

**NOT MEASUREMENT  
SENSITIVE**

**MIL-HDBK-735 (MR)**

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**MILITARY HANDBOOK**

**MATERIAL DETERIORATION PREVENTION  
AND  
CONTROL GUIDE FOR ARMY MATERIEL,  
PART ONE, METALS**



**AMSC N/A**

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### **FOREWORD**

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**MIL-HDBK-735(MR)****LIST OF ACRONYMS AND ABBREVIATIONS**

|  |  |
|--|--|
| ACI = Alloy Casting Institute  | JAN = Joint Army-Navy                                |
| AISI = American Iron and Steel Institute                             | LQ = limiting quality                                |
| AMC = US Army Materiel Command                                       | LSA = logistic support analysis                      |
| AN = Army-Navy   | LSAR = logistic support analysis record              |
| AND = Army-Navy design   | MACOM = major command                                |
| ANSI = American National Standards Institute                         | mdd = milligrams per square decimeter per day        |
| AQAPs = Allied Quality Assurance Publications                        | MIG = metal inert gas                                |
| AQL = acceptable quality level                                       | mpy = mils per year                                  |
| ASTM = American Society for Testing and Materials                    | MSC = major subordinate command                      |
| atm = atmosphere   | NACE = National Association of Corrosion Engineers   |
| BCC = body-centered crystal  | NAMLT = Nitric Acid Mass Loss Test                   |
| CARC = chemical-agent-resistant coating                              | NASA = National Aeronautics and Space Administration |
| CASS = Copper-Accelerated Acetic Acid-Salt Spray                     | NASN = National Air Surveillance Networks            |
| CID = commercial item description                                    | NATO = North Atlantic Treaty Organization            |
| CPAB = Corrosion Prevention and Advisory Board                       | NBC = nuclear, biological, and chemical              |
| CPC = corrosion prevention and control                               | NDT = nondestructive testing                         |
| CPSC = Consumer Product Safety Commission                            | NG = nitroguanidine                                  |
| CRT = cathode-ray tube   | NGS = non-Government standards                       |
| CTX = center of excellence   | NGSB = non-Government standards body                 |
| DARCOM = US Army Materiel Development and Readiness Command          | OC = operating characteristic                        |
| DCB = double cantilever base   | OSHA = Occupational Safety and Health Administration |
| DoD = Department of Defense  | ppm = parts per million                              |
| DODISS = Department of Defense Index of Specifications and Standards | QSTAGs = Quadripartite Standardization Agreements    |
| DoT = Department of Transportation                                   | RTV = room temperature vulcanizing                   |
| EC = electrolytic corrosion  | SCC = stress-corrosion cracking                      |
| EMF = electromotive force  | SMD = standardized military drawing                  |
| EPS = Environmental Protection Agency                                | SRET = scanning reference electrode technique        |
| EXCO = exfoliation corrosion   | STANAGSs = Standardization Agreements                |
| FAA = Federal Aviation Administration                                | TIG = tungsten inert gas                             |
| FACT = Ford Anodized Aluminum Corrosion Test                         | TNI = thermal nondestructive inspection              |
| FCC = face-centered cubic crystal                                    | TNT = trinitrotoluene                                |
| FIPS = Federal Information Processing Standards                      | TRADOC = US Army Training and Doctrine Command       |
| FMEA = failure mode and effects analysis                             | UNS = Unified Numbering Standard                     |
| GMR = General Motors Research  | UV = ultraviolet                                     |
| gr/ep = graphite-epoxy   | VCI = volatile corrosion inhibitors                  |
| IEC = International Electrochemical Commission                       |  |
| ILS = integrated logistics support                                   |  |
| ipy = inches per year  |  |
| ISO = International Organization for Standardization                 |  |

## MIL-HDBK-735(MR)

## CHAPTER 1

# INTRODUCTION

*Deterioration of Army materiel results from the reaction of metals and nonmetals with the environments to which the materiel is exposed. However, the corrosion process of metals can be prevented or limited. This requires knowledge and diligence on the part of those engaged in the design, acquisition, and use of Army materiel. This handbook provides the necessary knowledge. The basis for defining the content of the handbook is discussed, and an explanation is given for directing the handbook to those in a position to take the action necessary to prevent or control corrosion. The environments to which Army materiel may be exposed, and that may therefore result in corrosion reactions, are outlined. Finally, the organization of the information in the handbook is summarized.*

### 1-1 PURPOSE

Corrosion of metals reduces the effectiveness of Army materiel and limits its useful life; therefore, corrosion results in increased cost and decreased readiness. Corrosion of metals does not have to be inevitable; it can be prevented or controlled at an acceptable level if maintenance procedures are carried out in accordance with systems requirements. The key to effective corrosion control is performance of the required maintenance in supply depots and in field activities in addition to the application of state-of-the-art corrosion control methods during the design and fabrication of materiel. Corrosion prevention and control measures require appropriate actions by responsible individuals. The purpose of this handbook is to provide information needed to avoid or control corrosion of metals used in Army materiel. To the extent that this information is applied, the objectives of reducing costs and improving readiness are achieved.

### 1-2 SCOPE

The scope of this handbook is broad. Information is presented that can be used to anticipate, prevent, recognize, and control the deterioration of metals used in Army materiel. The metals considered in this handbook been used and are likely to be used in Army materiel.

Corrosion of a metal depends upon the environment to which it is exposed and the condition of the metal. The condition of a metal is influenced by the environments to which it has been exposed previously. This handbook includes the effects of environments encountered in production, transportation, storage, and use.

Corrosion occurs through a variety of processes and mechanisms, and the effects of corrosion appear in several modes of deterioration and failure. A discussion of the likely appearance, the possible intensity, and probable mechanisms of the various types of corrosion is presented.

Several different metals and nonmetals are often combined in an item of Army materiel. Some combina-

tions have high corrosion risk, whereas others have little risk. Information on the possible corrosion risk of metal-to-metal and metal-to-nonmetal interfaces is presented.

Several means are available for intervening in a corroding system to prevent or control the corrosion process. In some cases, however, it may be desirable to allow corrosion to occur. In these cases allowances for the corrosion effects or provision for periodic replacement of the damaged component should be made in the design. This handbook discusses means for preventing and controlling corrosion and allowing for the effects of corrosion.

The sources of most practical corrosion information are testing and operational experience. Thus this handbook discusses

1. Laboratory and field testing
2. The use of accelerated testing
3. The documentation of test results
4. Assessment of test significance.

The importance of feedback of operational experience to the design process is also covered.

Means of corrosion prevention and control should be built into all Army materiel. Therefore, this handbook also describes inspection and quality assurance procedures that relate to corrosion.

Emphasis is placed on lessons learned by Army and other organizations through research and development, testing and evaluation, and operational experience. This cumulative experience includes both successes and failures associated with corrosion of materiel. Examples of corrosion of Army materiel are given.

This information is presented so that it can be used easily by the many individuals who have an opportunity to reduce the effects of corrosion on Army materiel. This part, *Part One*, of the *Material Deterioration Prevention and Control Guide for Army Materiel* discusses corrosion of metals; Part Two of the guide considers deterioration of nonmetals.

**MIL-HDBK-735(MR)****1-3 FOCUS**

This handbook focuses on actions that can be taken to avoid or reduce the effects of metal corrosion, and it is written for those individuals who are in a position to take such actions.

An item of Army materiel comes under the control or influence of numerous individuals. These individuals have different interests in and opportunities for action to control corrosion or its effects. The soldier maintains *his* weapon because his effectiveness and survival depend on it. A design engineer, however, can influence the serviceability of *all* weapons issued to Army personnel.

Because of the wide range of skill, expertise, and interest of those involved in preventing and controlling corrosion in Army materiel, this handbook is addressed to those whose technical expertise in the area of corrosion may be limited but whose appropriate and timely action to avoid or control corrosion is crucial. There are many sources of corrosion information that may be consulted. These include technical reports, journal articles, symposium collections, and textbooks.

**1-4 ARMY ENVIRONMENTS**

The environment is defined as "the totality of natural and induced conditions occurring or encountered at any one time and place" (Ref. 1). An environment is important only as it relates to objects that are exposed to it and activities that are conducted within it. A definition of environment that relates more specifically to Army materiel and the conditions that it experiences is "the integrated total of all stresses that influence the performance capability of men and equipment during transit, in storage, or under field operating conditions" (Ref. 2). For the purposes of this handbook, the production environment for Army materiel must also be included.

In this handbook the important environmental factors are those that influence the corrosion of metal components in items of Army materiel throughout its useful life. The most meaningful way of characterizing environments is by climatic factors. Therefore, environments may be described as temperate, arctic, desert, and tropical. They may be further specified as industrial, rural, coastal, inland, or shipboard.

Induced environmental factors include radiation of all types, mechanical stresses, and airborne and waterborne pollutants.

At least 23 environmental factors have been identified as important in influencing the performance of Army materiel. The natural environmental factors are listed in Table 1-1. The induced environmental factors are given in Table 1-2.

Although climatic factors relate to the long-term manifestation of weather, wide variability in weather conditions occurs. Weather variability can be regular, such as the temperature difference between day and night

**TABLE 1-1. NATURAL ENVIRONMENTAL FACTORS (Ref. 3)**


---

Terrain  
 Temperature  
 Humidity  
 Pressure  
 Solar radiation  
 Rain  
 Solid precipitation  
 Fog and whiteout  
 Wind  
 Salt, salt fog, and salt water  
 Ozone  
 Macrobiological organisms  
 Microbiological organisms

---

**TABLE 1-2. INDUCED ENVIRONMENTAL FACTORS (Ref. 4)**


---

Atmospheric pollutants  
 Sand and dust  
 Vibration  
 Shock  
 Acceleration  
 Acoustics  
 Electromagnetic radiation  
 Nuclear radiation  
 Chemical agents  
 Decontaminants

---

or the precipitation patterns between winter and summer. Weather variability can also occur randomly, as in the case of severe storms.

Terrain refers to topographic features as well as soil conditions. Soil is any unconsolidated land that is not rock and includes such materials as clay, sand, and gravel. The environment for an article resting on or buried in a soil is influenced by the conditions of the soil.

Macrobiological organisms are those living organisms that are sufficiently large to be observed individually by the unaided eye. Conversely, microbiological organisms are too small to be observed individually by the unaided eye.

Corrosion can occur as the result of exposure of metal surfaces to a specific environment that causes corrosion. Metal components of Army materiel can also experience corrosion at any time as a result of previous or continuing long-term environmental encounters. For example, residual stresses and heat-affected zones in metals can result from production processes; these regions or zones may be more susceptible to corrosion. Additionally, shock and vibration during transportation and exposure to very high temperatures and humidities may later lead to severe corrosion problems.

**MIL-HDBK-735(MR)****1-5 OVERVIEW OF PART ONE**

Corrosion of metals leads to degraded performance and failure of Army materiel. It is possible to avoid or reduce corrosion through proper material selection, design considerations, corrosion prevention strategies, maintenance procedures, and other measures that are described in this handbook. All of the classical types of corrosion are possible in Army materiel because of the wide varieties of metals and alloys used and the wide range of environments that may be experienced. Chapter 2 discusses

1. Evidence of materiel damage
2. Environmental conditions that lead to corrosion
3. Mechanisms of corrosion
4. Selection of metals for Army materiel
5. Methods of protecting metals from corrosion.

Corrosion environments are described in terms of natural and induced conditions and of the status of the materiel (production and field) when the corrosion processes occur.

Because a typical item of Army materiel is fabricated of many components of both metallic and nonmetallic origin, potential modes of interaction are discussed. The interaction at the interface—where part meets part—is of most concern. However, interaction at a distance that results from chemical emissions released by materiel is also an important interface consideration.

Generic means of mitigating corrosion are discussed in Chapter 3 and include

1. Design configuration and layout considerations
2. Specifying materials that are less susceptible to corrosion
3. Avoiding process and fabrication conditions that sensitize the material
4. Using surface treatments and coatings to separate material from corrosive environments
5. Applying packaging concepts to protect materiel in transit and storage
6. Modifying the environment through the use of corrosion inhibitors.

Each metal and alloy of potential use in Army materiel is discussed in Chapter 4 in terms of the types of corrosion that may occur the environments to which each may be exposed. Corrosion problems that may occur at an interface with other metals and nonmetals are also considered. Applicable methods of preventing or mitigat-

ing corrosion are described. Specific examples of successful and unsuccessful applications of these methods to Army materiel are presented.

Because the factors controlling the rate of corrosion are often complex, testing is the only reliable way to determine the suitability of a metal for a particular application. The useful approaches to corrosion testing are described in Chapter 5 and include

1. Closely controlled laboratory tests performed with small specimens
2. Field tests performed with actual materiel items and with test specimens
3. Accelerated corrosion testing during which the action of critical controlling factors is intensified.

The documentation of corrosion testing is discussed. Any type of corrosion testing documentation should fully describe corrosion effects, the test environment, the test article, the test calibration, and the significance of the test for applications in Army materiel.

Quality assurance strategies are discussed in Chapter 6. A quality article of Army materiel reliably performs its design mission. Standards and specifications are a means of communication among the designer, fabricator, and inspectors in order to achieve a quality end item. Inspection strategies are based upon inspection of all items produced or examination of a statistically valid production sample. Destructive testing requires a sampling approach. Nondestructive means are available to inspect materials for surface and subsurface defects. Quality assurance extends beyond production of quality items to include packaging and inspection and maintenance during both storage and operation.

**REFERENCES**

1. MIL-STD-1165, *Glossary of Environmental Terms (Terrestrial)*, 25 March 1968.
2. AMCP 706-119, *Engineering Design Handbook, Environmental Series, Part Five, Glossary of Environmental Terms*, July 1975.
3. AMCP 706-116, *Engineering Design Handbook, Environmental Series, Part Two, Natural Environmental Factors*, April 1975.
4. AMCP 706-117, *Engineering Design Handbook, Environmental Series, Part Three, Induced Environmental Factors*, January 1976.

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## CHAPTER 2

# CORROSION PROCESSES

*The corrosion of a metal is a chemical process by which the metal is oxidized. The tendency to corrode in a given environment varies with the particular metal. This chapter discusses the chemical reactions that lead to corrosion and the various types of corrosion. Although there are different perspectives from which corrosion may be classified, this chapter discusses the types of corrosion as uniform, galvanic, pitting, crevice, intergranular, selective leaching, erosion-corrosion, fretting, liquid metal corrosion, high-temperature oxidation, high-temperature sulfidation, and biological. The discussion of each type of corrosion includes manifestation or characteristic appearance, conditions conducive to the process, mechanism of the process, limitations or constraints on the use of the metals involved and protective measures, and an Army example of the type of corrosion.*

### 2-1 CHEMISTRY OF CORROSION

Corrosion is the result of a chemical reaction between a metal and its surroundings during which the metal is oxidized. In most corrosion reactions the oxidation is the result of a transfer of electrons between the metal and its surroundings.

#### 2-1.1 OXIDATION-REDUCTION REACTIONS

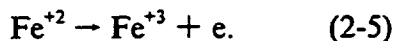
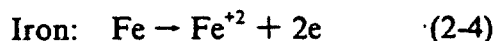
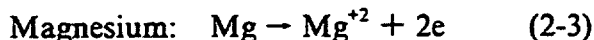
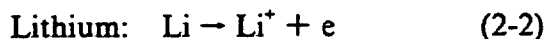
An electrochemical reaction is the term used for a chemical reaction during which a transfer of electrons takes place. The species that loses electrons is oxidized and thus is the reducing agent. The oxidation reaction is



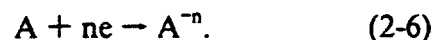
where

M = any metal capable of being oxidized  
n = number of electrons transferred  
e = an electron.

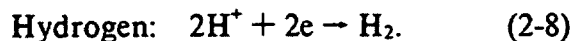
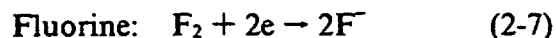
Some oxidation examples are



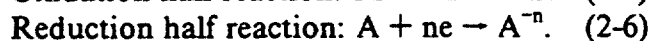
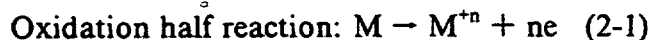
Oxidation is only half of the electrochemical reaction. The species that gains an electron is said to be reduced and thus is the oxidizing agent. The reduction reaction is



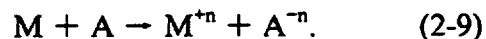
Some reduction examples are



Whenever there is an oxidation half reaction, there is a corresponding reduction half reaction:



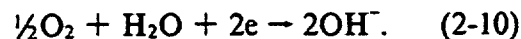
The overall reaction is the sum of these two half reactions:



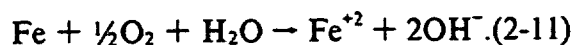
The corrosion of iron in water containing dissolved oxygen is a familiar corrosion process. Iron can be oxidized to either +2 or +3. The half reaction for the first step is



In this half reaction iron is oxidized to the  $Fe^{+2}$  oxidation state, which releases two electrons. The corresponding reduction half reaction is



The overall reaction is



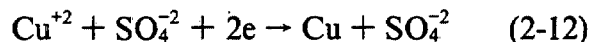
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In the formation of common red-brown rust,  $\text{Fe}^{+2}$  is further oxidized to  $\text{Fe}^{+3}$ . If an iron nail is dropped into a solution of copper sulfate,  $\text{CuSO}_4$ , the reactions that follow occur:

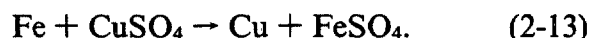
Oxidation half reaction:



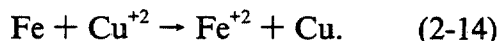
Reduction half reaction:



Overall reaction:



Because no change actually happens to the sulfate ion  $\text{SO}_4^{-2}$  the overall reaction can be written as



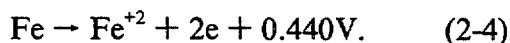
Part of the iron has gone into solution as  $\text{Fe}^{+2}$ , and the copper metal has deposited onto the surface of the nail. Fe has been oxidized to  $\text{Fe}^{+2}$ , and  $\text{Cu}^{+2}$  has been reduced to metallic Cu.

### 2-1.2 ELECTROMOTIVE FORCE SERIES

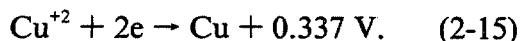
As can be seen from the example of the reaction in Eq. 2-14,  $\text{Cu}^{+2}$  has a greater affinity for electrons than does metallic iron Fe. If zinc metal Zn had been used instead of Fe, the tendency for the reaction to occur would have been stronger. If aluminum metal Al had been used, the tendency for the reaction to occur would have been even stronger. Conversely, if silver metal Ag had been substituted for Fe, no reaction involving the oxidation of silver would have occurred.

Accordingly, different metals have different affinities for electrons, and these affinities influence their reactivity in electrochemical reactions such as corrosion. These affinities are expressed as standard oxidation potentials. The hydrogen oxidation half reaction is assigned a value of zero, and the oxidation potentials of other elements are measured against the standard hydrogen oxidation potential. In this manner, the electromotive force (EMF) series of Table 2-1 is constructed.

The EMF series can be used to determine the tendency for an electrochemical reaction to occur. An example is Fe and  $\text{CuSO}_4$  from the previous paragraph. From Table 2-1, the oxidation half reaction and voltage are



The reduction reaction is



The reduction reaction is the reverse of the oxidation reaction, and the sign of the voltage changes from

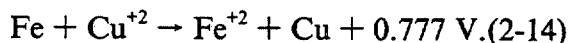
TABLE 2-1. ELECTROMOTIVE FORCE SERIES (Ref. 1)

| ELECTRODE REACTION                     | STANDARD OXIDATION POTENTIAL at 25°(77°F), V* |
|--|---|
| $\text{K} = \text{K}^+ + e^-$          | 2.925   |
| $\text{Na} = \text{Na}^+ + e^-$        | 2.714   |
| $\text{Mg} = \text{Mg}^{++} + 2e^-$    | 2.363   |
| $\text{Al} = \text{Al}^{+3} + 3e^-$    | 1.662   |
| $\text{Zn} = \text{Zn}^{++} + 2e^-$    | 0.763   |
| $\text{Cr} = \text{Cr}^{+3} + 3e^-$    | 0.744   |
| $\text{Fe} = \text{Fe}^{++} + 2e^-$    | 0.440   |
| $\text{Cd} = \text{Cd}^{++} + 2e^-$    | 0.403   |
| $\text{Co} = \text{Co}^{++} + 2e^-$    | 0.277   |
| $\text{Ni} = \text{Ni}^{++} + 2e^-$    | 0.250   |
| $\text{Sn} = \text{Sn}^{++} + 2e^-$    | 0.136   |
| $\text{Pb} = \text{Pb}^{++} + 2e^-$    | 0.126   |
| $\text{H}_2 = 2\text{H}^+ + 2e^-$      | 0.000   |
| $\text{Cu} = \text{Cu}^{++} + 2e^-$    | -0.337  |
| $2\text{Hg} = \text{Hg}_2^{++} + 2e^-$ | -0.788  |
| $\text{Ag} = \text{Ag}^+ + e^-$        | -0.799  |
| $\text{Pd} = \text{Pd}^{++} + 2e^-$    | -0.987  |
| $\text{Pt} = \text{Pt}^{++} + 2e^-$    | -1.2  |
| $\text{Au} = \text{Au}^{+3} + 3e^-$    | -1.498  |

\*Standard reduction potentials have the opposite sign.

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negative to positive. The overall reaction is obtained by summing the oxidation and reduction reactions



The relatively high positive voltage indicates that there is a strong tendency for the reaction to occur. If the flow of electrons between the  $\text{Cu}^{+2}$  and the Fe can be made to occur in an external circuit, the reaction is a chemical source of electricity, or a battery. An overall reaction voltage that is negative would not occur spontaneously but would require that an electrical current of the proper voltage be applied to the system. This is what happens during electroplating, such as plating chromium onto copper.

### 2-1.3 GALVANIC SERIES

The standard oxidation potentials in Table 2-1 apply to situations in which all reactants and products are at unit activity. The term "unit activity" has specific meaning to the chemical thermodynamicist but is rarely achieved in practical situations such as corrosion.

Galvanic series have been prepared that more accurately describe whether an electrochemical reaction will take place in an environment of practical concern. Such a

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TABLE 2-2. GALVANIC COMPATIBILITY OF MATERIALS IN SEAWATER (Ref. 2)

| METAL B →<br>METAL A ↓                       |   | METAL B          |      |                 |         |                          |           |                                |                    |                   |                 |                      |                     |                     |                        |                     |   |                   |                                   |                     |                                   |                                 |   |
|--|---|------------------|------|-----------------|---------|--------------------------|-----------|--------------------------------|--------------------|-------------------|-----------------|----------------------|---------------------|---------------------|------------------------|---------------------|---|-------------------|-----------------------------------|---------------------|-----------------------------------|---------------------------------|---|
|  |   | Magnesium alloys | Zinc | Aluminum alloys | Cadmium | Mild steel, wrought iron | Cast iron | Low-alloy, high-strength steel | Brasses, Mn bronze | Copper, Si bronze | Lead-tin solder | Tin bronze (G and M) | 90/10 Copper-nickel | 70/30 Copper-nickel | Nickel-aluminum bronze | Silver braze alloys | Types 302, 304, 321 and 347 stainless steel | Alloys 400, K-500 | Types 316 and 317 stainless steel | Alloy 20, Alloy 825 | Titanium, Alloys C, C-276 and 625 | Graphite, graphitized cast iron |   |
| Magnesium alloys                             | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Zinc   | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Aluminum alloys                              | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Cadmium                                      | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Mild steel, wrought iron                     | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Cast iron                                    | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Low-alloy, high-strength steel               | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Brasses, Mn bronze                           | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Copper, Si bronze                            | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Lead-tin solder                              | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Tin bronze (G and M)                         | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| 90/10 Copper-nickel                          | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| 70/30 Copper-nickel                          | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Nickel-aluminum bronze                       | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Silver braze alloys                          | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Types 302, 304, 321, and 347 stainless steel | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Alloys 400, K-500                            | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Types 316 and 317 stainless steel            | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Alloy 20, Alloy 825                          | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Titanium, Alloys C, C-276 and 625            | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
| Graphite, graphitized cast iron              | S | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |
|  | E | ●                | ●    | ●               | ●       | ●                        | ●         | ●                              | ●                  | ●                 | ●               | ●                    | ●                   | ●                   | ●                      | ●                   | ●   | ●                 | ●                                 | ●                   | ●                                 | ●                               | ● |

S—Small Metal A to Metal B Area Ratio  
 E—Equal Area Ratio  
 L—Large Metal A to Metal B Area Ratio

● Unfavorable—Galvanic Acceleration Expected  
 x Uncertain—Variable Direction and/or Magnitude of Galvanic Effect  
 o Compatible—No Galvanic Acceleration Expected

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galvanic series for commercial alloys and metals in seawater is given in Table 2-2. This table can be used to determine the likelihood of a galvanic reaction between two different metals in a seawater environment. The seawater galvanic series is also used to approximate the probable galvanic effects in other environments for which there are no data.

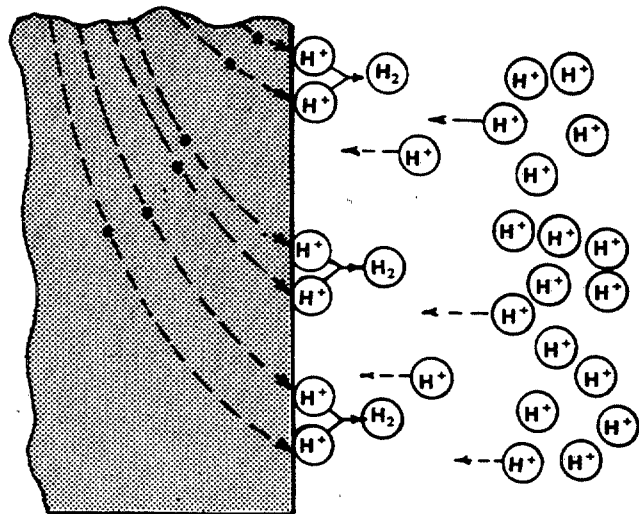
### 2-1.4 POLARIZATION AND MIXED POTENTIAL THEORY

When electrical current flows between two electrodes in an electrolyte, the potential of each electrode is changed from its equilibrium potential. The direction of potential change always opposes the flow of current. Thus the anode becomes more cathodic and the cathode becomes more anodic. The extent of potential change is called polarization.

Concentration polarization occurs when reactants are in short supply at an electrode. Fig. 2-1 illustrates a situation in which the reduction rate is controlled by the diffusion of hydrogen ions to the metal surface, and the diffusion of hydrogen ions is limited by the mass transport properties that control diffusion.

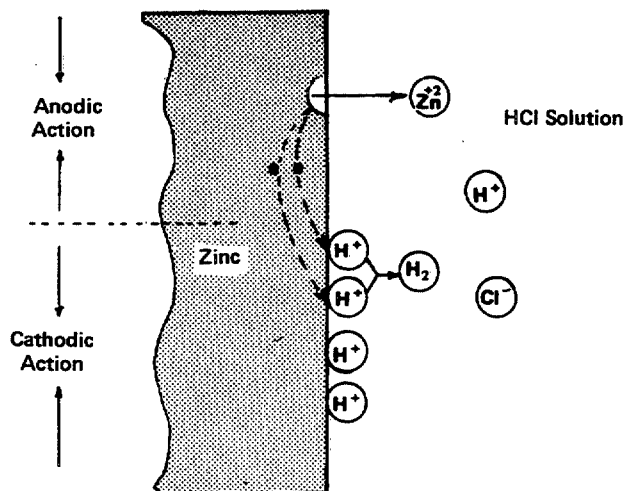
Activation polarization results from a slow electrode reaction. The reduction of hydrogen ions at a platinum electrode is controlled by the rate at which adsorbed hydrogen atoms coalesce into bubbles of gaseous hydrogen molecules. This rate-limiting step is illustrated in Fig. 2-2.

Concentration and activation polarization overpotentials are additive. Therefore, the overall reaction rate is determined by an appropriate combination of activation



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**Figure 2-1. Concentration Polarization During the Cathodic Reduction of Hydrogen Ions (Ref. 3)**



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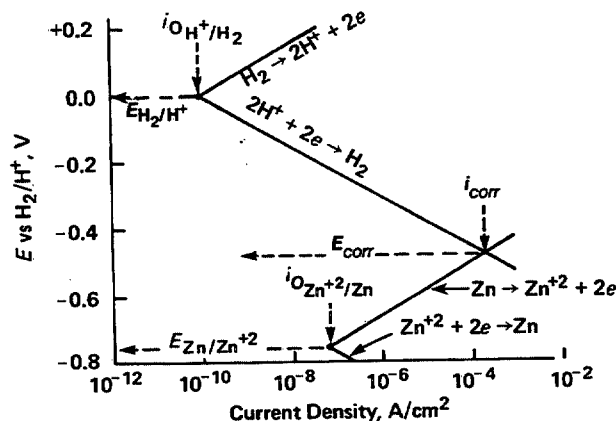
**Figure 2-2. Activation Polarization During the Corrosion of Zinc in Air-Free Hydrochloric Acid (Ref. 3)**

and concentration polarization. Mixed potential theory indicates how cathodic and anodic polarization plots are combined to determine the rate of an electrochemical reaction. The theory states

1. Any electrochemical reaction can be expressed by two or more partial oxidation and reduction reactions.
2. There can be no net accumulation of charge during an electrochemical reaction.

Accordingly, during the corrosion of a metal sample, the total rate of oxidation must equal the total rate of reduction.

An example of the mixed potential theory is shown in Fig. 2-3. Zinc immersed in hydrochloric acid will rapidly



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**Figure 2-3. Example of Mixed Potential Theory—Pure Zinc in Acid Solution (Ref. 1)**



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corrode with the evolution of hydrogen gas. The system consists of a zinc electrode in equilibrium with its ions and a hydrogen-electrode reaction occurring on a zinc surface under equilibrium conditions. Each of these electrodes has a reversible potential at the corresponding exchange current density. Also each of these electrodes has polarization current density-electrode potential relationships.

The total rate of oxidation must equal the total rate of reduction; therefore, the only point at which this equality occurs is the intersection of the zinc dissolution plot with the hydrogen gas evolution plot. This point characterizes the corrosion current density  $i_{corr}$  and the corresponding potential  $E_{corr}$ . A simple application of Faraday's law converts  $i_{corr}$  to the rate of metal corrosion.

Cathode and anode areas are equal for uniform corrosion. However, unequal areas are characteristic of local corrosion attack. Because the total rate of oxidation must equal the total rate of reduction, corrosion of an anodic area one-tenth the size of a cathodic area will penetrate 10 times faster than it would if the anodic area were equal to the cathodic area. Therefore, pitting corrosion can rapidly penetrate a pipe wall, even though the amount of metal corroded is relatively small.

There are at least four types of electrochemical cells responsible for corrosion attack. Dissimilar electrode cells have been discussed in terms of the standard electromotive force series and the galvanic series. Fig. 2-4 illustrates a dissimilar metal cell. If the concentration of electrolyte surrounding each electrode is different, a concentration cell is established, even though the electrodes are similar, as in Fig. 2-5. If the concentration of dissolved oxygen in the electrolyte surrounding each electrode is different, a form of concentration cell called a differential aeration cell is established. Fig. 2-6 illustrates a differential aeration cell. If one electrode has a passive oxide surface film and the other does not, a passive-active cell is formed. This type of cell can exist on the surface of a

metal where discontinuities in the passive film exist. The discontinuities are the anode and the protected surface becomes the cathode, as shown in Fig. 2-7.

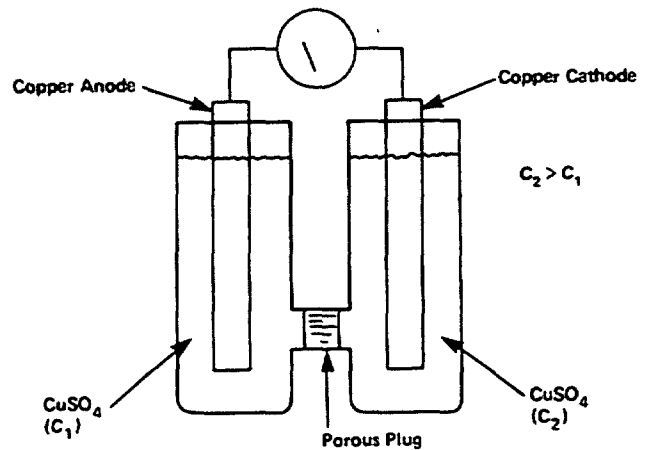


Figure 2-5. Dissimilar Concentration Cell

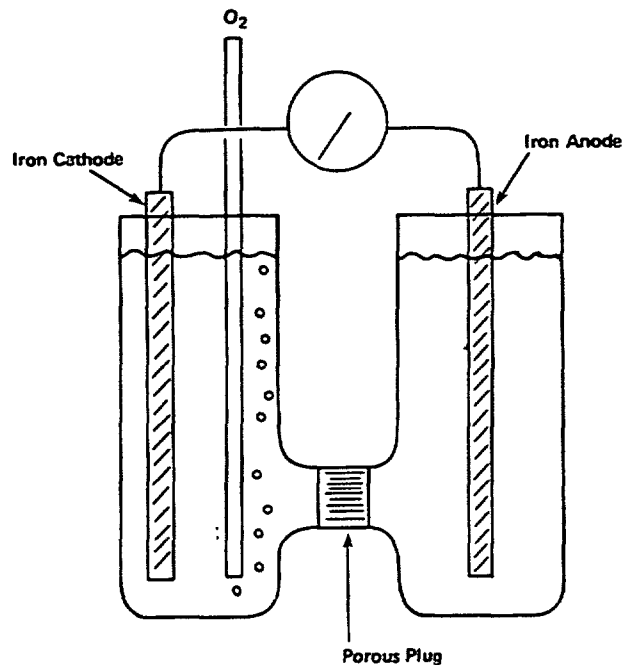


Figure 2-6. Differential Aeration Cell

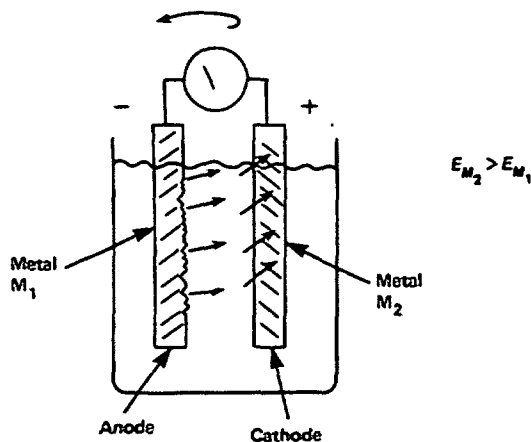


Figure 2-4. Dissimilar Metal Cell

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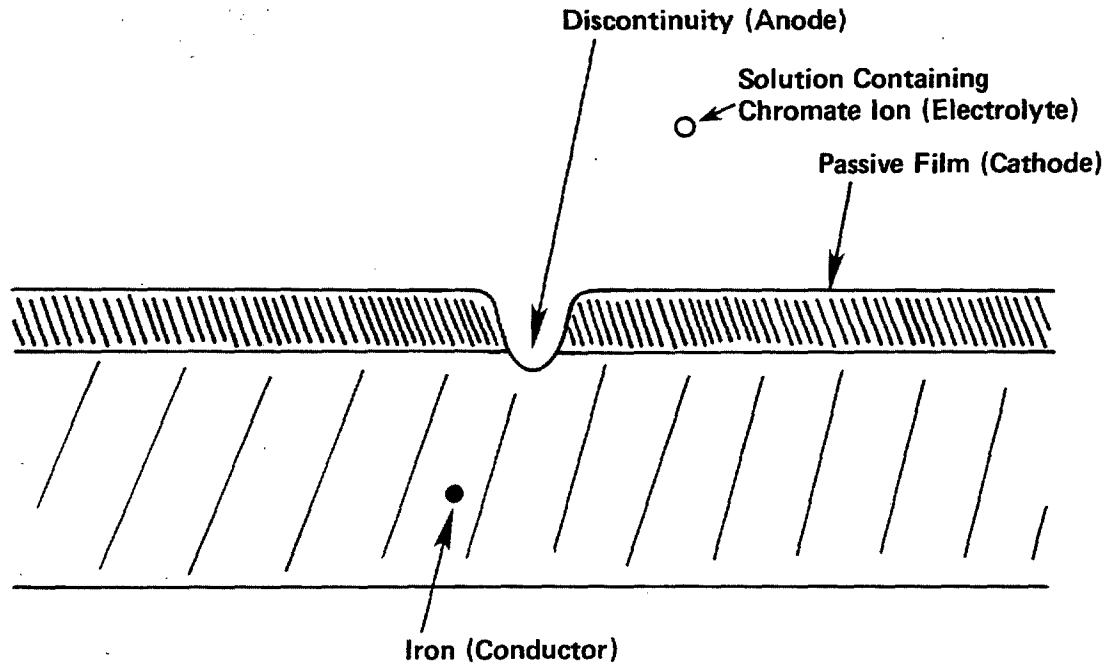


Figure 2-7. Example of Passive-Active Cell

## 2-2 TYPES OF CORROSION

### 2-2.1 UNIFORM CORROSION

Uniform corrosion describes corrosion attack uniformly distributed on a metal surface, as illustrated in Fig. 2-8.

#### 2-2.1.1 Manifestation and Quantification

The effect of uniform corrosion may be characterized as the weight loss per unit area of the surface per unit time.

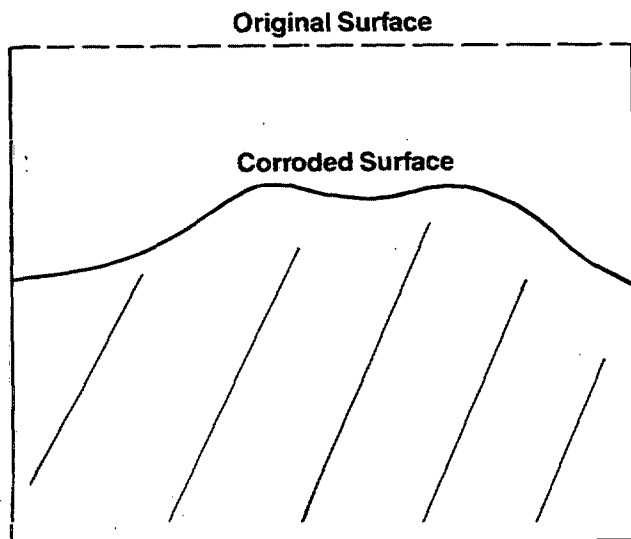


Figure 2-8. Uniform Corrosion

The commonly used units in the corrosion literature are milligrams per square decimeter per day, abbreviated as mdd. Uniform corrosion may also be expressed as the rate of thickness loss of the metal per unit time. This is commonly expressed as mils per year (mpy) and inches per year (ipy).

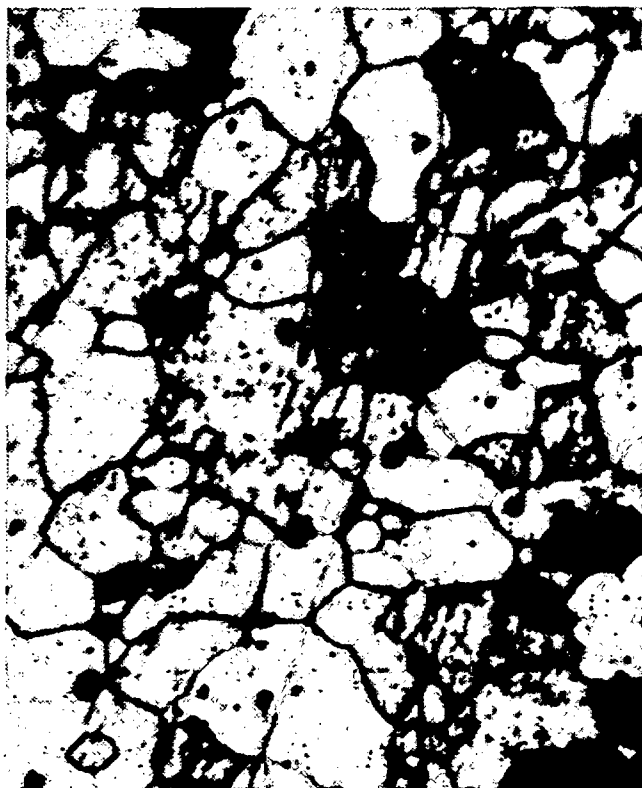
#### 2-2.1.2 Conducive Conditions

Conducive conditions for uniform corrosion are a surface on which anodic and cathodic sites are uniformly distributed and that is exposed to an electrolyte. An example, as shown in Fig. 2-9, is the microstructure of relatively pure iron with sulfide inclusions distributed on the surface. Given these basic conditions, the several factors listed in Table 2-3 determine whether and to what extent corrosion will occur.

Metals are composed of a mass of crystalline grains. A smooth surface presents grains of different composition that have different orientations with respect to the crystalline structure. The grains are separated by grain boundaries along which materials of a composition different from that of the crystalline grains may be deposited. If such a surface is exposed to water containing dissolved salts or some other electrolyte, uniform corrosion can occur.

#### 2-2.1.3 Mechanisms

The uniformly distributed grains of varying composition and crystalline orientation together with the grain boundaries at the surface of a metal act as microscopic

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**Figure 2-9. Relatively Pure Iron With Sulfide Inclusions (Ref. 4)**

anodes and cathodes when covered with an electrolyte. The electrolyte can consist of as little material as an absorbed layer. Thus the mechanism of uniform corrosion is galvanic action, but the uniform corrosion occurs at a microscopic level uniformly distributed on a metallic surface. This process is illustrated in Fig. 2-10.

If the metal does not form a protective oxide film, i.e., it is not passivating, the corrosion rate is a linear function of the corrosion potential, as indicated in Fig. 2-11(A). If, however, the metal can form a passivating film, the corrosion rate can be very low as long as the corrosion potential is maintained in the passivating range, as indicated in Fig. 2-11(B). The corrosion rate may be high in either the active or the transpassive potential ranges.

#### 2-2.1.4 Application Constraints and Protection Approaches

Uniform corrosion can be classified into the following categories:

1. Corrosion proceeds because of the solubility or nature of the corrosion products.
2. A passivating film that stifles further attack is formed on the metal surface.
3. The metal or alloy is immune to attack in the particular environment.
4. The metal dissolution process is artificially controlled by manipulating the corrosion potential.

Uniform corrosion of sheet metal is a widespread phenomenon. Sheet metal is widely used in a great many material items, so prevention of uniform corrosion is of

**TABLE 2-3. FACTORS INFLUENCING CORROSION IN SOLUTION (Ref. 5)**

| CHARACTERISTICS OF THE METAL  |
|---|
| Composition and chemical homogeneity of the metal   |
| Surface properties; inherent protective films   |
| Effective electrode potential of the metal in solution  |
| Overtoltage of hydrogen and oxygen on the metal that must be overcome   |
| Surface condition; physical homogeneity of the metal  |
| Protective deposits formed as a result of contact with the solution (environment)   |
| CHARACTERISTICS OF THE SOLUTION (ENVIRONMENT)   |
| Hydrogen ion activity in the solution   |
| Oxygen content of the solution  |
| Presence of oxidizing or reducing agents  |
| Characteristics and distribution of other ions in the solution  |
| Motion of solution in relation to metal   |
| Temperature   |
| EFFECT ON PROGRESS OF CORROSION BY PRODUCT OF CORROSION   |
| The oxide may inhibit corrosion by combining with other elements in the solution to form a protective layer on the surface of the metal.              |
| The formation of oxides may consume the available oxygen where the supply of oxygen is limited. This action would lessen or retard further corrosion. |

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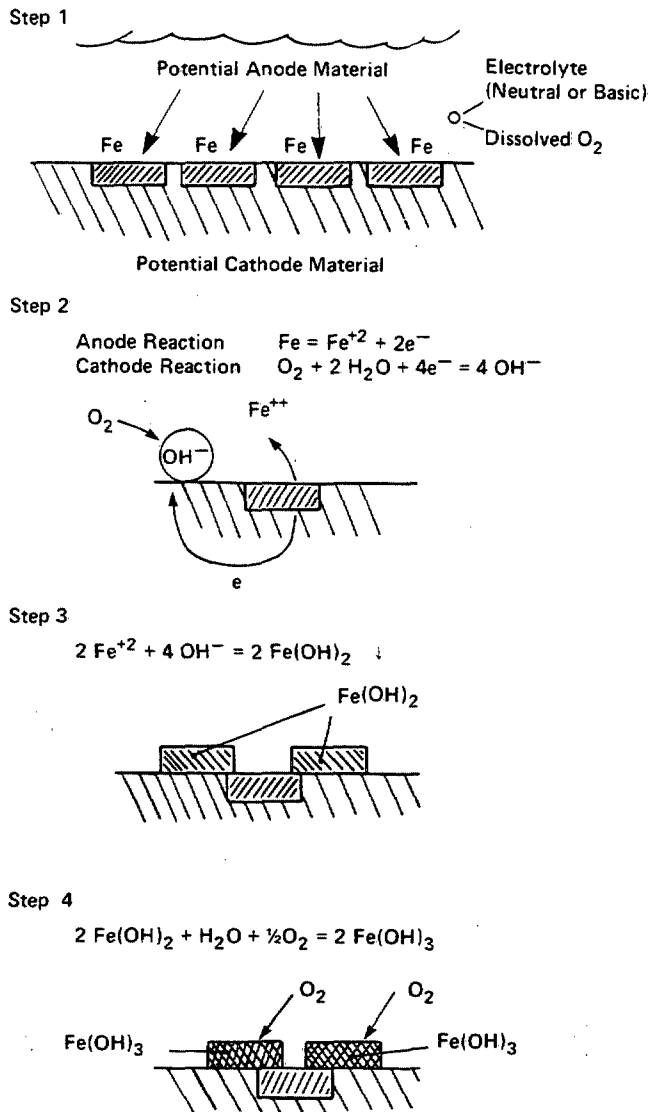
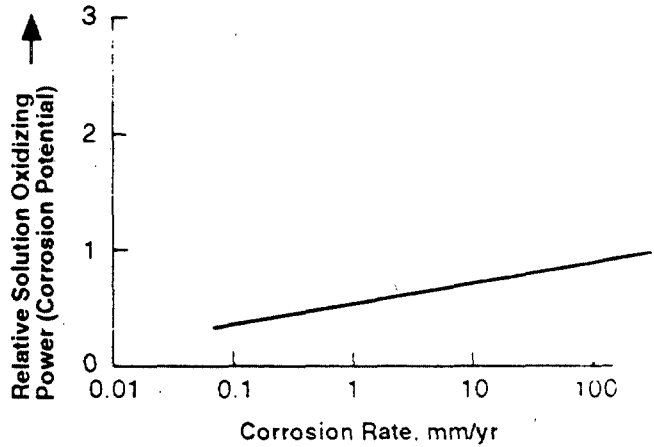


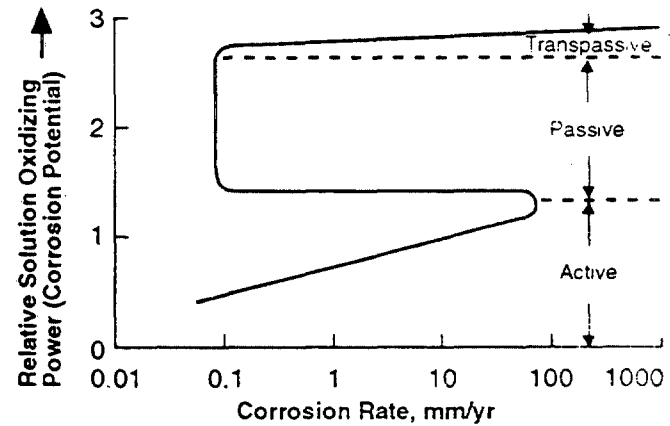
Figure 2-10. Steps in Uniform Corrosion

high priority and great importance. Fig. 2-12 illustrates the stages of corrosion of painted sheet metal. Preventing uniform corrosion of sheet metal and surfaces of other metal items is usually accomplished by coating the metal surfaces with a suitable protective finish.

If an item of material is to be stored for a long period, protection during storage can be accomplished by storing the item in a naturally dry climate, if practical, or in a



(A) Corrosion Rate of a Nonpassivating Metal as a Function of Solution Oxidizing Power (Corrosion Potential)



(B) Corrosion Rate of a Passivating Metal as a Function of Solution Oxidizing Power (Corrosion Potential)

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Figure 2-11. Comparison of Corrosion Rate Functions of Nonpassivating Metals (Ref. 3)

humidity-controlled storage space. Also the rate of uniform corrosion can be greatly reduced by lowering the storage temperature. Table 2-4 indicates the general susceptibility of metals and alloys to uniform corrosion.

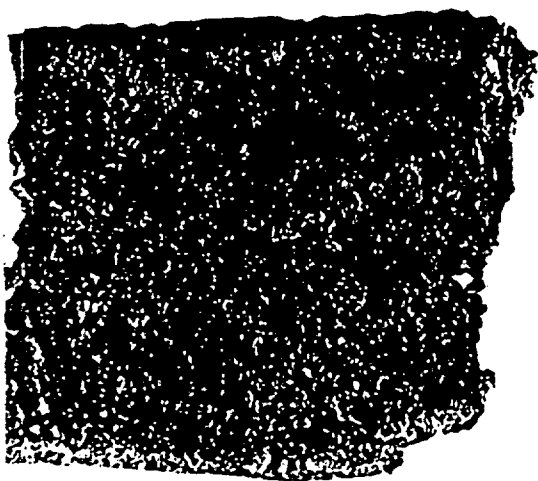
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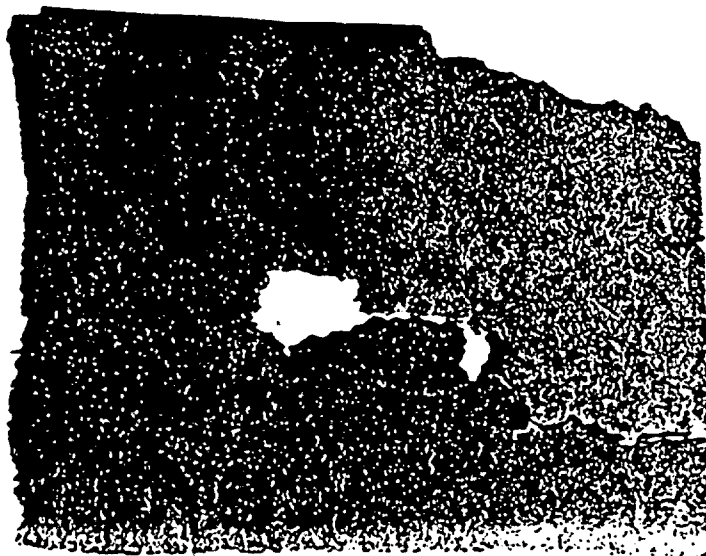
Stage 1



Stage 2



Stage 3



Stage 4

**Figure 2-12. Stages of Corrosion for Painted Metal Surfaces**

**MIL-HDBK-735(MR)****TABLE 2-4. GENERAL CORROSION OF METALS AND ALLOYS (Ref. 6)****LIGHT METALS**

**Magnesium.** Subject to attack in acid and neutral solutions, but resistant to attack by hydrofluoric acid. Shows passive behavior in alkaline solutions

**Aluminum.** Subject to attack in strongly acid or alkaline environments, but not attacked by concentrated nitric acid. Forms naturally protective oxide film

**FERROUS METALS**

General corrosion of iron and low-carbon steel in many natural environments

Low-alloy steels (per ASTM A243) exhibit uniform attack in mild atmospheric environments; resulting corrosion products prevent further attack

**STAINLESS STEELS**

Form protective oxide film

**LEAD, TIN, ZINC**

Amphoteric metals often exhibit uniform attack

**COPPER AND COPPER-BASE ALLOYS**

Show slow uniform attack in natural environments

**NICKEL ALLOYS**

Behave in manner similar to copper-base alloys. Are inherently resistant to caustic solutions and nonoxidizing acids

**CHROMIUM-NICKEL ALLOYS**

Tend to be resistant like stainless steels

**COBALT ALLOYS**

Usually contain chromium and are therefore resistant

**REACTIVE METALS**

Titanium alloys rely on passive film for corrosion resistance. Zirconium has broader range of resistance than titanium. Tantalum exhibits severe hydrogen pickup at low corrosion rates.

**NOBLE METALS**

Inherently resistant to natural environments

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**2-2.1.5 Example**

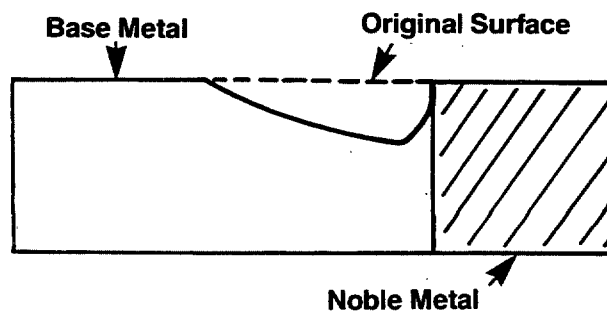
A common example of uniform corrosion is the rusting of vehicle bodies, which is most common where chemicals are used to melt ice and snow on roadways. Rapid corrosion of inadequately protected vehicle body sheet metal occurs in regions near the seacoast that experience high humidities, high temperatures, salt entrained in atmospheric moisture, and the regular formation of nocturnal dew.

**2-2.2 GALVANIC CORROSION**

Although all forms of corrosion are galvanic in nature, the term galvanic corrosion refers to localized attack resulting from the electrolytic coupling of dissimilar metals.

**2-2.2.1 Manifestation and Quantification**

In galvanic corrosion one metal is the anode upon which the attack occurs and the other metal is the cathode. This relationship is illustrated in Fig. 2-13. The



**Figure 2-13. Galvanic Corrosion Effect**

## MIL-HDBK-735(MR)

galvanic series, Table 2-2, applies particularly to this form of corrosion and assumes, of course, that the conditions of exposure approximate those of the series.

Because galvanic attack is localized, the extent of attack has meaning in terms of how the functional capability of the assembly of dissimilar metals is affected. Galvanic corrosion often occurs at structural joints where dissimilar metals are joined or where dissimilar fasteners are used. Therefore, relatively little corrosion can result in a great deal of damage.

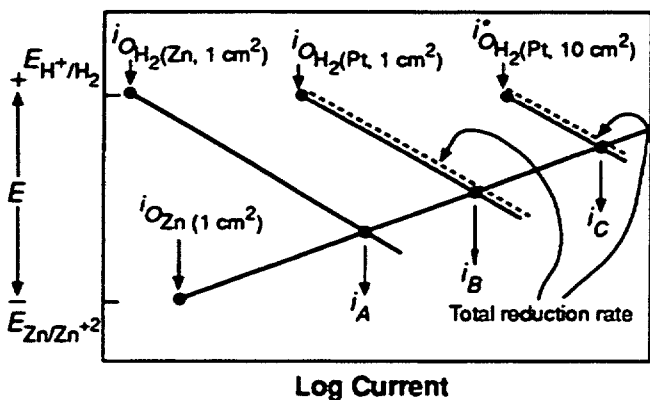
### 2-2.2.2 Conducive Conditions

Metals that have a relatively large difference in electrochemical potential are subject to galvanic corrosion if they are in good electrical contact and if the ionic charge transfer mechanism is effective, i.e., if an electrolyte is present. The extent and nature of polarization of the electrodes establish the electrochemical potential, which, in turn, sets the corrosion current. A couple whose anode area is small relative to the cathode area experiences a high current density that can lead rapidly to functional failure. The exchange current for an electrode equals the current density times the electrode area.

The effect of anode-to-cathode area ratio in a galvanic couple on the corrosion rate of the anode can be expressed as follows:

1. As the size of the cathode increases, the corrosion rate of the anode increases.
2. If the relative area of the anode increases, its overall corrosion rate decreases.

Fig. 2-14 shows the effect of cathode-to-anode area ratio for galvanic corrosion of zinc-platinum couples. The exchange current for a 1-cm<sup>2</sup> (0.16-in.<sup>2</sup>) platinum cathode is  $i_B$ , whereas the exchange current for a 10-cm<sup>2</sup> (1.6-in.<sup>2</sup>) platinum cathode is  $i_B^*$ .



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Figure 2-14. Area Effect of Galvanic Corrosion (Ref. 1)

### 2-2.2.3 Mechanisms

The mechanism of galvanic corrosion is the classical electrochemical reaction between dissimilar metals in an electrolyte, as illustrated in Fig. 2-15. The anode is oxidized and reduction occurs at the cathode. The rate of reaction depends upon the extent and nature of anode and cathode polarization, the relative areas of anode and cathode materials, and the distance between the anode and cathode over which ionic charge transfer must occur.

As the distance between the anode and cathode increases, the ionic charge transfer mechanism in the electrolyte becomes less efficient. Therefore, the rate or extent of dissolution of the anode is a function of the distance from the cathode, as illustrated in Fig. 2-16.

The general susceptibility of metals to galvanic corrosion is described in Table 2-5.

Graphite possesses valuable lubricating properties and is therefore used as an additive in some greases and lubricating oils. Graphite, however, behaves as a noble metal. Accordingly, graphite can cause corrosion of most metals to which it is coupled. Fig. 2-17 shows the severe galvanic corrosion of 5052 aluminum alloy caused by coating the aluminum alloy with graphite grease.

### 2-2.2.4 Application Constraints and Protection Approaches

The effects of galvanic corrosion can be avoided or reduced by choosing materials that are not widely separated in the galvanic series for the environmental conditions of interest. The galvanic reaction rate can be reduced by introducing a metal into the system that is more active and therefore serves as a sacrificial anode. Anodic current density and hence corrosion rates can be reduced by increasing the anode-to-cathode surface area ratio.

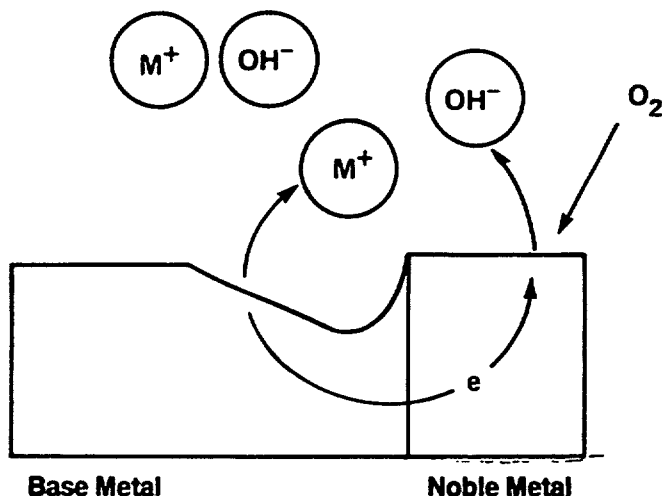


Figure 2-15. Galvanic Corrosion Mechanism

**MIL-HDBK-735(MR)****TABLE 2-5. SUSCEPTIBILITY OF METALS TO GALVANIC CORROSION (Ref. 6)**

---

**LIGHT METALS**

Magnesium is extremely susceptible to galvanic corrosion.

Aluminum is susceptible to galvanic corrosion in solutions containing chloride ion. In the absence of chlorides, aluminum is less active due to the stability of the oxide film that forms on the surface and inhibits further attack.

**FERROUS METALS**

Iron and steel undergo galvanic corrosion when coupled to more noble alloys. They are more noble than aluminum and its alloys in chloride solutions.

**STAINLESS STEELS**

In the passive state stainless steels assume a more noble position. In solutions containing chloride ion, localized corrosion of many stainless steels occurs in couples with copper or nickel and their alloys.

**LEAD, TIN, AND ZINC**

An oxide film on these metals can shift their potential to more noble values. Zinc is widely used as a sacrificial anodic coating.

**COPPER ALLOYS**

Copper and its alloys are not readily polarized in aqueous solutions containing chloride ion. They can cause severely accelerated corrosion of more active metals, such as aluminum and the ferrous metals.

**NICKEL ALLOYS**

Nickel and its alloys are not readily polarized and therefore cause accelerated corrosion of more active materials, such as aluminum and ferrous alloys.

**CHROMIUM-NICKEL ALLOYS**

Combination of a passive surface with inherent resistance of nickel-base alloys places them in more noble positions.

**COBALT-BASE ALLOYS**

These alloys, most of which are chromium bearing, are resistant to galvanic corrosion due to their noble position.

**REACTIVE METALS**

Titanium, zirconium, and tantalum are extremely noble due to their passive film.

**NOBLE METALS**

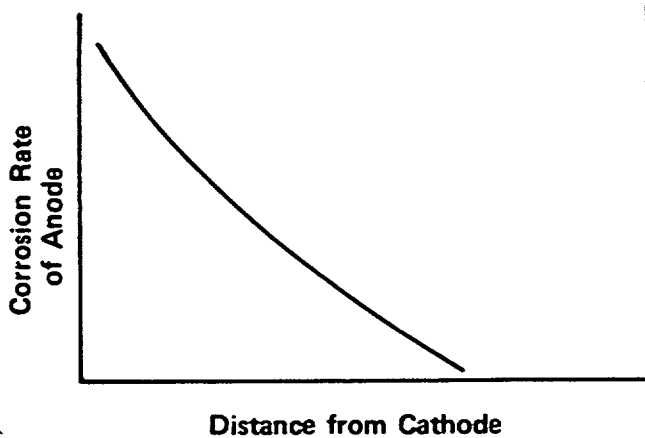
This designation, applied to gold, silver, and platinum, describes their position in the galvanic series and their resistance to galvanic corrosion.

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**Figure 2-16. Corrosion Rate of Anode as Function of Distance From Cathode**

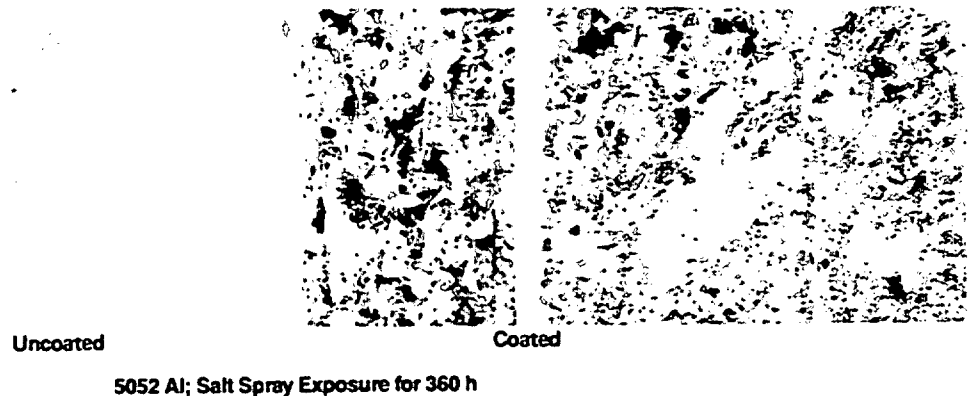
### 2-2.3 PITTING CORROSION

Pitting is a form of localized corrosion in which small areas on a metal surface corrode preferentially and cavities or pits form. If the metal is thin or if the pitting attack is severe, perforation can occur.

#### 2-2.3.1 Manifestation and Quantification

Fig. 2-18 illustrates pitting corrosion, and an example of pitting corrosion is shown in Fig. 2-19. The extent of pitting can be characterized differently, as described in Table 2-6.

The selection of the manner in which pitting behavior is characterized depends upon the effect of pitting on the intended use of the metal. Pitting that results in diminished visual appeal of a piece of decorative metal is characterized differently from pitting that can lead to perforation or other forms of structural damage.



**Figure 2-17. Galvanic Corrosion Caused by Graphite Grease**

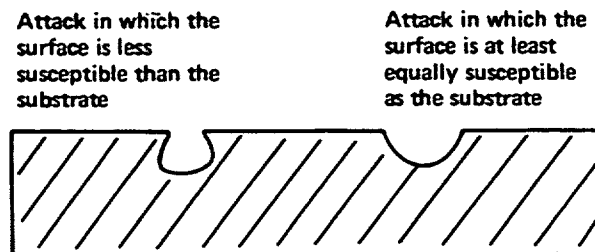
#### 2-2.2.5 Examples

Fasteners such as bolts or rivets generally have small surface areas relative to the metal sections they are joining; therefore, it is imperative that fastener metals be cathodic.

Steel fasteners are usually cadmium plated. However, it is important that the plating be sufficiently thick. An effort to reduce weight in a helicopter application by reducing the thickness of the cadmium plating resulted in corrosion.

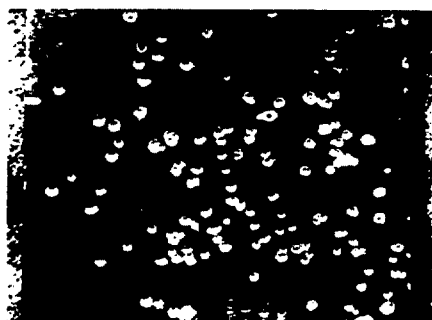
Aluminum coating applied by ion vapor deposition can protect the part, and the process does not generate hydrogen. Flame-sprayed aluminum is used on steel deck hardware and the superstructure of marine vessels.

Galvanizing sheet steel or iron pipe with zinc is an example of a sacrificial anode. If the surface is scratched and the underlying metal exposed, the large zinc anode protects the small exposed cathode from attack. Galvanized sheet steel is used for some parts of tactical vehicles that are especially susceptible to corrosion.

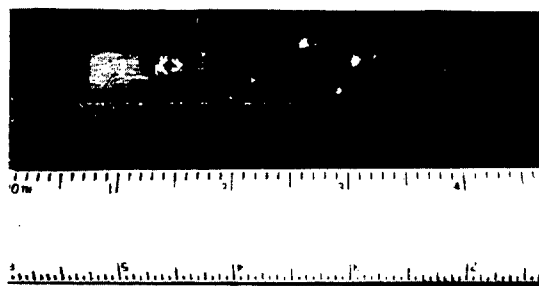


**Figure 2-18. Pitting Corrosion**

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(A) Small Corrosion Pits  
Randomly Distributed (Ref. 7)



(B) Pitting in Tubing With Low  
Velocity Seawater (Ref. 6)

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Figure 2-19. Examples of Pitting Corrosion

### TABLE 2-6. PITTING CHARACTERIZATION

1. Metal surfaces are examined visually and under low magnification to determine the number of pits. The pit density or number of pits per unit area is determined.
2. Nondestructive methods can be used to locate and count pits.
3. Metal weight loss alone is not a satisfactory procedure for determining the extent of pitting, but it may be used with other data such as the pit density to determine the average amount of metal removed per pit.
4. Pit depths can be determined by the following techniques:
  - a. Microscopic measurement of a cross-sectioned pit that has been mounted metallographically.
  - b. Determination of the difference in metal thickness before and after machining a specimen to the bottom of a pit. A refinement of this technique is to count the number of remaining pits after successive increments are machined off.
  - c. Measurement of a pit depth by the use of a micrometer, pit depth gage, or microscope that has a graduated focusing knob.
5. Standard charts can be used to describe the degree of pitting in terms of density, size, and depth of pits. Fig. 2-20 is an example of such a chart.
6. Measurement of the maximum pit depth or the average depth of a number of the deepest pits is often a meaningful way to express the extent of pitting damage.
7. Statistical methods can be used to show the probability that pitting will occur, to show the relationship between pit depth and time of exposure, and to estimate the maximum pit depth on the basis of an examination of a portion of the exposed metal surface.
8. The change in a particular mechanical property of a metal can be used to show the effect of pitting under some conditions.

Fig. 2-20 is a pitting chart for visual comparison of pits in metal.

#### 2-2.3.2 Conductive Conditions

Pitting occurs on certain metals that form passive oxide layers, such as aluminum and stainless steels. The pitting sites are usually stagnant flow conditions, and most pitting failures are caused by electrolytes that contain chloride or chloride-containing ions. Given the same alloy, pitting is less likely to occur on polished than on etched or ground metal surfaces. Table 2-7 lists the susceptibility to pitting of different metals.






#### 2-2.3.3 Mechanism

The pitting process is illustrated in Fig. 2-21. Fig. 2-21(A) shows the conditions for pit initiation. These are

1. An imperfection in a normally protective oxide surface layer
2. Presence of corrosive ions, such as those in an aerated salt solution.

Fig. 2-21(B) shows the pit initiation stage. An active-passive cell is established having a potential difference of about 0.5 volt. The resultant high current density of the large cathode-small anode causes rapid dissolution of the metal.

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|   | Density   | Size                 | Depth  |
|---|---|----------------------|--------|
| 1 | <br>25/dm <sup>2</sup>   | 0.5 mm <sup>2</sup>  | 0.4 mm |
| 2 | <br>100/dm <sup>2</sup>  | 2.0 mm <sup>2</sup>  | 0.8 mm |
| 3 | <br>500/dm <sup>2</sup>  | 8.0 mm <sup>2</sup>  | 1.6 mm |
| 4 | <br>1000/dm <sup>2</sup> | 12.5 mm <sup>2</sup> | 3.2 mm |
| 5 | <br>5000/dm <sup>2</sup> | 24.5 mm <sup>2</sup> | 6.4 mm |

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**Figure 2-20. Chart for Rating Pits According to Their Density, Size, and Depth (Ref. 8)**

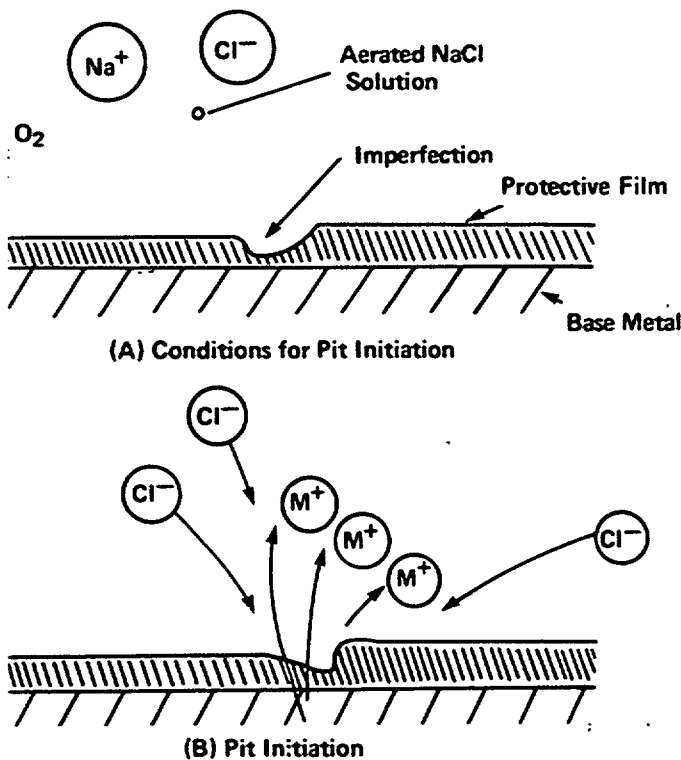
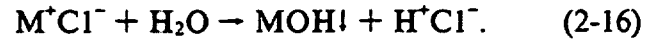


Fig. 2-21(C) shows the self-stimulating and self-propagating stage of pit growth. The rapid dissolution of metal produces an excess of positive metal ions. Chloride ions migrate to the pit to maintain electrical neutrality. A high concentration of  $M^+Cl^-$  is formed within the pit. A hydrolysis reaction occurs and forms a high concentration of hydrogen ions.

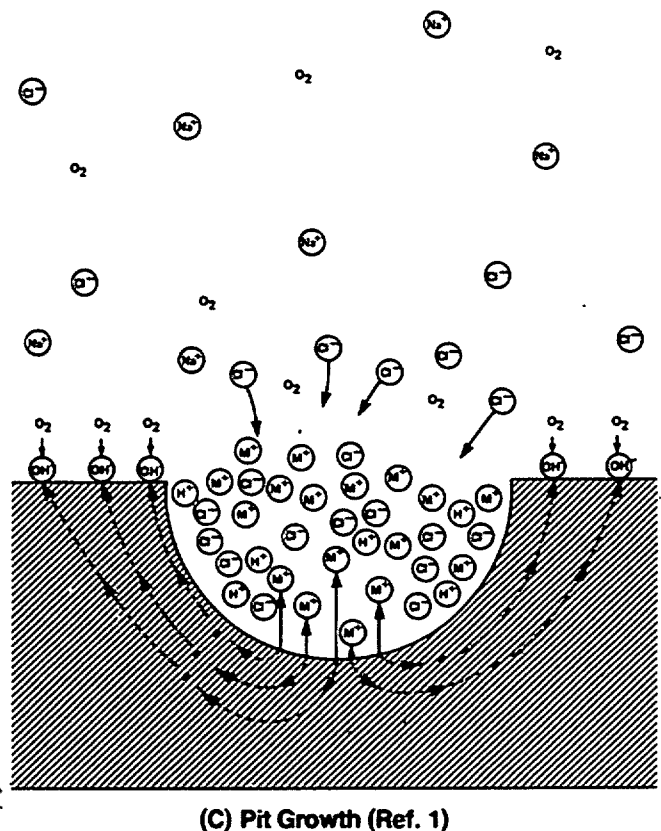


High concentrations of hydrogen ions lower the pH in the pit and stimulate further metal dissolution.

High flow velocity past a potential pit site hinders pit formation and growth by sweeping away the reacting species, especially the hydrogen and chloride ions. Stagnant flow conditions are conducive to pit growth. Pits tend to form more readily on horizontal than on vertical surfaces.

#### 2-2.3.4 Application Constraints and Protection Approaches

In addition to their effects on the esthetic properties of a surface or functional characteristics of a pitted member, pits form starting points for stress concentration that can cause or accelerate stress corrosion or corrosion fatigue attack.



**Figure 2-21. Illustration of Pitting Process**

**MIL-HDBK-735(MR)**

**TABLE 2-7. SUSCEPTIBILITY OF METALS TO PITTING (Ref. 6)**

---

**LIGHT METALS**

Metal ions (Cu, Fe, Pb, or Hg) can plate out of solution onto magnesium and aluminum surfaces. Microgalvanic cells are formed, which promote pitting.

Aluminum is susceptible to chloride pitting and crevice corrosion.

**FERROUS METALS**

Steels are susceptible to pitting under deposits, in crevices, and at breaks in otherwise protective films, e.g., mill scale, sulfide films, and at holidays in paint.

**STAINLESS STEELS**

Stainless steels are notoriously susceptible to chloride pitting, crevice corrosion due to chloride or oxygen concentration cells, and to simple oxygen cells in corrosive acids.

**LEAD, TIN, ZINC**

Lead will pit in sulfuric acid if the normal lead sulfate film is dissolved.

Tin may pit in aqueous environments rich in chlorides, sulfates, or nitrates.

Sheet zinc will pit in many aqueous environments.

**COPPER ALLOYS**

There is no inherent tendency for copper alloys to pit, but they are subject to pitting under deposits.

**NICKEL ALLOYS**

Except for localized attack under marine deposits in seawater, pitting of nickel is rare.

**CHROMIUM-NICKEL ALLOYS**

The basic Ni-Cr-Fe (Alloy 600) is subject to pitting and crevice corrosion in a manner analogous to the austenitic stainless steels.

**COBALT ALLOYS**

In practice, the chromium-bearing cobalt alloys seem to be highly resistant.

**REACTIVE METALS**

Titanium resists chloride pitting on boldly exposed surfaces but can suffer severe crevice corrosion in some environments.

Zirconium tends to be resistant to pitting but can corrode in crevices where corrosive species accumulate or concentrate.

Tantalum is usually resistant to pitting.

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The preventive measures include (Ref. 9)

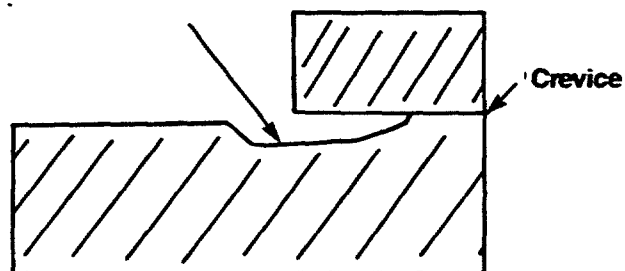
1. Select a metal that does not pit in the application.
2. Adjust the design geometry to prevent aggressive conditions such as stagnant flow areas on horizontal surfaces.
3. Allow for pitting by adjusting the material thickness. Because of the self-propagating nature of pitting, this method is not reliable if prevention of perforation is required.
4. Control the corrosive media by means such as removing chloride ions or using suitable inhibitors.
5. Use a protective coating on the metal surface.
6. Insure conditions such that the passive film is continuous and sound.

**2-2.4 CREVICE CORROSION**

Crevice corrosion is the intense localized corrosion that frequently occurs within crevices and other shielded areas exposed to a corrosive medium.

**2-2.4.1 Manifestation and Quantification**

A crevice is formed between two mating surfaces, such as those caused by gaskets, lap joints, surface deposits,

**Corrosion Damage**

**Figure 2-22. Crevice Corrosion**

bolts, and rivet heads. Crevice corrosion is illustrated in Fig. 2-22.

Because crevice corrosion is localized to the shielded area, it can be characterized in descriptive terms that relate to the area of attack and geometric distortion and degradation resulting from the attack. Further characterization of crevice corrosion is in terms of its effect on functional properties. For example, Fig. 2-23 shows crevice corrosion damage on the sealing face of a pipe flange.



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**Figure 2-23. Crevice Corrosion at Gasket Surface of Large Stainless Steel Pipe Flange (Ref. 1)**

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## 2-2.4.2 Conductive Conditions

Gaps or opening geometries favorable for crevice corrosion are those that are large enough for entry of liquid yet small enough to maintain a stagnant zone within the crevice. For aqueous media this size is approximately 10 to 100  $\mu\text{m}$  (0.4 to 4 mils) (Ref. 1). Fibrous material that provides a wicking action and thereby maintains corrosive materials at the metal interface is conducive to crevice corrosion. This type of corrosion is often called poultice corrosion.

Crevice corrosion, like pitting, occurs most commonly on passive layer or oxide-film-protected metals such as aluminum, magnesium, and stainless steel. Table 2-7 lists the susceptibilities of various metals to pitting corrosion, and similar susceptibilities apply to crevice corrosion. Crevice corrosion susceptibilities of corrosion-resistant steels are ranked in Table 2-8.

## 2-2.4.3 Mechanism

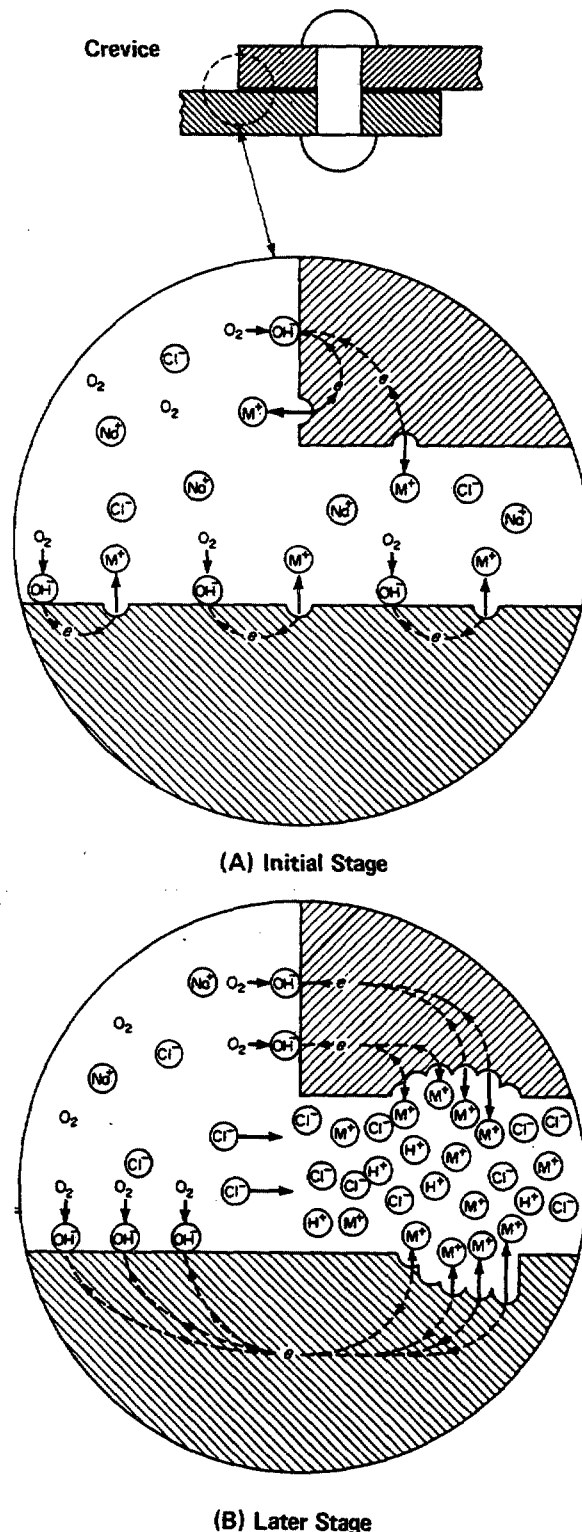
Except for the initiating sequence, the mechanism of crevice corrosion is very similar to pitting. The crevice corrosion sequence is illustrated in Fig. 2-24.

Fig. 2-24(A) shows the initial stage. Initially, the corrosion reaction of metal oxidation-oxygen reduction occurs uniformly over the entire surface of the metal including the wetted crevice surfaces. However, movement of the liquid within the crevice is restricted and oxygen is depleted. Oxygen reduction ceases but metal oxidation continues and creates an excess of positive charges within the crevice.

Fig. 2-24(B) shows the self-propagating stage of crevice corrosion, which is identical to that of the pit growth process described in par. 2-2.3.3.

**TABLE 2-8. CREVICE CORROSION SUSCEPTIBILITY RATING OF CORROSION-RESISTANT STEELS (Ref. 10)**

| ALLOY TYPE          | CREVICE CORROSION SUSCEPTIBILITY |
|---------------------|----------------------------------|
| 410                 | Poorest Resistance               |
| 17-10 (P) Annealed  | ↑                                |
| 17-4 (Cu) Annealed  |                                  |
| 316                 |                                  |
| 321                 |                                  |
| 17-7 Annealed       |                                  |
| 21-6-9              |                                  |
| 310                 |                                  |
| 14-8 (Mo) Annealed  |                                  |
| AM350 Annealed      | ↓                                |
| 35-35-20-10 (MP35N) | Best Resistance                  |



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**Figure 2-24. Illustration of Crevice Corrosion Process (Ref. 1)**

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Poultice corrosion occurs when an absorptive material is in contact with a metal surface that is wetted periodically. No corrosion occurs when the entire assembly is dry and little occurs when it is wet. During the drying period, however, adjacent wet and dry areas develop. Differential aeration develops near the edges of the wet zones and leads to pitting corrosion, as it does for crevice corrosion.

**2.2.4.4 Application Constraints and Protection Approaches**

Several opportunities exist for combating crevice corrosion in the design, fabrication, and operation of materiel items. These are (Ref. 1)

1. Reduce crevices to the minimum necessary by using larger and fewer parts.
2. Use butt-welded joints instead of riveted or bolted joints.
3. Close crevices in lap joints by continuous welding, caulking, soldering, or brazing.
4. Specify sound welding techniques to insure complete penetration and to avoid porosity.
5. Prevent ingress of corrodent by close fit of faying surfaces, by use of impervious joining materials, by encapsulation, by enveloping, and by sealing.
6. Avoid fibrous or absorbent packings and gaskets.
7. Avoid sharp corners and stagnant areas.
8. Specify (and design in the capability) complete removal of scale or foreign matter from metal surfaces.
9. Select materials that are not susceptible to crevice corrosion.
10. Design the system to provide a uniform environment.
11. Inhibit the environment in crevices or stagnant areas.
12. Design the system to facilitate surface cleaning and application of protective coatings.
13. In storage or operation keep surfaces clean by washing, draining, and keeping flowing fluids clean, which is done by filtering out suspended solids.

**2-2.4.5 Example**

Poultice corrosion is a form of crevice corrosion that occurs on the sheet metal of tactical vehicles. Soil, debris, and salt deposits accumulate in the semienclosed sections of the body and underbody. Severe corrosion occurs on the metal surfaces within or just adjacent to these deposits. The result is the characteristic penetration of body panels from the inside.

**2-2.4.6 Filiform Corrosion**

Filiform corrosion is a special type of crevice corrosion that occurs on metal surfaces under protective films. A common example of filiform corrosion is attack of the metal surfaces of food and beverage cans under the protective enamel and lacquer surfaces.

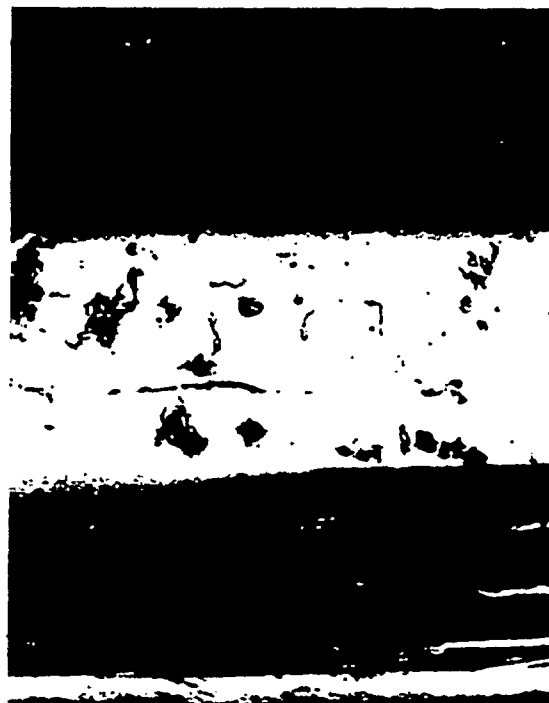
**2-2.4.6.1 Manifestation and Quantification**

Filiform corrosion appears as a network of threadlike corrosion product trails. The filaments are 2.54 mm (0.1 in.) or less in width. Examples of filiform corrosion are shown in Fig. 2-25.

Filiform corrosion does not usually result in loss of functional capability, such as weakening or destroying metallic components. It does, however, affect surface appearance. The extent of surface damage can be characterized as the area covered and the density of the



(A) Example of Filiform Corrosion on Alclad Aluminum Skin



(B) Filiform Corrosion Found Under Paint Coating on Landing Gear Strut

**Figure 2-25. Examples of Filiform Corrosion (Ref. 11)**

## MIL-HDBK-735(MR)

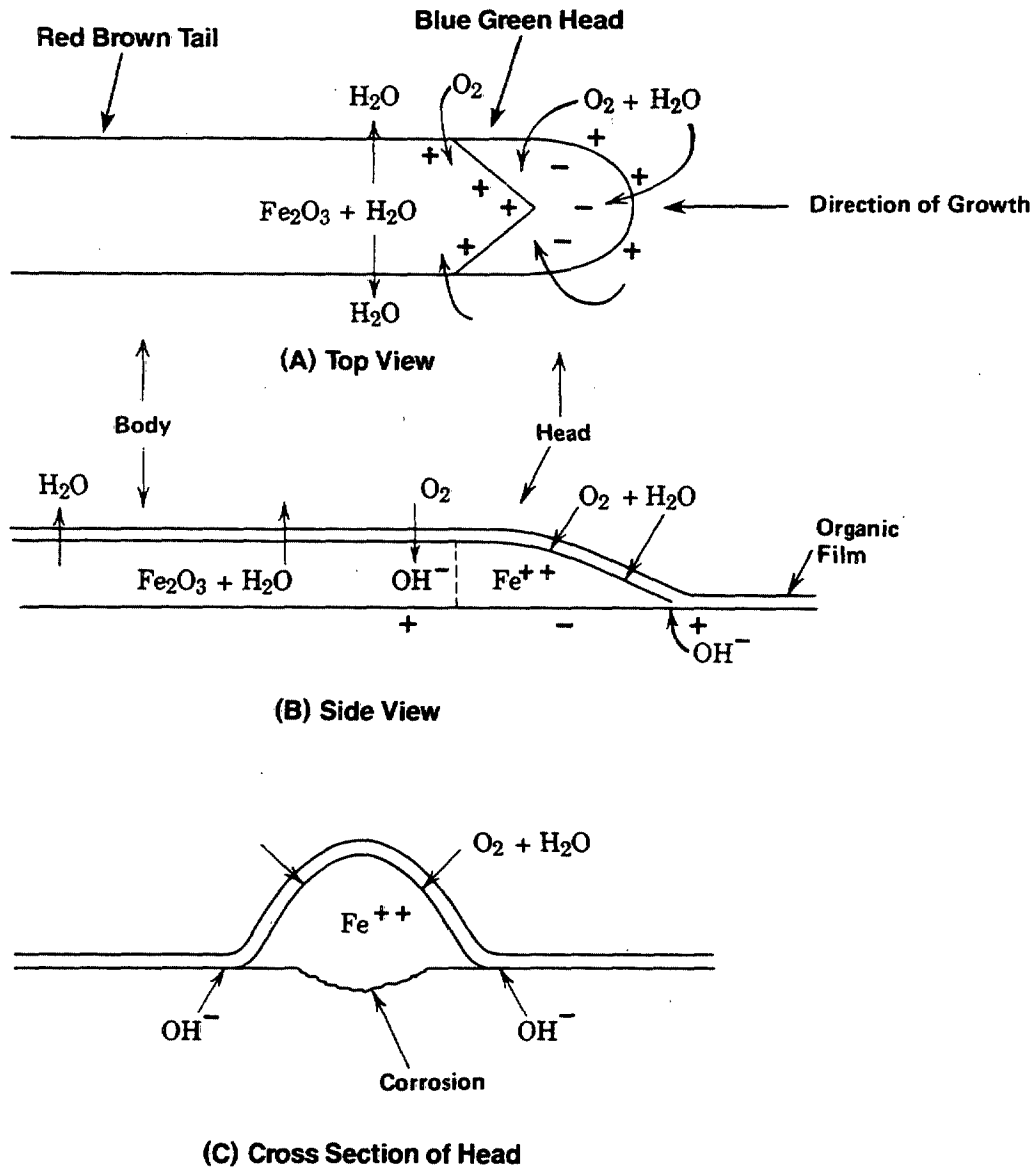
corrosion tracks. Perhaps a more important measure is the subjective response of the consumer to a product that exhibits filiform corrosion.

## 2-2.4.6.2 Conducive Conditions

Filiform corrosion has been observed on a variety of metal surfaces under an assortment of coatings. The metals include steel, magnesium, aluminum, zinc, and chromium-plated nickel surfaces. The coatings include tin, silver, gold, phosphate, enamel, lacquer, and adhesive bonded paper. Metals are unaffected by filiform corrosion when the humidity is under 65%, but above 90% humidity the corrosion appears as blisters rather than threads.

## 2-2.4.6.3 Mechanisms

The basic mechanism of filiform corrosion is formation of a differential oxygen cell between the head and the body of the corrosion filament, as illustrated in Fig. 2-26. The head is a relatively concentrated solution of ferrous salts, whereas the tail is precipitated ferric hydroxide. Water is absorbed in the region of the head from the atmosphere by osmosis, and water is lost in the region of the tail by osmosis. Oxygen diffuses through the film and reaches higher concentrations at the interface of the head and body and at the periphery of the head. The anode of the differential oxygen cell is in the central and forward portions of the head where ferrous ions  $Fe^{+2}$  are formed.



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Figure 2-26. Corrosion Filaments Showing Details of Differential Oxygen Cell (Ref. 12)



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All regions in which the film makes contact with the head and in which hydroxyl ions  $\text{OH}^-$  are liberated comprise the cathode. The  $\text{OH}^-$  ions diffuse toward the center of the head. There they react with  $\text{Fe}^{+2}$  to form ferrous hydroxide, which is oxidized by oxygen to form insoluble ferric hydroxide. The filament will continue to grow, usually in a straight line, as long as the conditions necessary to maintain the chemistry exist.

The only satisfactory way to prevent filiform corrosion is to store coated metal surfaces in low-humidity environments. Protective films of very low water permeability can also prevent filiform corrosion.

**2-2.5 INTERGRANULAR**

Intergranular corrosion consists of preferential attack at or adjacent to the grain boundaries of a metal or alloy.

**2-2.5.1 Manifestation and Quantification**

Metals and alloys consist of individually oriented crystals. At the boundaries between crystals, precipitates can form and alloying and residual elements can concentrate. Also adjacent crystal faces can be depleted in those elements that comprise the precipitates.

Preferential attack of grain boundaries can leave all the grains in place but result in complete loss of mechanical properties. If there is also significant attack of the grains along their faces, grains are readily dislodged, the geometry is affected, and the mechanical properties are diminished. Intergranular corrosion can cause an appreciable decrease in elongation before any significant loss of ultimate tensile strength or yield strength can be detected. In severe cases there can be a significant loss of tensile properties, even though only a small volume of metal has corroded. Intergranular attack during which there is increased volume of the corrosion product over that of the uncorroded material can cause swelling. In this situation both geometry and mechanical properties are affected. Fig. 2-27 is an example of intergranular attack.

A unique form of intergranular attack occurs in aluminum alloys in which the grains are flattened by rolling or extrusion. Intergranular attack proceeds laterally through the plate or sheet in planes parallel to the surface. The corrosion products force the metal away from the body of the materials in layers or sheets. This type of corrosion is referred to as exfoliation and is illustrated in Fig. 2-28.



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**Figure 2-27. Intergranular Corrosion of Sensitized Type 316 Stainless Steel (Ref. 6)**

## MIL-HDBK-735(MR)



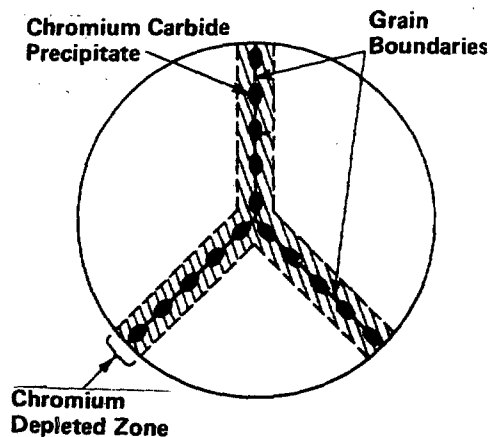
Reproduced with permission from *Basic Corrosion and Oxidation* by J. M. West, published in 1980 by Ellis Horwood Limited, Chichester, England.

**Figure 2-28. Exfoliation of Aluminum Alloy After Exposure to Marine Atmosphere (Ref. 13)**

### 2-2.5.2 Conducive Conditions

Conditions conducive to intergranular attack are brought about by grain boundary precipitates that are anodic to the surrounding zones or grain boundary precipitates that are cathodic to the adjacent denuded zones. In both cases the grain boundary becomes enriched in some component at the expense of the adjacent zones, as illustrated in Fig. 2-29. The tendency for these conditions to occur depends upon the chemical composition of the alloy, the thermal and mechanical history of the structural element, and the specific environment.

Chrome-nickel austenitic stainless steels such as American Iron and Steel Institute (AISI) 304 are sensitized to intergranular attack by precipitating chromium carbide ( $\text{Cr}_{23}\text{C}_6$ ) in the grain boundaries. The result is that the matrix near the fine platelets of grain boundary chromium carbide is less resistant to attack by both oxidizing and reducing acids. Sensitization results from exposure to temperatures in the range of  $427^\circ$  to  $871^\circ\text{C}$  ( $800^\circ$  to  $1600^\circ\text{F}$ ). So-called weld decay corrosion occurs in the

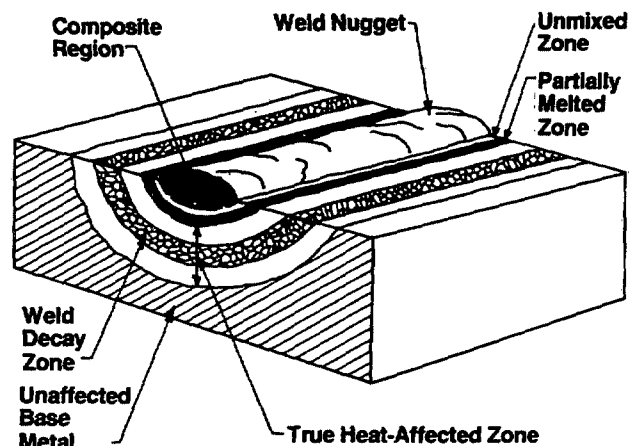


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**Figure 2-29. Grain Boundary in Sensitized Type 304 Stainless Steel (Ref. 1)**

heat-affected zone of weldments of austenitic stainless steels, as shown in Fig. 2-30. The time-temperature histories of several points at various distances from the deposited weld metal are related to the sensitized zone. The intergranular corrosion resulting from corrosion of the sensitized zone is illustrated in Fig. 2-31.

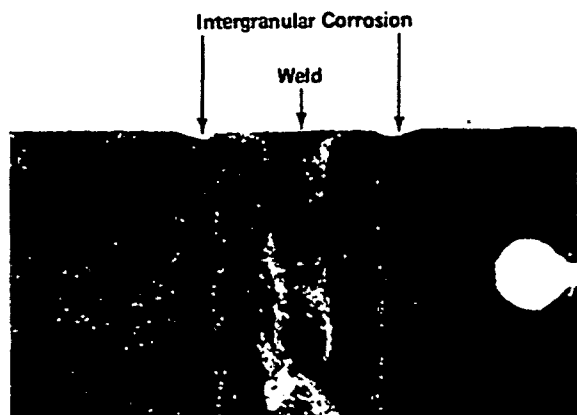
Strong carbide formers called stabilizers are added to austenitic stainless steel to control sensitization. However, under certain conditions stabilized austenitic stainless steels such as AISI 347 form grain boundary precipitates of chromium carbides in a narrow band that is a few grains wide on both sides of a weld. Intergranular attack by oxidizing solutions of this very narrow heat-affected zone is called knife-line attack.



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**Figure 2-30. Weldment in Austenitic Stainless Steel (Ref. 6)**

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**Figure 2-31. Weld Decay in Stainless Steel (Ref. 12)**

The sensitizing temperature range for ferritic stainless steels (Fe-Cr) such as AISI 430 is above 925°C (1700°F). In ferritic stainless steels, chromium-iron nitride (CrFe)<sub>2</sub>N precipitates may also form. Their sensitizing effect is similar to that of chromium carbides.

High strength is developed in several aluminum alloys by precipitating copper aluminide (CuAl<sub>2</sub>) from solid solution along slip planes and grain boundaries. This precipitation increases the susceptibility to exfoliation attack. Extensive cold work can also produce grain boundary precipitates. Exfoliation attack is very likely in situations where the flattened dimensions of the grain are exposed.

Table 2-9 summarizes the susceptibility of various alloys to intergranular corrosion.

### 2-2.5.3 Mechanisms

The mechanism of intergranular corrosion is galvanic corrosion at the microscopic scale. The driving force of intergranular corrosion is the difference in corrosion potential that develops between a thin grain boundary zone and the bulk of the immediately adjacent grains. This difference in potential may result from differences in chemical composition of the two zones. This can develop as a result of impurities or alloying elements migrating to the grain boundaries. A precipitate may form if the concentration of alloying elements in the grain boundary region is sufficiently large. If the precipitate is anodic to the adjacent denuded zone, it corrodes preferentially, but if the grain boundary precipitate is cathodic to the denuded zone, it remains intact and local cell action develops a crack in the denuded zone. Fig. 2-32 illustrates the mechanism of intergranular attack.

Examples of anodic constituents are Mg<sub>2</sub>Al<sub>3</sub>, MgZn<sub>2</sub> in aluminum alloys, and Fe<sub>4</sub>N in iron alloys. Corrosion of anodic constituents is illustrated in Fig. 2-32(A). Examples of cathodic constituents are FeAl<sub>3</sub> and CuAl<sub>2</sub> in aluminum alloys and Fe<sub>3</sub>C in iron alloys. Corrosion of cathodic constituents is illustrated in Fig. 2-32(B).

Intergranular corrosion can develop into a pit, and corrosion may continue with a pitting mechanism. However, further intergranular corrosion may proceed from the walls of the pit.

Most intergranular corrosion is the result of small differences in composition at grain boundaries. Heat treatment and cold-working affect not only the size and shape of the grains but also the composition, location, amount, and size of the constituents. The metallurgical history of the alloy can be as important as its chemical composition in influencing intergranular corrosion.

**TABLE 2-9. SUSCEPTIBILITY OF METALS TO INTERGRANULAR CORROSION (Ref. 6)\***

#### LIGHT METALS

**Magnesium Alloys.** Only rare instances of intergranular corrosion reported

**Aluminum Alloys.** Conventional intergranular corrosion occurs perpendicular to the surface of recrystallized alloys. In unrecrystallized alloys exfoliation occurs. The table roughly outlines the behavior of more common wrought alloys.

| Immune | Partly Susceptible <sup>1</sup> | Susceptible         |
|--------|---------------------------------|---------------------|
| A91100 | A95056                          | A92NNN <sup>2</sup> |
| A93003 | A95083                          | A96351              |
| A95052 | A95086                          | A97NNN              |
| A95454 | A95154                          |                     |
|        | A95456                          |                     |
|        | A96061                          |                     |
|        | A96063                          |                     |
|        | A97075 T73 <sup>3</sup>         |                     |

<sup>1</sup>Depending on % Mg, aging, cold-working

<sup>2</sup>May be clad with A91100 for cathodic protection

<sup>3</sup>May be clad with A97072 for cathodic protection

(cont'd on next page)

**MIL-HDBK-735(MR)****TABLE 2-9. (cont'd)****FERROUS METALS**

Intergranular corrosion has not been reported in cast irons and steels.

**STAINLESS STEELS**

Martensitic Grades. Intergranular corrosion is not a practical problem.

Ferritic Grades. AISI 430 and 446 can be sensitized to corrosion in oxidizing acids.

Newer grades (S44403, 44625, 44026) can be sensitized by the heat of welding if specified limits of carbon and nitrogen are exceeded.

Austenitic grades. Grades of 18-8 variety are subject to intergranular corrosion unless stabilized or extra-low-carbon variety.

Stabilized varieties are subject to highly localized attack known as knife-line attack in the fusion zone.

Special and superaustenitic grades of high nickel content (N08020, 08825, etc.) are more susceptible than 18-8 grades.

**LEAD, TIN, ZINC**

Lead and zinc are reported to experience intergranular corrosion in highly specialized conditions.

**NICKEL ALLOYS**

Commercially pure nickel (Alloy 200, N02200) is subject to intergranular corrosion at high temperatures.

Nickel-copper alloys (Alloy 400, N04400) have suffered intergranular corrosion in certain hydrofluoric acid and chromic acid solutions.

Intergranular corrosion can occur in the nickel-molybdenum alloys (Alloy BB10001) in hot hydrochloric acid and sulfuric acid.

**CHROMIUM-NICKEL ALLOYS**

Alloys of the Inconel variety are subject to intergranular corrosion.

Intermediate super alloys (Alloy 825, N08825; Alloy 20Cb3, N08020; Alloy G, N06007) are stabilized against attack.

Molybdenum-bearing grades are subject unless stabilized (Alloy 625, N06625) or of reduced carbon content (Alloy C276, N10276).

**COBALT ALLOYS**

Intergranular corrosion has not been reported in these alloys.

**REACTIVE METALS**

Not reported in either titanium or tantalum.

Commercial zirconium is subject to corrosion of the weld-heat-affected zone in mineral acids contaminated with oxidation cations such as Fe<sup>3+</sup>.

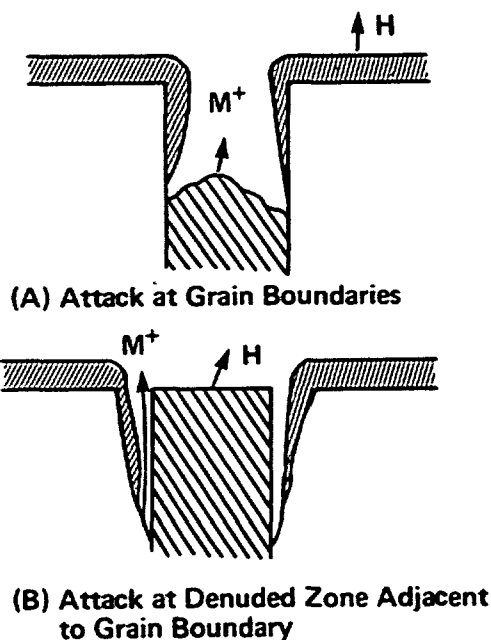
**NOBLE METALS**

Not encountered in silver, gold, or platinum.

\*This table uses the Unified Alloy Numbering System unless otherwise specified.

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From *An Introduction to Metallic Corrosion* by Ulick R. Evans, published by Edward Arnold Publishers. Copyright © 1981. Reprinted with permission.

**Figure 2-32. Galvanic Mechanism of Intergranular Attack (Ref. 14)**

#### 2-2.5.4 Application Constraints and Protection Approaches

Approaches to preventing intergranular corrosion are simple in concept but complex in practice. The approaches include

1. Select materials that are not susceptible to grain boundary depletion, e.g., low-carbon austenitic stainless steel.
2. Select suitable heat treatment for precipitation hardening alloys such as type 7075 aluminum.
3. Avoid specifying heat treatment or welding in the susceptible range.
4. Avoid cold work that can result in increased susceptibility.

Approaches to controlling intergranular corrosion of austenitic stainless steel follow:

1. Employ high-temperature solution heat treatment, commonly called quench annealing or solution quenching. This process consists of heating at 1050° to 1100°C (1920° to 2010°F) followed by water quenching. Most austenitic stainless steels are supplied in this condition. Rapid cooling from the solution temperature is essential. Problems exist in cooling shapes having large cross sections and in quench annealing following welding.

2. Add elements that are strong carbide formers. Columbium (or columbium plus tantalum) and titanium produce the stabilized types AISI 347 and 321 stainless steels, respectively. These elements are added in sufficient

quantity to combine with all the carbon in the steel. However, they may be susceptible to knife-line attack.

3. Lowering the carbon content below 0.03% (AISI type 304L) does not permit sufficient chromium carbide to form to result in susceptible low-chromium alloy adjacent to the grain boundary.

4. The solution to knife-line attack of the stabilized austenitic stainless steels is to heat the structure after welding to 1050°C (1920°F). The rate of cooling from 1050°C (1920°F) is not important.

The problem of exfoliation of aluminum alloy 7075 T6 can be adequately solved in most applications by using alloy 7075 T73. This involves a change in heat treatment and a loss of strength. The T6 temper optimizes strength by causing precipitation along the grain boundaries. "Overaging" to the T73 temper results in a more uniform dispersion of relatively small precipitate particles. This dispersion almost eliminates susceptibility to intergranular corrosion with relatively little loss in strength.

#### 2-2.5.5 Examples

Important examples of intergranular corrosion susceptibility are sensitized austenitic stainless steel and aluminum alloys that derive their strength from the precipitation of copper aluminide ( $\text{CuAl}_2$ ) along slip planes and grain boundaries. Use of high-strength aluminum alloys in Army tactical vehicles is increasing.

#### 2-2.6 SELECTIVE LEACHING

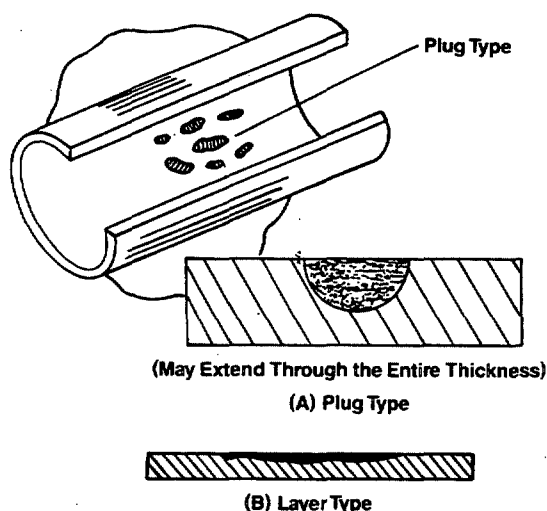
One constituent of an alloy is preferentially removed in selective leaching corrosion. This phenomenon is also called "dealloying" or "parting". Terms are also used that indicate the loss of specific alloying constituents such as "dezincification" to connote the loss of zinc from the original copper-zinc alloy; "destanification", "denickelification", and "dealuminification" are also used. "Graphitic corrosion" is used to describe the dealloying of gray cast iron.

##### 2-2.6.1 Manifestation and Quantification

Dealloying usually results in a color change. However, there is usually no visible evidence of loss of metal such as pits, dimension changes, cracks, or grooves. The surface geometry is unaffected. The fine detail including irregularities or roughness on the original surface remains, but the affected metal becomes lighter and porous. It also becomes brittle and has a very low tensile strength. Detection may be difficult if inspection cannot be readily accomplished.

A dealloying attack that occurs in a local area and proceeds inward rather than along the surface is called plug-type dealloying. Dealloying that proceeds over the whole surface is termed uniform or layer-type dealloying. The types of selective leaching attack are illustrated in Fig. 2-33.

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**Figure 2-33. Selective Leaching Attack**

Selective leaching is frequently misdiagnosed as erosion-corrosion. Selective leaching often occurs on pump housings and impellers made of bronze, brass, or gray cast iron from which the dealloyed corrosion product is swept away by high fluid velocities. Selective leaching has been observed in aluminum-, iron-, copper-, nickel-, and cobalt-base alloys as well as in other alloys. It is a significant engineering problem in applications of copper-base alloys and in cast iron. Generally the less corrosion-resistant element (anode) is removed and the cathodic matrix is left behind.

#### 2-2.6.2 Conducive Conditions

Brasses that contain 15% zinc or less (red brasses) are usually immune to dezincification attack in aqueous or atmospheric environments. Dezincification is more common in brasses that contain more than 20% zinc (yellow brasses). However, yellow brasses having up to 37% zinc can be made resistant to moderately corrosive environments, such as drinking and cooling water, if the alloys contain tin plus arsenic (Admiralty B alloy), antimony (Admiralty C alloy), or phosphorus (Admiralty D alloy).

Brasses are susceptible to selective leaching in soft water. High carbon dioxide concentration increases susceptibility. Susceptibility in water is also increased by high temperature, high chloride content, high flow velocity, crevices, and deposits such as sand on the metal surface (Ref. 6).

Phosphor-tin bronzes have undergone destanification in aggressive chemical environments. Aluminum bronzes (copper-aluminum alloys) are sometimes subject to dealuminification. Silicon bronzes have undergone desilicification in isolated cases involving high-temperature steam and acidic species (Ref. 6).

Graphitic corrosion, or "graphitization", is a form of selective leaching. Gray cast iron is corroded, and the residual graphite grain boundary precipitates are left. It is

usually plug-type corrosion proceeding uniformly inward from the surface, and it leaves a porous matrix of graphite. The graphite second phase in gray cast iron frequently forms long, almost continuous, intergranular strings between the iron-rich ferrite matrix grains. White cast iron does not have this structure and is more resistant to graphitization. Graphitization occurs in salt waters, acidic mine waters, dilute acids, and soils, especially in those containing sulfates and sulfate-reducing bacteria (Ref. 15).

#### 2-2.6.3 Mechanism

The dealloying mechanism may consist of the following:

1. Selective removal of one or more alloy constituents, which leaves a residual substrate
2. The whole alloy can dissolve with one or more constituents redeposited.
3. Both of the above can occur simultaneously.

For example, the  $\alpha/\beta$  brasses, which contain the relatively zinc-rich  $\beta$  phase (40% zinc), are prone to dezincification in near boiling, soft domestic water supplies containing chloride ions. Zinc atoms in this  $\beta$  phase are leached out preferentially if the oxygen potential of the water is low. However, in aerated waters, the process proceeds through two stages: first the  $\beta$  phase dissolves uniformly, then porous copper redeposits.

#### 2-2.6.4 Application Constraints and Protection Approaches

Control of dealloying corrosion is normally achieved by using an alloy that is more resistant to this kind of corrosion. For example, brasses containing more than 85% copper are less susceptible than those containing more than 15% zinc. Gray cast irons can be replaced with white cast iron, malleable or nodular "ductile" cast irons, and nickel, chromium, or silicon cast irons to avoid graphitization.

Reducing the aggressiveness of the corroding environment may be a feasible alternative in some situations. For example, dezincification can be reduced by deoxygenation.

#### 2-2.6.5 Examples

Dealloying attack can be expected on brass valves and fittings exposed to seawater and gray cast iron exposed to acidic chemical plant wastewater.

#### 2-2.7 EROSION-CORROSION

Erosion-corrosion is a general term that refers to a corrosion process enhanced by the action of flowing fluids. The process can also be characterized by whether the fluid contains solid particles, is in the form of impinging droplets, or is undergoing cavitation. Cavitation is the formation and sudden collapse of vapor bubbles in a liquid.

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## 2-2.7.1 Manifestation and Quantification

Erosion-corrosion can result in general corrosion that occurs at a higher rate than would be expected under stagnant conditions. In this case the measure of erosion-corrosion would be the rate of surface waste or the rate of penetration. The more usual effect of erosion-corrosion, however, is localized attack, which can appear as grooves, gullies, waves, rounded holes, etc., and usually exhibits a directional pattern that correlates with the direction of flow. Erosion-corrosion is illustrated in Fig. 2-34.

The appearance of cavitation damage is similar to pitting. However, the pitted areas are closely spaced and

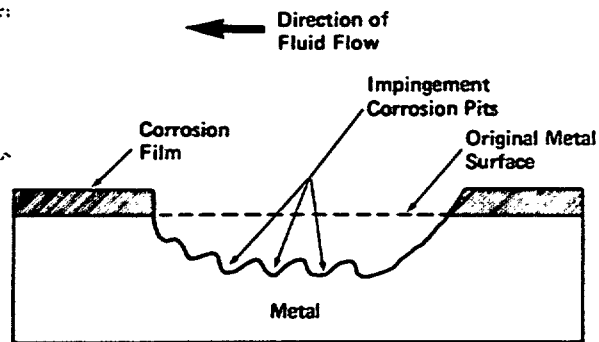


Figure 2-34. Erosion-Corrosion

the surface is usually considerably roughened. Severe cavitation damage can completely remove sections of metal. Cavitation damage that results from fluid movement relative to the metal surface can usually be correlated with the direction of flow. Cavitation-enhanced corrosion is illustrated in Fig. 2-35.

## 2-2.7.2 Conducive Conditions

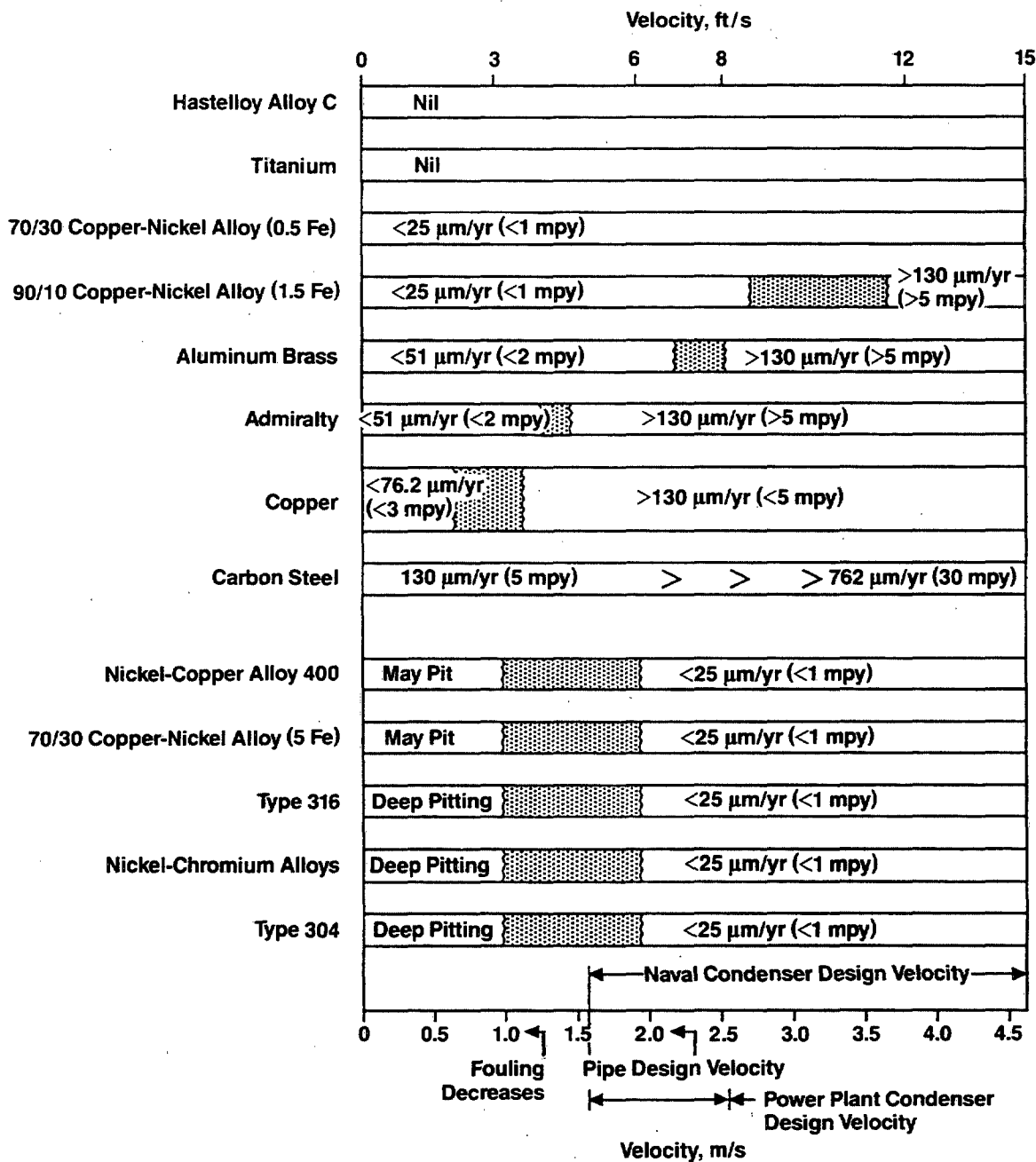
A condition conducive to erosion-corrosion is the flow of corrosive fluids (gas or liquid) relative to a metal surface. The rate of corrosion depends upon the flow rate of the fluid. Turbulent flow results in much higher corrosion rates than laminar flow. Hard particles entrained in the flowing fluid can enhance erosion-corrosion. Cavitation damage is caused by flow discontinuities that result in the formation and subsequent collapse of vapor bubbles on a metal surface. High-velocity drop impingement, such as raindrops on a helicopter rotor, can also result in rapid surface damage. Fig. 2-36 indicates the effect of velocity on the corrosion rate of several metals in seawater. Table 2-10 gives the relative resistance to cavitation of several materials. Fig. 2-37 shows the erosion-corrosion of several metals in seawater at speeds that can be achieved by watercraft hydrofoils. Fig. 2-38 shows the cavitation rates for several of the same materials in seawater.



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Figure 2-35. Cavitation-Enhanced Corrosion of Pump Impeller (Ref. 6)

**MIL-HDBK-735(MR)**



**(A) Seawater Velocity (Pipe and Tube Ranges)**

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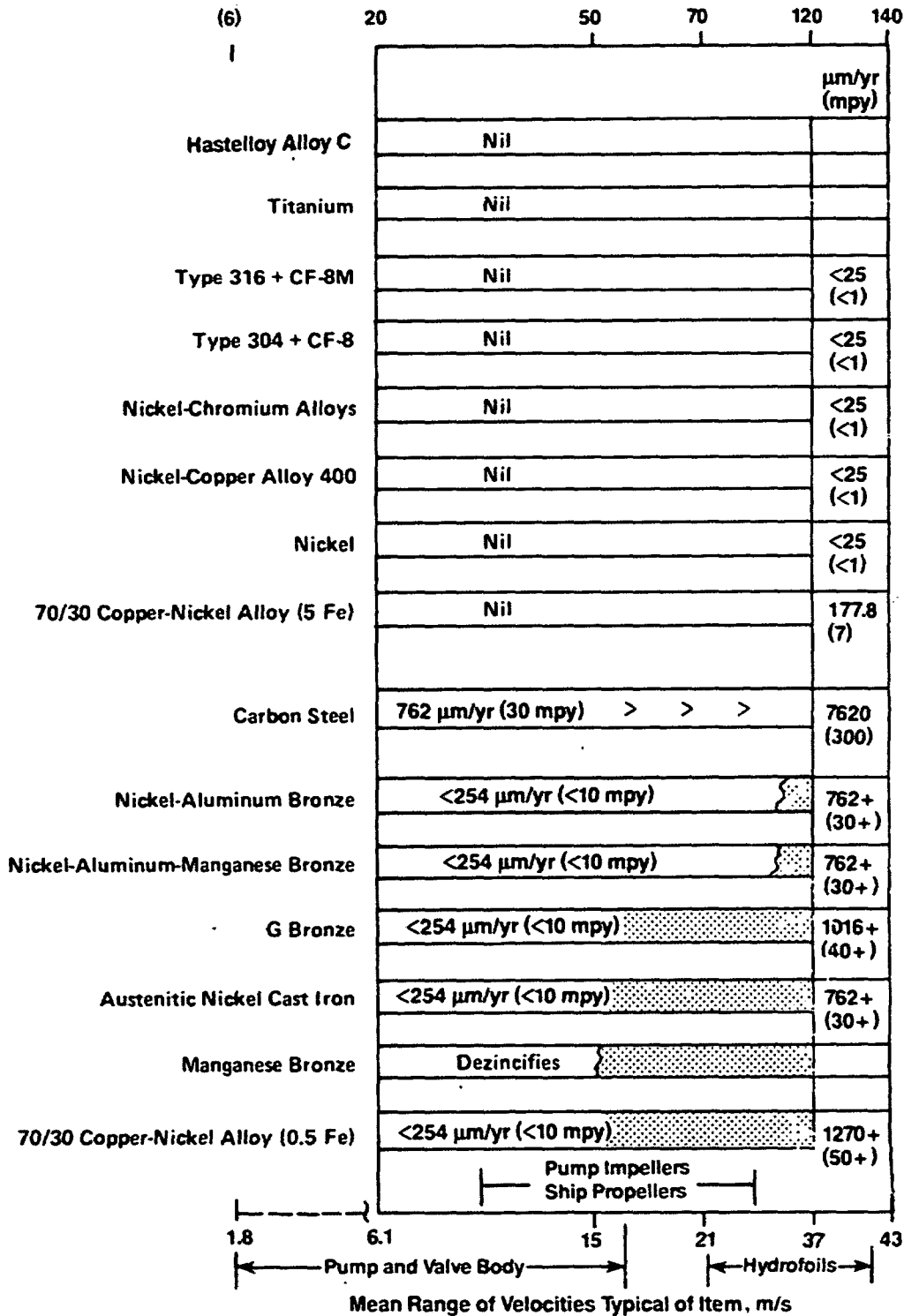
**Figure 2-36. The Effect of Velocity on the Corrosion Rate of Several Metals in Seawater (Ref. 16)**

(cont'd on next page)



**MIL-HDBK-735(MR)**

Mean Range of Velocities Typical of Item, ft/s



**(B) Seawater Velocity (Pump-to-Hydrofoil Ranges)**

**Figure 2-36. (cont'd)**

**MIL-HDBK-735(MR)****TABLE 2-10. CAVITATION RESISTANCE (Ref. 16)**

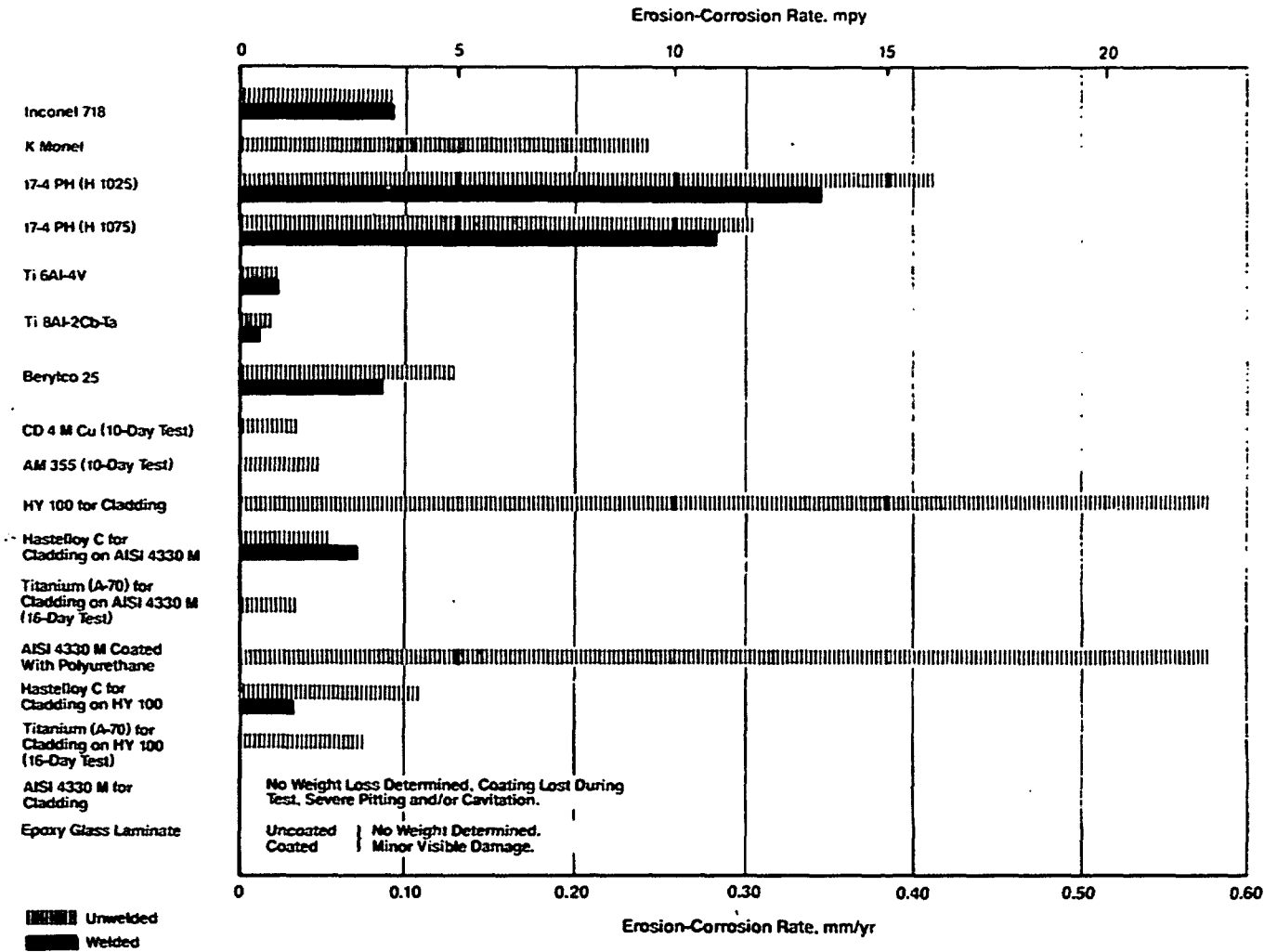
| RELATIVE CAVITATION RESISTANCE   |    |  |
|----------------------------------|----|--|
| BASED ON FIELD EXPERIENCE        |    | BASED ON LABORATORY TEST                   |
| STELLITE*                        | 1  | STELLITE*                                  |
| 17-7 Cr-Ni stainless steel weld  | 2  | Two layers 17-7 Cr-Ni stainless steel weld |
| 18-8 Cr-Ni stainless steel weld  | 3  | 18-8 Cr-Ni stainless steel weld            |
| AMPCO** No. 10 weld              | 4  | AMPCO** No. 10 weld                        |
| 25-20 Cr-Ni weld                 | 5  | Cast AMPCO** No. 18 bronze                 |
| Eutectic-Xyron 2-24 weld         | 6  | Nickel-aluminum bronze                     |
| AMPCO** bronze castings          | 7  | 18-8 Cr-Ni cast stainless                  |
| 18-8 Cr-Ni cast stainless        | 8  | 13% Cr, cast stainless                     |
| Nickel-aluminum bronze, cast     | 9  | Manganese bronze, cast                     |
| 13% Cr, cast stainless           | 10 | Cast steel                                 |
| Manganese bronze, cast           | 11 | Bronze                                     |
| 18-8 stainless spray metallizing | 12 | Cast iron                                  |
| Cast steel                       | 13 | Sprayed stainless 18-8 Cr Ni               |
| Bronze                           | 14 | Rubber                                     |
| Rubber                           | 15 | Aluminum                                   |
| Cast iron                        | 16 |  |
| Aluminum                         | 17 |  |

\*Trademark of Cabot Corporation

\*\*Trademark of Ampco Metals, Inc.

From "Resistance of Various Materials to Cavitation Damage" by W. M. Rheingans, published in *Report of the 1956 Cavitation Symposium*. Copyright © 1957. Reprinted with permission from The American Society of Mechanical Engineers.

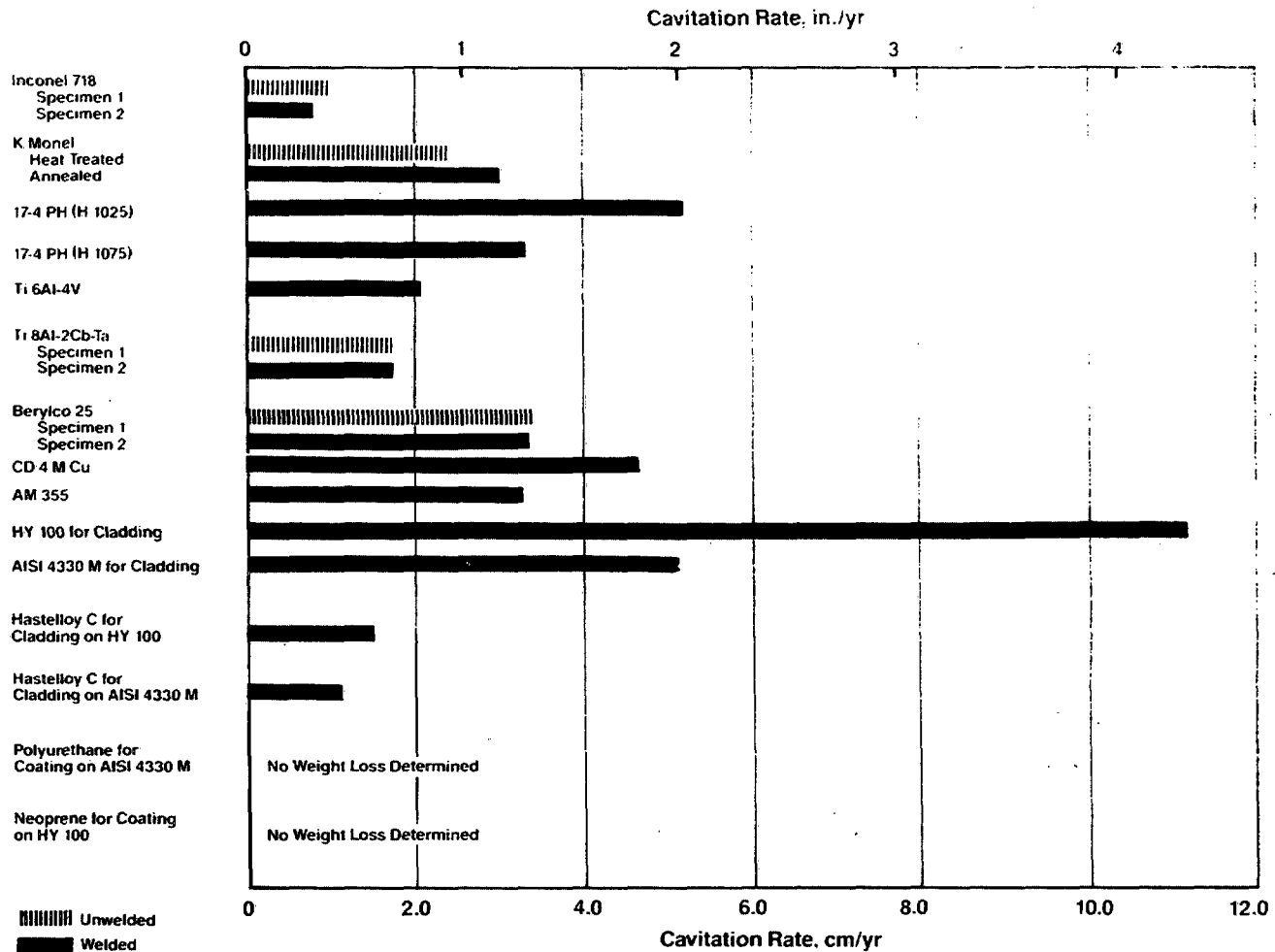
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**Figure 2-37. Rates for Jet Erosion-Corrosion in Seawater. Exposure 30 Days at 90 Knots (Ref. 17)**

## MIL-HDBK-735(MR)



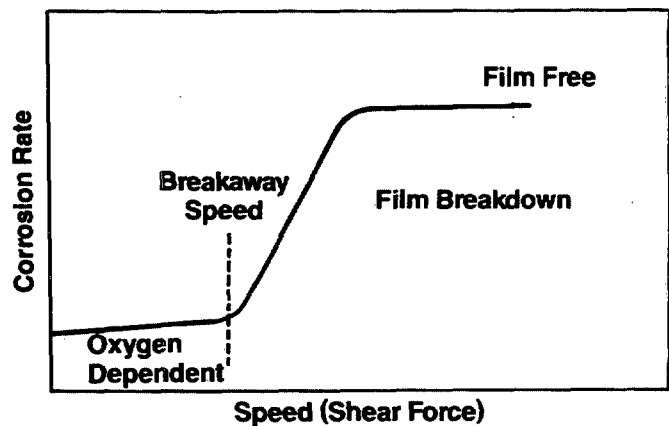
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**Figure 2-38. Cavitation Rates in Seawater, Double Amplitude  $25.4 \mu\text{m}$  (0.001 in.), Frequency 22,000 cycles per second (Ref. 17)**

### 2-2.7.3 Mechanism

Erosion-corrosion implies that the fluid medium is potentially corrosive to the metal. Erosion facilitates the corrosion process. This fact distinguishes erosion-corrosion from pure erosion or mechanical wear. Erosion-corrosion influences the rate of corrosion by changing the conditions of local cell action. The corrosion process is accelerated if the fluid speed is sufficient to remove weakly adhered corrosion products from the surface. Removal of these products reduces their polarizing or inhibitive effect. This phenomenon is illustrated in Fig. 2-39. At the breakaway speed the fluid begins to remove the corrosion film and the corrosion rate increases. A steady corrosion rate is achieved at the speed at which the film is completely removed. Fluid flow also maintains a uniform concentration of corrodent at the metal surfaces.

Impingement of suspended hard particles can accelerate the damage to the protective film and can cause



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**Figure 2-39. Corrosion Rate of Copper Alloys as Function of Flow Speed (Ref. 6)**

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mechanical damage to the underlying metal. Impingement of droplets on a metal surface can be viewed in terms of a similar model that combines corrosion and wear.

Fig. 2-40 illustrates the process of cavitation-enhanced corrosion. Rapidly collapsing vapor bubbles, such as those produced by cavitation, can produce shock waves with relatively high pressures. The shock wave destroys the corrosion film beneath it. The newly exposed metal surface corrodes and the film reforms. A new cavitation bubble forms and collapses at the same spot. The process repeats itself and deep holes or pits can result. An imploding cavitation bubble has sufficient force to tear metal particles from the surface; therefore, cavitation combines chemical and mechanical action (Ref. 1).

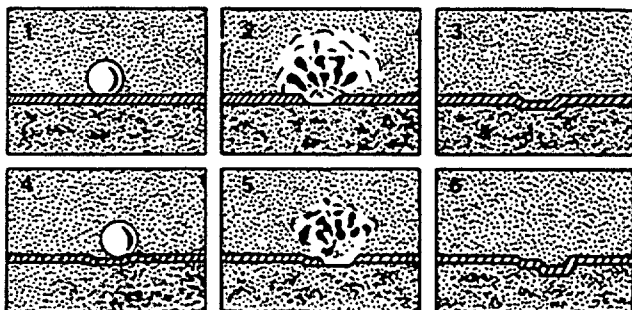
### 2-2.7.4 Application Constraints and Protection Approaches

Several methods for preventing or minimizing damage resulting from erosion-corrosion are available (Ref. 9). They include

1. *Material selection.* Select materials with better resistance to erosion-corrosion.

2. *Design considerations.* Streamline the flow; avoid designs that create turbulence. Minimize abrupt changes in flow direction. Introduce smooth aerodynamic or hydrodynamic flow channels; avoid roughly textured surfaces. Carefully align pipe sections. Avoid flow obstructions in design or obstructions that can arise under operations, increase the thickness of material in vulnerable areas, install renewable impingement plates or baffles, and design for easy repair by using interchangeable parts.

3. *Alteration of environment.* Decrease fluid stream speed to achieve laminar flow, regulate the concentration of dissolved oxygen in the environment to achieve optimal film-forming characteristics, provide filters for



Note: Numbers indicate sequence of events.

From *Corrosion Engineering* by Mars G. Fontana and Norbert D. Greene, published by McGraw-Hill Publishing Company. Copyright © 1978 by McGraw-Hill Publishing Company. Reprinted with permission.

**Figure 2-40. Process of Cavitation-Enhanced Corrosion (Ref. 1)**

removal of suspended solids, and provide condensed moisture traps in vapor lines.

4. *Specification of suitable coatings or linings.* Use of hard-facing may be helpful in some situations and resilient barriers may be helpful in others, e.g., cavitation.

5. *Cathodic protection.* Provide cathodic protection whenever possible.

### 2.2.7.5 Examples

Helicopter rotor blades are subject to impingement attack by water droplets, dust, and sand. Gas turbine blades and vanes are damaged by erosion-corrosion. Erosion-corrosion is a component of the process of gun tube wear.

The coolant side of diesel engine cylinder walls is subject to cavitation damage. The hydrofoils and driving propellers of watercraft can undergo cavitation.

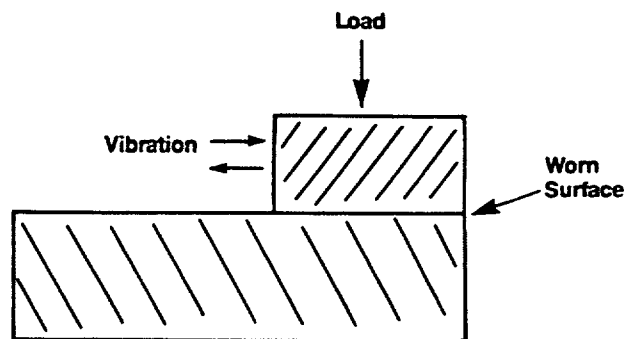
## 2-2.8 FRETTING CORROSION

Fretting corrosion is defined as metal deterioration caused by repetitive slippage at the interface between two surfaces in contact.

### 2-2.8.1 Manifestation and Quantification

Fretting corrosion results in wear between two mating metal surfaces and in the generation of oxidized wear products. Conditions required for fretting are illustrated in Fig. 2-41. The surface wear appears as depressions, pits, or grooves. Fretting is usually accompanied by the generation of visible amounts of corrosion products. Fretting on cast iron and steel surfaces produces reddish-brown iron oxides. Local attack may initiate fatigue cracks, especially where stresses concentrate and mating areas are pitted. Wearing away of protective surfaces can initiate galvanic or concentration cell corrosion. In the absence of oxygen and moisture, fretting results in less damage and the products are different.

Because the effects are localized, fretting may be characterized by descriptions of the surface effects and



**Figure 2-41. Fretting Corrosion**

**MIL-HDBK-735(MR)**

the corrosion products produced. This characterization could include a geometric description of the affected area and the specific wear patterns produced. The more significant indications of fretting, however, are degradation of functional capability such as loosening of hubs on shafts, loosening of bolted or riveted parts, seizing and galling of mating parts, loss of dimensional tolerances, fouling of precision mechanisms by debris, destruction of bearing surfaces, and accelerated fatigue when both fretting and fatigue load patterns are present. The fretting resistance of various materials is shown in Table 2-11.

**2-2.8.2 Conducive Conditions**

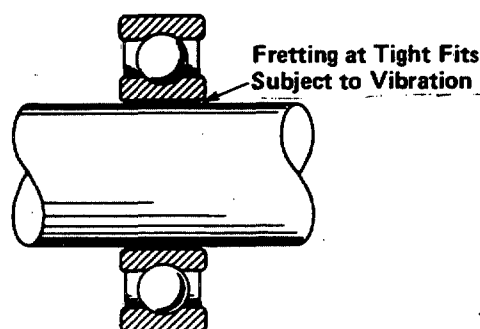
Fretting between two metal surfaces occurs under the following conditions (Ref. 1):

1. A load is transmitted across the interface.
2. There is repeated relative motion between the two surfaces. The necessary relative motion is extremely small. Fretting does not occur on surfaces in continuous motion.
3. Slippage or deformation must be produced on the surfaces.

Fig. 2-42 is an example of a typical fretting corrosion condition.

**2-2.8.3 Mechanism**

The wear process in fretting is not well understood. The debris produced can be either an oxide, if oxidation conditions exist, or very fine metal particles. Fretting has been observed on almost every kind of surface including noble metals, mica, glass, and ruby. Two different mechanisms have been used to describe the fretting



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**Figure 2-42. Typical Fretting Corrosion Condition (Ref. 1)**

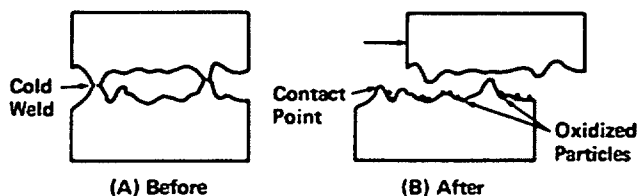
process. In one proposed explanation, fretting is due to cold-welding of microscopic high spots on the two surfaces. Relative motion causes these welded high spots to rupture. It also causes the high spots, or asperities, to plow into the opposing surface. Both actions dislodge metal particles, which eventually are partly or completely converted into oxides. This fretting corrosion mechanism is illustrated in Fig. 2-43. In the other mechanism, abrasion due to the relative motion of the surfaces removes the protective surface film. The fresh metal surface then oxidizes. The corrosion products formed are also removed from the surface by the abrasive action.

**TABLE 2-11. FRETTING RESISTANCE OF VARIOUS MATERIAL SURFACE COMBINATIONS (Ref. 18)**

| POOR   | AVERAGE                                   | GOOD  |
|--|---|---|
| Aluminum on cast iron                          | Cast iron on cast iron                    | Laminated plastic on gold plate                         |
| Aluminum on stainless steel                    | Copper on cast iron                       | Hard tool steel on tool steel                           |
| Magnesium on cast iron                         | Brass on cast iron                        | Cold-rolled steel on cold-rolled steel                  |
| Cast iron on chrome plate                      | Zinc on cast iron                         | Cast iron on cast iron with phosphate coating           |
| Laminated plastic on cast iron                 | Cast iron on silver plate                 | Cast iron on cast iron with coating of rubber cement    |
| Bakelite on cast iron                          | Cast iron on copper plate                 | Cast iron on cast iron with coating of tungsten sulfide |
| Hard tool steel on stainless                   | Cast iron on amalgamated copper plate     | Cast iron on cast iron with rubber gasket               |
| Chrome plate on chrome plate                   | Cast iron on cast iron with rough surface | Cast iron on cast iron with Molykote lubricant          |
| Cast iron on tin plate                         | Magnesium on copper plate                 | Cast iron on stainless with Molykote lubricant          |
| Cast iron on cast iron with coating of shellac | Zirconium on zirconium                    |   |

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**Figure 2-43. Fretting Corrosion Action (Ref. 1)**

#### 2-2.8.4 Application Constraints and Protection Approaches

There are three basic approaches to preventing or mitigating the effect of fretting. They are (Refs. 1 and 9)

1. Prevent relative motion between the two surfaces:
  - a. Avoid a structural design that transmits vibration to the surfaces.
  - b. Increase the friction of the surfaces by roughening them.
  - c. Increase the load to stop motion.
  - d. Isolate moving components from stationary ones.
2. Allow the relative motion, but prevent or reduce the fretting damage:
  - a. Select materials that are not susceptible to fretting. Hard materials are more resistant than soft ones. Increasing surface hardness by shot peening or cold-working increases fretting resistance.
  - b. Introduce barriers between the metal surfaces that allow slippage.
  - c. Select a suitable lubricant, specify protective coating of a porous (lubricant-absorbing) material, improve lubrication design, and arrange better accessibility for lubrication.
  - d. Decrease the load at the bearing surface. This method is not always successful, because very small loads are capable of producing damage.
3. Prevent contamination by oxidized wear particles:
  - a. Arrange the flushing of debris by the motion of the lubricant.
  - b. Design for exclusion of oxygen on the bearing surface.

#### 2-2.8.5 Examples

Fretting can result from the relative motion of load-bearing surfaces during transportation. Some examples are

1. Fretting between packing crates and enclosed metal parts
2. Fretting in close tolerance parts such as bearings

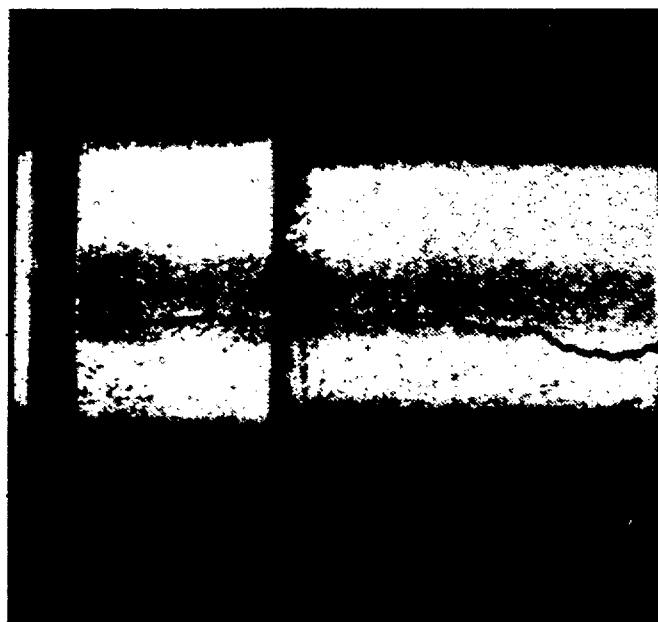
3. Fretting between layers of sheet steel in coils or in stacks.

### 2-2.9 STRESS-CORROSION CRACKING

Stress-corrosion cracking is the apparently spontaneous failure of metals that results from the combined actions of a corrosive environment and tensile stress. The tensile stress may be applied or may be the result of thermal treatment and mechanical working of the metal.

#### 2-2.9.1 Manifestation and Quantification

An example of a stress-corrosion crack is shown in Fig. 2-44. This crack on a fitting of high-strength, precipitation-hardening stainless steel, designed Unified Numbering Standard (UNS) S35500, occurred as a result of stresses imposed by assembly. The fitting was then exposed to a marine environment. A ductile metal will deform under tensile (stretching) forces without fracture. The metal is extended in length and reduced in cross section as it is drawn out. A brittle metal, however, breaks rather than deforms under tensile load. These are, of course, relative terms, and any metal reaches a limit at which it will break rather than be drawn out farther. The tensile load at which a metal begins to deform is the yield strength, and the tensile load at fracture is the ultimate strength. Generally, because they are brittle, stress-corrosion cracks occur before the onset of general yielding. Fracture occurs on a plane that is nominally perpendicular to the tensile axis. Stress-corrosion cracking is catastrophic because it occurs without a readily apparent warning.



**Figure 2-44. Stress-Corrosion Crack (Ref. 19)**

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The measure of practical interest in stress-corrosion cracking is "How long will this component or that structure last?" The answer depends upon the sequence of events involved in stress-corrosion cracking. Fig. 2-45 illustrates this sequence. For a specimen that initially is smooth, the total time to failure usually represents the sum of the times for surface film breakdown, pit initiation and growth, and stress-corrosion crack initiation and

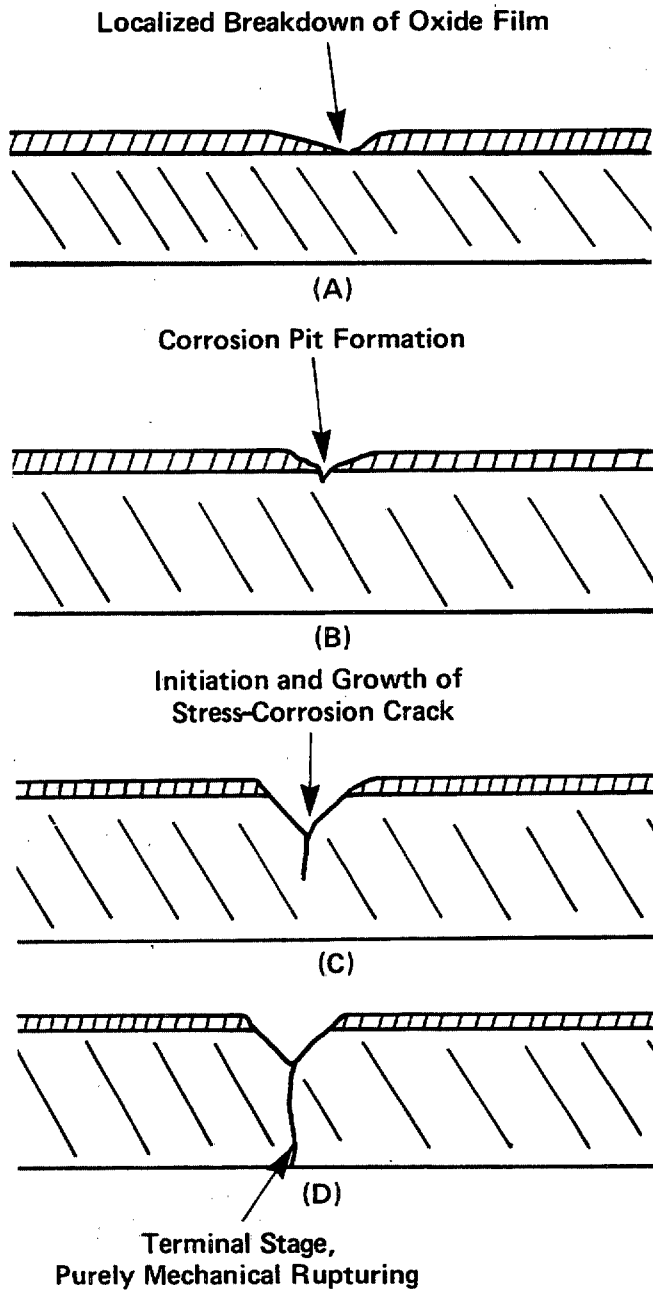


Figure 2-45. Sequence of Events in Stress-Corrosion Cracking (Ref. 19)

growth to an arbitrary crack size, or to failure of the specimen. When the time to failure is plotted as a function of initial stress, it typically shows a horizontal asymptote. The implication of the asymptote is that there is an induction period before failure at a given stress level and a given stress level below which failure will not occur. The existence of a horizontal asymptote-line, and therefore a threshold stress, is not always easily provable. The stress-time relationship is illustrated in Fig. 2-46.

The existence of a crack-like surface in a metal specimen defect completely alters its response to stress-corrosion cracking. A major portion of the service life of a component is determined by how rapidly stress-corrosion cracks propagate from some critically sized surface flaw.

The approach of linear elastic fracture mechanics has been applied to give an indication of the depth of such critical flaws (Ref. 19). When a piece of metal containing a crack is stressed so that the crack opens and extends, the nominal stress is intensified near the crack tip. This stress intensity is characterized as  $K_I$ , which has units of  $\text{MPa}\cdot\sqrt{\text{m}}$  or  $\text{ksi}\cdot\sqrt{\text{in.}}$ . Linear elastic fracture mechanics relates stress intensity to the crack geometry, the nominal stress, and the yield strength of the metal. If the assumptions of a long, thin flaw and the existence of yield point stresses are made, the critical flaw depth for propagating stress-corrosion cracking  $a_c^{sc}$  is given by

$$a_c^{sc} = 0.2 \left( \frac{K_{Isc}}{\sigma_y} \right)^2, \text{ m (in.)} \quad (2-17)$$

where

$a_c^{sc}$  = critical flaw depth, m(in.)

$K_{Isc}$  = critical stress intensity,  $\text{MPa}\cdot\sqrt{\text{m}}$   
( $\text{ksi}\cdot\sqrt{\text{in.}}$ )

$\sigma_y$  = yield strength, MPa (ksi).

Studies of the growth rate of stress-corrosion cracking as a function of stress intensity  $K_I$  indicate that there is a threshold intensity for propagation of stress-corrosion cracking  $K_{Isc}$ . Fig. 2-47 illustrates the general relationship

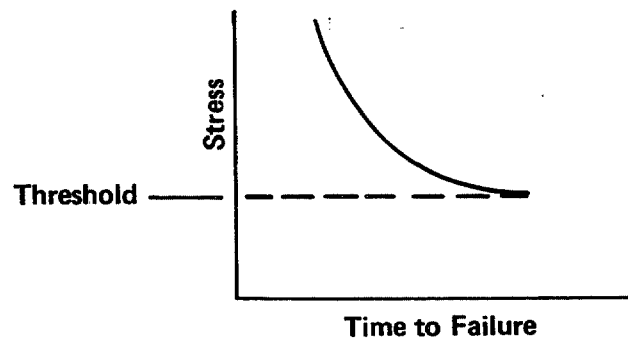
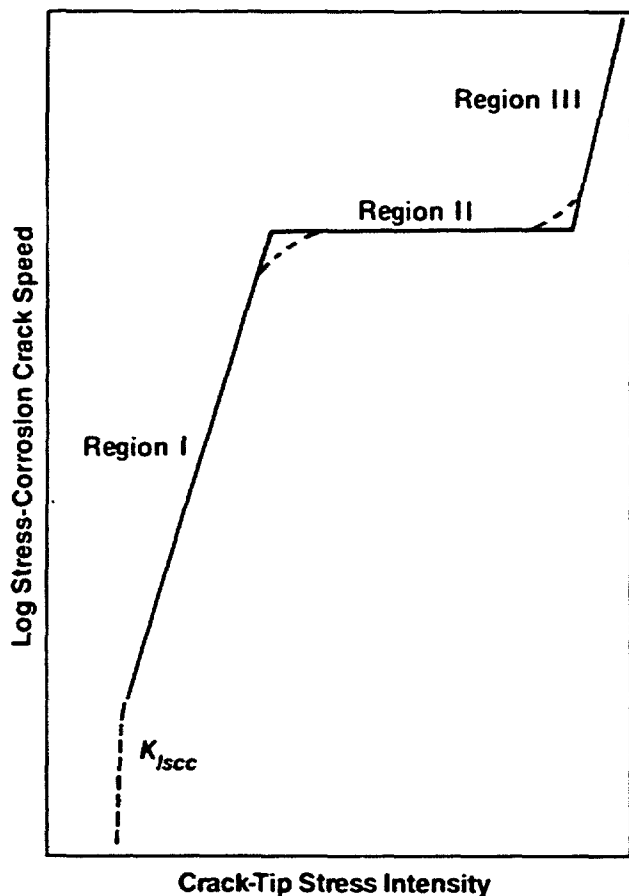


Figure 2-46. Representation of Relationship Between Stress and Time to Failure for Smooth Specimens (Ref. 19)



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**Figure 2-47. Effect of Stress Intensity of the Rate of Propagation of a Stress-Corrosion Crack (Ref. 19)**

between the stress intensity at the crack tip and the rate of stress-corrosion cracking propagation.

Eq. 2-17 can be plotted for various values of  $a_c^{sc}$ , as shown in Fig. 2-48. Point X on the diagram represents a safe  $K_{Isc}$  for flaws no deeper than 0.25 mm (0.01 in.). However, stress-corrosion cracking may occur if flaws are as deep as 2.5 mm (0.1 in.). The plot can be used in various ways to assess the stress-corrosion characteristics of a cracked specimen:

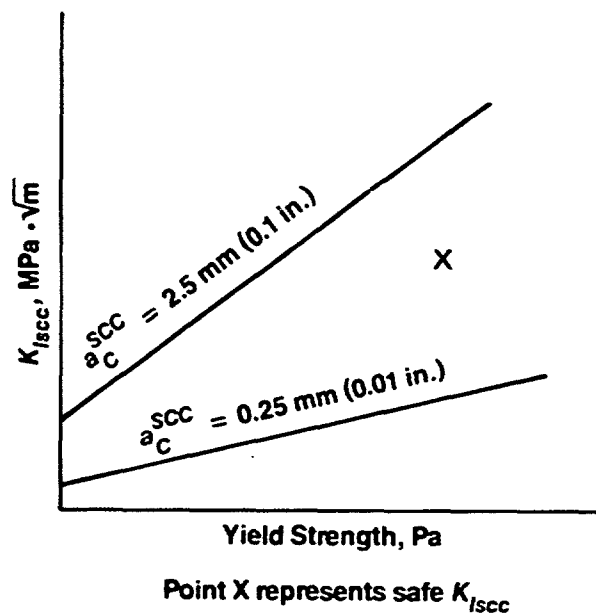
1. The  $K_{Isc}$  of a given material can be evaluated to determine whether the corresponding surface defect size is greater or less than a critical crack size.

2. The fact that a certain minimum crack size cannot be ruled out would specify the  $K_{Isc}$  that a suitable material must have.

3.  $K_{Isc}$  can be viewed as linearly proportional to the load-carrying capability of a component containing some standard-sized flaw.

### 2-2.9.2 Conductive Conditions

Sustained tensile stress is a principal requirement for stress-corrosion cracking. The effective tensile stress may



**Figure 2-48. Threshold Stress Intensity as a Function of Yield Strength for Two Values of Critical Flaw Depth (Ref. 19)**

be a vector sum of the tensile components of the following:

1. Working or applied stress
2. Assembly or fit-up stress, for example, tensile stress resulting from interference fits
3. Residual stress from cold work, such as spinning, drawing, sinking, roll forming, or stamping.

The dangerous stress levels may be only a small fraction of the yield strength. Specifying thicker sections is seldom effective in reducing susceptibility because this measure alone does not reduce residual or assembly stresses. Castings, however, usually have reduced residual stresses compared to those of unannealed wrought products.

Stress-corrosion cracking is selective to specific alloy-environment pairs, as given in Table 2-12. The essential chemical species in the environment may not be needed in either high concentrations or large amounts. Also the most severe alloy-environment conditions tend to be those in which the alloy is almost, but not quite, inert to the environment. Critical chemical species can be identified for stress-corrosion cracking. For example, chloride ion is a critical species for austenitic stainless steel, ammonia is for copper alloys, caustic is for carbon steels, and hydrogen is for high-strength steels. Elimination of critical species from the environment can control stress-corrosion cracking.

Alloy susceptibility varies with respect to the tensile stress orientation, which is relative to the grain orientation of rolled, extruded, forged, or other wrought conditions. This is illustrated in Fig. 2-49. The American Society for Testing and Materials (ASTM) has developed a code for

**MIL-HDBK-735(MR)****TABLE 2-12. ENVIRONMENTS CONDUCTIVE TO STRESS-CORROSION CRACKING (Ref. 9)**

| ALLOY   | ENVIRONMENT   |
|---|---|
| Aluminum (most susceptible are copper-bearing (2XXX), magnesium-bearing (5XXX), and zinc-bearing (7XXX) alloys) | Water and steam; NaCl, including sea atmospheres and seawaters; air; water vapor  |
| Copper (the higher the percentage zinc, the higher the susceptibility of the brasses)                           | Tropical atmospheres; mercury; HgNO <sub>3</sub> ; bromides; ammonia; ammoniated organics   |
| Aluminum bronzes  | Water and steam; H <sub>2</sub> SO <sub>4</sub> ; caustics  |
| Austenitic stainless steels   | Chlorides, including FeCl <sub>2</sub> , FeCl <sub>3</sub> , NaCl; sea environments; H <sub>2</sub> SO <sub>4</sub> ; fluorides; condensing steam from chloride waters  |
| Ferritic stainless steels   | Chlorides, including NaCl; fluorides; bromides, iodides; caustics; nitrates; water; steam   |
| Carbon and low alloy steels   | HCl; caustics; nitrates; HNO <sub>3</sub> ; HCN; molten zinc and Na-Pb alloys; H <sub>2</sub> S; H <sub>2</sub> SO <sub>4</sub> -HNO <sub>3</sub> ; H <sub>2</sub> SO <sub>4</sub> ; seawater                                   |
| High-strength alloy steels (yield strength 1240 MPa (180 ksi) plus)   | Sea and industrial environments   |
| Magnesium   | NaCl, including sea environments; water and steam; caustics; N <sub>2</sub> O <sub>4</sub> ; rural and coastal atmosphere; distilled water  |
| Lead  | Lead acetate solutions  |
| Nickel  | Bromides; caustics; H <sub>2</sub> SO <sub>4</sub>  |
| Monel   | Fused caustic soda; hydrochloric and hydrofluoric acids   |
| Inconel   | Caustic soda solutions; high-purity water with few ppm oxygen   |
| Titanium  | Sea environments; NaCl in environments 288° C (550° F); mercury; molten cadmium; silver and AgCl; methanols with halides; fuming red HNO <sub>3</sub> ; N <sub>2</sub> O <sub>4</sub> ; chlorinated or fluorinated hydrocarbons |

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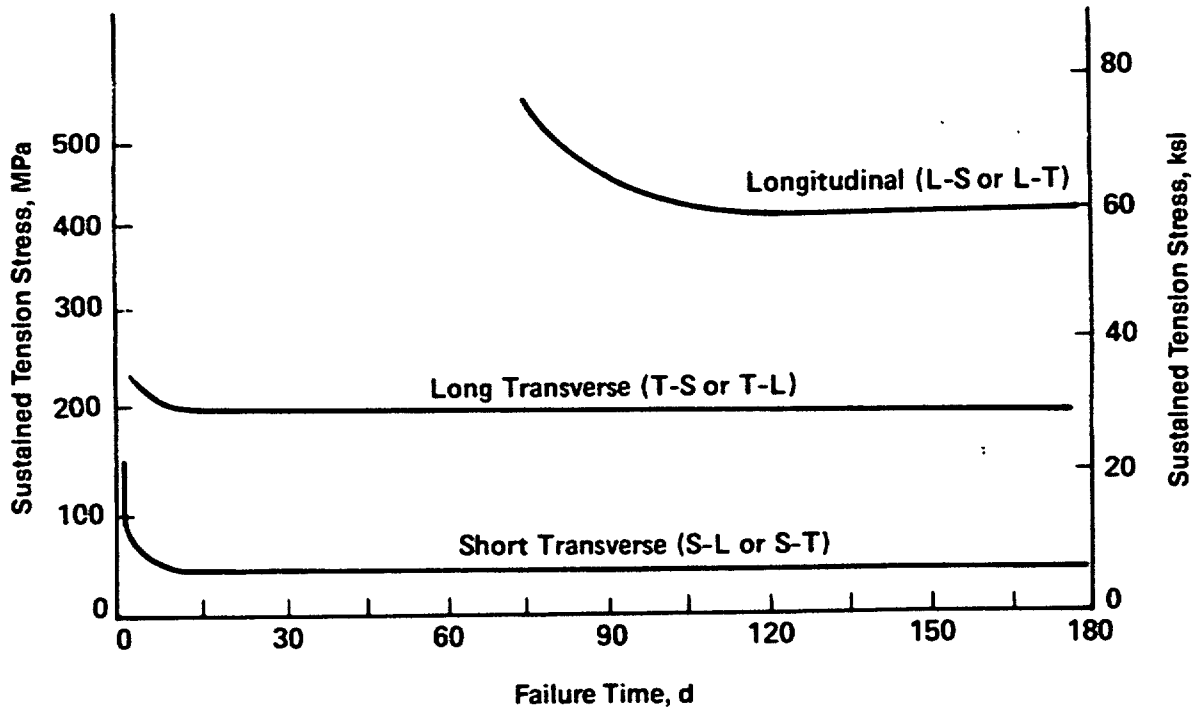


Figure 2-49. Effect of Orientation of Aluminum Alloy 7075-T6 Extruded Section on Resistance to Stress-Corrosion Cracking (Ref. 19)

describing both the orientation of the fracture plane with respect to grain texture and the direction of the propagation of cracking on that plane. This code employs two letters: The first indicates the stress axis, and the second indicates the direction of crack propagation. For long plates the letters are L for longitudinal, S for short transverse, and T for long transverse, as shown in Fig. 2-50. For an extruded or drawn cylinder C refers to

circumferential and R refers to radial orientations, as shown in Fig. 2-51. The grain orientation is the important consideration, not the product shape. Also the external shape of complicated forgings may give no indication of the internal grain texture.

Almost all aluminum alloy service failures involve the short transverse properties, and the fractures would be designated S-L or S-T. (Refer to Fig. 2-50.) Machining wrought aluminum alloy shapes can expose the vulnerable short transverse texture, as illustrated in Fig. 2-52. For example, machining off the forging lines may improve the

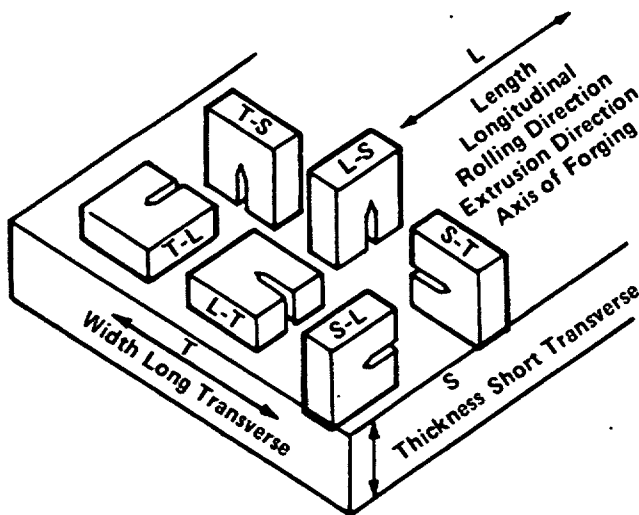


Figure 2-50. Crack Plane Orientation for Rolled Plate (Ref. 19)

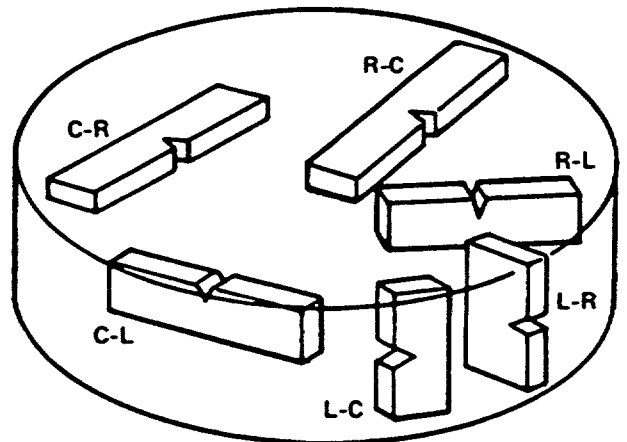
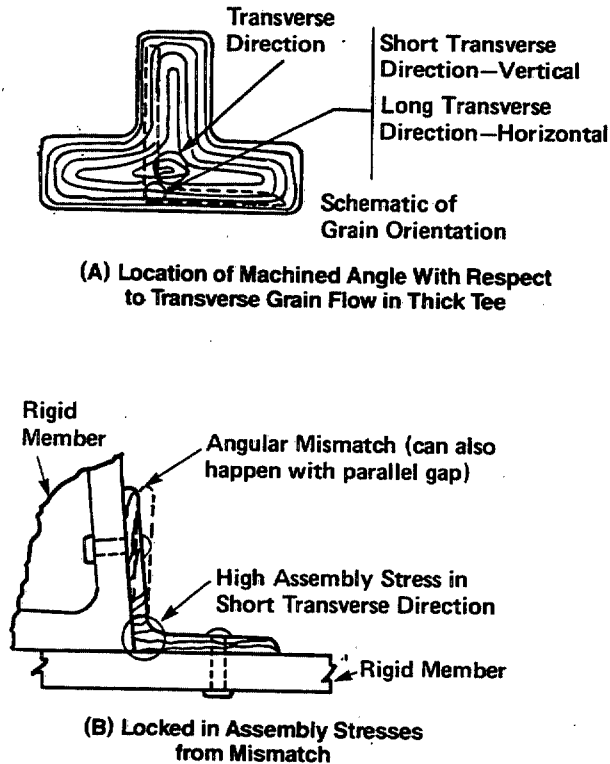


Figure 2-51. Crack Plane Orientation for Drawn Bars (Ref. 19)

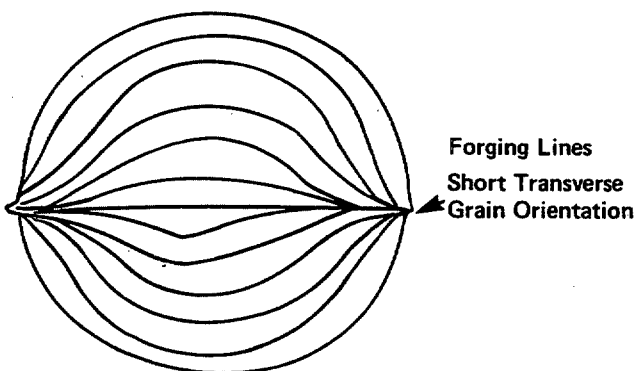
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**Figure 2-52. Example of Generating High Sustained Stress Across the Short Transverse Direction (Ref. 19)**

appearance, but it also exposes the vulnerable grain texture, as illustrated in Fig. 2-53. This figure represents the grain flow in the cross section of a forged bar. The forging process leaves surface ridges that run the length of the bar. Machining off the ridges to produce a uniform surface exposes the short transverse grain orientation.

High-strength aluminum alloys are strengthened by age-hardening or precipitation-hardening heat treatments. First, the alloy is heated to dissolve one or more elements. It is then rapidly cooled so that these solute



**Figure 2-53. Orientation of Grain Structure in Forging**

elements are retained in solid solution. Aging the alloy at room temperature or above, a process called precipitation heat treatment, produces controlled precipitation. Age hardening may be supplemented by cold work. Overaging, which is aging past the point of maximum strength, insures stabilization of the grain structure. Certain alloys strengthened by cold work (strain hardening) may also be given stabilizing anneals. The term used for these straining and thermal treatments is temper. The temper of an alloy can greatly influence its susceptibility to stress-corrosion cracking. For example, wrought alloys 7075 and 7475 in the T6 temper have low resistance to stress-corrosion cracking, whereas the same alloys in the T73 temper have high resistance.

Quenching a specimen usually places the surface in compression while the interior of the piece is in tension. Machining off the surface layers can expose the interior, which may be susceptible to stress-corrosion cracking. However, quenching stresses may be reduced by mechanical stretching.

Exfoliation is closely related to stress-corrosion cracking. The source of stress is the wedging action of bulky corrosion products in a crack. A stress-corrosion crack in one end of a long piece may propagate the entire length because of corrosion product wedging.

There appears to be an electrochemical potential range within which stress-corrosion cracking occurs. At potentials more oxidizing or more reducing than this range, cracking will not occur. The potential range for cracking is specific to the alloy and the corrosive environment. For a given alloy changing the oxidizing potential of the solution can move the system into or out of the stress-corrosion range. This movement can be accomplished by altering the chemical composition of the environment or by polarizing the metal by either galvanic action or impressed currents. Both cathodic and anodic polarization can be used to control stress-corrosion cracking.

Cathodic protection may act to reduce pitting on initially smooth specimens. Pits can act as a stress intensifier, and a chemical environment conducive to crack initiation may be produced within the pit. Cathodic protection may delay the initiation of stress-corrosion cracks and decrease the crack velocity when it is above  $K_{Isc}$ . In applying cathodic protection, care should be exercised so that hydrogen is not generated on the metal surface because hydrogen generation on the surface leads to hydrogen cracking (par. 2-2.10).

In general, stress-corrosion cracking becomes more severe as temperature increases, and it occurs over a broader range of solution composition and occurs more rapidly in a given solution.

**MIL-HDBK-735(MR)****2-2.9.3 Mechanisms**

Several mechanisms have been proposed to explain the various instances and conditions of stress-corrosion cracking. The search for understanding has focused on the microscale fractures and processes involved in crack initiation and growth. There is no unifying theory or mechanism; a variety of pictures has emerged, which can be classified as (Ref. 20):

1. *Dissolution mechanism.* This mechanism involves rupture of the surface film followed by crack propagation and dissolution at the tip.

2. *Mechanical-fracture mechanisms:*

a. *Based on ductile fracture.* Formation of rows of corrosion pits that lengthen into an array of parallel corrosion tunnels. The uncorroded walls between the tunnels ultimately rupture mechanically to produce crack advance.

b. *Based on brittle fracture.* Several processes have been suggested:

(1) Adsorption and interaction of environmental species with strained crystal bonds. The bond strength is reduced and permits continuous brittle fracture at low stresses.

(2) Hydrogen embrittlement

(3) Stress-accelerated dissolution

(4) Brittle film formation and rupture that is repeated cyclically.

In recent years application of the scanning electron microscope to the study of stress-corrosion fracture surfaces has led to significant advances in characterizing these surfaces. As a result, the fractographic details can be correlated with the mechanism proposed for the propagation of stress-corrosion cracking as listed above (Ref. 20). The film rupture mechanism is consistent with the fractography of the majority of intergranular failures but not with that of transgranular stress-corrosion cracking. The fractographic evidence for transgranular cracking indicates a bulk embrittlement mechanism, such as hydrogen embrittlement, or a mechanism based on selective dissolution. On the basis of fractographic evidence, the tunnel mechanism, the adsorption mechanism, and the brittle film mechanism do not appear to be supported.

**2-2.9.4 Application Constraints and Protection Approaches**

Stress-corrosion cracking should be avoided because of its catastrophic nature. The only way to accommodate stress-corrosion cracking in design is to use redundant structural members so that failure of one component does not result in complete functional failure. All five fundamental corrosion control methods are applicable to controlling environmental cracking (Refs. 6 and 9). Each is discussed:

1. *Change the material:*

a. Select material more suitable for the critical environmental species.

b. Trade off lower strength material for one with greater stress-corrosion cracking resistance.

c. Make minor compositional changes such as low-carbon or stabilized grades of austenitic stainless steels.

d. Select heat treatment and cold-working tempers to achieve a microstructure resistant to stress-corrosion cracking.

2. *Modify the environment:*

a. Exclude critical environmental species or lower concentration to a level that does not promote cracking.

b. Eliminate oxidizing agents if they are a factor in stress-corrosion cracking.

c. Maintain service temperature as low as possible.

d. Eliminate condensation of moisture in a gaseous system by dehumidifying and maintaining the temperature above the dew point.

e. Eliminate minor constituents that aggravate stress-corrosion cracking.

f. Prevent all types of corrosion in critical space by any suitable means.

g. Eliminate possible corrodants or use suitable inhibitors.

3. *Coatings:*

a. Specify vacuum or ion plating, metallizing, or cladding in stressed area. Electroplating may introduce hydrogen and lead to hydrogen embrittlement. (See par. 2-2.10.)

b. Select suitable surface coatings. Specify passive surface films, organic coatings (possibly incorporating inhibition), or other types of barrier coatings.

c. Specify input of compressive surface stresses by shot peening or other suitable means.

4. *Electrochemical techniques:*

a. Use anodic or cathodic means to polarize an alloy to an oxidizing potential out of the range that will promote stress-corrosion cracking.

b. Polarization can be controlled by galvanic action of dissimilar electrodes or by impressed currents.

c. Use caution in cathodic protection so that hydrogen cracking is not induced.

5. *Change the design:*

a. Minimize applied stress. Reduce stress concentrations, or redistribute stress. Increase the size of critical load-bearing members. Achieve sufficient load path flexibility so that applied stresses are transmitted in the most direct path. Compensate for loss of structural stiffness resulting from removal of metal by holes, penetrations, etc. Design simple joints under stress; avoid lap welding, riveting, or bolting. Butt or fillet welding is preferred. Specify techniques that produce sound welds. Require careful preparation and finishing of welds. Specify and design for elimination of stress raisers.

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Exercise caution in imposing short transverse tensile loads.

b. Minimize residual stress. Avoid misalignment of sections joined by riveting, bolting, or welding. Avoid specifying any machining, assembling, or welding operation that imparts residual stress. Exercise care in cutting, machining, and forming alloys to avoid exposing grain structure in tension.

c. Avoid geometries in which solutions can become concentrated or in which critical environmental species can accumulate. By design, prevent surfaces that in operation will be subject to alternate wetting and drying.

d. Avoid material incompatibility. Contact of dissimilar materials can polarize one into the potential range for environmental cracking. Chemical species specifically introduced into the environment for one purpose may result in stress-corrosion cracking. Use materials in assembly with similar coefficients of expansion to avoid stresses resulting from unequal expansion.

e. Always conduct detailed stress analyses by using techniques amenable to computer manipulation. Hand calculations can be applied to simple models that may give only approximate results.

### 2-2.9.5 Examples

The classic example of stress-corrosion cracking is the so-called "season cracking" of cartridge brass due to the presence of ammonia. High-strength aluminum 7075 T6 alloy aircraft landing gear components have failed in the forging parting plane or flash line where the short transverse grain structure is exposed. Aerospace pressure vessels constructed of Ti-6Al-4V alloy containing  $N_2O_4$  have failed by stress-corrosion cracking. Aircraft bolts of high-strength martensitic steel inevitably crack when in contact with atmospheric moisture if they are not electroplated with cadmium. (The electroplated cadmium is then baked to remove the hydrogen generated in electroplating.)

## 2-2.10 HYDROGEN STRESS

Hydrogen stress cracking, or hydrogen embrittlement, is a special case of stress-corrosion cracking in which the absorption of atomic hydrogen into the metal plays a crucial role in the cracking mechanism of metals under tensile stress.

### 2-2.10.1 Manifestation and Quantification

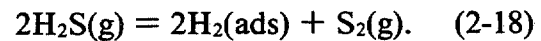
Hydrogen stress cracking failure paths can be either intergranular or transgranular. Susceptibility to hydrogen embrittlement increases with increasing tensile strength. Higher residual and applied tensile stresses cause cracking to occur more rapidly. Higher concentrations of hydrogen in the metal increase the tendency for hydrogen embrittlement. Chemicals in the environment can have a marked

effect on hydrogen embrittlement to the extent that they inhibit or promote the formation and absorption of atomic hydrogen.

### 2-2.10.2 Conducive Conditions

High-tensile-strength steels are subject to hydrogen stress cracking. The rule of thumb for steels is that embrittlement becomes more severe as strength levels increase above 690 MPa (100 ksi), and the corollary is that steels with strengths below that level tend not to exhibit hydrogen embrittlement.

Hydrogen can originate from the molten state, e.g., in steel refining and especially in welding. Usually, however, it originates from atomic hydrogen adsorbed on the surface of solid metal. This development can be produced by gas dissociation such as



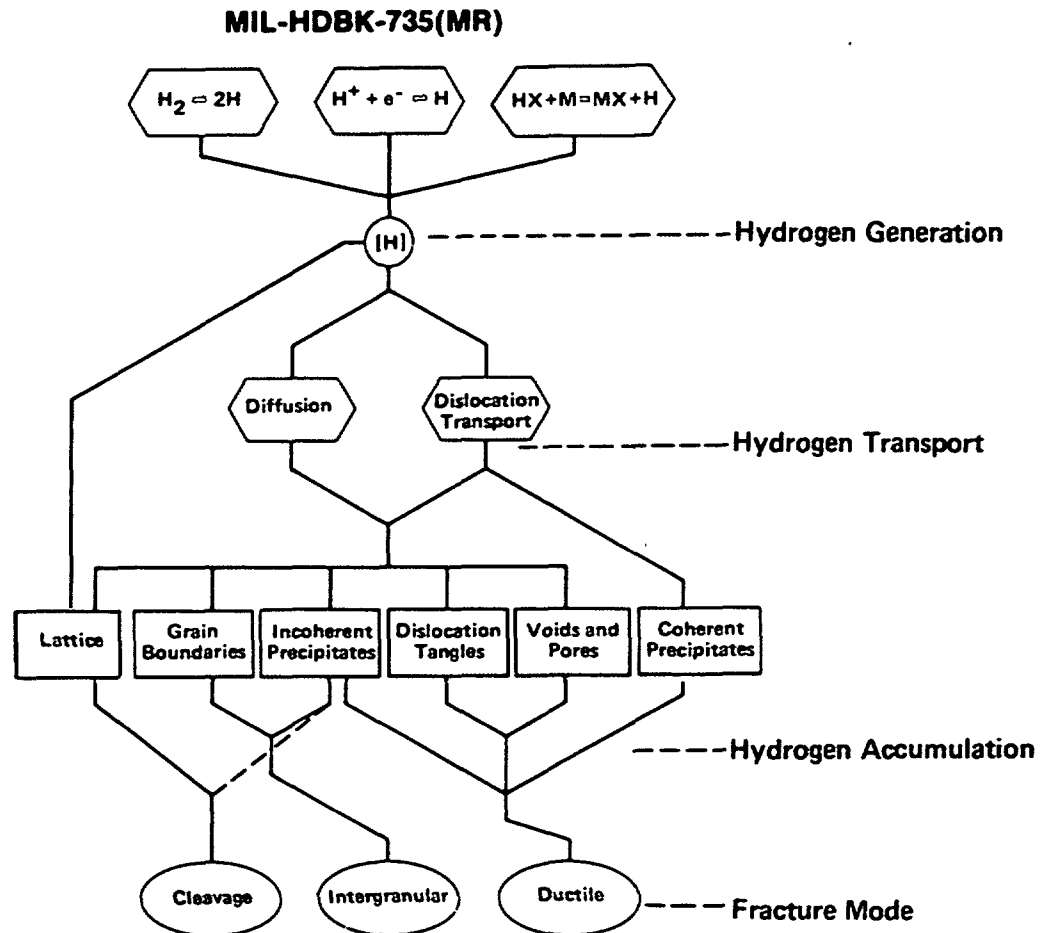
In practice, corrosion can usually generate the surface hydrogen necessary for embrittlement. Hydrolysis of salts in pits and cracks leads to acidity and consequently to hydrogen evolution. In addition, hydrogen may be produced on a metal surface by cathodic protection, by electroplating, and by acid pickling.

Some of the hydrogen atoms combine on the metal surface to form gaseous molecular hydrogen  $H_2$  and some atomic hydrogen is absorbed into the metal. Hydrogen diffuses rapidly in most metals; however, hydrogen can be transported more rapidly as it accompanies moving dislocations in the crystal lattice structure. This latter process accounts for the instances in which observed cracking rates exceed the rate predicted by hydrogen diffusion (Ref. 21).

Hydrogen tends to accumulate at a wide variety of locations in an alloy. These locations include grain boundaries, inclusions, voids, dislocations and dislocation arrays or other lattice defects, and in solid solution. The occurrence of hydrogen embrittlement depends upon attaining a critical hydrogen concentration at points of stress concentration. Therefore, the points of hydrogen accumulation most sensitive to fracture will control the magnitude of hydrogen effects.

If the metal is under high tensile stress, brittle fracture can occur and intergranular fractures are common. Cleavage or transgranular fractures can also occur either in the matrix or through a precipitated hydroxide phase. Many materials exhibit ductile fracture in the presence of hydrogen. Fig. 2-54 is a diagram of the hydrogen processes that lead to hydrogen cracking.

Chemicals in the environment can have a significant effect on hydrogen embrittlement. Sodium chromate inhibits the absorption of hydrogen, but sodium disilicate promotes absorption. By inhibiting the tendency of



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**Figure 2-54. Schematic of Hydrogen Processes (Ref. 22)**

hydrogen atoms to combine to form harmless molecular hydrogen, hydrogen sulfide and some arsenic compounds increase the tendency toward hydrogen embrittlement.

Hydrogen will egress from the metal as well as enter it to achieve equilibrium with the external environment. Therefore, an alloy that displays a combination of high hydrogen solubility and low egress diffusivity is said to have a high hydrogen affinity. Such an alloy would be expected to exhibit susceptibility to hydrogen stress cracking. Recent research suggests, however, that within a group of similar alloys, increased resistance to hydrogen embrittlement may be accompanied by an increase in hydrogen affinity (Ref. 23). Improved resistance to hydrogen embrittlement in given alloys resulted from thermomechanical treatment that increased hydrogen affinity (Ref. 24). Apparently hydrogen is immobilized, and thus its availability to the stress cracking process is limited. Hydrogen fracture behavior in many alloys can be greatly modified by relatively minor variations in the alloy chemistry and in the metallurgical condition.

### 2-2.10.3 Mechanisms

Several classes of mechanisms have been proposed to account for the role of hydrogen in reducing the ductility and/or fracture strength of materials. Factors such as hydrogen solubility, hydrogen diffusivity, and hydride stability differ widely among systems embrittled by hydrogen. Therefore, it is expected that certain mechanisms may be applicable in some situations, whereas others may appear to be more generally applicable. There may be situations in which several mechanisms interact to produce the observed effect.

Hydrogen has unique characteristics, with respect to a metal lattice, that could control its effect on fracture processes. The apparent mechanism depends on which of these characteristics dominates in a particular system. Suggested mechanisms include the following general classifications:

1. Hydrogen can affect the binding forces between metal atoms, particularly the interatomic cohesive force at or near the crack tip.
2. Adsorbed hydrogen lowers the surface energy of the metal within the crack and facilitates crack propagation.

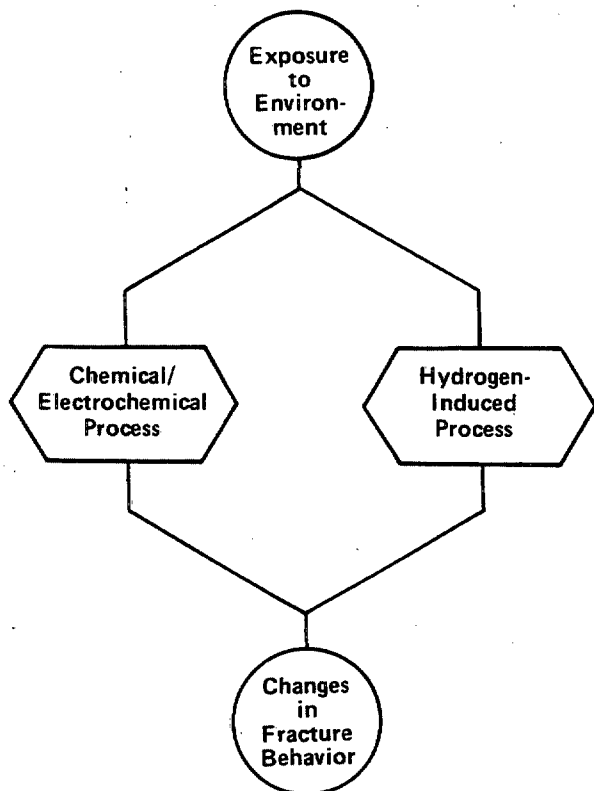
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3. Hydrogen gas (molecular hydrogen) accumulates in internal cracks, and the resultant gas pressure exerts an internal stress that assists fracture.

4. Hydrogen can induce changes in crystal lattice dislocation mobility, particularly a reduction of the local stresses required for dislocation motion.

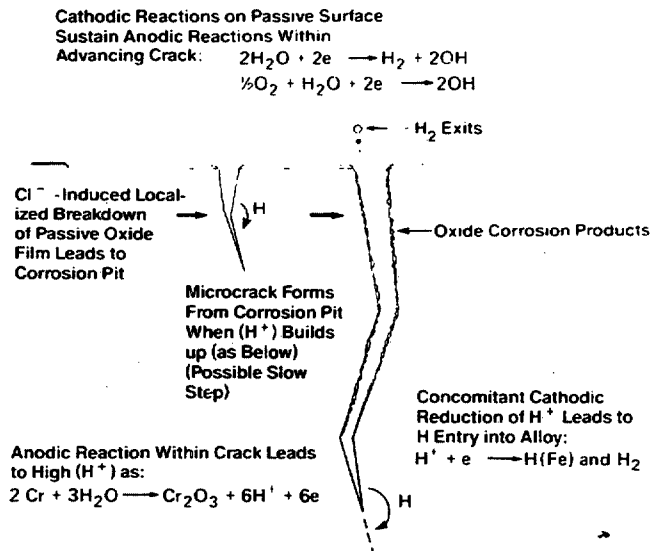
5. Many metals that exhibit severe hydrogen embrittlement form hydrides. In some systems precipitated hydrides have been shown to nucleate cracks.

In environmental cracking the chemical/electrochemical processes of stress-corrosion cracking often occur with the hydrogen-induced process of hydrogen cracking. Sometimes one or the other may be sufficient to account for environmental cracking. Anodic dissolution of titanium alloys in  $N_2O_4$  is a case of electrochemical cracking, but hydrogen processes account for the cracking of most high-strength steels in aqueous environments. However, in most cases, both processes occur. This dual nature of environmental cracking is represented in Fig. 2-55. Fig. 2-56 illustrates chemical/electrochemical processes and hydrogen-induced processes acting together in the cracking of austenitic stainless steel in a chloride environment.



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**Figure 2-55. Parallel Processes in Environmental Fracture (Ref. 22)**



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**Figure 2-56. Environmental Fracture Processes for Austenitic Stainless Steel in Chloride Environment (Ref. 22)**

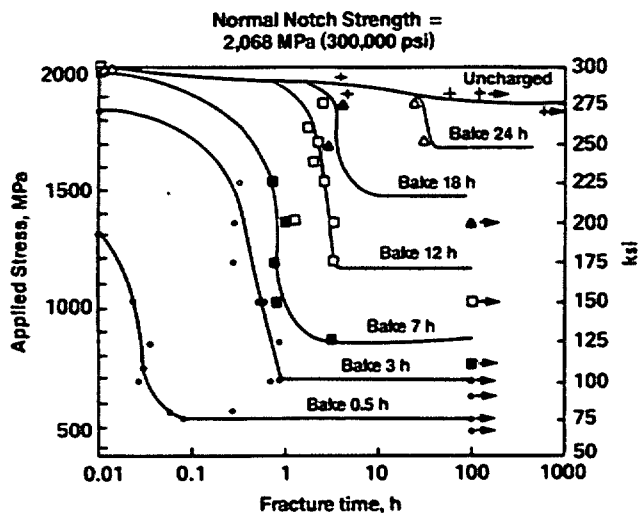
#### 2-2.10.4 Application Constraints and Protection Approaches

Hydrogen embrittlement may be prevented by application of one or more of the following measures (Ref. 1):

1. Avoid incorrect pickling procedures. Use inhibitors to eliminate base-metal corrosion and consequent hydrogen pickup.
2. Avoid incorrect plating procedures. Make the proper choice of plating baths, and carefully control plating current.
3. Select low-hydrogen welding rods, and specify that welding be carried out in dry conditions.
4. Select the correct surface preparation and treatment. Carefully control the processes.
5. Provide control of media chemistry, e.g., use inhibitors and remove sulphides, arsenic compounds, cyanides, and phosphorus-containing ions from the environment.
6. Carefully control cathodic protection potential to avoid generation of hydrogen.
7. Avoid anodic metallic coatings.
8. Remove hydrogen from metal by baking at  $93^\circ$  to  $149^\circ C$  ( $200^\circ$  to  $300^\circ F$ ). Hydrogen embrittlement is a reversible process. Fig. 2-57 illustrates the effect of baking on environmental stress cracking of high-strength steel.
9. Select a resistant material, i.e., homogeneous or clad. The materials most susceptible to hydrogen embrittlement are very high-strength steels. Alloying with nickel or molybdenum reduces susceptibility.



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**Figure 2-57. Environmental Stress Cracking Curves of 4340 Steel for Various Concentrations of Hydrogen (Hydrogen Content Changed by Baking at 149°C (300°F)) (Ref. 25)**

10. Induce compressive surface stresses, e.g., by shot peening.

#### 2-2.10.5 Example

Cadmium plating is used on high-strength steels in aerospace applications because it provides improved resistance to corrosion fatigue; however, hydrogen embrittlement is a problem. Proper plating techniques and baking out the hydrogen after plating are required to avoid this problem.

### 2-2.11 CORROSION FATIGUE

Corrosion fatigue is the reduction of the ability of a metal to withstand cyclic or repeated stress. This condition results from the action of a corrosive environment combined with the application of cyclic or repeated stress.

#### 2-2.11.1 Manifestation and Quantification

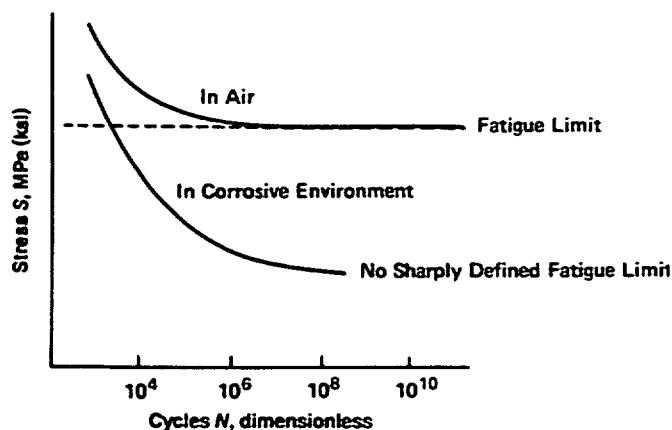
Fatigue failures occur at stress levels below the tensile yield point and after many applications of the stress. There is, however, usually a stress level below which failure will not occur regardless of the number of cycles. This level is designated the "fatigue limit".

If the stress level  $S$  is plotted against the number of cycles  $N$  to cause failure at that stress level, an  $S-N$  curve is obtained. This curve tends to approach a stress limit as the number of cycles is increased. This limit is the fatigue limit. In a noncorrosive environment the fatigue limit is fairly well defined. The frequency of stressing should be specified because that factor influences the endurance limit.

In a corrosive environment failure at a given stress level usually occurs within a fewer number of cycles and a sharply defined fatigue limit is not observed. Fig. 2-58 compares fatigue in a corrosive and a noncorrosive environment. Cracking at the affected sites is usually transgranular (except for lead and tin) in both ordinary fatigue and corrosion fatigue. Prior to failure damage due to corrosion fatigue is greater than the sum of corrosion damage plus fatigue damage. The final stages of corrosion fatigue are identical to those of ordinary fatigue. The supporting metal is reduced by cracking until final fracture is purely mechanical. Fig. 2-59 illustrates corrosion fatigue failure and compares the appearance of a corrosion fatigue failure with an ordinary fatigue failure.

There are two distinct modes of corrosion fatigue cracking. Fracture occurs in a plane 45 deg to the applied stress in shear mode cracking. This is the direction that receives the greatest resolved shear stress, and fracture is roughly normal to the stress direction in tensile mode cracking.

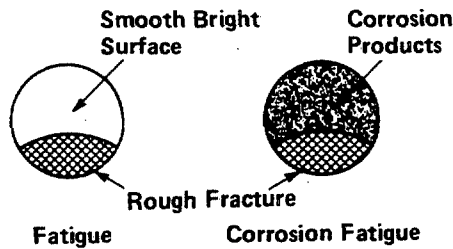
Published values of corrosion fatigue properties are usually unreliable for use in engineering design because it is very difficult to match all of the chemical and physical characteristics of an operating environment to those in which experimental values are obtained. However, experimental corrosion fatigue data can indicate the ranking of different metals under identical experimental conditions.



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**Figure 2-58. Typical  $S-N$  Curve for Fatigue Failure (Ref. 26)**

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(A) Illustration of Fatigue and Corrosion Fatigue Failures (Ref. 1)

From *Corrosion Engineering* by Mars G. Fontana and Norbert D. Greene, published by McGraw-Hill Publishing Company. Copyright © 1978 by McGraw-Hill Publishing Company. Reprinted with permission.



(B) Corrosion Fatigue Photograph (Ref. 7)

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## Figure 2-59. Fatigue and Corrosion Fatigue

### 2-2.11.2 Conducive Conditions

Factors that influence corrosion fatigue include the following:

1. Corrosion fatigue may occur in even a mildly corrosive environment, especially with alloys that form protective surface films.
2. Many aqueous environments cause corrosion fatigue, and they are not specific as in stress-corrosion cracking. For example, steel is subject to corrosion fatigue in fresh water, seawater, combustion product condensates, and chemical environments.
3. Anodic polarization accelerates and cathodic polarization retards corrosion fatigue in an aqueous environment. If the alloy is susceptible to hydrogen cracking, however, hydrogen generated by cathodic polarization will reduce the number of cycles to failure through a combination of corrosion fatigue and hydrogen embrittlement.
4. The nature of the corrosion environment, such as oxygen concentration, temperature, pH, and solution composition, influences corrosion fatigue.
5. Local corrosion, such as pitting or intergranular corrosion, has a greater accelerating effect on fatigue than does uniform surface corrosion.

6. Corrosion fatigue is most pronounced at low stress cycle frequencies.

7. Nonalignment of moving parts can lead to stress cycling, which must have a tensile component. If the member also carries a sustained tensile load, e.g., taut wires or stranded cables, failure may occur below the fatigue limit.

### 2-2.11.3 Mechanism

If a piece of metal is subjected to alternating tensile and compressive stress over a range insufficient to cause immediate fracture, slipping may occur within some of the grains. When the dislocations reach a grain boundary, they are halted, and when the stress is reversed, the dislocations retrace their movement along the slipping plane until the opposite grain boundary is reached. Ideally, dislocations would move to and fro along the slip plane and no damage would result. In practice, however, a great many stress cycles can occur without apparent damage. However, slight irregularities prevent smooth slipping indefinitely. The original slip plane becomes rough, and movement becomes difficult; therefore, at a certain point, slipping will start on a parallel plane. Ultimately, bands of material become disorganized. If the stress range is low, slipping will cease and the alternating stress will produce only elastic changes. If the stress range exceeds a certain level, the slipping will become irregular and will cause separation between the moving surfaces. Local gaps will coalesce into cracks, and the piece of metal will separate along the disorganized band. The number of stress cycles at which this separation occurs is the fatigue limit.

The disorganized or deformed band is exposed at the surface. Therefore, in a corrosive environment the direct or indirect interaction of the environment with the slip band interferes with the slip process and accelerates the deterioration process. Failure or cracking results at a lower number of stress cycles than would occur in vacuum or an inert gas.

Corrosion fatigue in gaseous or aqueous environments is a highly complex interaction between the environment and metal mechanical properties. The specific mechanisms for how the gaseous species act to reduce fatigue resistance are generally characterized as

1. Interference with otherwise reversible slip
2. Prevention of slip band crack rewelding
3. Surface energy reduction at the crack tip due to gas phase adsorption
4. Bulk oxide interference with slip processes.

Theories of aqueous corrosion fatigue have generally relied on one or more of the following mechanisms:

1. Stress concentration at the base of hemispherical pits created by corrosive media
2. Electrochemical attack at plastically deformed areas of metal with nondeformed metal acting as the cathode

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3. Electrochemical attack at ruptures in an otherwise protective film

4. Lowering the surface energy of the metal due to environmental adsorption and increased propagation of microcracks.

For aqueous environments, as in the gaseous situation, the specifics of environmentally affected crack initiation and growth are functions of the aggressiveness of the environment and the mechanical properties of the metal or alloy.

The application of linear elastic fracture mechanics and related small-scale crack tip plasticity provides a basis for describing fatigue crack propagation. The crack growth rate per cycle  $da/dN$  is primarily controlled by the alternating stress intensity  $\Delta K$  through an expression of the form:

$$\frac{da}{dN} = C(\Delta K)^n \quad (2-19)$$

where

$C$  = scaling constant

$n$  = scaling constant

$\Delta K$  = difference between the maximum and minimum stress intensities for each cycle:

$$\Delta K = K_{max} - K_{min}. \quad (2-20)$$

The fatigue crack growth expression of Eq. 2-19 is shown schematically in Fig. 2-60.

When a corrosive environment is simultaneously present with fatigue stressing, the tendency to crack spontaneously is increased. The threshold  $\Delta K_0$  is lowered, and the crack growth rate per cycle is increased. The increase is independent of cycling frequency or stress intensity ratio  $K_{min}/K_{max}$ . This situation is called the "true" corrosion fatigue and is indicated by the solid line in Fig. 2-61. There is a much larger increase in crack growth per cycle at low cycle frequencies and high stress intensity ratios. This is due to stress-corrosion cracking superimposed on the true corrosion fatigue. The upper dotted line in Fig. 2-61 is the curve of Fig. 2-47 superimposed on the line of Eq. 2-19. The practical implication of this is that the enhancement of the crack propagation rate in corrosion fatigue is not really significant unless the stress cycling rate is sufficiently slow (at or below 1 Hz) for stress-corrosion cracking to take effect.

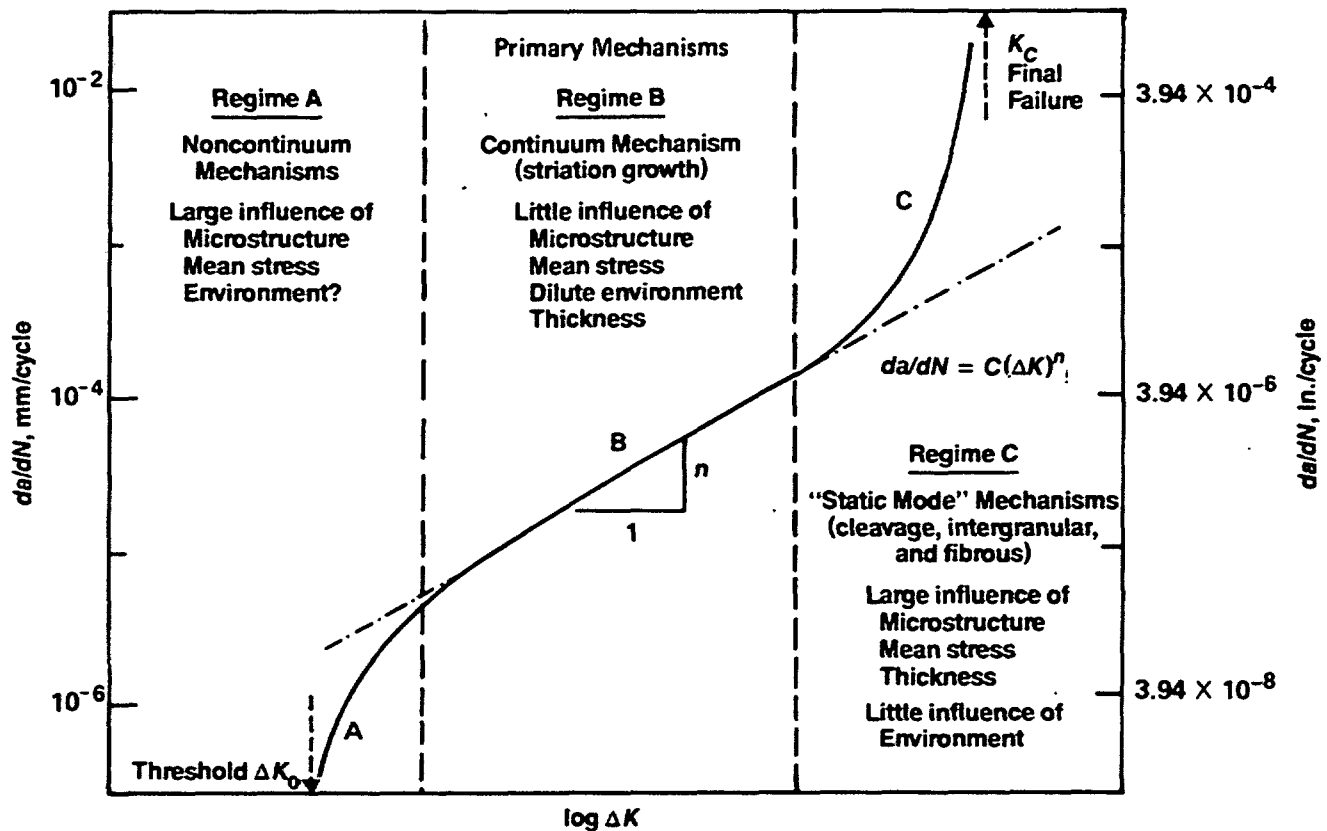
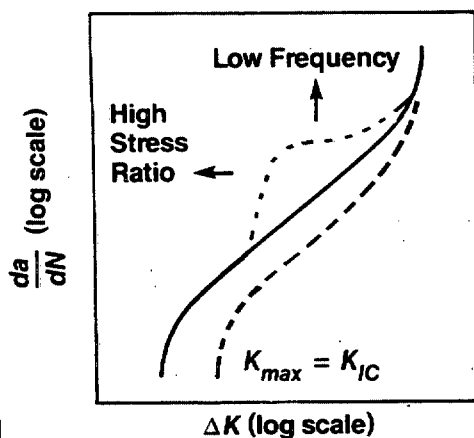


Figure 2-60. Schematic Variation of Fatigue Crack Growth Rates ( $da/dN$ ) With Alternating Stress Intensity ( $\Delta K$ ) (Ref. 27)

## MIL-HDBK-735(MR)



## Legend

- Fatigue in argon  
 — True corrosion fatigue  
 - - - - Stress corrosion fatigue

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**Figure 2-61. Influence of Stress Intensity Range on Incremental Crack Propagation in Fatigue and Corrosion Fatigue (Ref. 13)**

### 2-2.11.4 Application Constraints and Protection Approaches

Basic approaches to eliminate the danger of corrosion fatigue are to design to stay below the  $S-N$  curve with the given loading, material, and environment. If this cannot be achieved, the objective should be to modify loading, material, and environment to improve the applicable  $S-N$  curve to achieve, if possible, a true fatigue limit that is above the design requirements. The measures that follow are applicable:

1. Select suitable materials.

a. Materials exist that combine resistance to corrosion fatigue with good mechanical strength, e.g., austenitic stainless steels. Table 2-13 lists the corrosion fatigue measurements of some materials.

b. Certain materials are made especially sensitive to corrosion fatigue by the presence of notches on their surface. Other materials, such as gray cast iron, are saturated with surface notches because of their microstructure, and adding more notches has little effect on their corrosion fatigue susceptibility.

c. Machine or structural components exposed to vibration at frequencies close to their natural frequency experience resonance oscillations that may lead to cor-

**TABLE 2-13. EFFECT OF CORROSION ON FATIGUE-STRENGTH**  
 (S. F. DOREY, BASED ON D. J. McADAM) (Ref. 14)

| MATERIAL                                   | ULTIMATE TENSILE STRENGTH |         | ENDURANCE LIMIT APPROXIMATELY<br>$5 \times 10^7$ CYCLES |        |             |        |            |        |
|--|---------------------------|---------|---|--------|-------------|--------|------------|--------|
|  |                           |         | AIR   |        | FRESH-WATER |        | SALT-WATER |        |
|  | MPa                       | (ksi)   | MPa   | (ksi)  | MPa         | (ksi)  | MPa        | (ksi)  |
| 0.16% Carbon steel (hardened and tempered) | 404.0                     | (58.6)  | 220.6   | (32.0) | 122.7       | (17.8) | 55.2       | ( 8.0) |
| 0.24% Carbon steel                         | 342.0                     | ( 49.6) | 142.0   | (20.6) | 104.8       | (15.2) | —          | —      |
| Copper steel (0.98 Cu, 0.14 C)             | 379.2                     | ( 55.0) | 197.2   | (28.6) | 122.7       | (17.8) | 48.3       | ( 7.0) |
| 1.09% Carbon steel                         | 637.1                     | ( 92.4) | 246.1   | (35.7) | 129.6       | (18.8) | —          | —      |
| Ni steel (3.7 Ni, 0.26 Cr, 0.28 C)         | 558.5                     | ( 81.0) | 303.4   | (44.0) | 139.3       | (20.2) | 97.9       | (14.2) |
| Cr-V steel (0.88 Cr, 0.14 V)               | 926.7                     | (134.4) | 413.7   | (60.0) | 110.3       | (16.0) | —          | —      |
| Ni-Cr steel (1.5 Ni, 0.73 Cr, 0.28 C)      | 854.9                     | (124.0) | 417.8   | (60.6) | 99.3        | (14.4) | 85.5       | (12.4) |
| Stainless iron (12.9 Cr, 0.11 C)           | 551.6                     | ( 80.0) | 337.8   | (49.0) | 234.4       | (34.0) | 179.3      | (26.0) |
| Stainless steel (14.5 Cr, 0.23 Ni, 0.38 C) | 579.2                     | ( 84.0) | 319.9   | (46.4) | 220.6       | (32.0) | 220.6      | (32.0) |
| Ni-Si steel (3.1 Ni, 1.6 Si, 0.5 C)        | 1544.4                    | (224.0) | 671.5   | (97.4) | 103.4       | (15.0) | —          | —      |
| Monel metal (fully annealed)               | 503.3                     | ( 73.0) | 220.6   | (32.0) | 160.0       | (23.2) | 172.4      | (25.0) |
| Pure nickel                                | 468.8                     | ( 68.0) | 204.1   | (29.6) | 143.4       | (20.8) | —          | —      |
| Nickel (cold-rolled)                       | 809.4                     | (117.4) | 307.6   | (44.6) | 179.3       | (26.0) | 147.5      | (21.4) |
| Duralumin                                  | 427.5                     | ( 62.0) | 107.6   | (15.6) | 62.1        | ( 9.0) | 49.6       | ( 7.2) |
| Aluminum bronze (7.5 Al)                   | 554.3                     | ( 80.4) | 199.9   | (29.0) | 154.4       | (22.4) | 135.1      | (19.6) |
| Pure copper (annealed)                     | 187.5                     | ( 27.2) | 57.9  | ( 8.4) | 62.1        | ( 9.0) | —          | —      |

NOTE: The "freshwater" was well water containing calcium carbonate. The "saltwater" was river water with a salinity about one sixth of that of seawater. Speed of tests = 1450 cycles per minute.

From *An Introduction to Metallic Corrosion* by Ulick R. Evans, published by Edward Arnold Publishers. Copyright © 1981. Reprinted with permission.

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rosion fatigue failure. However, materials with high damping capacity will resist this type of failure.

**2. Design to avoid stress concentrations.**

a. Avoid raising stress locally through the shape of a stressed member or component.

b. Avoid surface defects that can act as stress raisers, such as oil holes, tool marks, flaws and grooves, rough surface finish, and corrosion and wear pits and grooves.

c. Conduct an adequate stress analysis of a critical part or component.

**3. Specify stress-relieving measures including tensional surface stresses.**

a. Specify stress-relieving heat treatment.

b. Induce compressional surface stresses by shot peening, swaging, rolling, vapor blasting, tumbling, etc. Compressional stresses can be created on certain ferrous metals by creating nitride surface layers that are hard and voluminous.

**4. Specify surface coatings.**

a. Specify electrodeposition of zinc, chromium, nickel, copper, or nitride coatings by techniques that do not produce tensile stresses or charge the metal with hydrogen.

b. Specify suitable surface coatings. Paint systems that provide good protection against corrosion generally are also effective against corrosion fatigue.

**5. Modify the loading.**

a. Minimize or eliminate the stress-corrosion cracking component of corrosion fatigue. In terms of linear elastic fracture mechanics, this means to avoid low-frequency cyclic loads, high-stress ratios, and high values of alternating stress intensity.

b. Avoid fluttering and vibration-producing and -transmitting designs.

c. Provide against rapid changes of loading, temperature, or pressure.

d. Provide sufficient flexibility in the assembly to reduce overstressing by thermal expansion, vibration, shock, and working loads.

e. Conduct an adequate stress analysis of the assembly.

**6. Modify the environment.**

a. Use appropriate corrosion inhibitors. Water-soluble inhibitors have been effective in aqueous solutions. Film-forming inhibitors have also been successful. Their efficacy depends upon the strength of the film and their insolubility in the filming and contacting fluids.

b. Apply cathodic protection. Cathodic protection is effective if the initial mode of cracking is at 45 deg (the shear mode), but it is not effective if the initial mode of cracking is at 90 deg (the tensile mode) to the stress.

c. Modify the corrosive environment to reduce or eliminate both uniform and local attack.

**2-2.11.5 Examples**

An early example of corrosion fatigue was the failure of paravane towing ropes. Paravanes are towed from minesweepers to cut the mooring cables of mines. Numerous instances of corrosion fatigue failure have been reported for ships (propeller shafts and rudders), aircraft, railways (axles exposed to dripping salt water from refrigerator cars), boilers, and motor vehicles (steering arms and axles).

**2-2.12 LIQUID METAL CORROSION**

Liquid metals interact with solid metals in two different types of corrosion phenomena. Liquid metal cracking is a form of embrittlement that results from the combined action of a tensile stress and a liquid metal in contact with a solid metal surface. Liquid metal corrosion results from the mutual solubility of the liquid and solid phases.

**2-2.12.1 Manifestation and Quantification**

Liquid metals exhibit several forms of interactions with solid metals. They are

1. Embrittlement that results from the combined action of a tensile stress and a liquid metal in contact with the alloy surface

2. Dissolution of the solid alloy or selected components of the microstructure by the liquid metal

3. Diffusion of liquid into solid metal

4. Chemical reaction of the liquid with the solid metal to form intermetallic compounds

5. Mass transfer through the liquid metal media as a result of a composition difference or a temperature difference.

Liquid metal embrittlement can result in structural damage and functional failure. Dissolution, diffusion, and chemical reaction between liquid and solid phases can result in uniform and local deterioration of the solid phase. Liquid metals can facilitate the transfer of material between dissimilar metals. This reaction results in material degradation of the donor metal and a reduction of its mechanical properties. Material is deposited on the surface of the acceptor metal. The deposition can degrade fluid flow and heat transfer properties and can change the characteristics of the alloy surface by diffusion into the elements of the microstructure of the acceptor metal.

Temperature gradient mass transfer moves material from the hot zone and deposits it on the cold zone surfaces. As with concentration gradient mass transfer, the buildup at the cold zone can diminish heat transfer efficiency and plug fluid flow channels. The loss of material at the hot zone can also result in degradation of mechanical properties and eventual perforation or failure.

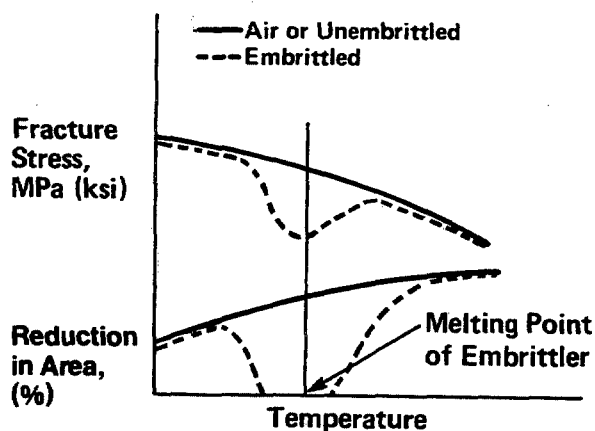
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## 2-2.12.2 Conducive Conditions

Liquid metals are usually used as a heat transfer medium in the flowing systems in which they are confined by a solid metal. This establishes the basic solid metal/liquid metal combination, the temperature gradient between the hot and cold zones, the concentration gradient that may exist between dissimilar metals in the system, and the fluid flow conditions. Fluid flow may result from forced circulation or thermal convection.

Some liquid metal effects result not from purposeful design of liquid metal systems but from contamination. For example, liquid metal cracking of high-strength aluminum alloys is most commonly associated with mercury contamination, e.g., from antifouling paint on aluminum ship hulls.

Because of its potentially catastrophic consequences, much of the information concerning liquid metal corrosion focuses on liquid metal embrittlement. The phenomenon of liquid metal embrittlement has long been recognized; recently, however, it has received more attention because of the potential use of liquid metals as a heat transfer medium in nuclear reactors. In addition, solid-metal-induced embrittlement has recently been identified as an extension of liquid metal embrittlement. The degree of embrittlement caused by environmental species often changes continuously as the environment is transformed from a solid to a liquid phase. However, not all environments capable of producing liquid metal embrittlement have an effect in the solid state. For example, 2024-T4 Al is embrittled by mercury only at temperatures above  $-39^{\circ}\text{C}$  ( $-38^{\circ}\text{F}$ ), the melting point of mercury. Nevertheless, any assessment of liquid metal embrittlement should include related solid-metal-induced embrittlement. Generally, a solid metal environment must be heated to within 75% of its melting point for effects on the mechanical properties of the substrate metal to occur. Embrittlement is a maximum at the melting point of the environment and is then reduced as temperature is increased further, as illustrated in Fig. 2-62. For example, the reduction in area mechanical property of internally leaded (free machine 4145 steel) steels decreases from about  $200^{\circ}\text{C}$  ( $392^{\circ}\text{F}$ ) and reaches a minimum at  $327^{\circ}\text{C}$  ( $621^{\circ}\text{F}$ ), which is just above the melting point of lead. Ductility returns at a higher temperature, i.e., in the range of  $371^{\circ}$  to  $454^{\circ}\text{C}$  ( $700^{\circ}$  to  $849^{\circ}\text{F}$ ). Recovery of ductility at



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**Figure 2-62. Effect of Temperature on Embrittlement Due to Solid and Liquid Metals (Ref. 28)**

higher temperatures is general for liquid metal embrittlement regardless of whether solid metal embrittlement occurs. Relatively little attention has been given to the effect of liquid metal embrittlement on cyclic loading phenomena. Also there is evidence of significant deterioration of fatigue properties of a variety of metals exposed to liquid metals.

A significant problem associated with identification of embrittling couples and the tables listing them is uncertainty regarding the precise experimental conditions that lead to embrittlement. Solid substrate and liquid environment composition are significant embrittling parameters as are grain size of the substrate, test temperature, strain rate, and notch (or crack) geometry. Many combinations of environment and substrate have not yet been tested, and for others there was insufficient control of experimental variables to provide confidence in the test results. Also there is no consensus by which to establish the degree of loss of ductility or fracture stress before a couple can be considered embrittling. Table 2-14 lists some alloy-liquid metal combinations that can result in cracking. Table 2-15 shows some, but not all, embrittling couples.

**MIL-HDBK-735(MR)****TABLE 2-14. SUSCEPTIBILITY OF ALLOYS TO LIQUID METAL CRACKING (Ref. 6)**

| ALLOYS                     | LIQUID METAL CRACKING  |
|----------------------------|--|
| Magnesium                  | No information   |
| Aluminum                   | Hg (30°C (86°F)), Ga (50°C (122°F)), In (180°C (356°F)),<br>Na (125°C (257°F)), Sn (260°C (500°F)), Zn (450°C (842°F)) |
| Carbon steels              | Cu, Zn (450°C (842°F)), In (180°C (356°F)), Li (210°C (410°F)),<br>Cd (350°C (662°F))                                  |
| High-strength steels       | Cu, Cd   |
| 18% maraging steel         | 50:50 Pb-Bi  |
| Martensitic SS             | No information   |
| Ferritic SS                | No information   |
| Austenitic SS              | Zn, Cd, Al, Cu   |
| Precipitation-hardening SS | Zn, Cd, Al, (Cu?)  |
| Superaustenitics           | Zn, Cd, Al, (Cu?)  |
| Lead, tin, zinc            | No information   |
| Copper alloys              | Hg   |
| Nickel N02200              | S, Hg, Bi, Li, Pb, Sn  |
| Monel N04400               | S, Hg, Bi, Li, Pb, Sn  |
| Alloy B, N10001            | Al, Cd, Li   |
| Inconel N06600             | S, Zn, Cd, Al  |
| Alloy C N10002             | S, Zn, Cd, Al  |
| Alloy C 276 N10276         | S, Zn, Cd, Al  |
| Vitallium (Cobalt)         | No information   |
| Titanium                   | Hg (30°C (86°F)), Cd (350°C (662°F)), Ag   |
| Zirconium                  | No information   |
| Silver, gold, platinum     | No information   |

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TABLE 2-15. SUMMARY OF EMBRITTLEMENT COUPLES (Ref. 27)

| SOLID | LIQUID | Hg  | Cs  | Ga  | Na  | In  | Li  | Sn  | Bi   | Tl  | Cd  | Pb  | Zn  | Te  | Sb  | Cu   |
|-------|--------|-----|-----|-----|-----|-----|-----|-----|------|-----|-----|-----|-----|-----|-----|------|
|       |        | P A | P P | P A | P P | P A | P P | P A | P A  | P P | P P | P A | P P | P P | P P | P P  |
| Sn    | P      | X   |     | X   |     |     |     |     |      |     |     |     |     |     |     |      |
| Bi    | P      | X   |     |     |     |     |     |     |      |     |     |     |     |     |     |      |
| Cd    | P      |     | X   | X   | X   | X   |     | X   |      |     |     |     |     |     |     |      |
| Zn    | P      | X   | X   | X   |     |     |     | X   |      |     |     |     |     |     |     |      |
|       | LA     |     | X   |     |     |     |     |     |      |     |     | X   |     |     |     |      |
| Mg    | CA     |     |     |     | X   |     |     |     |      |     |     |     |     |     |     | X    |
| Al    | P      | X   | X   | X   |     | X   |     | X   |      |     | X   |     |     |     |     |      |
|       | CA     | X   | X   | X   |     | X   |     | X   |      |     |     |     |     |     |     | X    |
| Ge    | P      |     |     | X   |     | X   |     | X   |      |     | X   | X   | X   |     |     |      |
| Ag    | P      | X   | X   | X   | X   |     |     | X   | X    | X   | X   | X   |     |     |     | X    |
|       | LA     |     |     |     |     |     |     | X   |      |     |     |     |     |     |     |      |
| Cu    | CP     | X   | X   |     | X   |     |     | X   |      | X   | X   |     | X   |     |     |      |
|       | LA     | X   |     |     |     |     |     | X   |      |     |     |     |     |     |     |      |
|       | CA     | X   | X   |     |     | X   | X   | X   | X(?) | X   |     |     | X   |     |     |      |
| Ni    | P      | X   |     |     |     |     |     | X   |      |     |     |     | X   |     |     |      |
|       | LA     |     |     |     |     |     |     | X   |      |     |     |     | X   |     |     |      |
|       | CA     |     |     |     |     |     |     | X   |      |     |     |     | X   |     |     |      |
| Fe    | P      |     |     |     |     |     |     | X   |      |     |     |     |     |     |     | X(?) |
|       | LA     | X   | X   |     |     |     |     | X   |      |     |     |     |     |     |     |      |
|       | CA     |     |     |     |     |     |     | X   | X    |     |     | X   | X   | X   | X   | X    |
| Pd    | P      |     |     |     |     |     |     | X   |      |     |     |     |     |     |     |      |
|       | LA     |     |     |     |     |     |     | X   |      |     |     |     |     |     |     |      |
| Ti    | CA     |     | X   |     |     |     |     |     |      |     |     |     |     |     |     |      |

P = element (nominally pure) A = alloy C = commercial L = laboratory

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### 2-2.12.3 Mechanism

Mass transfer liquid metal corrosion processes rely on solubility and diffusion processes, as illustrated in Figs. 2-63 and 2-64. Thermal gradient mass transfer depends upon the solubility of a solid metal in a liquid metal as a function of temperature. Fig. 2-65 is a schematic diagram of a typical solubility-temperature relationship. Solid Metal A is more soluble in liquid Metal B at 816°C (1500°F) than at 704°C (1300°F). Therefore, if liquid Metal B contacts solid Metal A at 816°C (1500°F) and is then cooled to 704°C (1300°F), some dissolved Metal A will precipitate as a solid. If this process is carried out in a closed recirculating system, solid Metal A will be transferred from the 816°C (1500°F) zone to the 704°C (1300°F) zone. The difference in solubilities does not have to be large to cause considerable damage because the recirculation rate of liquid metals is high in most applications.

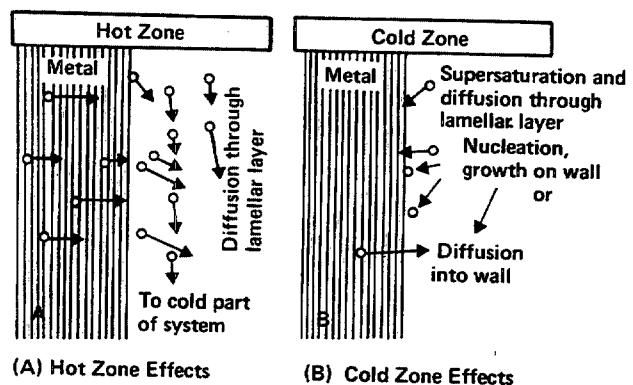
Similarities exist between various types of environmental embrittlement. There are common features of hydrogen and liquid metal embrittlement, such as (Ref. 28)

1. Tensile stress must exist in the base metal.

2. Preexisting cracks or stable obstacles to dislocation must be present.

3. Embrittling species must be present at the obstacle and subsequently at the tip of the propagating crack.

4. Low mutual solubilities, little tendency to form compounds, and strong binding energies are characteristic of embrittlement couples.

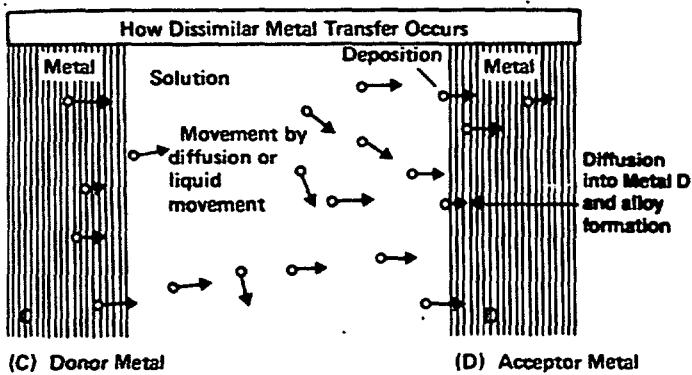


(A) Hot Zone Effects (B) Cold Zone Effects  
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Figure 2-63. Thermal Gradient Mass Transfer (Ref. 29)

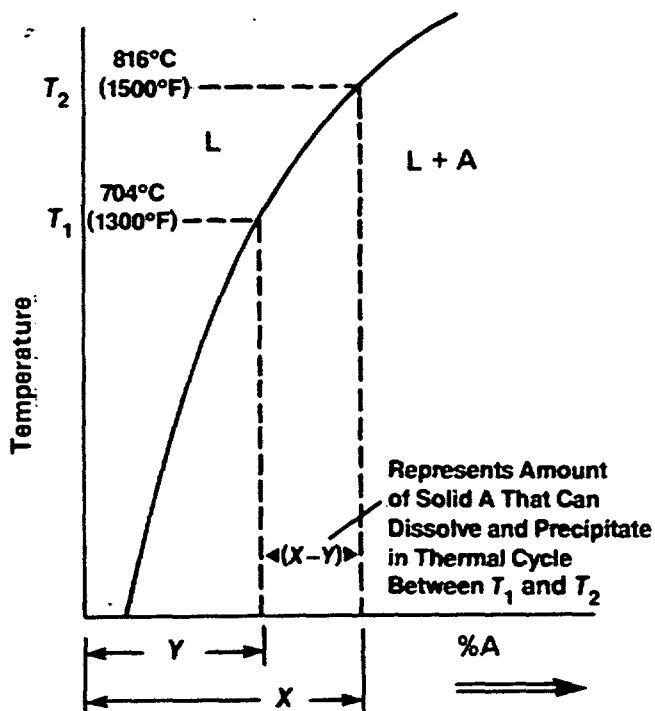


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**Figure 2-64. Dissimilar Metal Mass Transfer (Ref. 29)**



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**Figure 2-65. Solubility of Solid Metal A in Liquid Metal B (Ref. 30)**

The degree of embrittlement between any combination of environment and substrate depends on several variables. The most significant of which is the strength of interaction between the environment and structural material (Ref. 28). Chemisorption-induced lowering of bond strength at the crack tip is widely accepted as the mechanism for liquid metal embrittlement. However, the concept of chemisorption alone is not sufficient because many liquid metals that adsorb on a solid do not cause any change in mechanical behavior.

The question of specificity of a liquid metal/solid metal pair toward embrittlement is a matter of degree. Strong interactions will tend toward embrittlement under a wide variety of conditions, whereas weak interactions require a very precise combination of conditions. Even a strong solid-liquid interaction, however, will not lead to embrittlement if mutual solubility is high or if grain size, temperature, or other experimental conditions are unfavorable. Similarly, competing chemical reactions, e.g., intermetallic compound formation, can overcome the tendency toward embrittlement. Material dissolution or intermetallic compound formation may be viewed as competitive reactions, which may rapidly remove the adsorbed species from potential embrittlement sites.

#### 2-2.12.4 Application Constraints and Protection Approaches

The measures that follow can be used to reduce the potential for liquid metal embrittlement:

1. Select a liquid metal/solid metal combination that exhibits low susceptibility to liquid metal embrittlement at the planned operating temperature. This selection may be in the form of a nonsusceptible cladding on a susceptible substrate.
2. Control operating conditions to minimize embrittlement. For example, embrittlement is a maximum near the melting point of the environment but is then reduced as temperature is increased through the brittle-to-ductile transition.
3. Control grain size and cold-work to reduce tendencies to embrittlement. Small grain size is less susceptible to liquid metal embrittlement, and cold-work can provide beneficial effects.
4. Control the chemistry of the substrate. For example, tin and arsenic increase the susceptibility of AISI 3340 steel, whereas phosphorus causes a modest decrease in embrittlement.
5. Control the chemistry of the environment. Elements that form stable compounds with the substrate when added to the environment inhibit liquid metal embrittlement.
6. Remove preexisting cracks in the substrate metal. These or other stable obstacles to dislocation are necessary for liquid metal embrittlement.
7. Reduce the tensile stress level through design considerations. The time to failure decreases with increasing stress levels.
8. Use a metal or alloy having lower strength. Embrittlement increases with increasing strength levels.
9. Keep mercury away from high-strength aluminum alloys. Mercury embrittles 2024-T4 aluminum severely at room temperatures.
10. Create compressive stress on the surfaces of a solid metal through shot peening, etc. A tensile stress is needed for embrittlement.

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### 11. Apply a suitable nonmetallic coating.

In liquid metal systems in which heat transfer takes place, select materials or control the chemistry of the environment so that substrate components are not dissolved at the hot zone to be subsequently deposited at the cold zone. For example, the addition of 1 to 10 parts per million of titanium to mercury reduces the rate of attack on carbon steels to a very low rate.

Minimize the occurrence of concentration-gradient mass transfer by using the same material throughout the system or by minimizing solubility from the donor surface by means similar to those suggested for the hot zone.

Use an inert gas blanket to keep oxygen at low levels when using liquid sodium, potassium, and sodium-potassium alloys; oxides of these liquid metals are very corrosive.

#### 2-2.12.5 Examples

Much information concerning liquid metal corrosion and embrittlement involves the application of liquid metals as working fluids in power systems. These applications include heat transfer through liquid to vapor phase transitions, thermal convection, and forced convection. A wide range of liquid to solid metal couples has been examined in these applications. Sodium, sodium-potassium alloys, bismuth, lead, lithium, and many other metals have been considered as coolants, and all have caused some degree of mass transfer failure.

Premature fractures of cadmium-plated steels and titanium alloys as well as internally leaded steels have been observed at temperatures well below the respective melting points of cadmium or lead. This should raise a caution signal for many applications involving plating, soldering, brazing, and welding. Alpha brass is very susceptible to liquid metal embrittlement by mercury. Therefore, exposure to mercury is a sensitive test for residual stresses in this material.

A serious liquid metal corrosion problem is the tanks used to hold molten zinc for galvanizing.

#### 2-2.13 HIGH-TEMPERATURE OXIDATION AND/OR EROSION

Any metal exposed to oxygen at high temperatures reacts with the oxygen. The oxygen will be adsorbed on the surface and may then react to form an oxide. If the film or scale is continuous, adherent, and nonporous, a degree of protection from further reaction with the oxygen is afforded. The degree of protection depends upon the thickness of the film and the rates at which reactants can diffuse through the film, i.e., oxygen moving in and/or metal moving out.

##### 2-2.13.1 Manifestation and Quantification

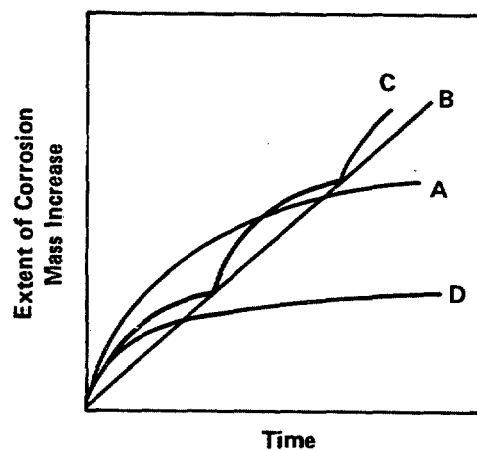
Oxidation scale breakdown can result from the following processes:

1. Thermal cycling in which differential rates of expansion and contraction of the scale and base metal cause the scale to crack and spall.
2. In flowing gas systems the scale can be cracked and/or abraded by forces generated by fluid dynamics or by particles in the gas stream.
3. Chemical reactions can change the characteristics of the scale.
4. Mechanical forces that are generated by moving parts in machinery.

If the oxidation film is nonprotective, oxidation of the substrate metal continues unabated. If the oxidation film provides temporary protection for a time, fails, and rebuilds in a repetitive manner, oxidation of the substrate metal continues in incremental steps. If the oxidation film provides protection, the extent of oxidation of the substrate metal approaches a limit. The growth laws of oxidation represented by the previous conditions are, respectively, linear, quasi-linear, and parabolic. Other empirical growth relations have been observed, e.g., logarithmic and cubic. Fig. 2-66 shows the growth laws of oxidation. The nature of the growth relationship depends upon the rate-controlling step of the oxidation process.

Catastrophic oxidation occurs when the metal reacts with oxygen at continuously increasing rates. This reaction can occur under the following conditions:

1. The surface temperature of the metal continuously increases.
2. Volatile oxides are formed.
3. A low-melting eutectic oxide forms beneath the scale.



- A. Parabolic  
B. Rectilinear  
C. Quasi-Rectilinear  
D. Logarithmic

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Figure 2-66. Growth Relations of Oxidation (Ref. 13)

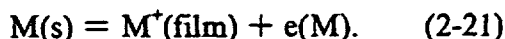
## MIL-HDBK-735(MR)

Internal oxidation occurs when dilute components of an alloy form a more stable oxide than the base metal, and this oxidation occurs below the external surface of the metal or below the metal-scale interface. This occurs when the diffusion rate of oxygen in the base metal of the alloy is greater than the diffusion rate of the alloying addition. In some cases no external oxide scale is formed and only internal oxidation takes place. However, if an external film is formed with the base metal, such as in Ni-Cr alloys, the internally oxidized particles become incorporated into the scale. As the internally oxidized NiO zone moves inward, the  $\text{Cr}_2\text{O}_3$  particles that were previously formed internally are incorporated into the NiO film. The phenomenon of internal oxidation of Ni-Cr alloy is illustrated in Fig. 2-67. Cu- and Ni-base alloys containing Cr, Al, and Si are among those subject to internal oxidation.

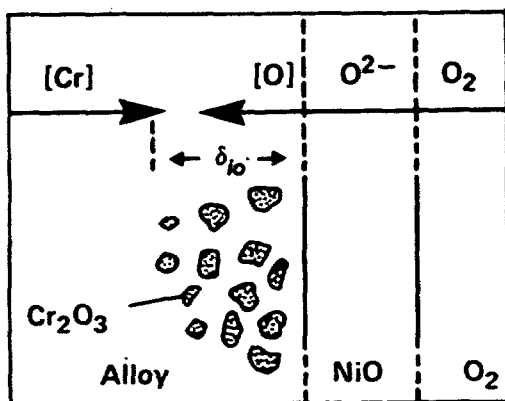
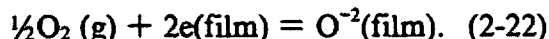
## 2-2.13.2 Conducive Conditions

Under high temperatures a surface oxide film is almost always formed. Because of this film, high-temperature corrosion processes depend upon a spacial separation of simultaneous oxidation and reduction reactions that closely parallel the anodic and cathodic reactions of electrochemical reactions in ionic solutions:

1. At the metal/film interface



2. At the film/air interface



$\delta_{io}$  = depth of internally oxidized zone

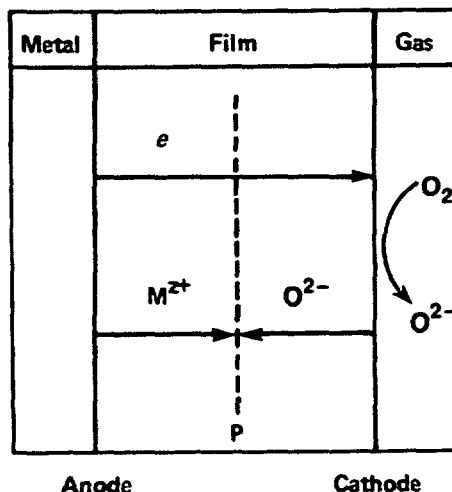
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Figure 2-67. Internal Oxidation of Ni-Cr (Ref. 13)

After the initial film is formed, oxidation continues if the film conducts not only cations but also electrons for the external cathodic process of oxygen reduction. Therefore, the transport mechanism through a coherent film is a combination of diffusion from high to low concentration and electron migration from high to low electrical potential. This is illustrated schematically by Fig. 2-68. As the scale thickens, everything else remaining constant, the diffusion rate decreases. Therefore, the rate of scale growth decreases and is inversely proportional to its actual thickness at any point in time. These conditions result in the parabolic growth relationship, which is illustrated by Curve A on Fig. 2-66.

If the oxide scale fails or is porous or otherwise nonprotective, corrosive gas has easy access to the metal surface and therefore reacts readily with the base metal. In this case, the rate of oxidation is constant, and the oxidation weight change is a linear function with time. This situation is illustrated by Curve B on Fig. 2-66.

The tendency for an oxide scale to fail mechanically depends upon the volume of the scale formed relative to the volume of the metal reacting. If the ratio is less than one, as it is only for alkali and alkaline earth metals, the surface scale is under tensile stress and can be expected to rupture. If, however, the ratio is much greater than one, which it is for most engineering metals, the oxide scale is in compression. As the film grows, mechanical failure can occur, particularly at flaws in the film. Table 2-16 lists protective and nonprotective oxide films. Protective scales tend to have oxide-to-metal volume ratios between



P = Plane of film growth

Diffusion of oxygen is inward.

Diffusion of metal ions and electrons is outward.

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Figure 2-68. Oxidation Process (Ref. 13)

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TABLE 2-16. OXIDE METAL VOLUME RATIOS (Ref. 31)

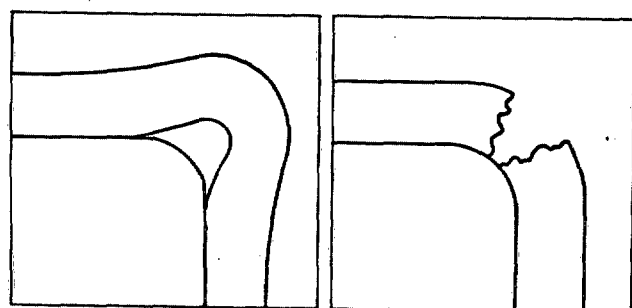
| PROTECTIVE OXIDES |      | NONPROTECTIVE OXIDES |      |
|-------------------|------|----------------------|------|
| Be                | 1.59 | Li                   | 0.57 |
| Cu                | 1.68 | Na                   | 0.57 |
| Al                | 1.28 | K                    | 0.45 |
| Si                | 2.27 | Ag                   | 1.59 |
| Cr                | 1.99 | Cd                   | 1.21 |
| Mn                | 1.79 | Ti                   | 1.95 |
| Fe                | 1.77 | Mo                   | 3.40 |
| Co                | 1.99 | Cb                   | 2.61 |
| Ni                | 1.52 | Sb                   | 2.35 |
| Pd                | 1.60 | W                    | 3.40 |
| Pb                | 1.40 | Ta                   | 2.33 |
| Ce                | 1.16 | U                    | 3.05 |
|                   |      | V                    | 3.18 |

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one and two. Whether under tension or compression, scales can separate from the base metal at corners. This occurrence is illustrated in Fig. 2-69.

When the corrosion product is volatile or when it is sufficiently fluid to run off the surface, no film is formed to provide protection. The oxides of vanadium, molybdenum, and tungsten melt relatively easily, as indicated by Table 2-17. The oxide of molybdenum sublimates and therefore affords no protection above approximately 1000°C (1832°F). Alloys containing even small quantities of molybdenum and vanadium frequently oxidize catastrophically. In this case, a low-melting eutectic mixture produces a liquid beneath the scale. Alloys will nearly always lead to the formation of mixed oxides, which, if mutually soluble, will lower the melting point of the film.

Oxidation can proceed without an external scale or



(A) At Metal/Film Interface  
(Compression)

(B) Within the Film (Tension)

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Figure 2-69. Scale Failure at Corners  
(Ref. 13)

TABLE 2-17. MELTING POINTS OF METAL OXIDES (Ref. 13)

| METAL | OXIDE                          | MELTING POINT, °C (°F) |
|-------|--------------------------------|------------------------|
| Al    | Al <sub>2</sub> O <sub>3</sub> | 2020 (3668)            |
| Cu    | Cu <sub>2</sub> O              | 1230 (2246)            |
| Fe    | FeO                            | 1371 (2500)            |
| Cr    | Cr <sub>2</sub> O <sub>3</sub> | 2280 (4136)            |
| Ni    | NiO                            | 1960 (3560)            |
| V     | V <sub>2</sub> O <sub>5</sub>  | 670 (1238)             |
| Mo    | MoO <sub>3</sub>               | 795 (1463)             |
| W     | WO <sub>2</sub>                | 1270 (2318)            |

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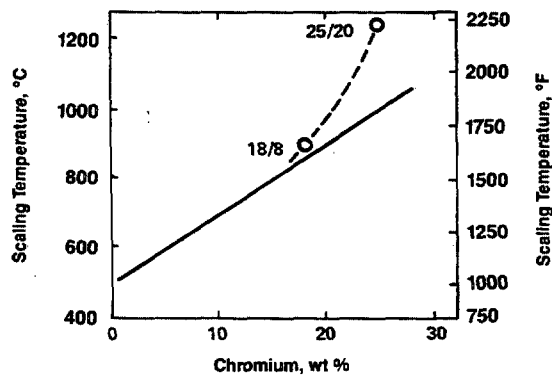
beneath the external scale provided that certain conditions are met:

1. The alloy must contain as a minor ingredient an element that is considerably more reactive than its major constituent. Silicon in copper and chromium in nickel are examples.

2. The rate at which the minor ingredient diffuses toward the surface must be less than that at which oxygen diffuses inwardly.

Internal oxidation of this kind often occurs in the iron, nickel, and cobalt alloys commonly used in high-temperature applications. (See Fig. 2-67.) Forming internal oxide precipitates precludes preferential oxidation of these elements, which would form the surface scale. Chromium and aluminum are added to these alloys to form a protective external scale.

Fig. 2-70 shows scaling temperatures for iron-chromium alloys in air. Scaling temperature is defined as that



18/8 = 18 Cr, 8 Ni, Remainder Fe  
25/20 = 25 Cr, 20 Ni, Remainder Fe

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Figure 2-70. Scaling Temperature of Iron-Chromium Alloys in Air (Ref. 13)

## MIL-HDBK-735(MR)

temperature below which the oxidation rate in air is less than 0.5 mm/yr (0.02 in./yr). Addition of chromium progressively raises the scaling temperature from about 500°C (932°F) to over 1000°C (1832°F). Addition of nickel further raises the scaling temperature until it exceeds 1200°C (2192°F) at a composition of 25% chromium and 20% nickel.

## 2-2.13.3 Mechanism

The process of high-temperature oxidation has been described in terms of oxide- or film-forming capabilities. During the formation of a metal oxide film, metal ions diffuse out of and oxide ions move into the plane of film growth. Electrons move out of the metal surface to the film-gas interface. This mechanism is controlled by the semiconducting properties of oxide films.

## 2-2.13.4 Application Constraints and Protection Approaches

There are four basic approaches to minimizing high-temperature oxidation:

1. Use a material that is stable at the operating conditions of interest.
2. Modify the operating conditions.
3. Limit exposure to the adverse conditions.
4. Apply a specially designed coating.

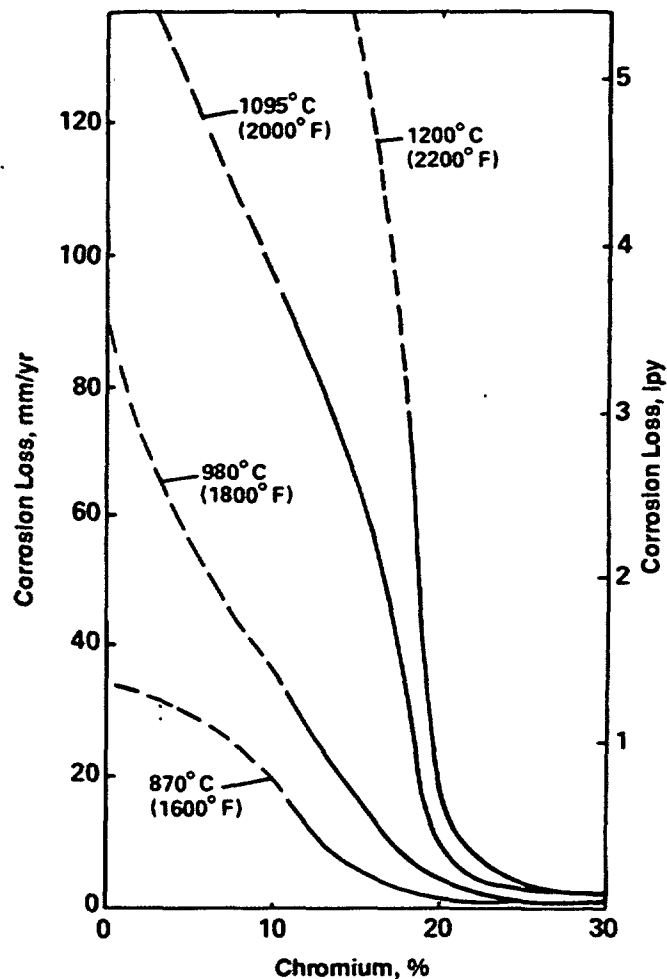
A stable material is one that forms a protective oxide file. To be effective, a protective oxide should (1) have low volatility, (2) be free of pores and fissures, and (3) be adherent. These criteria are met by chromium sesquioxide ( $\text{Cr}_2\text{O}_3$ ), alumina ( $\text{Al}_2\text{O}_3$ ), and silicon dioxide ( $\text{SiO}_2$ ). The concentration of film-forming elements in an alloy should be sufficient to form the initial oxide film as well as to replace it whenever it is lost under service conditions.

The effect of chromium on decreasing the corrosion of iron in the temperature range from 870°C (1600°F) to 1200°C (2200°F) is shown in Fig. 2-71. More than 20% chromium has little additional effect.

Nickel improves the high-temperature corrosion properties of an 11% chromium-iron alloy, as shown in Fig. 2-72. Nickel alone, however, does not significantly improve the high-temperature properties of iron. Also additions of nickel with chromium do not significantly degrade the mechanical properties of an alloy.

As shown in Fig. 2-73, additions of up to 12% aluminum achieve significant reductions in high-temperature corrosion, but the use of aluminum is not favored because of a significant decrease in the mechanical properties of the alloy. Nevertheless, aluminum-rich surfaces can be created by high-temperature diffusion of aluminum into metal surfaces. This cementation process is known as "calorizing".

The  $\text{Al}_2\text{O}_3$  scale that is formed reduces the diffusion of oxygen to the substrate, but its adhesion to the substrate is poor. Rare earth additions, such as hafnium (Hf) and



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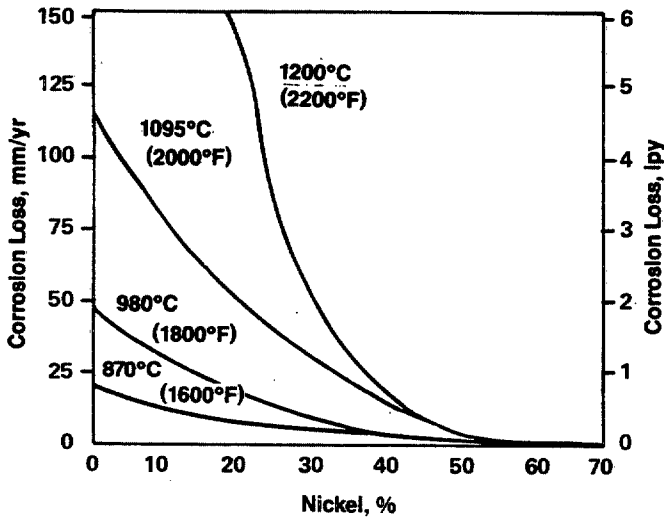
**Figure 2-71. Effect of Adding Chromium to Iron on Corrosion in Air at High Temperatures (Ref. 30)**

yttrium (Y), form numerous oxide penetrations into the substrate alloy. These pegs consist predominantly of  $\text{Al}_2\text{O}_3$  that has grown inwardly and encapsulated the Hf- and Y-rich internal particles. The presence of these oxide protrusions plays a decisive role in maintaining scale adhesion over long exposure periods.

Silicon can improve the corrosion resistance of steels at high and moderate temperatures. However, the use of silicon is limited to about 2% because it has a negative effect on ductility. The effect of silicon addition to the high-temperature oxidation of a commercial steel containing 5% chromium and 0.5% molybdenum is shown in Fig. 2-74.

The data for Figs. 2-71 and 2-72 are based on 100-h tests. Since the relationship of the extent of corrosion with time follows one of the oxidation growth relations of Fig. 2-66, the rate of corrosion based on a short time will be conservative, i.e., higher than the rate of corrosion for

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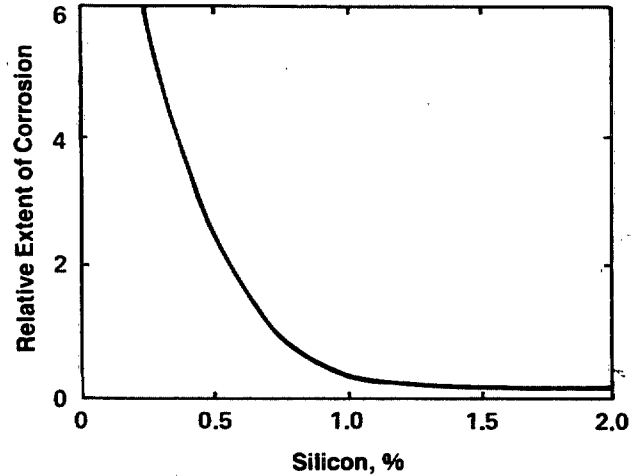


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Figure 2-72. Effect of Adding Nickel to Fe-11 Cr Alloy on Corrosion in Air at High Temperatures (Ref. 30)

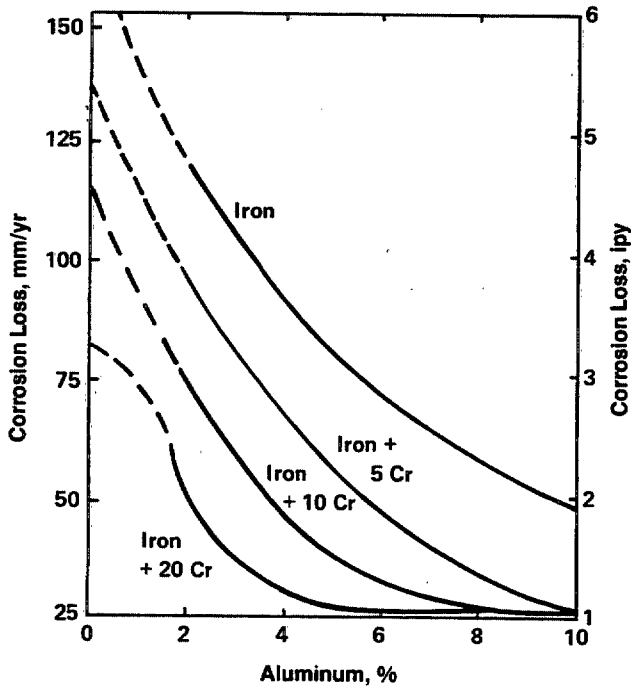
a longer time. This fact is illustrated in Fig. 2-75 for a parabolic growth relationship.

The melting point of some metals is shown in Fig. 2-76. The high-temperature utility of metals and alloys is summarized in Table 2-18.



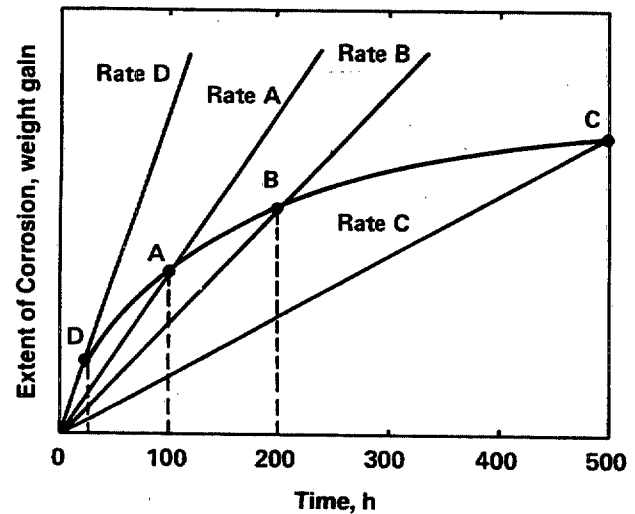
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Figure 2-74. Effect of Increasing Silicon Content in a 5-Cr-1/2Mo Steel on Resistance to Corrosion in Air at 815°C (1500°F) (Ref. 30)



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Figure 2-73. Effect of Adding Aluminum to Iron and to FeCr Alloys on Corrosion in Air to 1095°C (2000°F) (Ref. 30)



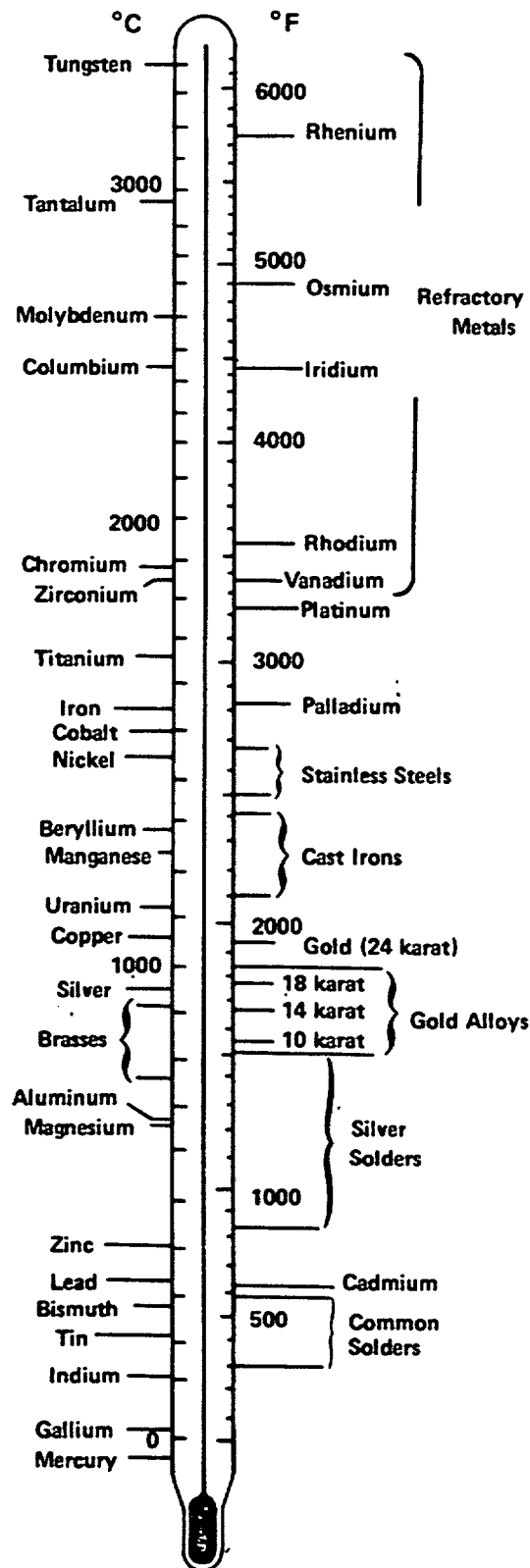
$$\text{Rate} = \frac{\text{Extent of Corrosion}}{\text{Time}}$$

Rate D > Rate A > Rate B > Rate C

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Figure 2-75. Extent of Corrosion vs Time (Ref. 30)

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**Figure 2-76. Melting Points of Metals (Ref. 30)**

**MIL-HDBK-735(MR)****TABLE 2-18. HIGH-TEMPERATURE UTILITY OF STRUCTURAL OR BASE METALS AND ALLOYS (Ref. 6)****LIGHT METALS**

Aluminum and magnesium are not considered to be suitable for high-temperature service. Their limiting temperature is less than 230°C (450°F).

**FERROUS METALS**

Carbon steel has little useful strength and oxidation resistance above 425°C (800°F).

Graphitization of carbon steel (formation of graphite nodules) occurs at about 470°C (875°F).

Molybdenum alloy steel (0.5%) combats graphitization, and various amounts of chromium are added to improve resistance to hydrogen attack.

**STAINLESS STEEL**

Austenitic stainless steels resist oxidation by air and steam to 815°C (1500°F). They will also resist high-temperature sulfidation at concentrations at which the chromium-molybdenum alloy steels are unsuitable. Chromium content of 25%, such as type 310, is required for good oxidation resistance. The maximum service temperature in air is 1150°C (2102°F) for type 310.

**LEAD, TIN, ZINC**

Low-melting alloys are not suitable for high-temperature service.

**COPPER AND ITS ALLOYS**

These are not considered high-temperature alloys.

**NICKEL ALLOYS**

Because of its protective oxide film, nickel is useful up to 595°C (1100°F).

Nickel-chromium alloys have extended resistance to high-temperature oxidation that depends on chromium content. Nickel-base superalloys have a nominal chromium content of 20%. The limiting temperature for oxidation is about 705°C (1300°F). In sulfur-free reducing atmospheres containing hydrogen or carbon monoxide, the limiting temperature is about 980°C (1800°F). Hydrogen sulfide reduces the limiting temperature to 540°C (1000°F).

**COBALT ALLOYS**

Cobalt has poor oxidation resistance, but alloys containing 25% chromium are resistant to 980°C (1800°F); 30% chromium alloy is resistant to 1150°C (2100°F). Cobalt-base superalloys have a nominal chromium content of 30%.

**REACTIVE METALS**

Zirconium and tantalum are not useful at elevated temperatures. The air corrosion at 1206°C (2200°) of zirconium and tantalum is 59 and 1100 times, respectively, that of type 310 stainless steel. Titanium can be used up to 600°C (1112°F) in air.

**PRECIOUS METALS**

Gold and platinum retain their luster in air up to their melting points.

Silver is readily attacked by sulfurous gases. Platinum is resistant to 980°C (1800°F). Gold is resistant.

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**MIL-HDBK-735(MR)****2-2.14 HIGH-TEMPERATURE  
SULFIDATION AND/OR EROSION**

In environments containing high sulfur concentrations, sulfide scales form at high temperatures instead of oxide scales. However, in most environments of practical interest, such as combustion products of hydrocarbon fuels, sulfur occurs in relatively low concentration in complex multicomponent mixtures. These mixtures contain sulfur-bearing gases ( $H_2S$  and  $SO_2$ ) in addition to oxidants ( $CO_2/CO$  and  $H_2O/H_2$ ). Sulfidation of metals, therefore, is related to the interaction of alloys with these complex mixtures under the conditions of exposure.

**2-2.14.1 Manifestation and Quantification**

Iron-, nickel-, and cobalt-base alloys with chromium as a major constituent have been developed for use in high-temperature applications involving combustion gases. The corrosion behavior of these alloys in such complex environments is strongly influenced by the gas composition, alloy chemistry, and temperature. Depending upon the mode of corrosion attack that occurs, i.e., oxidation

or sulfidation, corrosion rates can vary significantly. In general, sulfidation is more destructive to metals than oxidation. Sulfide scale cracks and spalls more readily than oxide scales. As shown in Table 2-19, metal sulfides generally melt at lower temperatures than oxides. Under some environmental conditions, continuous sulfide scales cannot form, so corrosion attack continues unabated by the growth of a protective scale. For example, most eutectics formed by metal-metal sulfide combinations are molten at temperatures much lower than the melting point of the metal itself, as shown in Table 2-20. In comparison, metal-metal oxide eutectics melt at temperatures closer to the melting point of the metal. Formation of a molten phase prevents formation of a protective surface scale.

Accelerated corrosion of high-temperature gas turbine alloys in circumstances in which sodium chloride or other salts are ingested with combustion air is attributed to the presence of sodium sulfate, which is formed by the reaction between sodium chloride and sulfur in the fuel. Apparently, for most alloys there is an incubation period (100-1000 h) that may or may not be associated with the

**TABLE 2-19. MELTING POINTS OF SOME METAL SULFIDES AND OXIDES (Ref. 13)**

| METAL | OXIDE     | MELTING POINT, °C (°F) | SULFIDE   | MELTING POINT, °C (°F) |
|-------|-----------|------------------------|-----------|------------------------|
| Al    | $Al_2O_3$ | 2020 (3668)            | Unstable  | — —                    |
| Cu    | $Cu_2O$   | 1230 (2246)            | $Cu_2S$   | 1130 (2066)            |
| Fe    | $FeO$     | 1371 (2500)            | $FeS$     | 1190 (2174)            |
| Cr    | $Cr_2O_3$ | 2280 (4136)            | $Cr_2S_3$ | 1150 (2102)            |
| Ni    | $NiO$     | 1960 (3560)            | $Ni_2S_3$ | 790 (1454)             |
| V     | $V_2O_5$  | 670 (1238)             | $V_2S_3$  | d 600 (1112)           |
| Mo    | $MoO_3$   | 795 (1463)             | $MoS_2$   | s 450 ( 842)           |
| W     | $WO_2$    | 1270 (2318)            | $WS_2$    | d 1250 (2282)          |

s = sublimation

d = decomposition

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**TABLE 2-20. MELTING POINTS OF METALS AND METAL-SULFIDE EUTECTICS  
(Ref. 29)**

|    | METAL |      | METAL-SULFIDE<br>EUTECTIC |      |
|----|-------|------|---------------------------|------|
|    | °C    | °F   | °C                        | °F   |
| Co | 1495  | 2723 | 877                       | 1611 |
| Cr | 1850  | 3362 | 1350                      | 2462 |
| Cu | 1083  | 1981 | 1070                      | 1958 |
| Fe | 1539  | 2802 | 985                       | 1805 |
| Mn | 1136  | 2077 | 1240                      | 2264 |
| Ni | 1455  | 2651 | 645                       | 1193 |

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## MIL-HDBK-735(MR)

breakdown of a protective oxide layer (Ref. 32). After the incubation period, the hot corrosion reaction can be quite rapid.

### 2-2.14.2 Conducive Conditions

As an alloying component with iron and nickel, chromium reacts to sulfur in much the same manner that it reacts to oxygen. A chromium sulfide scale is formed regardless of the amounts of iron and nickel. However, when the chromium is depleted, that is, when it is completely converted to the sulfide or oxide, the base metal is rapidly attacked.

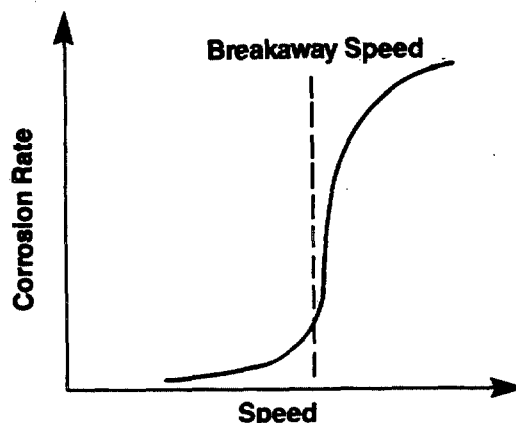
The rate of attack depends upon the form of the sulfur and the presence of oxygen. The gaseous forms of sulfur are sulfur vapor,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{S}$ , and organic sulfides. Because of the dissociation reaction of  $\text{SO}_3$  and  $\text{SO}_2$  to elemental sulfur and oxygen, oxygen is present with these compounds. With oxygen present a mixed oxide-sulfide scale is formed, and this mixed scale is more protective than a sulfide scale, such as that formed by pure  $\text{H}_2\text{S}$ .  $\text{H}_2\text{S}$  rapidly attacks nickel and nickel alloys, and the attack can be catastrophic and can have rapid intergranular penetration.

If an iron-chromium-nickel alloy with high chromium content is exposed to gases containing both oxygen and sulfur at high temperatures, there is, for a given sulfur concentration, a threshold oxygen concentration above which a continuous protective scale is formed. The threshold oxygen concentration is about 1000 times the oxygen concentration for the chromium oxide-chromium sulfide equilibrium. As the exposure time increases, a greater oxygen concentration is required to prevent catastrophic corrosion (Ref. 33).

In those environments containing appreciable concentrations of oxygen along with sulfur, chromium sesquioxide ( $\text{Cr}_2\text{O}_3$ ) protective scales form in preference to sulfides on those nickel- and iron-base alloys containing sufficient chromium. However, long-term exposure results indicate that the corrosion behavior of the material is influenced by the extent of sulfur diffusion through the oxide scale. Sulfide formation under the scale affects the adherence of the scale. This can explain the breakaway corrosion that has been observed with long-term evaluation of a number of alloys exposed to complex gas mixtures under flowing conditions. Breakaway corrosion is illustrated in Fig. 2-77.

If a protective oxide scale breaks down as a result of erosion, mechanical forces, thermal cycling, etc., there is real potential for sulfur to react with chromium to form a sulfide near the alloy surface. Once this reaction occurs, it interferes with the process of formation and maintenance of the protective oxide scale.

If all the available chromium becomes bound up as sulfide, less stable sulfides of the base metal, iron and nickel, can form. Because these sulfides form molten



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**Figure 2-77. Breakaway Corrosion at Speed Sufficient to Erode Protective Scale (Ref. 34)**

phases with components of the alloy and scale, they are responsible for accelerated sulfide attack. The molten phase is readily eroded away and attack continues unabated.

If sulfide forms in the alloy surface, sulfur tends to migrate into the alloy and to form sulfides at the grain boundaries or at chromium-enriched sites. This intergranular attack can result in localized stress concentrations, and severe attack can result in reduced load-bearing capability of the alloy.

Hot corrosion is the attack on Ni-Cr and Co-Cr superalloys at high temperatures. Fossil-fueled devices, such as gas turbines, are susceptible to rapid degradation of high-temperature alloy components when they are subjected to molten salt deposits (Ref. 32). Almost all fossil fuels contain some amounts of sulfur and alkali metals. In addition, the gases ingested to support combustion usually contain some sodium chloride. The corrosive deposits responsible for hot corrosion usually contain alkali sulfates, especially  $\text{Na}_2\text{SO}_4$ . At temperatures above the melting point of  $\text{Na}_2\text{SO}_4$ ,  $884^\circ\text{C}$  ( $1623^\circ\text{F}$ ), rapid sulfidation occurs with depletion of those elements added to form protective oxides, Cr and Al, in a near-surface zone.

At temperatures below the melting point of  $\text{Na}_2\text{SO}_4$ ,  $700^\circ\text{C}$  to  $884^\circ\text{C}$  ( $1292^\circ\text{F}$  to  $1623^\circ\text{F}$ ),  $\text{Na}_2\text{SO}_4$ - $\text{CoSO}_4$  liquid phases can form at very low partial pressures of  $\text{SO}_3$  (Ref. 35). At partial pressures about 10 to 15 times greater, a  $\text{Na}_2\text{SO}_4$ - $\text{NiSO}_4$  eutectic can form. Formation of these low-melting sulfate mixtures on alloy surfaces leads to rapid attack.

Particulate materials present in the combustion gas stream of gas turbines subject turbine rotor blades and nozzle guide vanes to erosion and contribute to the corrosion process. A variety of particulate materials, such

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as carbon, sea-salt debris, silicates, and iron-rich phases, impact and deposit on airfoil surfaces. In dusty environments, airborne sand particles cause erosion of compressor blades and possibly hot section components as well. Carbon particles produce erosion damage to turbine rotor blades. Also there is evidence that carbon particles intensify the hot corrosion process that results from ingested NaCl (Ref. 36).

### 2-2.14.3 Mechanism

The basic mechanism of sulfidation is closely related to that of high-temperature oxidation by air or gas streams containing oxygen. (See par. 2-2.13.3.) This mechanism involves film or scale formation in which the semiconducting characteristics of the film support an electrochemical reaction. Within the scale metal ions diffuse out of and sulfide ions move into the plane of film growth. Electrons move out of the metal surface into the film-gas interface.

The sulfidation reaction is complicated by the following considerations:

1. Because it cracks and spalls more readily, a sulfide scale is not as protective as an oxide scale.
2. Complex gas environments are usually involved in sulfide scale formation.
3. Sulfides form low-melting eutectics with the base metal.

There is no significant difference between the hot corrosion mechanisms for nickel and cobalt or alloys of these metals containing the same amount of chromium and/or aluminum. The resistance of such alloys to the initiation of hot corrosion is about the same, except for alloys containing both chromium and aluminum, in which case the cobalt alloys are more resistant.

In hot corrosion tests of alloys in a burner rig, nickel-base and cobalt-base alloys corroded at a similar rate at 954°C (1750°F) (Ref. 37). At 1038°C (1900°F), the cobalt-base alloys were more resistant. The following effects of alloying elements were noted for nickel-base alloys:

1. Increasing chromium is beneficial.
2. Increasing cobalt may increase corrosion resistance.
3. Molybdenum additions are increasingly detrimental as the temperature increases.
4. Tungsten has no effect at 954°C (1750°F), but it is detrimental at a higher temperature, 1038°C (1900°F).
5. Tantalum seems to improve resistance.
6. Rhenium and yttrium have no effect.
7. Titanium is not harmful and may be beneficial.
8. Aluminum is increasingly detrimental as a function of temperature in simple alloys but may be beneficial in complex alloys. This result, however, does not agree with other investigators who found aluminum to be particularly beneficial in nickel-base alloys.

The following effects of alloying elements were noted for cobalt alloys:

1. Twenty-five percent chromium provides sufficient resistance to attack, and larger amounts may not make a difference.
2. Yttrium is beneficial.
3. Carbon, copper, nickel, and tantalum additions do not have an effect.
4. Tungsten is usually harmless.
5. Molybdenum results in severe attack.

### 2-2.14.4 Application Constraints and Protection Approaches

Approaches for reducing the effects of high-temperature sulfidation in complex gas mixtures, such as combustion gases, are dependent on obtaining and maintaining a protective oxide film. These approaches include

1. Use fuels that are low in sulfur, vanadium, and alkali metals.
2. Use combustion conditions that favor the formation of oxides over sulfides.
3. Minimize mechanical forces acting upon the scale, and minimize or avoid thermal cycling.
4. Use an alloy composition with sufficient amounts of chromium or aluminum to form a protective Cr<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> scale under service conditions.
5. Use an active element, such as yttrium or hafnium, or a stable oxide dispersion in the alloy to improve the adherence of the Cr<sub>2</sub>O<sub>3</sub> or Al<sub>2</sub>O<sub>3</sub> scale (Ref. 38).
6. Apply a protective coating.

Coatings can be either ceramic or metallic. Refractory metal oxides maybe applied either as a slurry and subsequently sintered, or they may be flame sprayed in a high-temperature plasma. One such coating is a plasma or flame-sprayed layer of Y<sub>2</sub>O<sub>3</sub>-stabilized ZrO<sub>2</sub> deposited on a thin NiCrAlY or a CoCrAlY bond layer applied directly to the alloy surface (Ref. 39). These coatings appear to be very stable toward oxidizing environments to temperatures of at least 1000°C (1832°F). However, in the presence of salt deposits, such as those that form on hot gas path components in gas turbines, rapid failure of the ceramic coating may occur. The salt deposits result from burning fuels contaminated with sodium, sulfur, lead, and vanadium (Ref. 40).

Reactive metal coatings such as aluminum or chromium are applied by cladding, electrodeposition, deposition from the vapor phase or pack cementation, and hot dipping. After application, these coatings are often diffusion annealed to promote formation of intermetallic compounds with the substrate.

### 2-2.14.5 Example

The most important example of high-temperature oxidation and sulfidation and hot corrosion are the hot

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components of gas turbines. The approaches used in controlling these phenomena include

1. Less susceptible alloys
2. Composite materials
3. Resistant coatings
4. Control of surface temperatures by cooling
5. Reduction of contaminants in fuels.

**2-2.15 BIOLOGICAL CORROSION**

In their metabolic process, biological organisms ingest nutrients and eliminate a waste product. Biological corrosion is the interaction of the biological life process with corrosion mechanisms. Organisms are classified according to size:

1. The microorganisms implicated in corrosion processes are primarily bacteria. Table 2-21 lists some troublesome microorganisms.

2. Macroorganisms that cause material degradation include fungi or molds and aqueous organisms, such as barnacles, mussels, and algae.

The principal ways in which macroscopic and microscopic organisms influence corrosion are by locating differential aeration cells and by hydrogen depolarization. Microorganisms also produce aggressive species such as hydrogen ions and sulfide ions.

**2-2.15.1 Manifestation and Quantification**

Microbial corrosion may be suspected by one or a combination of the following conditions (Ref. 42):

1. Pitting-type corrosion
2. The presence of microbial slime masses
3. Hydrogen sulfide (rotten egg odor) in anaerobic systems

**TABLE 2-21. SOME TROUBLESOME MICROORGANISMS (Ref. 41)**

|                                   |              |
|-----------------------------------|--------------|
| <b>BACTERIA (Slime-Forming)</b>   | <b>ALGAE</b> |
| Flavobacterium                    | Chroococcus  |
| Mucoids                           | Oscillatoria |
| Aerobacter                        | Chlorococcus |
| Pseudomonas                       | Ulothrix     |
| B. Subtilis                       | Scenedesmus  |
| B. Cereus                         | Navicula     |
| <b>BACTERIA (Corrosive)</b>       | <b>FUNGI</b> |
| Desulfovibrio                     | Aspergillus  |
| Clostridia                        | Alternaria   |
|                                   | Penicillium  |
| <b>BACTERIA (Iron-Depositing)</b> | Trichoderma  |
| Gallionella                       | Torula       |
| Crenothrix                        | Monilia      |

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4. Ferric(ous) hydroxide in aerobic systems

5. Large bacterial or fungal populations.

Corrosion generated by bacteria may take distinctive forms (Ref. 43). Gallionella, a type of iron bacterium, on stainless steel produces subsurface cavities with only minute pinhole penetrations at the surface. Sulfate reducers, however, generally produce open pitting or gouging on stainless steel, and when they are active along the edges of gasketed joints, shallow crevice corrosion is often found under adjacent gasket areas. Attack by sulfate reducers on cast iron typically produces graphitization. Sulfate reducers produce conical pits containing concentric rings or steps on nickel, high-nickel alloys, and cupronickels. Under the hollow, hemispherical tubercles of iron bacteria will be hemispherical or conical pits that are almost as large in diameter as the tubercles. Tubercles are small knobby prominences. The corrosion will be irregular under irregular tubercles containing slime formers.

Bacteria-induced corrosion is usually accompanied by characteristic deposits (Ref. 43), which are usually discrete mounds. Tuberculation of steel may develop into a general, irregular buildup. Uniform, thin pseudomonas films are formed in heat exchangers and other moderate flow rate areas. Bacteria deposits most often have a slimy feeling when fresh and wet, and wet deposits are generally soft and easily deformed. Bacteria may also flourish in sludge layers. Sulfate reducers produce characteristic black deposits of ferrous sulfide (FeS) on steel and stainless steels. Iron bacteria deposits are usually some shade of brown. Gallionella deposits on stainless steels are often reddish, whereas beeggiatoa produce the yellow color of elemental sulfur. Slime deposits may be colored by the suspended solids they trap.

Confirmation that corrosion is bacteria induced usually requires analyses of accompanying deposits (Ref. 43). These should include an elemental analysis, determination of organic/inorganic ratio, and a microbiological analysis. Determination of the elements in a deposit can be useful even without bacteria analyses. High levels of iron, manganese, and chlorides usually indicate gallionella. A high sulfur level indicates sulfur oxidizers or sulfate reducers, and a high iron level could indicate iron bacteria.

**2-2.15.2 Conducive Conditions**

Microscopic and macroscopic organisms live and reproduce in mediums with a pH value between 0 and 11, at temperatures between  $-1^{\circ}\text{C}$  ( $30^{\circ}\text{F}$ ) and  $82^{\circ}\text{C}$  ( $180^{\circ}\text{F}$ ), and at pressures up to 10.34 MPa (1.5 ksi) (Ref. 1). Accordingly, biological activity can be expected to influence corrosion in a variety of environments including soil, fresh waters, seawater, petroleum products, and in oil-emulsion-cutting fluids.

The conducive conditions include the following (Ref. 42):

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1. The system can be either aqueous or nonaqueous, but it must allow the accumulation of water in some areas.

2. The temperature of the system must be below approximately 65°C (149°F) at some intervals and below 125°C (257°F) at all times.

3. Although the pH of a system is generally an unreliable indicator, most microorganisms will not grow in strongly acidic or strongly basic environments, i.e., below pH 4 or above pH 9.

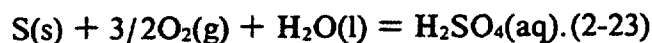
4. Light is not necessary for the growth of most bacteria and fungi; it is, however, necessary for the growth of algae.

**2-2.15.3 Mechanisms**

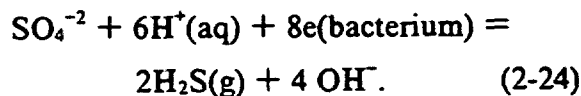
Biological organisms affect corrosion by one or a combination of the following mechanisms (Ref. 1):

1. Directly influencing anodic and cathodic reactions
2. Affecting protective surface films
3. Creating corrosive conditions
4. Producing deposits that result in differential aeration cells.

Most active microorganisms are bacteria about 1 to 5  $\mu\text{m}$  (0.04 to 0.2 mil) long that either oxidize or reduce sulfur compounds as some part of their life process. Aerobic bacteria use external oxygen to oxidize sulfur or sulfide to sulfuric acid:



This reaction lowers the pH to between 1 and 4. Another group of bacteria flourishes in anaerobic conditions and reduces sulfate to sulfide or  $\text{H}_2\text{S}$ :



The electrons for the reaction are supplied by oxidation of organic matter or hydrogen. Sulfate-reducing bacteria foster corrosion in circumstances where it would not otherwise be expected, namely, at neutral pH and in the absence of oxygen.

The reduction reaction of sulfates is normally slow, but anaerobic bacteria catalyze the reduction. There are two more effects of the bacteria in this process: Hydrogen ion reduction is stimulated. (Bacterial enzymes such as hydrogenase may be responsible for this reduction.)

A sulfide film is precipitated that is nonprotective and leads to enhanced attack if oxygen becomes available later.

Slime-forming bacteria are aerobic oxygen scavengers that can harbor sulfate reducers. If anaerobic bacteria are to exist in oxygen-rich environments, they must coexist with oxygen scavengers that create the required anaerobic conditions.

Filamentous iron bacteria, which appear as intertwined threads under a microscope, oxidize dissolved ferrous iron to insoluble ferric hydrate. Filamentous iron bacteria are responsible for the common, hollow, hemispherical tubercles seen in equipment below the waterline. These bacteria are aerobic and create oxygen depletion under the tubercles. Although this action is corrosive in itself, it is made even more so when it harbors sulfate reducers.

The metabolic deposits of gallionella are rich in iron and manganese chlorides. This richness causes uniform corrosion of steel and rapid pitting of austenitic stainless steel.

Macroorganisms contribute to corrosion by interfering with access of oxygen to the metal and by creating differential oxygen cells. Fungi liberate organic acids, such as oxalic and acetic, which accelerate the formation of unsightly tarnish films. Barnacles and mussels are common organisms in seawater. Pitting attack can result from the fouling of surfaces by these organisms, and fouling increases resistance to fluid flow and heat transfer.

**2-2.15.4 Application Constraints and Protection Approaches**

The following measures can be applied to specific instances of biological corrosion as appropriate:

1. Accurately diagnose the presence and relative contribution of biological corrosion to the material degradation problem. Microbiological corrosion rarely occurs without some degree of conventional corrosion. It is difficult to separate the two.

2. Accurately assess the source of biological organisms. In a closed system eliminating the source of contamination may solve the corrosion problem.

3. Control the environmental or media chemistry. Strongly acidic or strongly basic environments can prevent microorganism growth.

4. Use inhibitors and/or biocides. For example, icing inhibitor, MIL-I-27686, added at the rate of  $5.5 \times 10^{-4} \text{ m}^3$  per  $0.38 \text{ m}^3$  (1 pt per 100 gal) of diesel fuel controls corrosion by microorganisms.

5. Remove biological nutrients.

6. Select suitable resistant materials. For example, only titanium and most noble metals resist the iron-manganese chloride environment generated by gallionella (Ref. 43).

7. Use cathodic protection. For example, cathodic protection used in conjunction with linings seems to protect steel against the effects of sulfate reducers.

8. Provide designed-in accessibility for frequent and effective cleaning, sterilization, and decontamination.

9. Apply protective coatings. Thin, film coatings should be avoided. Tests should be made to determine whether the coating material is attacked by or is a nutrient for the bacteria.

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### 2-2.15.5 Examples

Biological corrosion has caused the failure of the M60 tank aluminum fuel cells. Dirt and water contamination of the diesel fuel results in the formation of colonies of microorganisms. Attack is reported to result from the formation of an acid by the microorganisms (Ref. 44). However, the formation of simple concentration cells is suggested as the mechanism for similar corrosion of jet aircraft fuel tanks (Ref. 42).

## 2-3 ENVIRONMENTS

The metal in an equipment item experiences different environments during fabrication and use. Corrosion results from the interaction of the metal with these environments. The basic environment for military materiel is the natural atmospheric environment of the field, which varies in different locations and in different seasons. The natural environment is also greatly affected by human activity.

The materiel design and procurement process must balance the goals of reliability, readiness, safety, and cost. To accomplish this task, corrosion processes must be considered an integral component of a materiel system. Within this context, corrosion processes are to be prevented altogether, controlled at some rate, or the damage is to be repaired after it occurs. Each of these approaches requires consideration of the potential for corrosion effects, and this potential can be assessed only by reference to the environments to which the metal may be exposed in the production phase and in the fielded phase. Environmental exposure in the production phase creates conditions in the metal that influence its susceptibility to corrosion, whereas environmental exposures in the field are directly responsible for the corrosion effects.

A distinction is drawn between natural and induced environmental factors. The key to the distinction is whether the environment is modified as a result of human activity. The induced environment should be considered in the setting of the natural environment. For example, calcium chloride (induced environment) is used in certain parts of the country to melt snow and ice on roadways (natural environment). This substance splashes on the underparts of vehicles and creates an induced environment. At normal winter temperatures (natural environment) when ice and snow can be expected, the corrosion rate of steel by the calcium-chloride-induced environment is relatively low. However, when the vehicle is driven into a heated garage (induced environment), the corrosion rate is much higher.

Packaging creates an induced environment. For example, some plastics release corrosive chemicals when heated. Therefore, a package containing these plastics and susceptible metals creates an induced corrosive environment when the package is exposed to the natural environment of solar radiation.

### 2-3.1 NATURAL ENVIRONMENT

The natural environmental factors are related to the basic climate types listed in Table 2-22, which are temperate, arctic, desert, and tropical. The various environmental factors or elements are qualitatively ranked according to their importance in a particular climate type. Thus terrain, high humidity, and microbiological organisms are key factors in the tropical environment. Solar radiation, rain, and salt are also important factors. Except for terrain, all of these factors are conducive to corrosion processes.

The general conditions that describe climate types are listed in Table 2-23. These are the specific quantitative parameters that describe the environment. For example, one of the sets of conditions in the tropical environment is outside air temperatures ranging from 24° to 35° C (75° to 95° F) plus a 4-h exposure to salt spray. Obviously, these conditions exist only in coastal areas, but they can be severe corrosion conditions. Temperate climate types are further classified as maritime, continental, and highlands in Table 2-23.

#### 2-3.1.1 Production

Most production activities occur in enclosed factory spaces, but buffer storage of raw materials, semifinished components, and finished items is often in the open. Transportation may also expose materials and components to the elements, especially materials that are shipped in large unit lots, such as rolls of sheet metal and components that are large.

Table 2-24 lists the environmental factors or elements that are most significant in the various forms of transportation. Accordingly, materiel carried in an open truck can be exposed to all of the environmental elements that are characteristic of the climate type of the region. In addition, it will be exposed to the shock and vibration resulting from road conditions of the route traversed.

Similar relationships between the type of storage accorded to the materiel and the significant environmental elements that can be experienced are shown in Table 2-25. Materiel in open storage experiences the environmental elements characteristic of the climate type of the region.

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TABLE 2-22. RELATIONSHIP OF NATURAL ENVIRONMENTAL FACTORS TO CLIMATE (Ref. 45)

| FACTOR                    | TEMPERATE | ARCTIC | DESERT | TROPICAL |
|---------------------------|-----------|--------|--------|----------|
| Terrain                   | +++       | +++    | +++    | +++      |
| Low temperature           | ++        | +++    | 0      | 0        |
| High temperature          | +         | 0      | +++    | ++       |
| Low humidity              | 0         | 0      | ++     | 0        |
| High humidity             | ++        | +      | 0      | +++      |
| Pressure                  | 0         | 0      | 0      | +        |
| Solar radiation           | +         | ++     | +++    | ++       |
| Rain                      | ++        | +      | +      | ++       |
| Fog                       | ++        | ++     | 0      | 0        |
| Solid precipitation       | ++        | ++     | 0      | 0        |
| Whiteout and ice fog      | 0         | ++     | 0      | 0        |
| Salt, salt fog, saltwater | +         | +      | +      | ++       |
| Wind                      | +         | ++     | +      | +        |
| Ozone                     | *         | *      | *      | *        |
| Macrobiological organisms | +         | 0      | 0      | +        |
| Microbiological organisms | +         | 0      | 0      | +++      |

+++ Key factor

++ Important factor

+ Active factor

0 Unimportant or absent factor

\* Little or no climatic relationship

TABLE 2-23. A CLIMATE CLASSIFICATION SYSTEM (Ref. 45)

| CLIMATE TYPE      | DESCRIPTION   |
|-------------------|---|
| Icecap and arctic | -54°C (-65°F) outside air temperature plus blowing snow at 24 km/h (15 mph) and higher (4-h duration)   |
| Desert            | +52°C (+125°F) outside air temperature plus 1292 W/m <sup>2</sup> (120 W/ft <sup>2</sup> ) solar radiation (4-h duration)   |
| Tropic            | <ol style="list-style-type: none"> <li>+24° to 35°C (+75° to 95°F) outside temperature plus 100 mm/h (4 in./h) of rain (2-h duration)</li> <li>+24° to 35°C (+75° to 95°F) outside air temperature plus salt spray (4-h duration)</li> <li>+35°C (+95°F) outside temperature plus 1292 W/m<sup>2</sup> (120 W/ft<sup>2</sup>) solar radiation (4-h duration)</li> <li>+24° to 32°C (+75°F to 90°F) outside temperature plus fog (4-h duration)</li> </ol>   |
| Temperate:        |   |
| Maritime          | <ol style="list-style-type: none"> <li>+18°C (+65°F) outside air temperature plus fog (4-h duration)</li> <li>+27°C (+80°F) outside air temperature plus 90% relative humidity (4-h duration)</li> <li>+21°C (+70°F) outside air temperature plus salt spray (4-h duration)</li> <li>+24°C (+75°F) outside air temperature plus 10 cm/h (4 in./h) of rain (2-h duration)</li> <li>+38°C (+100°F) outside air temperature plus 1292 W/m<sup>2</sup> (120 W/ft<sup>2</sup>) solar radiation (4-h duration)</li> </ol> |
| Continental       | <ol style="list-style-type: none"> <li>+32°C (+90°F) outside air temperature plus 1292 W/m<sup>2</sup> (120 W/ft<sup>2</sup>) solar radiation (4-h duration)</li> <li>+27°C (+80°F) outside air temperature plus sand and dust (4-h duration)</li> <li>+32°C (+90°F) outside air temperature plus 95% relative humidity (4-h duration)</li> <li>-7°C (+20°F) outside air temperature plus blowing snow at 64 km/h (40 mph) and higher (4-h duration)</li> </ol>   |
| Highland          | Highlands are those regions above 1829 m (6000 ft) altitude. Climates between highland areas vary widely; therefore, no typical conditions can be specified.  |

**MIL-HDBK-735(MR)**

**TABLE 2-24. RELATIONSHIPS BETWEEN TRANSPORT MODES AND  
THE ENVIRONMENT EXPERIENCED BY MATERIEL IN THE PRODUCTION PHASE  
(Ref. 45)**

| <b>TRANSPORT TYPE</b> | <b>ENVIRONMENTAL EXPOSURE</b>  | <b>MOST SIGNIFICANT ELEMENTS</b>   |
|-----------------------|--|--|
| <b>Truck:</b>         |  |  |
| Open                  | 1. Ambient climatic and natural factors  | 1. Temperature, humidity, solar radiation, rain, solid precipitants, natural and induced wind                                  |
|                       | 2. Low- to high-level shock and vibration  | 2. Terrain (road surfaces)   |
|                       | 3. Sand and dust   | 3. Terrain and wind  |
| Closed                | 1. Modified climatic and natural factors (can intensify or reduce effect of certain factors)               | 1. Temperature, solar radiation, humidity  |
|                       | 2. Low- to high-level shock and vibration  | 2. Terrain (road surfaces)   |
| <b>Rail:</b>          |  |  |
| Open                  | 1. Ambient climatic and natural factors  | 1. Temperature, humidity, solar radiation, rain, solid precipitants, natural and induced wind                                  |
|                       | 2. High-level shock  | 2. Switching operation, run-in and run-out   |
|                       | 3. Sand and dust (less severe than for open truck because vehicle induces far less airborne sand and dust) | 3. Wind and terrain  |
| Closed                | 1. Modified climatic and natural factors (can intensify or reduce effect of certain factors)               | 1. Temperature, solar radiation, humidity  |
|                       | 2. High-level shock  | 2. Switching operations and run-in and run-out   |
| <b>Ship:</b>          |  |  |
| Above decks           | 1. Ambient climatic and natural factors  | 1. Saltwater, salt spray, salt fog, humidity, temperature, solar radiation, rain, solid precipitation                          |
|                       | 2. Shock, vibration, and acceleration significantly less than for rail or truck                            | 2. Wave impact and drive train vibration   |
| Below decks           | 1. Modified ambient climatic and natural factors   | 1. Humidity, temperature, solar radiation, macrobiological and microbiological organisms                                       |
|                       | 2. Shock, vibration, and acceleration significantly less than for rail or truck                            | 2. Wave impact and drive train vibration   |
| <b>Air:</b>           |  |  |
| Exterior transport    | 1. Ambient climatic and natural factors  | 1. Low temperature, pressure, fluctuation (altitude), rain, solid precipitation, induced wind                                  |
|                       | 2. Shock, vibration, and acceleration  | 2. Structurally transmitted shock and vibration resulting from landing, maneuvers, aerodynamic forces and aircraft components  |
|                       | 3. Sand and dust   | 3. Helicopter rotor wash, aircraft prop wash, jet engine exhaust   |
| Interior transport    | 1. Modified ambient climatic and natural factors   | 1. Low temperature, pressure fluctuation (altitude)  |
|                       | 2. Shock, vibration, and acceleration  | 2. Structurally transmitted shock and vibration resulting from landing, maneuvers, aerodynamic forces, and aircraft components |



**MIL-HDBK-735(MR)****TABLE 2-25. RELATIONSHIPS BETWEEN STORAGE TYPE AND THE ENVIRONMENT EXPERIENCED BY MATERIEL IN THE PRODUCTION PHASE (Ref. 45)**

| <b>STORAGE TYPE</b>     | <b>ENVIRONMENTAL EXPOSURE</b>                  | <b>MOST SIGNIFICANT ELEMENTS</b>   |
|-------------------------|--|--|
| Open                    | All ambient climatic and natural factors       | Varies with climatic type<br><br>Arctic: solid precipitants, low temperature, wind, rain<br>Desert: high temperature, solar radiation, sand and dust, low humidity, wind<br>Tropical: fungi, high temperature, high humidity, solar radiation, rain, macrobiological organisms, salt spray, and fog<br>Industrial: ozone and atmospheric pollutants can be important during open storage in industrialized areas |
| Sheltered               | Protection provided from most climatic factors | Varies with climatic type<br><br>All climates: temperature and macrobiological organisms<br>Additional tropical and some temperate: high humidity and fungi<br>Additional desert: low humidity and sand and dust   |
| Sheltered, dehumidified | High degree of protection from exposure        | Temperature, macrobiological organisms, and sand and dust can occasionally cause some problems.  |

**2-3.1.2 Field**

Natural environments for the field deployment of Army materiel represent the range of climatic conditions in many parts of the world. Climatic conditions that represent combinations of the natural environmental factors of temperature, humidity, and solar radiation are described in Table 2-26. The worldwide occurrence of climate regions is indicated in Fig. 2-78. The ranges of climatic conditions that relate to climatic type are shown in Table 2-27. These ranges, which represent the diurnal cycle, should be considered in the development of military materiel.

The relative interdependence of pairs of environmental factors can be determined from Table 2-28. For example, temperature has little interdependence on salt but some interdependence on biological organisms. The direction of interdependence is given in Table 2-29. The implications of high and low temperatures for the various environmental factors are indicated in a qualitative way. High and low temperatures are, of course, related to the range of naturally occurring temperatures. Microorganisms cannot exist, for example, if the temperature is either too high or too low.

Atmospheric sea salt is an environmental factor of great importance to corrosion. Atmospheric sea salt is a function of geographic location relative to bodies of salt water and the humidity of the region. It is, of course, highest in coastal regions and occurs usually in the form

of salt spray, mist, or fog. Regions subject to these conditions are indicated in Fig. 2-79.

**2-3.2 INDUCED ENVIRONMENT**

Processing conditions must be considered as part of the induced environment during the production of Army materiel because it may create residual conditions that can influence corrosion. For example, cold-forming metal shapes can generate residual stress, welding can affect the microstructure of the molten and adjacent heat-affected zone, and pickling parts in an acid bath can influence the corrosion characteristics of a metal surface by removing mill scale and rust and exposing clean metal.

The internal atmosphere of a production plant, such as a forge shop or a plating shop, may be corrosive to some metals. The so-called industrial environment created by the uncontrolled or partially controlled effluents of a concentration of industries in an area is generally more corrosive than other atmospheres.

Induced environments for the field deployment of Army materiel are caused by the modification of the natural environment that results from normal human activity as well as by that resulting from military operations. A materiel storage depot located in an industrial region will experience an induced environment caused by the pollutants in the atmosphere. Materiel in a training or combat environment experiences the atmospheric contaminants and the sustained and cyclic stresses of operations.

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TABLE 2-26. CLIMATE CATEGORIES (Ref. 46)

| TYPE                     | DESCRIPTION   |
|--------------------------|---|
| Wet-warm                 | Typified by conditions under the canopy of heavily forested tropical areas with temperatures very close to 24°C (75°F), a relative humidity above 95%, and negligible solar radiation   |
| Wet-hot                  | Typified by open tropical areas with wet-hot conditions occurring frequently or seasonally. Temperatures range from 26° to 35°C (78° to 95°F), relative humidity ranges from 74 to 100 %, and solar radiation can be intense.   |
| Humid-hot coastal desert | Typified by coastal regions around water bodies with high surface temperatures. Temperatures range from 29° to 38°C (85° to 100°F), humidities range from 63 to 90 %, and solar radiation can be intense.   |
| Hot-dry                  | Desert regions with temperatures from 32° to 52°C (90° to 125°F), humidities under 20 %, and intense solar radiation  |
| Intermediate             | Seasonal dry periods of wet-hot regions as well as large regions of the mid-latitude of both hemispheres where high temperatures range from 21° to 43°C (70° to 110°F), humidities range from 20 to 85 %, and solar radiation can be intense. This climatic category may be seasonal and alternate with an intermediate cold climate. |
| Intermediate cold        | This climate is found in mid-latitude regions of the northern hemisphere where low temperatures range from -32° to -21°C (-25° to -5°F), relative humidities are near 100 %, and solar radiation is negligible.   |
| Cold northern            | Cold conditions found in the northern hemisphere where minimum temperatures range from -46° to -37°C (-50° to -35°F), humidity is close to 100 %, and solar radiation is negligible.  |
| Extreme cold             | Those arctic regions where temperatures of -57°C (-70°F) occur for periods of 6 h or longer.  |

### 2-3.2.1 Production

An item of Army materiel can contain a great many parts and components. The production phase terminates after these parts and components have been assembled into a functioning item of materiel and are shipped from the supplier's facility to a receiving and storage depot. As a corrosion-related concept, the production phase begins when environmental exposure can influence the corrosion of finished items of materiel. For metals this is the last solidification from a molten phase because it establishes the final chemistry of the alloy. Fig. 2-80 is a flowchart of metal in production processing and field use. The microstructure can be influenced by further heating and cooling, working, and forming. The metal chemistry can be influenced locally by joining processes, such as welding, and by thermally induced diffusion processes.

The primary metal producer manufactures the basic metal ingot. The secondary metal producer manufactures mill products that include such standard forms as sheet, strip, plate, bar, wire, pipe, welding electrodes, and forging stock. In many cases the primary and secondary

metal producers are integrated. The chemical composition is specified in terms of maximum levels for some components and a range for others. Mechanical properties are given as typical or minimum values. If nonstandard materials such as close tolerances on the alloy composition, special heat treatments, and hot- and cold-working schedules are required, consideration should be given during production to the potential corrosion effects of the environmental exposure experience.

A piece of raw material is fashioned into an equipment item by a wide variety of processes. These processes influence the internal stress, microstructure, surface finish, and chemistry of a metal part. These influences are induced by production processes that form, cut, clean, treat, and join metal. Therefore, the induced environmental parameters include those inherent in production processes. Also included are the influences of shock and vibration in transportation and exposure to industrial pollutants in storage. Induced environmental parameters to which materiel is unintentionally exposed are more important in the operational, or field, phase.

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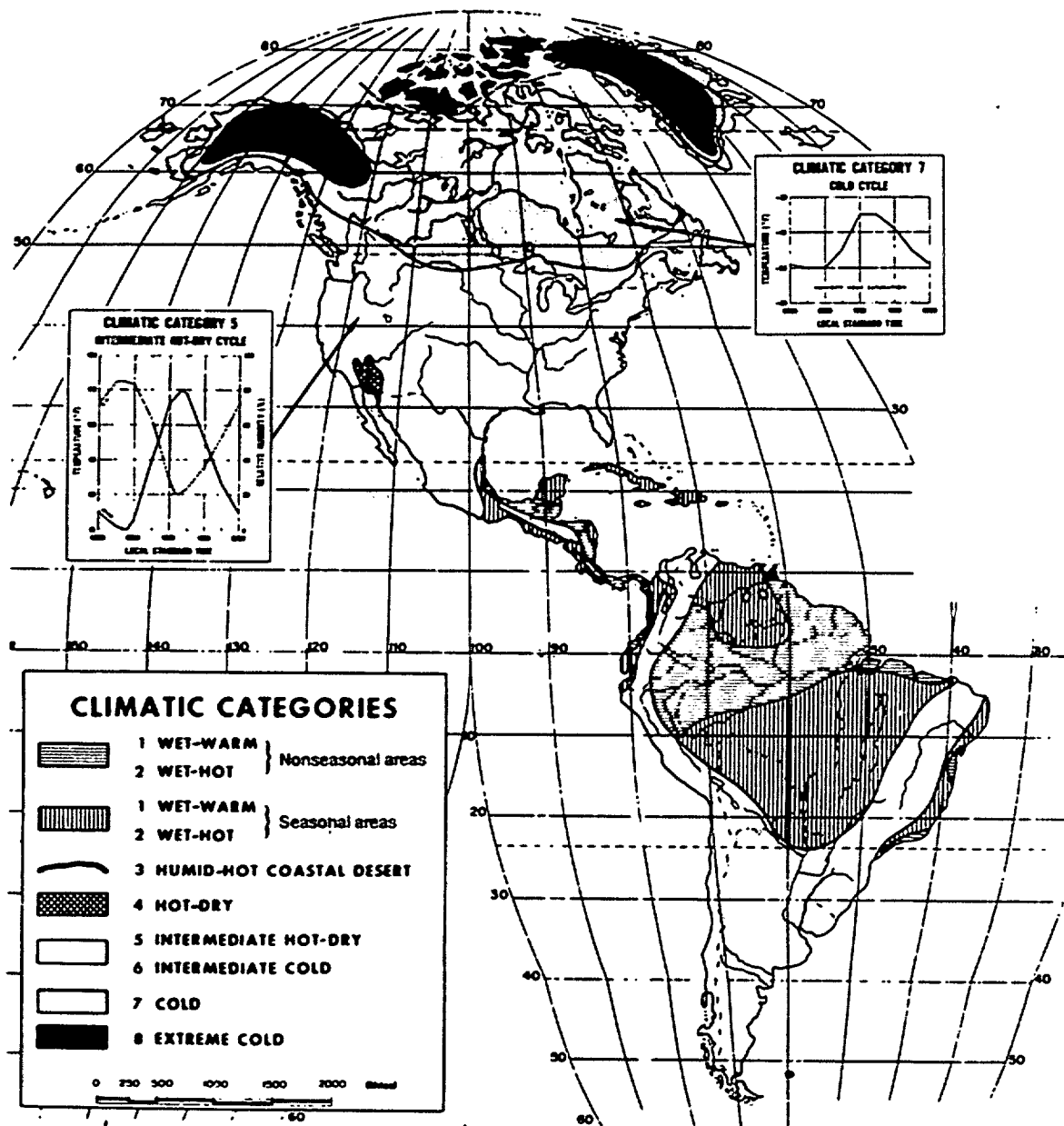


Figure 2-78. Areas of Occurrence of Climate Categories (Ref. 46)

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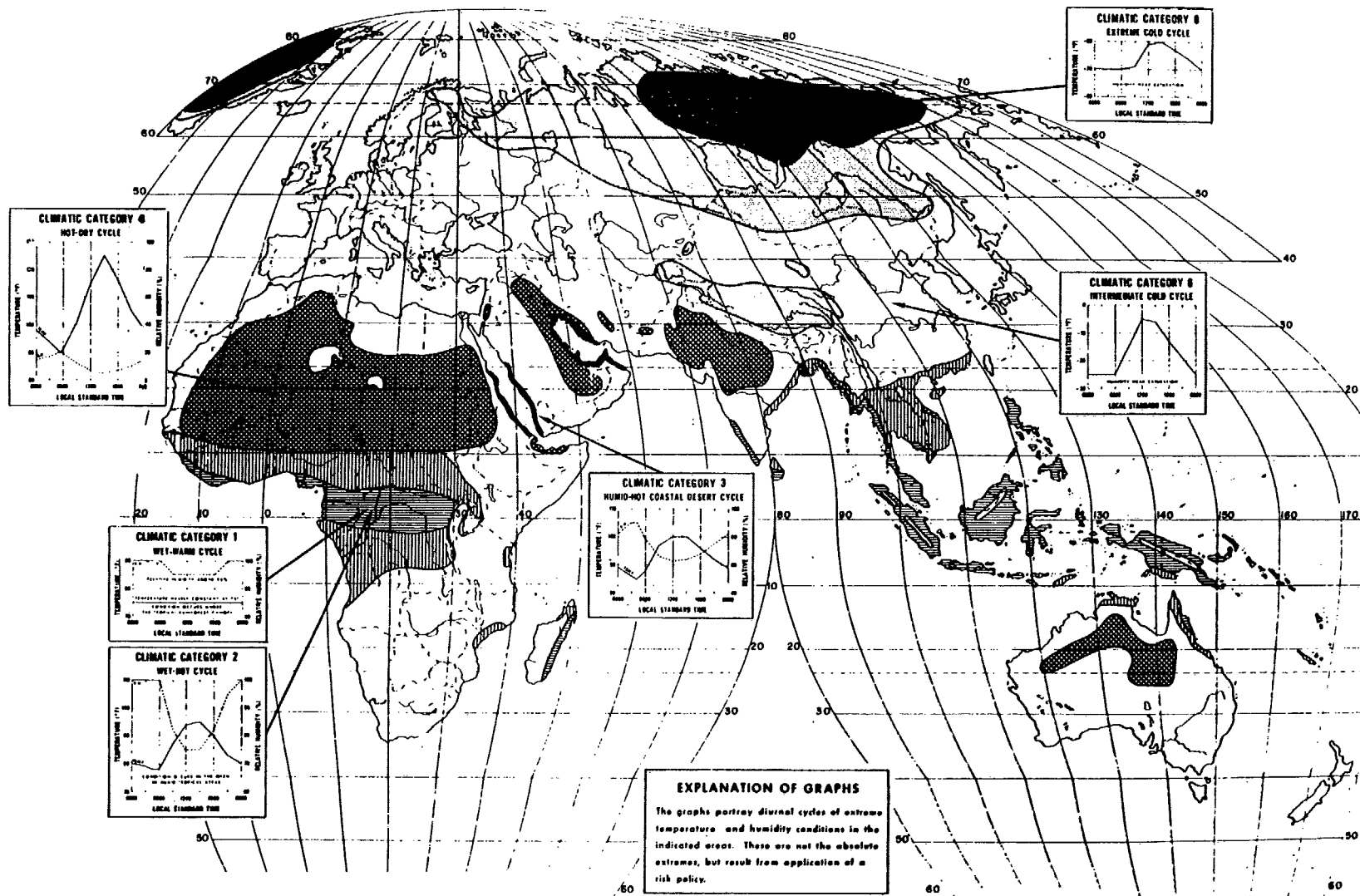


Figure 2-78. (cont'd)

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**MIL-HDBK-735(MR)****TABLE 2-27. TEMPERATURE, SOLAR RADIATION, AND RELATIVE HUMIDITY  
DIURNAL CYCLES FOR CONSIDERATION IN THE DEVELOPMENT  
OF MILITARY MATERIEL (Ref. 46)**

| CLIMATIC<br>TYPE                    | CLIMATIC CONDITIONS           |   |                            |                               |                            |
|-------------------------------------|-------------------------------|---|----------------------------|-------------------------------|----------------------------|
|                                     | OPERATIONAL                   |   |                            | STORAGE AND TRANSIT           |                            |
|                                     | Temperature,<br>°C (°F)       | Solar<br>Radiation,<br>W/m <sup>2</sup><br>(Btu/(ft <sup>2</sup> -h)) | Relative<br>Humidity,<br>% | Temperature,<br>°C (°F)       | Relative<br>Humidity,<br>% |
| 1<br>Hot-Dry                        | 32 to 52<br>(90 to 125)       | 0 to 1135<br>(0 to 360)   | 5 to 20                    | 32 to 71<br>(90 to 160)       | 2 to 50                    |
| 2<br>Wet-Warm                       | Nearly<br>Constant<br>24 (75) | Not<br>Applicable   | 95 to 100                  | Nearly<br>Constant<br>27 (80) | 95 to 100                  |
| 3<br>Wet-Hot                        | 26 to 35<br>(78 to 95)        | 0 to 1135<br>(0 to 360)   | 75 to 100                  | 32 to 71<br>(90 to 160)       | 10 to 85                   |
| 4<br>Humid-Hot<br>Coastal<br>Desert | 29 to 38<br>(85 to 100)       | 0 to 1135<br>(0 to 360)   | 63 to 90                   | 32 to 71<br>(90 to 160)       | 10 to 85                   |
| 5<br>Intermediate<br>Hot-Dry        | 21 to 43<br>(70 to 110)       | 0 to 1135<br>(0 to 360)   | 20 to 85                   | 21 to 63<br>(70 to 145)       | 5 to 90                    |
| 6<br>Intermediate                   | -32 to -21<br>(-25 to -5)     | Negligible  | High                       | -34 to -23<br>(-30 to -10)    | High                       |
| 7<br>Cold                           | -46 to -37<br>(-50 to -35)    | Negligible  | High                       | -46 to -37<br>(-50 to -35)    | High                       |
| 8<br>Extreme<br>Cold                | -57 to -51<br>(-70 to -60)    | Negligible  | High                       | -57 to -51<br>(-70 to -60)    | High                       |

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TABLE 2-28. INTERDEPENDENCE OF NATURAL ENVIRONMENTAL FACTORS (Ref. 47)

|                           | TERRAIN | TEMPERA-<br>TURE | HUMIDITY | PRESSURE | SOLAR<br>RADI-<br>ATION | RAIN | SOLID<br>PRECIP-<br>ITANTS | FOG | WIND | SALT | OZONE | MACROBIO-<br>LOGICAL<br>ORGANISMS | MICROBIO-<br>LOGICAL<br>ORGANISMS |
|---------------------------|---------|------------------|----------|----------|-------------------------|------|----------------------------|-----|------|------|-------|-----------------------------------|-----------------------------------|
| Terrain                   |         | 2                | 2        | 2        | 2                       | 2    | 2                          | 2   | 1    | 2    | 1     | 3                                 | 1                                 |
| Temperature               | 2       |                  | 2        | 1        | 3                       | 2    | 3                          | 2   | 1    | 1    | 1     | 3                                 | 3                                 |
| Humidity                  | 2       | 2                |          | 1        | 3                       | 4    | 2                          | 2   | 1    | 1    | 1     | 2                                 | 3                                 |
| Pressure                  | 2       | 1                | 1        |          | 1                       | 2    | 1                          | 1   | 2    | 1    | 1     | 1                                 | 1                                 |
| Solar radiation           | 2       | 3                | 2        | 1        |                         | 2    | 4                          | 1   | 1    | 1    | 2     | 2                                 | 1                                 |
| Rain                      | 2       | 2                | 4        | 2        | 4                       |      | 4                          | 2   | 1    | 1    | 1     | 2                                 | 1                                 |
| Solid precipitants        | 2       | 3                | 3        | 1        | 4                       | 4    |                            | 2   | 1    | 1    | 1     | 2                                 | 1                                 |
| Fog                       | 2       | 2                | 4        | 1        | 4                       | 3    | 3                          |     | 3    | 2    | 1     | 1                                 | 1                                 |
| Wind                      | 2       | 1                | 3        | 2        | 1                       | 2    | 1                          | 3   |      | 1    | 2     | 1                                 | 1                                 |
| Salt                      | 1       | 1                | 2        | 1        | 1                       | 2    | 1                          | 1   | 1    |      | 1     | 1                                 | 1                                 |
| Ozone                     | 1       | 1                | 1        | 1        | 1                       | 1    | 1                          | 1   | 1    | 1    |       | 1                                 | 1                                 |
| Macrobiological organisms | 2       | 2                | 2        | 1        | 1                       | 1    | 1                          | 1   | 1    | 1    | 1     |                                   | 4                                 |
| Microbiological organisms | 1       | 3                | 3        | 1        | 1                       | 1    | 1                          | 1   | 1    | 1    | 1     | 2                                 |                                   |

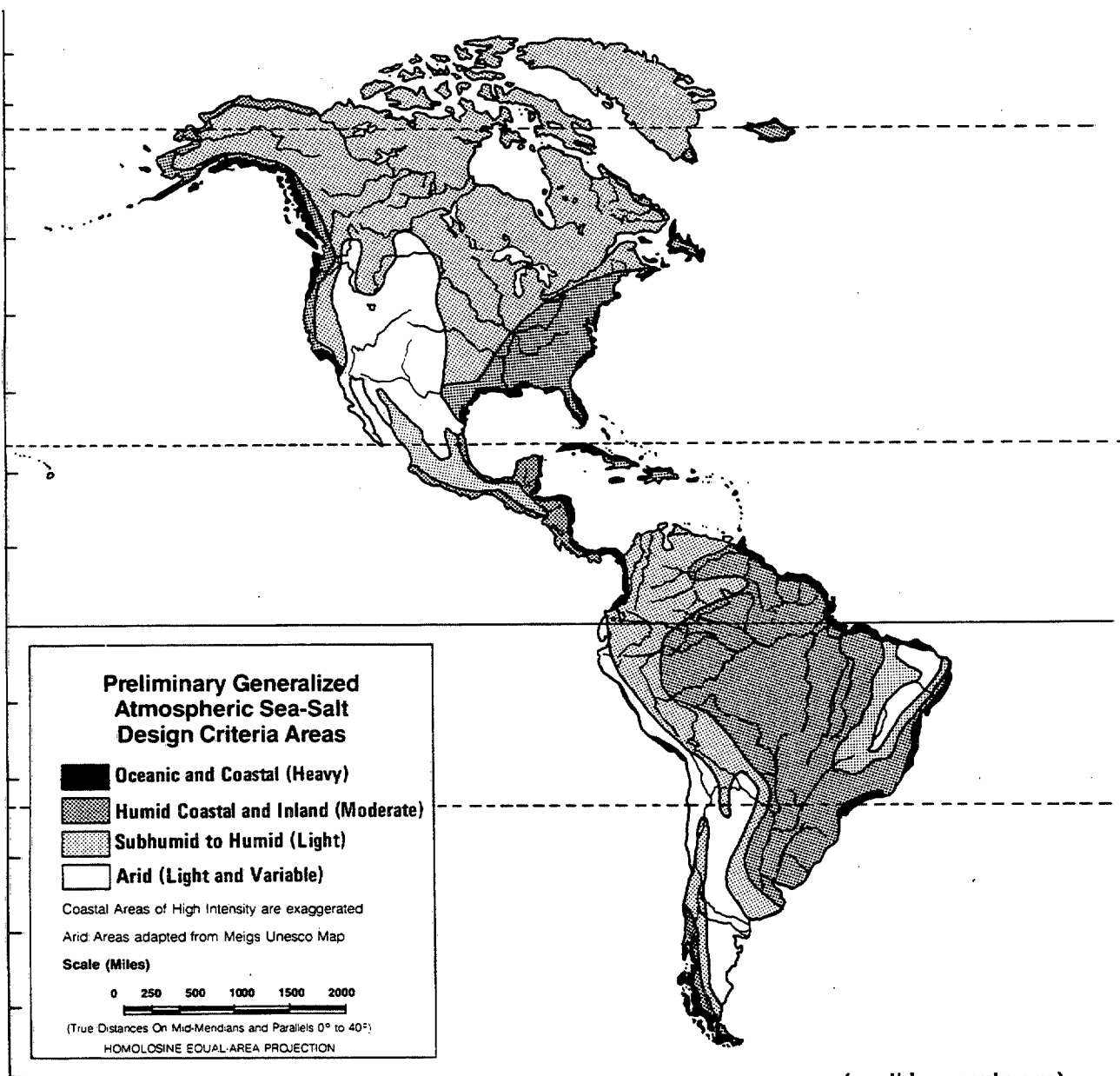
NOTE: Given knowledge of the factor in the left-hand column, the attendant knowledge about the factor at column heading is given by numerical index where 1 = no, 2 = little, 3 = some (or sometimes), and 4 = much.

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TABLE 2-29. TEMPERATURE SYNERGISMS (Ref. 48)

| FACTOR                | HIGH-TEMPERATURE EFFECT  | LOW-TEMPERATURE EFFECT  |
|-----------------------|--|---|
| Humidity              | High temperature tends to increase the rate of moisture penetration. The general deterioration effects of humidity are increased by high temperatures.   | Humidity decreases with temperature but low temperature induces moisture condensation and, if the temperature is low enough, frost or ice.                        |
| Solar radiation       | This is a natural combination that causes increasing effects on organic materials.   | Low temperature tends to reduce the effects of solar radiation, and vice versa.   |
| Shock and vibration   | Because both of these environments affect common material properties, they will intensify each other's effects. The amount the effects are intensified depends on the magnitude of each environment in the combination. Plastics and polymers are more susceptible to this combination than metals, unless extremely high temperatures are involved. | Low temperature tends to intensify the effects of shock and vibration. This effect is, however, a consideration only at very low temperatures.                    |
| Low pressure          | Each of these environments is dependent on the other. For example, as pressure decreases, outgassing of constituents of materials increases, and as temperature increases, the rate of outgassing increases. Hence each tends to intensify the effects of the other.   | This combination can accelerate leakage through seals, etc.   |
| Fungus                | A certain degree of high temperature is necessary to permit fungus and microorganisms to grow. But above 71°C (160°F) fungi and microorganisms cannot develop.   | Low temperature reduces fungus growth. At sub-zero temperatures, fungi will remain in suspended animation.  |
| Acceleration          | This combination produces the same effect as high temperature with shock and vibration.  | This combination produces the same effect as low temperature with shock and vibration.  |
| Salt spray            | High temperature tends to increase the rate of corrosion caused by salt spray.   | Low temperature reduces the corrosion rate of salt spray.   |
| Sand and dust         | The erosion rate of sand and dust may be accelerated by high temperature. However, high temperatures reduce sand and dust penetration.   | Low temperature increases dust penetration.   |
| Explosive environment | Temperature has very little effect on the ignition of an explosive atmosphere, but it does affect the air-vapor ratio, which is an important consideration.  | Temperature has very little effect on the ignition of an explosive atmosphere. It does, however, affect the air-vapor ratio, which is an important consideration. |
| Ozone                 | Starting at about 150°C (300°F) temperature starts to reduce ozone. Above about 270°C (520°F) ozone cannot exist at pressures normally encountered.  | Ozone effects are reduced at lower temperatures, but ozone concentration increases with lower temperatures.   |

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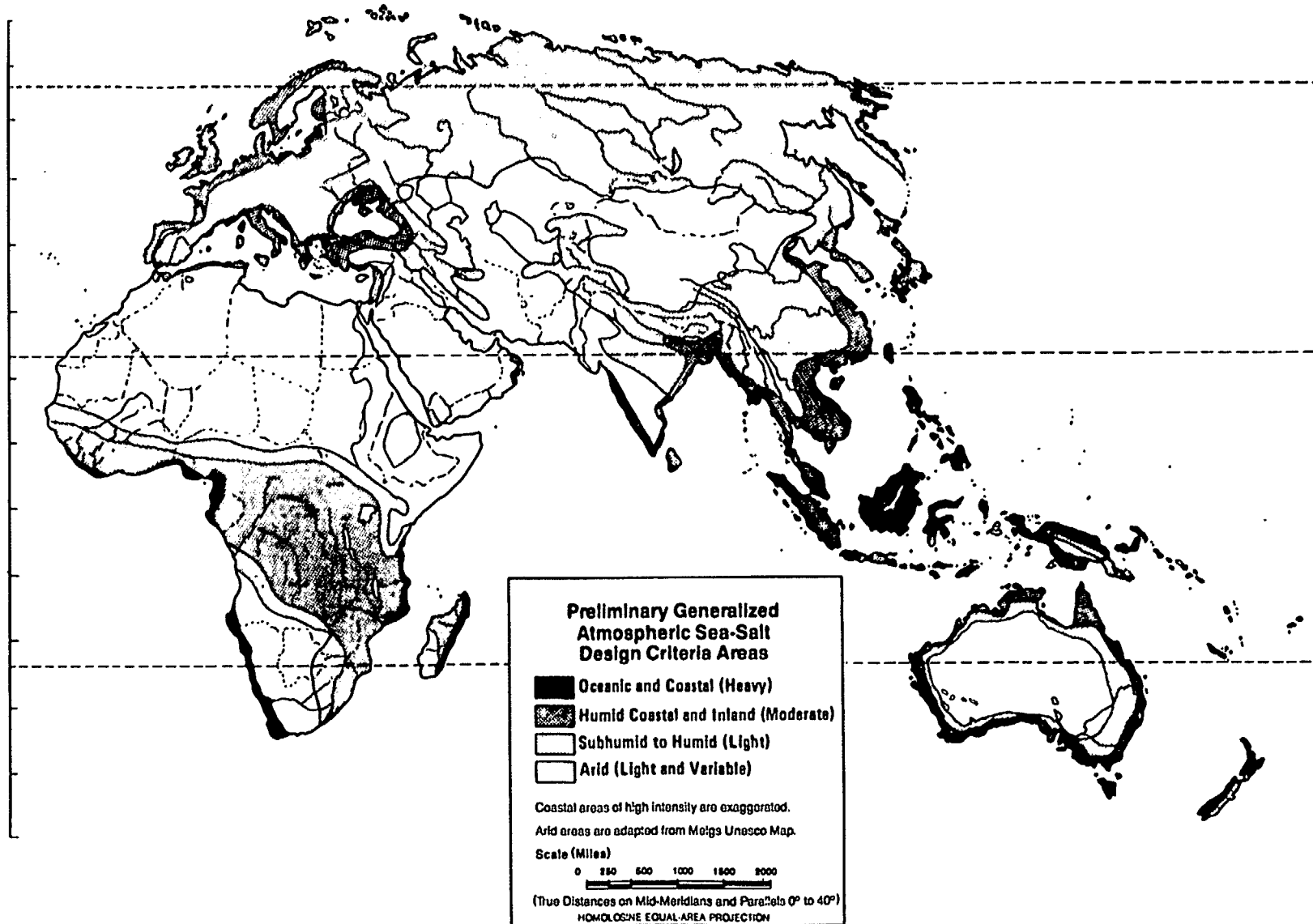
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**Figure 2-79. Preliminary Generalized Atmospheric Sea-Salt Design Criteria Areas (Ref. 49)**

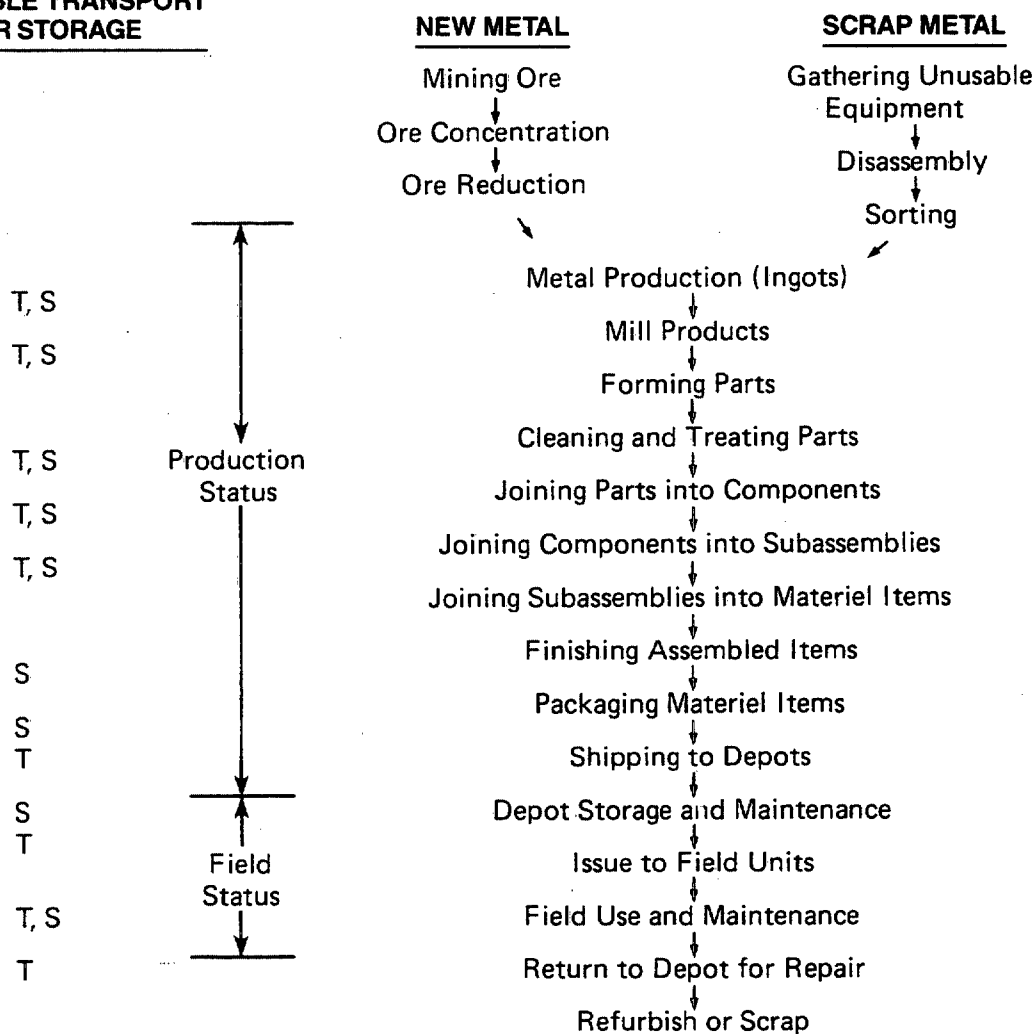


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Figure 2-79. (cont'd)

**MIL-HDBK-735(MR)****POSSIBLE TRANSPORT  
OR STORAGE****Figure 2-80. Production and Field Flowchart****2-3.2.2 Field**

The field environment is the operating environment for an item of Army materiel. The field phase begins when an item of materiel is received at a storage location from which it will be issued to operating personnel. Field storage facilities can be characterized as follows:

1. Buffer storage in the supply chain for materiel that is continually consumed. An example is an ammunition dump that is supplying troops engaged in combat. This materiel will not be given much protection from the environment because it is constantly being used and replenished.

2. Materiel deposited in locations in which national interests dictate an ability to respond rapidly to crises. Although this materiel is in potentially long-term storage, it must be available for operations on short notice. Therefore, the degree of protection from the environment that can be applied is compromised by the need for rapid

availability. For example, an antitank missile stored in its launch tube must function perfectly, regardless of the length of storage. The combat exposure of such equipment may be quite brief, if it occurs at all, but the storage exposure may be long and severe.

3. Permanent supply depots that maintain stock of a wide variety of materiel items for issue. Items that are not consumed are returned and maintained or refurbished and reissued. Considerable effort is expended to maintain stocks highly protected from environmental damage. Equipment such as tactical vehicles may also be exposed to long periods of storage. However, it is more likely that those available and in use in peacetime will be used by a combat force. Therefore, depot and field maintenance and repair must be a high-priority activity. Not only does this storage situation have implications for the materials of construction, but it also has serious implications for incorporating maintainability in the design.

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Most materiel storage sites are on land in different parts of the world; however, if land bases are unavailable in locations where vital interests are threatened, shipboard storage may be used. Materiel stored aboard ship will be stored so that it can be rapidly loaded and unloaded. Shipboard storage, however, presents environmental conditions that can cause severe corrosion.

Induced environmental factors to which materiel is exposed in field activities include

1. Atmospheric pollutants
2. Sand and dust
3. Vibration
4. Shock
5. Acceleration
6. Acoustics
7. Electromagnetic radiation
8. Nuclear radiation
9. Chemical, biological, and decontamination agents.

Many of these factors arise from natural causes as well as from man's activities.

Induced environmental effects can degrade materiel, its functioning, and its operators. An example of permanent damage to materiel is the effect of large electromagnetic pulses from nuclear weapons. These pulses induce electrical currents in electronic devices that can destroy

solid-state components. An example of functional degradation is electromagnetic interference from countermeasures and from other electrical and electronic equipment. In this case the materiel itself is not damaged, and it recovers when the sources of interference are removed. An example of temporary operator degradation is impairment of vision from sand and dust or smoke screens. The materiel and its functioning may not be affected in this case.

As indicated in Table 2-30, the deterioration of metals results from chemical and mechanical damage. The most significant induced environmental factor in chemical damage is air pollutants. Table 2-31 lists pollutant concentrations and compositions in urban and rural areas. Also this table indicates the significant differences in pollutants between urban and rural locations, and it indicates the presence of pollutant species that are potentially corrosive when dissolved in water. For example, corrosive species that can form include nitric, sulfuric, and hydrochloric acids.

Forty-five locations have been compared based upon corrosion of steel and zinc specimens over a period of time. This comparison is shown in Table 2-32. The trend indicated by the table is that the least corrosive locations are rural and inland, the most corrosive are coastal sites, and industrial and tropical locations are intermediate.

**TABLE 2-30. EFFECT OF ENVIRONMENTAL FACTORS (Ref. 45)**

| MAJOR EFFECT  | CAUSES  |
|---|---|
| Interference:   |   |
| Optical (reduction of visibility and loss of communications)  | Fog, ice fog, salt fog, whiteout, rain, snow, mirages, darkness, terrain, clouds, duststorms, vegetation, water (covering terrain), countermeasures   |
| Electromagnetic (nonoptical)  | Lightning, terrain, auroral phenomena, rotating machinery, electromagnetic pulses from nuclear weapons, electrostatic discharge, communication (radio and television) sources, microwave sources, transmission lines, industrial equipment            |
| Audio   | Gunfire, explosions, rotating machinery, vibration of materiel, impact or shock of materiel, thunder, wave impact, animal noise, traffic, construction, exhaust noise from engines.   |
| Mobility reduction<br>(embedment, trapping, loss of traction)   | Ice, snow, mud, wet salt flats, swamp, sand, relief (due to shape of terrain), rocks and boulders, vegetation, grade, water, step function interfaces in the terrain, barricades, and traps.  |
| Mechanical damage<br>(deformation, fracture, fatigue, loss of strength, change of state, change of viscosity for liquids) | Temperature, humidity, fog, water, rain, water pressure, wind loading and air pressure, ice and snow loads, blowing sand and dust, terrain (shock, vibration, and impact), microbiological organisms, shock, vibration, acceleration, solar radiation |
| Chemical damage<br>(deterioration and corrosion spoilage)   | Temperature, humidity, fog, salt fog, saltwater and spray, rain, ozone, air pollutants, microbiological organisms.  |

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TABLE 2-31. POLLUTANT CONCENTRATIONS AND COMPOSITIONS (Ref. 50)

| PARTICULATE POLLUTANTS IN URBAN AREAS*                            |  | GASEOUS POLLUTANTS                  |   |        |
|---|--|-------------------------------------|---|--------|
| Pollutant   | Typical Concentration,<br>$\mu\text{g}/\text{m}^3$ | Pollutant                           | Typical Concentration,<br>ppm by volume |        |
|   |  |                                     | Urban                                   | Rural  |
| Solid particles:  | 110†   | Organic gases:                      | 3.0*                                    | 1.0    |
| Combustible carbon/soot and<br>miscellaneous organic<br>particles | 25   | Hydrocarbons (90% CH <sub>4</sub> ) | 2.8                                     | 1.0    |
| Metal oxides, salts, and<br>noncombustible soot particles         | 75   | Others                              | 0.2                                     | 0.05   |
| Silicates and mineral dusts                                       | 10   | Total aldehydes                     | 0.05                                    | 0.01   |
| Liquid particles:   | 10   | Inorganic gases:                    |   |        |
| Total particulates  | 120  | Oxides of nitrogen:                 |   |        |
| Chemical content of<br>particulates:††                            |  | Nitric oxide                        | 0.05**                                  | 0.01   |
| Chloride  | 4  | Nitrogen dioxide                    | 0.05**                                  | 0.02   |
| Nitrate   | 4**  | Oxides of sulfur:                   |   |        |
| Phosphate   | 1  | Sulfur dioxide                      | 0.05*                                   | 0.005  |
| Sulfate   | 13**   | Sulfur trioxide                     | <0.001                                  | <0.001 |
| Aluminum  | 5  | Oxides of carbon:                   |   |        |
| Calcium   | 4  | Carbon monoxide                     | 7.0**                                   | 0.1    |
| Iron  | 3**  | Carbon dioxide                      | 350                                     | 315    |
| Ammonium  | 0.7**  | Others:                             |   |        |
| Lead  | 1**  | Ammonia                             | 0.1                                     | 0.01   |
| Silicon   | 4  | Hydrogen chloride                   | 0.05                                    | 0.005  |
| Zinc  | 0.5**  | Hydrogen fluoride                   | 0.01                                    | 0.003  |
|   |  | Hydrogen sulfide                    | 0.003                                   | <0.001 |
|   |  | Ozone                               | 0.05**                                  | 0.02   |

\*Rural values are approximately 30% of the urban values.

\*\*From National Air Surveillance Networks (NASN)

†Based on the NASN average for suspended particulates of  $100 \mu\text{g m}^{-3}$  and a dustfall value of  $0.1 \text{ kg m}^{-2} \text{ mo}^{-1}$  ( $300 \text{ tons mi}^{-2} \text{ mo}^{-1}$ )

††Fifteen other elements are known to be present at lower concentration levels.

Chemical environmental factors and mechanical forces interact to enhance metal deterioration. Stress-corrosion cracking, corrosion fatigue, fretting, and erosion-corrosion are examples of this type of effect. However, the local chemical environment that is acting in these cases is either a derivative of the larger operating environment or it is a specialized environment purposely incorporated to facilitate a function. An example of a derivative environment is a concentrated salt solution in a crevice. An example of a specialized environment is hydraulic fluid in

a vehicle brake system. The derivative environment must be considered on a case-by-case basis even though it may actually be more important than the larger environmental effects. The potential for corrosion exists as a function of the design, which facilitates the creation of the local environment when the conditions of the larger environment are favorable. The specialized environment must be considered in terms of the interface that exists with the materials of construction.

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TABLE 2-32. COMPARATIVE ORDER OF SEVERITY OF 45 LOCATIONS BASED ON STEEL AND ZINC LOSSES (Ref. 51)

| RANKING TO<br>STATE COLLEGE |      | LOCATION  | 2-YEAR EXPOSURE<br>GRAMS LOST, g |      | STEEL: ZINC<br>LOSS<br>RATIO |
|-----------------------------|------|---|----------------------------------|------|------------------------------|
| STEEL                       | ZINC |   | STEEL                            | ZINC |                              |
| 1                           | 1    | Norman Wells, Northwest Territory, Canada       | 0.73                             | 0.07 | 10.4                         |
| 2                           | 2    | Phoenix, AZ                                     | 2.23                             | 0.13 | 17.2                         |
| 3                           | 3    | Saskatoon, Saskatchewan, Canada                 | 2.77                             | 0.13 | 21.3                         |
| 4                           | 4    | Esquimalt, Vancouver Island, Canada             | 6.50                             | 0.21 | 31.0                         |
| 5                           | 15   | Detroit, MI                                     | 7.03                             | 0.58 | 12.1                         |
| 6                           | 5    | Fort Amidor Pier, Panama                        | 7.10                             | 0.28 | 25.4                         |
| 7                           | 11   | Morenci, MI                                     | 7.03                             | 0.53 | 13.3                         |
| 8                           | 7    | Ottawa, Ontario, Canada                         | 9.60                             | 0.49 | 19.6                         |
| 9                           | 13   | Potter County, PA                               | 10.00                            | 0.55 | 18.2                         |
| 10                          | 31   | Waterbury, CT                                   | 11.00                            | 1.12 | 9.8                          |
| 11                          | 10   | State College, PA                               | 11.17                            | 0.51 | 21.9                         |
| 12                          | 28   | Montreal, Quebec, Canada                        | 11.44                            | 1.05 | 10.9                         |
| 13                          | 6    | Melbourne, Australia                            | 12.70                            | 0.34 | 37.4                         |
| 14                          | 20   | Halifax (York Redoubt), Nova Scotia, Canada     | 12.97                            | 0.70 | 18.5                         |
| 15                          | 19   | Durham, NH                                      | 13.30                            | 0.70 | 19.0                         |
| 16                          | 12   | Middletown, OH                                  | 14.00                            | 0.54 | 25.9                         |
| 17                          | 30   | Pittsburgh, PA                                  | 14.90                            | 1.14 | 13.1                         |
| 18                          | 27   | Columbus, OH                                    | 16.00                            | 0.95 | 16.8                         |
| 19                          | 21   | South Bend, PA                                  | 16.20                            | 0.78 | 20.8                         |
| 20                          | 18   | Trail, British Columbia, Canada                 | 16.90                            | 0.70 | 24.1                         |
| 21                          | 14   | Bethlehem, PA                                   | 18.3                             | 0.57 | 32.1                         |
| 22                          | 33   | Cleveland, OH                                   | 19.0                             | 1.21 | 15.7                         |
| 23                          | 8    | Miraflores, Panama                              | 20.9                             | 0.50 | 41.8                         |
| 24                          | 29   | London (Battersea), England                     | 23.0                             | 1.07 | 21.5                         |
| 25                          | 24   | Monroeville, PA                                 | 23.8                             | 0.84 | 28.3                         |
| 26                          | 35   | Newark, NJ                                      | 24.7                             | 1.63 | 15.2                         |
| 27                          | 16   | Manila, Philippine Islands                      | 26.2                             | 0.66 | 39.7                         |
| 28                          | 32   | Limon Bay, Panama                               | 30.3                             | 1.17 | 25.9                         |
| 29                          | 39   | Bayonne, NJ                                     | 37.7                             | 2.11 | 17.9                         |
| 30                          | 22   | East Chicago, IN                                | 41.1                             | 0.79 | 52.0                         |
| 31                          | 9    | Cape Kennedy, 1/2 mile from ocean               | 42.0                             | 0.50 | 84.0                         |
| 32                          | 23   | Brazos River, TX                                | 45.4                             | 0.81 | 56.0                         |
| 33                          | 40   | Pilsey Island, England                          | 50.0                             | 2.50 | 20.0                         |
| 34                          | 42   | London (Stratford), England                     | 54.3                             | 3.06 | 17.7                         |
| 35                          | 43   | Halifax (Federal Building), Nova Scotia, Canada | 55.3                             | 3.27 | 16.9                         |
| 36                          | 38   | Cape Kennedy, 60 yds from ocean, 60-ft elev.    | 64.0                             | 1.94 | 33.0                         |
| 37                          | 26   | Kure Beach, NC, 800-ft lot                      | 71.0                             | 0.89 | 79.8                         |
| 38                          | 36   | Cape Kennedy, 60 yds from ocean, 30-ft elev.    | 80.2                             | 1.77 | 95.3                         |
| 39                          | 25   | Daytona Beach, FL                               | 144.0                            | 0.88 | 163.6                        |
| 40                          | 44   | Widness, England                                | 174.0                            | 4.48 | 38.3                         |
| 41                          | 37   | Cape Kennedy, 60 yds from ocean, ground level   | 215.0                            | 1.83 | 117.5                        |
| 42                          | 34   | Dungeness, England                              | 238.0                            | 1.60 | 148.8                        |
| 43                          | 17   | Point Reyes, CA                                 | 244.0                            | 0.67 | 364.2                        |
| 44                          | 41   | Kure Beach, NC, 80-ft lot                       | 260.0                            | 2.80 | 92.9                         |
| 45                          | 45   | Galeta Point Beach, Panama                      | 336.0                            | 6.80 | 49.4                         |

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## 2-4 INTERFACES

A complex item of materiel is composed of many parts and components that are designed to work together to provide some functional utility. Therefore, there will be many interfaces between parts and components that may be fixed or may allow for movement. They may place metal to metal, metal to nonmetal, or nonmetal to nonmetal. Interface environments may be potentially corrosive conditions that would diminish the functional capability of the materiel item.

An interface can result in the following conditions that can contribute to or provide resistance to material degradation:

1. A galvanic couple of dissimilar metals
2. An electrical path or insulating barrier
3. A boundary across which heat is transferred or barrier that insulates against heat flow
4. A boundary across which static, fluctuating, or cyclic stresses are transferred
5. Relative motion of one surface against the other
6. Stresses resulting from the buildup of deterioration products on one or both of the materials at the interface
7. A geometric configuration for collecting, maintaining, and concentrating liquids or gases
8. A geometric configuration that modifies flow conditions
9. A chemical environment corresponding to contained material
10. A chemical environment resulting from the deterioration of one or both of the materials at the interface.

## 2-4.1 METAL TO METAL

Metal-to-metal interfaces are primarily involved in providing

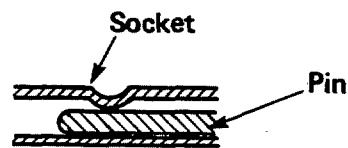
1. Structural integrity
2. Electrical conductivity
3. Heat transfer
4. Transfer of motion and stress.

Fig. 2-81 illustrates typical metal-to-metal interfaces.

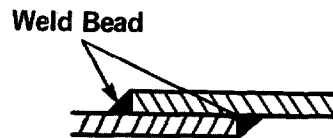
In accomplishing these functions, the following types of corrosion phenomena can become involved:

1. Galvanic corrosion between dissimilar metals
2. Electrolytic corrosion from stray direct current
3. Crevice and concentration cells
4. Differential temperature cells
5. Stress-corrosion cracking
6. Hydrogen embrittlement
7. Corrosion fatigue
8. Fretting corrosion
9. Erosion-corrosion
10. Liquid-metal- and solid-metal-induced embrittlement.

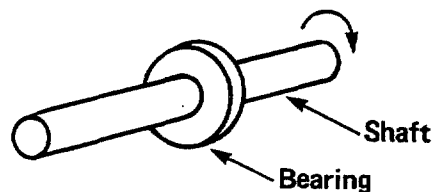
If the use of dissimilar metals cannot be avoided, the following general principles apply:



(A) Electrical Connector



(B) Structural Joint



(C) Rotating Joint

## Figure 2-81. Typical Metal-to-Metal Interfaces

1. Use metals that are compatible as indicated by a galvanic series in the environment of interest. (See Table 2-2 for a galvanic series.)

2. Condition the environment to minimize corrosion, e.g., remove all moisture, use inhibitors, etc.

3. Provide dielectric separation (electrical insulation) of noncompatible metals with insulating gaskets, tape, or spreadable sealant.

4. Avoid crevices between dissimilar metals and between metals and various types of plastics and elastomers.

5. If complete dielectric separation cannot be achieved,

a. An increase in the electrolytic path can be beneficial. In a marine atmosphere dielectric separation of approximately 50 mm (2 in.) should be effective.

b. A transition metal that reduces the potential difference between the two metals can be interposed.

6. Avoid the unfavorable area effect of a small anode and large cathode:

a. The more noble (cathodic) metal should be specified for key structural components.

b. Because the less noble (anodic) metal in a galvanic couple undergoes corrosion, it should expose sufficient surface area to the corroding medium and be sufficiently thick in the affected area so that structural performance remains adequate.

c. Provide for easy replacement of anodic structural units or components

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d. Brazing or welding alloys should be cathodic to at least one of the joined metals and should be galvanically compatible to both.

7. Avoid embrittling couples, such as liquid-metal to solid-metal contact.

8. Avoid friction and wear between surfaces undergoing repeated impacting and/or vibration motion:

a. Provide clamping forces to prevent the relative motion.

b. Use an effective lubricant.

c. Interpose an elastomeric material between the two metals.

d. Use a metal pair that is resistant to fretting.

**2-4.2 METAL TO NONMETAL**

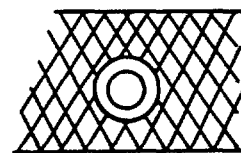
Metal-to-nonmetal interfaces are used primarily to provide

1. Electrical insulation
2. Dampening of shock and vibration
3. Sealing
4. Thermal insulation
5. Misalignment and thermal expansion allowance
6. Structural integrity
7. Transfer of motion and stress
8. Isolation from potentially corrosive environments.

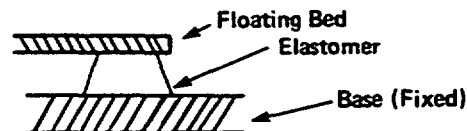
Nonmetals are used in combination with metals to mitigate some of the consequences that could result from a metal-to-metal interface. Nonmetals also provide some unique characteristics that cannot be achieved with metals. Fig. 2-82 illustrates typical metal-to-nonmetal interfaces.

The principal problem with metal-to-nonmetal interfaces is their propensity to release corrosive chemical species to the local interface environment. Even though the interface metal may be resistant, the released chemical species may migrate away from the interface to more sensitive areas. Some useful nonmetals possess a cellular structure that is open, so they may absorb environmental material and keep the interface metal exposed longer than necessary.

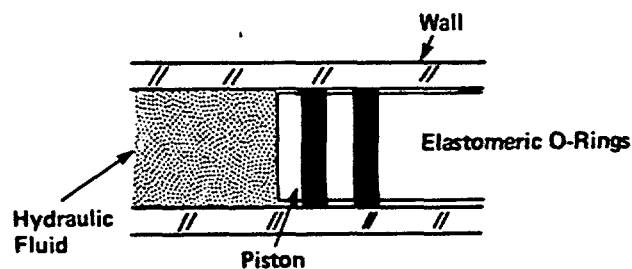
Metal-to-nonmetal interfaces can be involved in the containment of liquid or gaseous phases in static or flowing conditions. A metal-to-nonmetal interface also exists in contact between a metal and a solid nonmetal. Metal-to-nonmetal interfaces can be involved in a galvanic couple between two metals by providing a medium for ionic transport. Although metals can be liquid, but for a few exceptions, metals fulfill their functional role as solids. Nonmetals can be solids, but their functional role is often performed in a liquid or gaseous state. The importance of this fact in the consideration of interfaces related to material degradation is that the damaging metal or nonmetal phase can be mobile; it need not arise from material directly adjacent to it.



(A) Grommet in Fabric



(B) Shock Mount



(C) Hydraulic Cylinder

**Figure 2-82. Typical Metal-to-Nonmetal Interfaces**

Graphite and carbon, e.g., solid graphitized gaskets or packing, in pipe systems containing conducive media can cause damage to downstream components. Salts of copper, emanating from copper-base pipes and components, are dangerous to downstream carbon steel components. Condensate forming on copper surfaces and containing oxides of copper can damage aluminum on which it drips. Organic materials can give off vapors or release chemical species into leaching liquids that can be corrosive to metals with which they come in contact. Therefore, chemical compatibility is an important consideration in the corrosion of metals. The practices that follow exemplify measures that can reduce the chemical corrosion effect:

1. Avoid the use of materials in interfaces that are incompatible by reason of the chemical environment under particular conditions, e.g., vulcanized rubber, which contains sulfur.

2. Avoid materials that, under conditions which may be experienced, liberate fumes that are potentially corrosive to metals with which they may come in contact:

a. Partially cured or undercured organic materials. For example, room temperature vulcanizing silicone rubbers generate acetic acid on curing.

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b. Insulating materials, varnishes, or encapsulating compounds that emit phenolic vapors and are within unventilated spaces of electronic equipment containing cadmium- or zinc-plated or zinc-base alloy parts

c. Polyvinyl chloride coatings and parts that can emit hydrochloric acid vapors at temperatures over 66° C (150° F).

d. Certain woods and glues used to laminate plywood. For example, plywood glued with synthetic resin glues may release formaldehyde and ammonia from the resin bases, volatile acidic substances from the hardeners, and acetic acid from the wood. Douglas fir, which is commonly used in plywood, is moderately corrosive compared to other woods.

e. Vapors resulting from microbiological attack on organic materials

f. Paints and varnishes based on drying oils, urea formaldehyde and phenolformaldehyde glues, and vinyl and phenolic plastics and resins

3. Avoid metal-to-nonmetal interfaces in which leaching of the nonmetal can result in chemical corrosion of the metal and impair its functional utility:

a. Acid in wood

b. Wood or canvas impregnated with copper salts

c. Timber treated with zinc chloride.

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## CHAPTER 3

# CORROSION PREVENTION

*This chapter discusses the various measures available to prevent or control corrosion. The different categories of corrosion prevention measures discussed include mechanical design considerations to avoid potentially corrosive configurations and conditions, selection of corrosion-resistant materials of construction, specification of process and fabrication conditions to avoid sensitizing the metal to corrosion, the use of corrosion inhibitors in the environment that the metal will encounter, the use of various types of protective coatings, and the use of protective packaging.*

### 3-1 INTRODUCTION

Army materiel must meet several criteria:

1. It must achieve its intended function in the field with a high degree of reliability. Anticipating functional requirements within a reasonable planning horizon is difficult and uncertain.

2. It must be available and ready for use when needed. The time and place of potential conflict cannot be reliably predicted; therefore, materiel requires storage under a wide variety of conditions and/or rapid supply from central storage areas. Providing materiel to friendly nations throughout the world adds to the materiel readiness problem.

3. It must meet weight limits. Excess weight reduces the mobility of materiel items, but reducing the weight often sacrifices other functional characteristics. Therefore, the design process often requires a tradeoff.

4. It should be simple to produce, operate, and maintain. Modern military materiel can be highly sophisticated and therefore complex. This complexity can seriously reduce reliability and readiness, increase the technical skills needed by the soldier, and strain the technological and manufacturing capabilities of the nation. These considerations require diligence in order to design materiel that is easy to fabricate, assemble, operate, and maintain.

5. It should rely on established technology. As materiel systems advance the state of the art, problems arise that may be solved by the application of unusual materials, unfamiliar manufacturing processes, and/or specialized components. Such solutions can create shortages that limit the rate of production and can create unanticipated technical problems.

6. It must be cost-effective. Modern materiel systems tend to be costly. They can also be extremely effective in terms of both offensive capabilities and defensive countermeasures. Obviously, the more cost-effective military materiel systems are, the more capability can be acquired within fixed budgets. However, this capability may be concentrated in fewer units.

7. It must be durable under the conditions in which it will be employed.

Meeting these criteria places exacting demands on the materiel design process. Metallic parts and components are specified that exhibit certain mechanical properties and corrosion characteristics, and these properties and characteristics must be considered in the materiel design process. Therefore, if the mechanical properties of a metal are adequate but the corrosion characteristics are inadequate or questionable in a particular application, corrosion prevention strategies can be applied. Often corrosion prevention techniques permit the use of a less costly or more readily available material, and use of such a material significantly improves the cost-effectiveness of the materiel system.

Corrosion prevention techniques consist of intervening in the corrosion process to thwart or impede its progress. Corrosion prevention strategies for electrochemical processes include

1. Modifying materials to reduce the galvanic potential between anodic and cathodic areas
2. Electrically isolating the anode from the cathode so that electrons cannot be conducted between them
3. Isolating the anodic and/or cathodic areas (if only one, isolating the cathode is preferable) from the electrolyte so that ionic transport cannot occur between them
4. Modifying the electrolyte with inhibitors to impede the ionic transport mechanism
5. Using an applied electromotive force to maintain a protective oxide film that forms on the surface of some metals
6. Using an impressed current or sacrificial anodes to modify the galvanic relationship.

As described in Chapter 2, specific corrosion processes occur only when tensile stress is applied or the metal surface films are disrupted. Removing or modifying these conditions can be a necessary component of corrosion prevention strategies.

### 3-2 DESIGN CONSIDERATIONS AND PRACTICES

Corrosion is most effectively prevented by removing, reducing, or countering the factors conducive to its

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formation in the design configuration and operating characteristics of Army materiel. Design considerations and practices include

1. The interrelation of various materials within a materiel system that can influence the corrosion process
2. The configuration of the materiel system as it affects the presence and conditions of a corrodent
3. The functioning of the operating system as it influences the generation and distribution of stress, erosion, and wear
4. Active corrosion prevention systems that can only be incorporated into the system design.

### 3-2.1 MATERIAL COMPATIBILITY CONSIDERATIONS

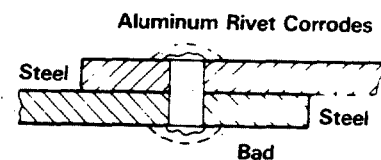
First, a designer must examine the array of materials that comprise a complex item of military materiel. Next the designer assesses the potential for interaction considering the external environments of transportation, storage, and use together with the internal environments of working fluids, consumable materials, and residual products. The characteristics that influence material compatibility are (Ref. 1)

1. The component metals and other materials of construction and the galvanic relationships they may establish
2. The relative size of anode to cathode in corroding couples
3. The geometric relationship of and the dimensions defining dissimilar materials
4. The degree and extent of exposure to corrosive environments
5. The electrical and electrochemical properties of the environment and corroding couples
6. The thermal properties and temperature variations
7. The fluid flow characteristics
8. The chemical compositions of aggressive agents in solvent waters and other media
9. The sources and conductive paths of stray direct currents
10. The development of corrosive reactant products
11. The impact of the effect on performance—beneficial or deleterious
12. The criticality of possible failures.

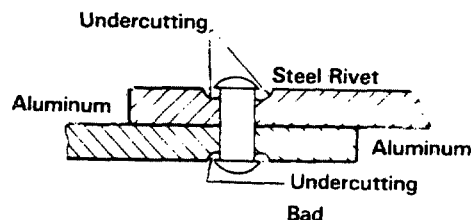
Design guidance covering the use of dissimilar metals (Refs. 1 and 2) includes

1. If possible, do not allow dissimilar metals to be in electrical contact. Electrical contact can result from intimate contact or through an electrical conductor. Refer to par. 2-1.3 for a discussion of galvanic corrosion and Table 2-2 for a galvanic series of metals. Fig. 3-1 illustrates corrosion resulting from faying surfaces of dissimilar metals.

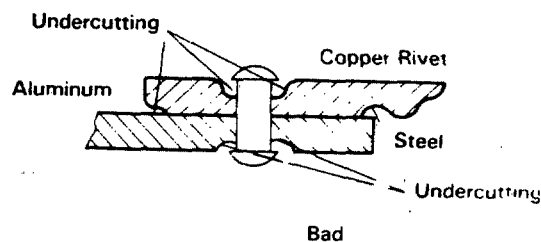
2. Faying surfaces of dissimilar metals should be separated by a dielectric, i.e., insulator, material. Similar



(A) Corrosion of Aluminum Rivet Heads. Aluminum Anodic to Steel



(B) Undercutting of Anodic Aluminum at Cathodic Steel Rivet



(C) Corrosion of Aluminum Plate at Junction With Steel Plate and Undercutting of Both Aluminum and Steel at Copper Rivet. Aluminum and Steel Both Anodic to Copper

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### Figure 3-1. Corrosion at Dissimilar Metal Joints (Ref. 1)

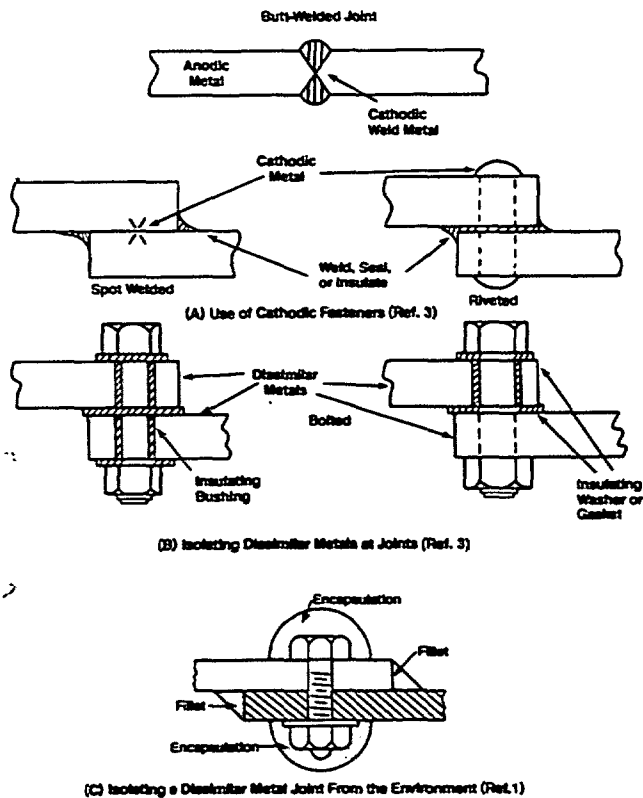
metals that are joined by a dissimilar metal connector may undergo galvanic corrosion in the area adjacent to the connector if the connector is cathodic, but the connector itself may corrode if it is anodic. A dissimilar metal joint is acceptable if it is completely isolated from the environment. These considerations are illustrated in Fig. 3-2.

3. Dielectric separation can be provided by using insulating gaskets, tapes, sealants, etc. as illustrated in Fig. 3-3. Sealant should extend over a sufficiently large area to isolate the metal from condensates or other electrolytes that might accumulate.

4. If electrical insulation between two metals is not feasible, a transition metal piece will divide the potential between them into two less damaging potentials. Metal transition joints are illustrated in Fig. 3-4.

5. Large cathode and small anode areas should be avoided. Insulating compound or sealant should extend

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### Figure 3-2. Acceptable Methods of Joining Dissimilar Metals

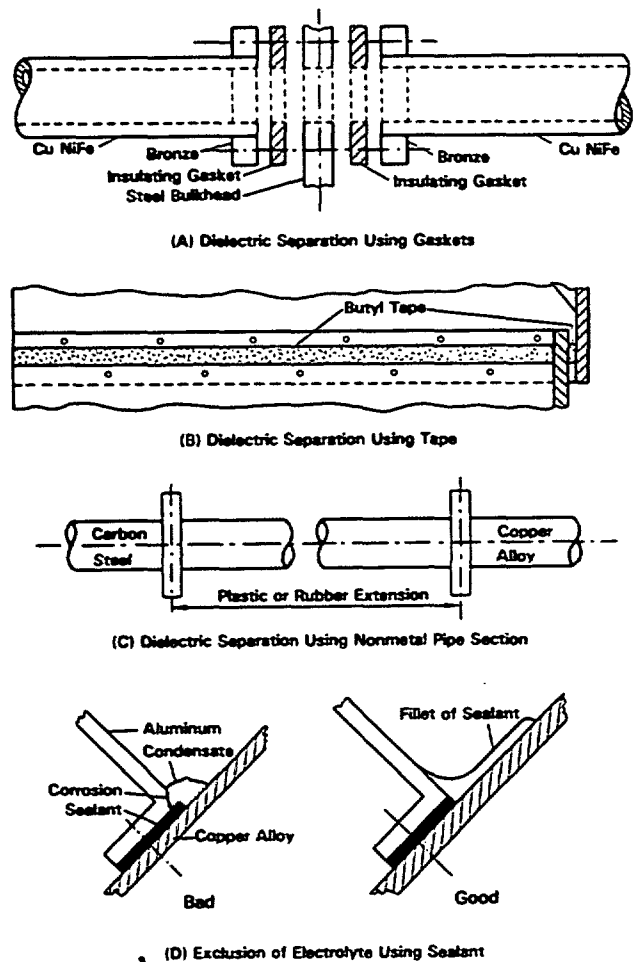
beyond the joint areas in the form of fillets, which should also cover nearby areas of high corrosion potential. These practices are illustrated in Fig. 3-5.

6. Avoid galvanic effects at structural joints between dissimilar metals by using clad metals. Because clad metals may be subject to galvanic corrosion along exposed edges, the edges should be insulated from the environment.

7. The galvanic effects of metal coatings on base metals should be assessed before the specification for corrosion prevention is prepared. Fig. 3-6 illustrates the galvanic characteristics of some metal coatings on steel.

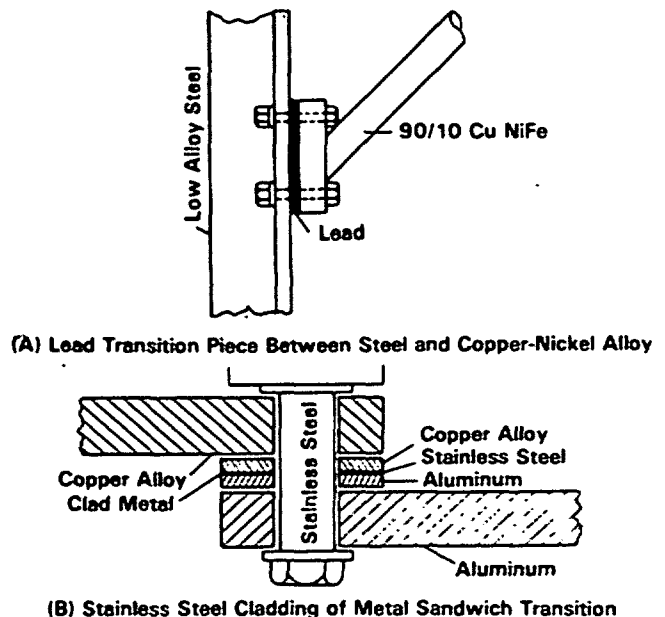
8. Coverage of an organic coating applied to a galvanic couple should be specified to obtain optimum protection, as illustrated in Fig. 3-7. An organic coating, however, does not provide the protection of full metal cladding.

9. The degree of dielectric insulation afforded by chemical conversion coatings on dissimilar metal couples can vary. As illustrated in Fig. 3-8, chromate- and phosphate-treated zinc and cadmium-coated metals are not dielectrically separated when in contact. However, chromate and phosphate treatment of both metals in a dissimilar couple can sometimes effect a reduction in corrosion.



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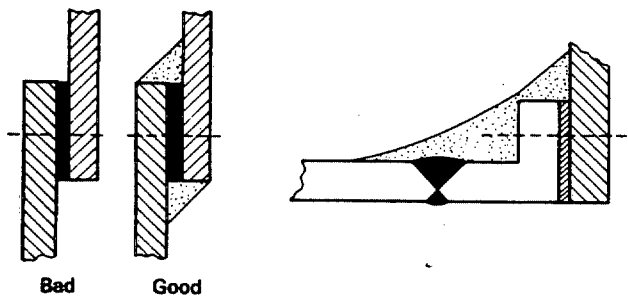
### Figure 3-3. Dielectric Separation (Ref. 1)



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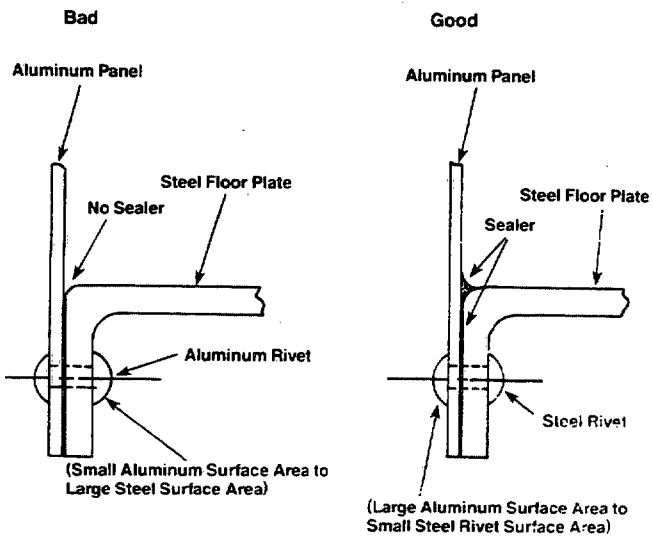
### Figure 3-4. Metal Transition Joints (Ref. 1)

MIL-HDBK-735(MR)



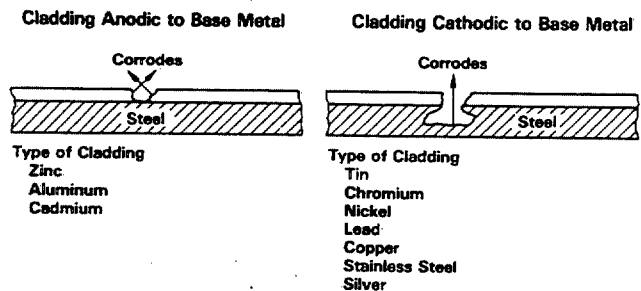
(A) Exclusion of Electrolyte by Use of Sealant Fillets (Ref. 1)

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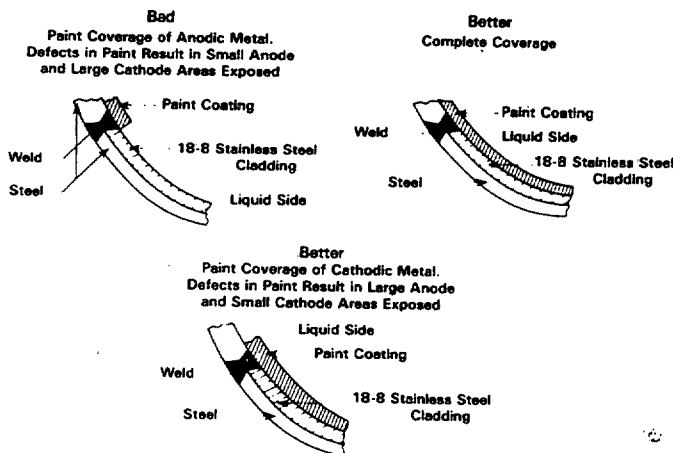
(B) Sealant Between Dissimilar Metals (Ref. 3)

Figure 3-5. Examples of Sealant Practices to Achieve Dielectric Separation.



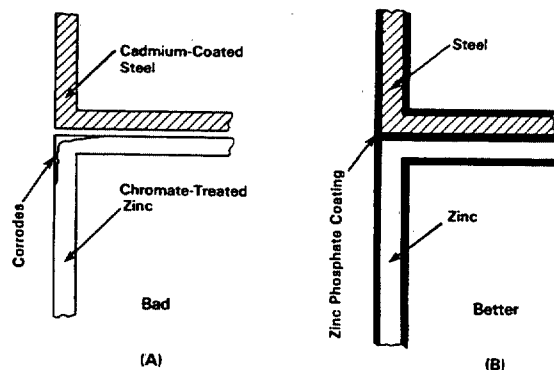
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Figure 3-6. Corrosion Characteristics of Clad Steel (Ref. 1)



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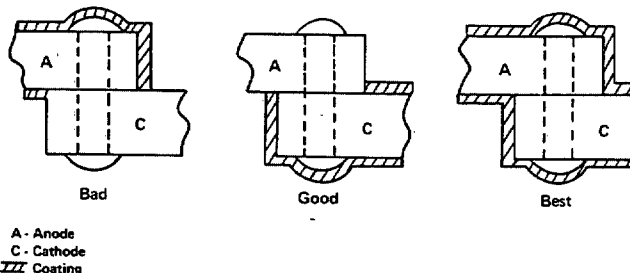
Figure 3-7. Paint Coverage of Galvanic Couple (Ref. 1)



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Figure 3-8. Effect of Selected Coatings on Galvanic Couple (Ref. 1)

10. Fig. 3-9 illustrates the proper practices for coating a dissimilar metal junction. The anode should not be coated unless the cathode is also coated. If the anode is coated and the cathode is not, a scratch, pinhole, or other defect in the coating can be a small area of locally intense corrosion. The corrosion of anode and cathode will always be balanced electrically; therefore, a small, exposed anodic surface area relative to the cathodic surface will result in deep penetration of the anode area.



A - Anode  
C - Cathode  
ZZZ Coating

Figure 3-9. Application of Coating to Galvanic Couple (Ref. 3)

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## 3-2.2 GEOMETRY CONSIDERATIONS

Configuration or geometry considerations (Refs. 1 and 3) require

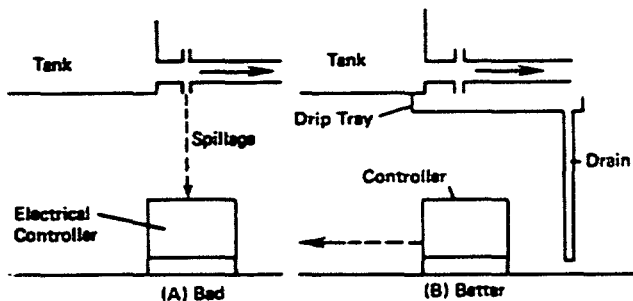
1. Arranging the components within a system to prevent an adverse effect of one part of the assembly on another during either normal operation or as the result of failure. Fig. 3-10 illustrates a potentially dangerous situation in which a critical controller is located beneath a flange that may leak a highly corrosive liquid.

2. Allowing for collection and/or drainage of corrosive fluids that may leak from screwed fittings, bolted flanges, shaft seals, etc. Design to prevent condensation drips onto components susceptible to corrosion.

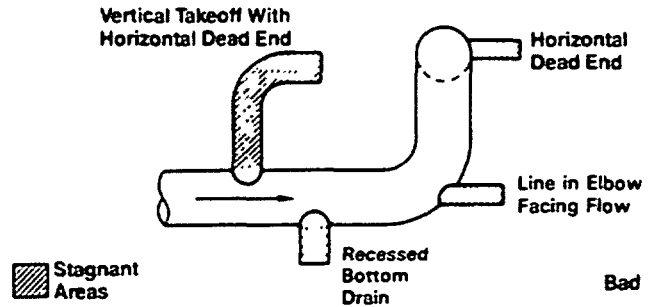
3. Avoiding liquid traps that cannot be drained. Fig. 3-11 illustrates good and bad practices in piping systems, and Fig. 3-12 illustrates good and bad practices in tanks. Prevent condensation in critical spaces by providing for adequate drainage and quick drying. Covers and boots that are intended to prevent the accumulation of moisture often retain moisture once it is present. Therefore, attempt to provide a design that inherently cannot accumulate moisture.

4. Preventing the accumulation of moisture by avoiding dead spaces. If weight is a consideration, spaces can be filled with a foam material. To be acceptable, the foam must be a closed-cell material that is expanded with an inert gas. Also it should not emit corrosive vapors if properly cured nor should it deteriorate or revert to a liquid under operating conditions. The foam should be fire-resistant to minimize flame propagation in closed spaces exposed to flammable vapors.

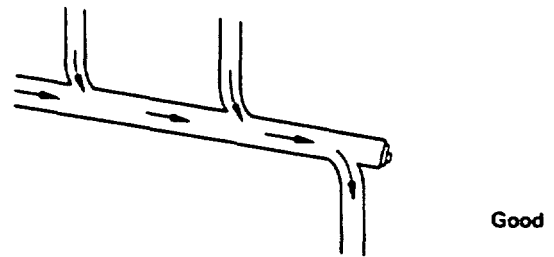
5. Preventing entrance of a corrodent into an unavoidable crevice. This solution can sometimes be accomplished by changing the geometry, fit, or surface texture of the materials forming the crevice. Avoid lap joints or seal them effectively. Laps should face downward on the exposed surfaces. Fig. 3-13 illustrates the application of lap joints.



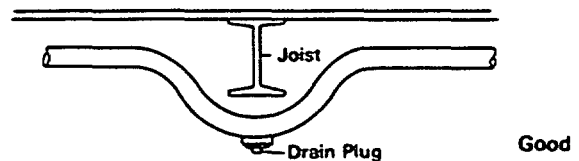
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Figure 3-10. Leakage Onto Critical Component (Ref. 1)



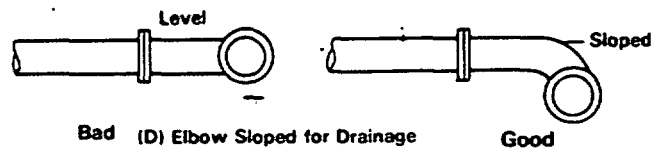
(A) Avoid Stagnant Areas in Pipe Stubs and Dead Ends



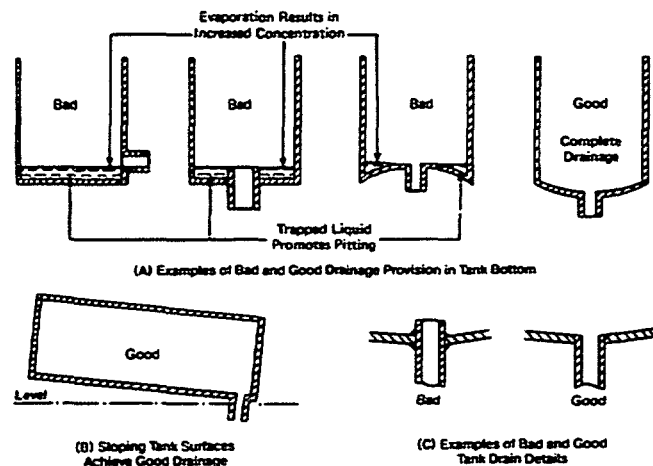
(B) Downstream Slope Facilitates Complete Emptying



(C) Provision for Drainage of Low Point

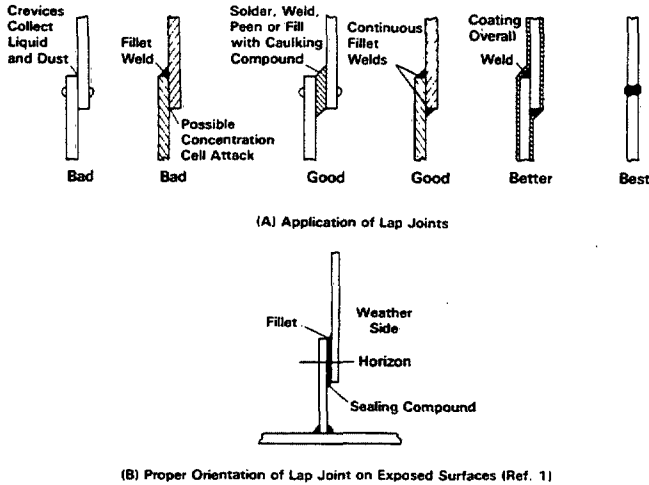


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Figure 3-11. Piping System Drainage Practices (Ref. 1)



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Figure 3-12. Tank Discharge Practices (Ref. 1)

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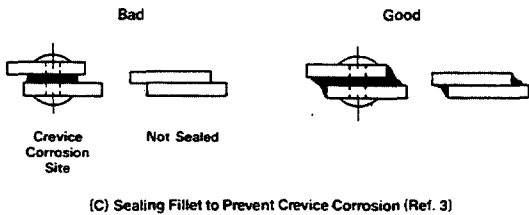
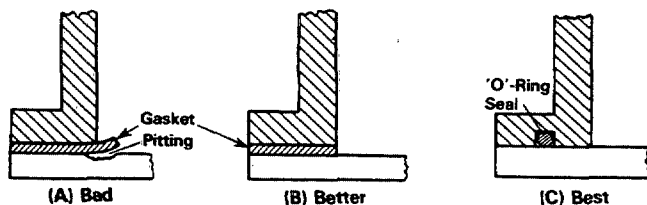


Figure 3-13. Lap Joint Applications

6. Designing seals to be effective. Seal flanges should be sufficiently rigid and compressive forces sufficiently uniform to compress the seal uniformly. It is easier to achieve a proper O-ring seal than a flat gasket seal. An O-ring, however, should be used only in a circular seal. Fig. 3-14 illustrates proper seal design.

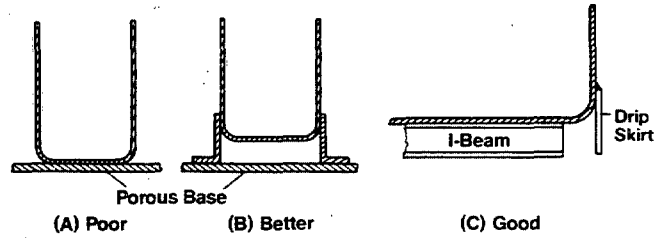
7. Allowing for complete flushing, draining, and drying of spaces that may accumulate liquids, such as spills, condensation, or cleaning fluids, from time to time. Fig. 3-15 illustrates designs that prevent accumulation of liquids beneath tanks.

8. Designing fluid systems to minimize turbulent flow, formation of gas bubbles, rapid surging, excessive agitation, and impingement. Fig. 3-16 illustrates the desirable flow channel dimensions when the direction of flow is changed. A sharp bend results in impingement and in accelerated corrosion in the affected area. Fig. 3-17 illustrates the potential generation of turbulence at pipe connectors. Turbulence can increase corrosion in the affected area.



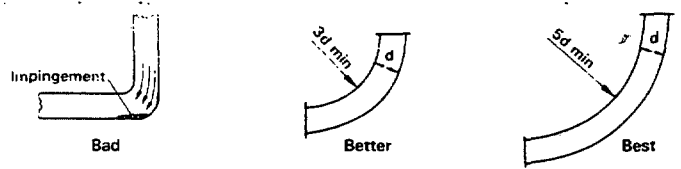
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Figure 3-14. Seal Design (Ref. 1)

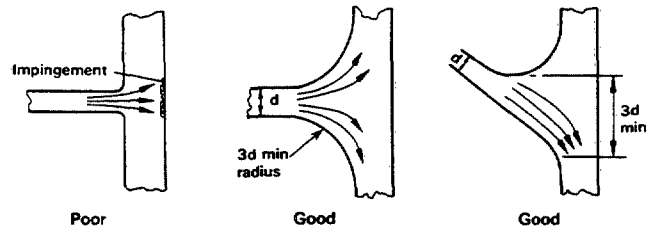


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Figure 3-15. Prevention of Accumulation Beneath Tanks (Ref. 1)



(A) Large Radius Bend Minimizes the Effect of Impingement on Corrosion



(B) Illustration of Pipe Tee Geometry on Impingement

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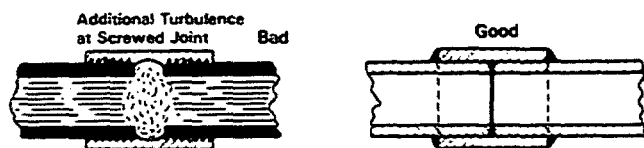
Figure 3-16. Flow Channel Ells and Tees (Ref. 1)

9. Considering dynamic as well as static operating conditions. Fig. 3-18(A) through (E) illustrate the effect on the flow of surface discontinuities. If the flowing medium contains fluid droplets or dust, the surface discontinuities cause their entrapment and accumulation, as indicated by the flow eddies. Accordingly, if the shapes Fig. 3-18(F) were oriented on a moving vehicle as indicated, they would trap liquid or dust particles, but the shapes in Fig. 3-18(G) would not trap suspended matter. Under operating conditions a road vehicle or an aircraft can accumulate moisture and dust through openings that would not collect water when the vehicle is parked.

10. Arranging the system layout for easy initial application of protective films and for repainting. Provide for easy replacement of components that are likely to suffer unavoidable deterioration.

11. Enclosing electrical and electronic equipment to impede buildup of damaging levels of moisture or particulate matter. Enclosures should prevent liquid traps and should drain moisture away from critical areas.

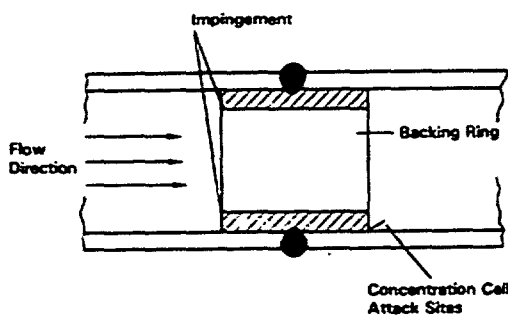
## MIL-HDBK-735(MR)



(A) Comparison of Turbulence Generation by Screwed and Welded Pipe Joints



(B) Gaskets That Protrude Into the Flow Channel Cause Turbulence



(C) A Welded Joint Backing Ring Causes Impingement on Upstream Face and Stagnant Area Downstream

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**Figure 3-17. Turbulence From Pipe Connectors (Ref. 1)**

12. Allowing for adequate ventilation for cooling and drying in the design of electrical and electronic circuitry. Arrange circuit boards vertically to provide drainage, and group components so that they can be readily protected by encapsulation, sealing, and enveloping. Seal all crevices, e.g., those formed by washers, threaded fasteners, and spot welds. Space conductors at different voltages as widely apart as possible to avoid electrolysis and silver migration.

13. Locating electrical and electronic equipment away from areas of air contamination and high humidity

14. Adequately grounding electrical and electronic equipment. Orient electrical sockets and plugs to avoid the effects of moisture. Moisture can corrode through a contact and cause an open circuit, partially corroded contacts can create high resistance, and moisture can form a conducting bridge, which creates a short circuit between contacts. Ensure that sockets and plugs are adequately sealed. Use a seal gasket on multiple pin connectors with the proper hole sizes for the wire to be used. Carefully plug all unused holes.

15. Laying out electrical cables and cable bundles to avoid areas of potential corrosion. If the cables and bundles cannot be laid out, enclose them in corrosion-resistant conduits.



(A) Effect of Projection on Flow



(B) Effect of Groove or Crevice on Flow



(C) Effect of Corner on Flow



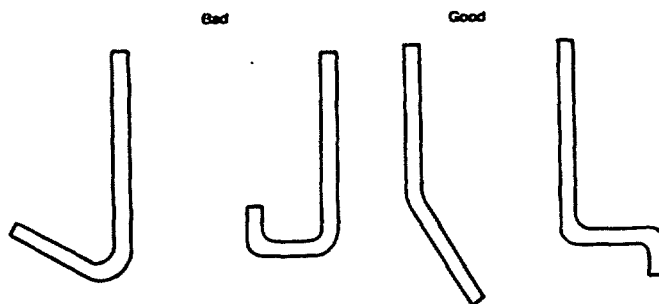
(D) Effect of Weir at Low Flow Velocity

(Ref. 1)



(E) Effect of Weir at High Flow Velocity

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(F) These Panel Configurations Can Trap Material

(G) These Panel Configurations Cannot Trap Material

(Ref. 3)

Front of Vehicle

Front of Vehicle

**Figure 3-18. Fluid Flow Discontinuities****3-2.3 MECHANICAL DESIGN CONSIDERATIONS**

Metals are used for their mechanical properties. The loads on metals in a component, however, can interact with some environments and result in damage and failure. Residual loadings are generated by the treatment that the metal undergoes in preparation and fabrication. Service loads are imposed by operating conditions.

Mechanical design considerations (adapted from Ref. 1) require

1. Applying precautions suggested to prevent stress corrosion cracking, par. 2-2.9; fatigue failure, par. 2-2.11; hydrogen cracking, par. 2-2.10; and fretting, par. 2-2.8

2. Using the lowest practical stress level in the design. Do not specify metals and alloys susceptible to stress-corrosion cracking or corrosion fatigue for highly loaded (tensile stress) and critical structures.

3. Considering the potential for hydrogen embrittlement that may result from cleaning, welding, surface treatment, cathodic protection, and operating conditions. Avoid potential hydrogen embrittlement in materials selected for critical structures.



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4. If possible, conducting all metal-forming operations in the annealed condition. Reduce or remove residual stresses by suitable stress-relieving processes. Minimize the effects of potential residual and applied stresses by specifying processes that increase local strength, improve fatigue strength, and introduce compressive surface stresses.

5. Watching for problems introduced by welding. Weld defects can be sites of high residual stress, weld material can be galvanically incompatible with the base material, hydrogen can be introduced into the base material, and heating can change the microstructure of the affected metal. Therefore, select processes and materials that produce sound welds. Specify postweld treatments to reduce problems associated with the welding process.

6. Designing a component to avoid locally high stress levels. These stresses can arise from abrupt changes in cross section and from stress raisers, such as notches, sharp corners, grooves, keyways, oil holes, screw threads, and surface scouring and scratches.

7. Avoiding residual stresses from material that is deformed around welds, rivets, bolts and from interference fits and shrink fits

8. Avoiding operational stresses that arise from differential thermal expansion and pressure differentials

9. Avoiding use of metals in a design so that critical loading is in a short transverse direction.

### 3-2.4 ANODIC AND CATHODIC PROTECTION

Active corrosion prevention techniques include cathodic and anodic protection.

Cathodic protection uses impressed currents or sacrificial anodes. Sacrificial anodes may be in the form of metal coatings anodic to the base metal, such as zinc, aluminum, or cadmium coatings on steel. They may also be in the form of discrete pieces of metal. Fig. 3-19 illustrates the two methods of cathodic protection.

Anodic protection is applied to active/passive metals, such as alloys of nickel, iron, chromium, titanium, and stainless steel, in weakly to strongly corrosive environments. The impressed electromotive force must be controlled to maintain the passive condition. Fig. 3-20 illustrates the principle of anodic protection using a potentiostat. A potentiostat is a device that maintains a constant applied potential regardless of the current. As indicated in Fig. 3-20, the corrosion current increases rapidly as the potential is increased from zero. As the potential is increased, a maximum corrosion current  $i_{critical}$  is reached, and then the current decreases to the passive value  $i_{passive}$ . The passive corrosion current, however, does not change over a range of increasing potential, and minimum corrosion occurs within this range. For the example shown, 1.0 V is in the center of the passive

region. At some higher value of potential, the corrosion current again increases with the evolution of oxygen.

If cathodic protection is used, the choice between using impressed currents or sacrificial anodes depends (Ref. 1) upon

1. The size and geometry of the article to be protected. Impressed current cathodic protection is usually used for large systems.

2. The ease of providing the required current from a suitable power supply

3. The possibility of problems at the interface between the anode and the material to be protected and the anode and the electrolyte. Problems experienced with impressed current systems include generation of gases such as chlorine at the anode with subsequent damage to the anode, hydrogen embrittlement of high-strength metals, damage to protective coatings on the metal, scale deposition on the metal, and increase in the pH value at the metal surface with subsequent metal damage.

4. The degree of safety from sparks and accumulation of hydrogen

5. The ease of replacing anodes

6. The lifetime or duty cycle requirements

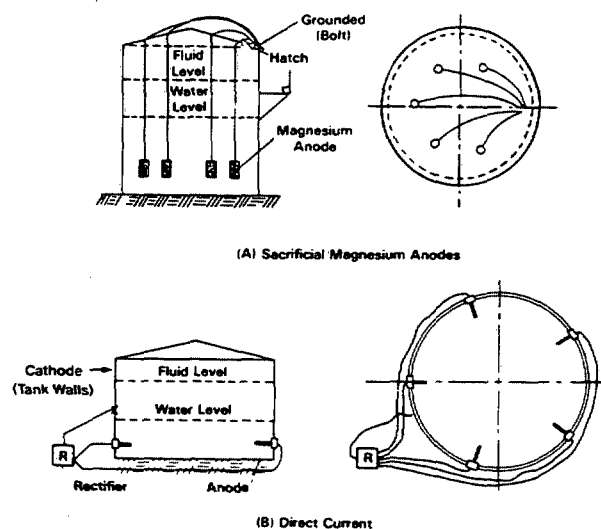
7. The relative cost.

The general design considerations of cathodic protection by sacrificial anodes (Ref. 1) include

1. The anode characteristics, such as the material, its geometry, and its electrochemical properties

2. The environment or electrolyte characteristics, such as chemical composition (including aeration, pH, and ionic properties), temperature, and fluid flow

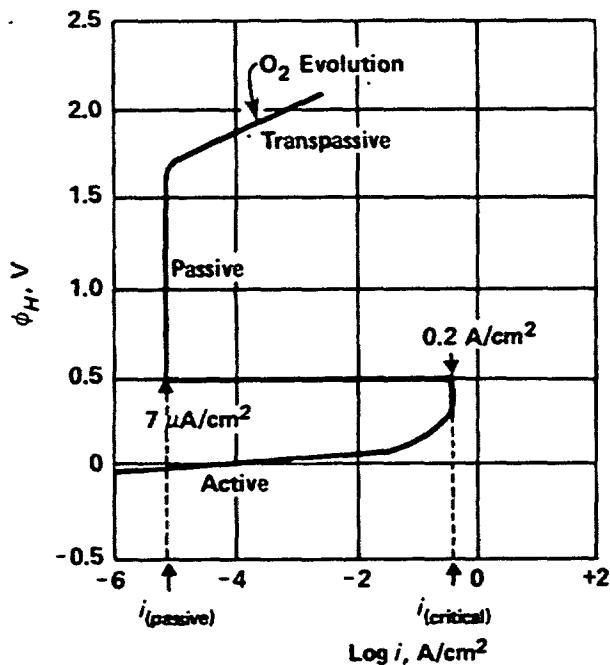
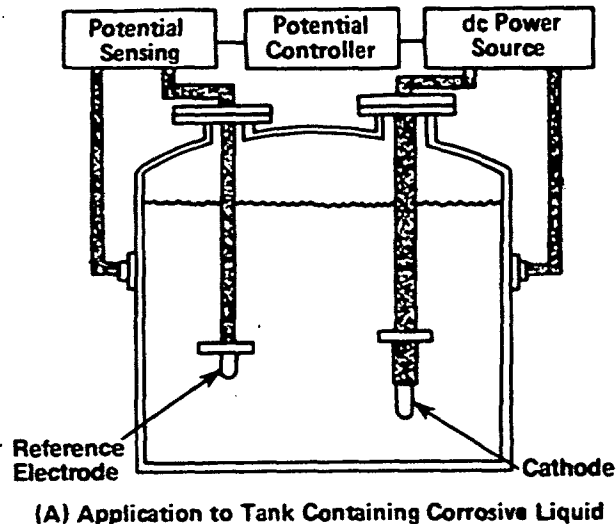
3. The protected article, or cathode, such as the material, its geometry, surface characteristics, and electrochemical properties



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**Figure 3-19. Cathodic Protection of Oil Field Tank (Ref. 1)**

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NOTE: Maintain Potential  
at 1.0 V

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Figure 3-20. Anodic Protection Using Potentiostat

4. The operating system, such as electrochemical cell properties, duty cycle, and required lifetime.

Many of the same considerations would apply to cathodic protection by impressed current and anodic protection by a controlled electromotive force. The power supplies and the means of controlling the impressed current or electromotive force, however, would be different.

### 3-2.5 OPERATIONAL PARAMETERS

The design of a materiel assembly is based upon operating parameters derived from mission requirements. To meet operating parameters, a design configuration incorporating material specifications is developed, and certain components will appear to be critical to the successful operation of a materiel assembly. The designer has alternative ways to deal with these critical component requirements. One way is to overdesign or to design conservatively so that the operational limits can be readily met. Another approach is to limit the controllable operational parameters so that critical levels are not exceeded. This control may be mandatory and built into the system, or it may be voluntary on the part of the operator. For example, a materiel item may have a maximum operating level that may be exceeded only in an emergency by overriding a detent on the control input mechanism.

A tendency exists to use the latest developments at their limits. Often there are valid reasons to do so, for example, to attain higher performance at less weight. Pushing the state of the art, however, adds an element of uncertainty into the design. If the design limits cannot be reliably projected, it is advisable to limit the operational parameters until experience reduces the design uncertainty.

Often the only practical way to assess the capability of a complex system is through operational experience. Operational failures include both random catastrophic failure of individual parts and progressive deterioration of performance. Corrosion effects combined with mechanical effects can influence both types of failure. This usually proceeds through three phases (Ref. 1):

1. The initial operational phase during which the failure rate decreases rapidly from an initial rate. Diligent maintenance and prompt correction of production shortcomings are required. Basic design shortcomings should be corrected based on this experience

2. A period of constant failure rate which represents experience under normal operating conditions. This period represents the condition(s) that can be improved through control of operating parameters.

3. The final phase is the wear-out phase. Although this phase represents a cumulation of previous measures, it is strongly determined by design considerations.

The effective lifetime of the hot components of a gas turbine engine is determined by operating parameters

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such as temperature and thermal cycling. Operating an engine at less than rated thrust will improve its lifetime as will running an engine for long periods at a constant power setting. Therefore, the operating parameters defined by the mission requirements will influence the selection of materials. The gas turbine engines of a cruise missile, a transport aircraft, a ground support aircraft, and a helicopter gunship must meet different sets of operating criteria.

**3-3 SELECTION OF MATERIALS**

Selection of metals and alloys for an article of Army materiel requires balancing material characteristics and costs to meet the required levels of functional capability, ease of fabrication, reliability, maintainability, and readiness. Selected materials should provide the necessary functional capability for the required period of time (storage and use) at acceptable life cycle costs.

Those parts and components of materiel items that are critical or that are expensive to fabricate and to replace should be made from materials that are more corrosion-resistant. The useful service life of a subassembly comprised of several materials is determined by the material having the shortest life. To assess materials, the corrosion prevention treatment, e.g., chromate passivation or cadmium plating, should be evaluated for suitability along with the base alloy. The effect(s) of corrosion products should also be considered during material selection. Corrosion products can create stresses, cause dimensional deformation, interact adversely with other materials, block flow channels, and decrease heat transfer, even though the extent of corrosion itself seems otherwise acceptable.

Great care should be exercised when trading mechanical properties for corrosion resistance because both characteristics can affect functional capability. If the environment can be reliably predicted or controlled, materials may be selected with confidence. For example, stainless steels, aluminum alloys, and lead may be used in most natural environments, even those containing pollutants. In coastal climates relatively cheap structural materials with added protection applied may be more economical than expensive corrosion resistant materials. Surface treatments and coatings that may be used to prevent corrosion are discussed in pars. 3-6 and 3-7. Under severe corrosion conditions, however, it is preferable in most cases to use a resistant material rather than a cheaper material with expensive treatment. If the corrosion environment is either very mild or severe, the choice of materials is simple. If the corrosion environment is moderately severe, the analysis governing a choice is more complex.

The choice of materials must also consider the cost of failure. If safety of personnel and/or success of a vital mission are involved, highly reliable materials must be

used. If the functional reliability can be easily maintained by realistic, regular maintenance, a balance can be achieved between life cycle costs involving high initial costs and life cycle costs involving high maintenance costs.

Factors other than the composition of an alloy affect its corrosion resistance in specific applications. Corrosion susceptibility can be increased by fabrication processes, such as welding, forming, machining, or heat treating. However, special processes can be incorporated to improve corrosion resistance, e.g., special welding techniques, stress relieving, shot peening, and cladding. Sometimes it is better to use a weaker alloy that is less sensitive to fabrication and assembly processes than to use a stronger alloy whose response to these processes is detrimental or unreliable. If heat treatment after fabrication is not feasible, materials and fabrication processes should be chosen that give adequate corrosion resistance in the as-fabricated condition. Stress relieving is not always a reliable cure for stress-corrosion cracking. Therefore, materials prone to stress-corrosion cracking should be avoided in environments conducive to failure. Table 2-12 indicates common metal-environment combinations subject to stress-corrosion cracking.

Allowances for corrosion can be made in the thickness of metal sections, provided that pitting does not occur or that perforation by pitting does not reduce the mechanical stability of the structure. If the objective is to reduce weight by using thinner sections of higher strength metal, a proportionately more resistant alloy or more reliable corrosion prevention measures should be used.

Long-term exposure of certain metals to an environment may result in deterioration of mechanical properties with few apparent surface effects or little weight change. Therefore, the basis of data supporting the assumed corrosion resistance of a material should be assessed and evaluated. A material whose corrosion resistance is based solely on weight change should be used with caution if working stresses are close to the strength limits of the material.

**3-4 PROCESS AND FABRICATION CONSIDERATIONS**

The fabricator receives a metal or alloy in the form of a mill product. While being transformed into a part, the mill product is sectioned into working blanks, these blanks are then formed into a raw part, the raw part may then be machined to a final dimension, and the finished part is joined into an assembly. In this sequence, the surface characteristics, the microstructure, and the alloy chemistry may be modified from those of the mill product, and all of these characteristics may affect the corrosion characteristics of a metal.

Some examples of process and fabrication influence on corrosion characteristics are

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1. Welding regular 300 series stainless steel sensitizes it to intergranular corrosion. Low-carbon alloys should be specified, e.g., 304L (0.03% carbon maximum), to avoid the problem.

2. 7075 aluminum alloy in the T6 temper is susceptible to exfoliation. The T73 or T76 tempers are less susceptible but also somewhat weaker. 2XXX series aluminum alloys are susceptible to exfoliation in the T3, T4, and T5 tempers. Resistance to exfoliation is improved in the T6 temper and is virtually eliminated in the T8 temper.

3. Stress relief annealing of 300 series stainless steel reduces its susceptibility to stress corrosion. Stress relief should be conducted below 427°C (800°F) to avoid sensitization.

4. Shearing an aluminum alloy subject to exfoliation to final dimension should be avoided. Shearing produces an edge that is loaded compressively at the leading edge of the cut but is in tension at the following edge.

5. Tools that make clean smooth cuts should be used. Control the cutting speed and depth to avoid chattering, jagged cuts, and nicks; these can act as stress raisers.

6. Extreme care should be exercised when cleaning the forging line. Removing too much material can expose the transverse grain and lead to exfoliation in aluminum alloys and intergranular corrosion in other metals.

7. Parts from rolled aluminum alloy sheets and plates should be cut with reference to the direction of rolling to avoid short transverse loading in the finished article. Stress-corrosion cracking can occur if the loading in the short transverse direction is as little as 10% of the short transverse yield strength (Ref. 4).

8. Sealant should be used on all fasteners in aluminum alloys to avoid exposing the transverse grain. Seal all edges exposed in lap joints.

Heating and cooling, plastic deformation, and local shearing are the principal conditions imposed upon a piece of metal in the fabrication process. Plastic deformation refers to processes that change the shape of the piece of metal. Heating and cooling occur in cutting, joining, annealing, and tempering processes. Local shearing results from metal-cutting processes.

### 3-4.1 COLD WORKING

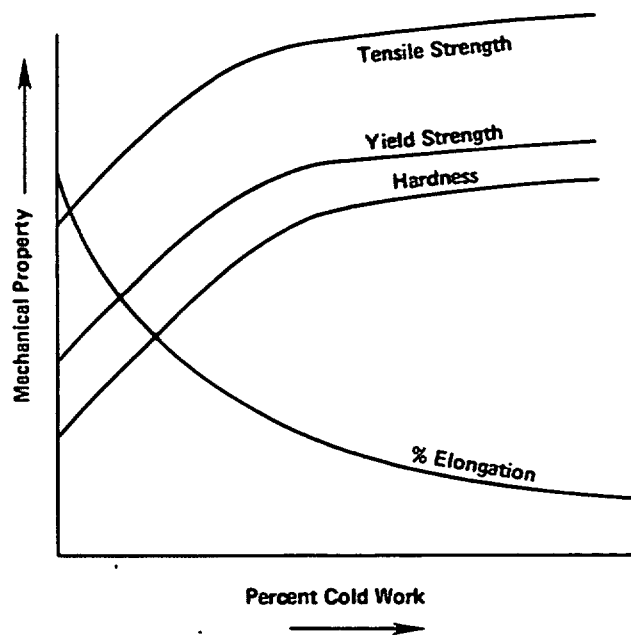
Plastic deformation within a temperature range in which no crystallization and no readjustment of structure take place is referred to as cold working. In highly deformed metals the grains are deformed and the grain structure is completely disrupted. For example, the grains in a cast billet are likely to have roughly the same dimension in all directions if the billet is cooled slowly. If that billet is cold-rolled into a flat sheet, the grains are deformed into thin platelets that are longer in the direction of rolling than they are wide. Cold working increases hardness and strength but reduces the ability of the metal to withstand more deformation, as shown in

Fig. 3-21. For example, the specified minimum tensile strength for seamless copper condenser tubing in the light drawn condition is 206.8 MPa (30 ksi), but in the hard drawn condition it is 310.3 MPa (45 ksi).

Cold working generally increases corrosion susceptibility. Tensile stresses induced by cold working render the metal more prone to stress-corrosion cracking. Cold working also increases dislocations in the crystal structure. Impurities or atoms of alloying metals migrate to these sites and change their electrochemical characteristics. These areas are usually subject to pitting attack and can be sites for hydrogen entrapment.

### 3-4.2 THERMAL EFFECTS

Effects of cold working can be removed by annealing (Ref. 5). Fig. 3-22 shows the change in properties as a function of annealing time or temperature. There are three stages in annealing: recovery, recrystallization, and grain growth. Annealing in the recovery stage is called stress relief. The cold-worked metal recovers some of its lost ductility but loses little in its strength properties. In the second stage, recrystallization, stress-free grains grow by diffusion and replace deformed material. As this occurs, ductility, hardness, and other strength properties return to their precold-worked level. Recrystallized grains grow at the expense of others in the last stage of annealing. Ductility improves, but the strength and hardness of the metal decrease.

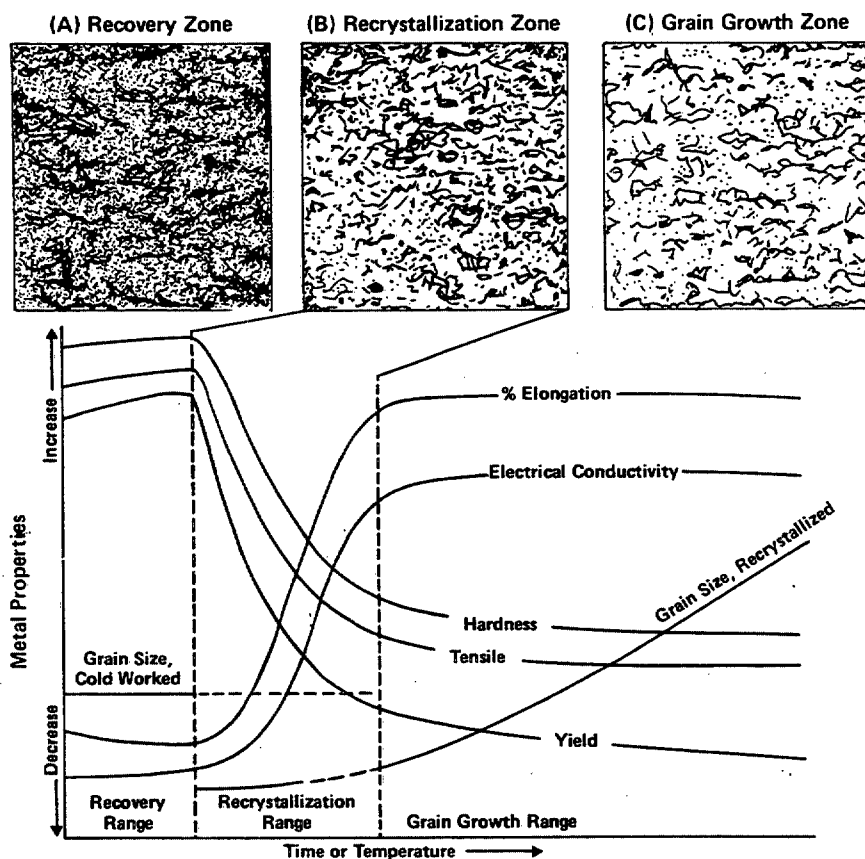


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Figure 3-21. Typical Effect of Cold Working on Mechanical Properties (Ref. 5)

## MIL-HDBK-735(MR)

## Typical Grain Structure Micrographs



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**Figure 3-22. Differences in Annealing Stages on Cold-Worked Brass (Ref. 5)**

When a molten alloy is cooled through the temperature range in which solid and liquid phases exist, the solid and liquid phases can have different compositions. If the rate of cooling is sufficiently slow, the composition of grains are uniform when the alloy has completely solidified. There is sufficient time for solid-state diffusion to homogenize the grains chemically as they solidify and grow. If, however, the rate of cooling is rapid, the grains may vary in composition between the interior and the surface. Rapid cooling through a two-phase solid-state region can also result in nonhomogeneous grains. Intergranular corrosion can result from this chemical nonhomogeneity. Grain homogenization through solid-state diffusion can be improved by annealing at temperatures close to the melting point.

Rapid cooling of many alloy systems produces supersaturation of one element in another. Through controlled reheating, it is often possible to control precipitation from a supersaturated phase. Because this controlled reheating improves the strength of the alloy, it is called age hardening or precipitation hardening. Aluminum, magnesium, nickel, copper, and some forms of stainless

steel are among the metals that can be strengthened by this method when they are alloyed with certain elements.

Aluminum containing about 4% copper can be strengthened by the controlled precipitation of fine, highly dispersed copper aluminide  $\text{CuAl}_2$  precipitates. The alloy adjacent to the  $\text{CuAl}_2$  is depleted of copper. The net result is that grain boundaries are anodic to the grains, and these high-strength aluminum alloys are susceptible to intergranular corrosion and stress-corrosion cracking, especially in the short transverse direction. Aluminum alloys can be age-hardened in a temperature range that reduces susceptibility to intergranular corrosion and stress-corrosion cracking. However, less than maximum mechanical strength is produced. Shastry, Levy, and Joshi (Ref. 6) showed that the size, number, shape, and distribution of coherent intermetallic particles are altered by varying the solid solution heat treatment temperature of 7075 alloy. The composition of the grain boundaries is also greatly affected. The 7075 alloy contains magnesium, copper, and zinc. By comparing the microstructure effects that result from age hardening with changes in mechanical properties and fracture mechanics parameters, the authors

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concluded that

1. Increasing the solid solution heat treatment temperature reduces the amounts of minor alloying intermetallic particles and develops higher strength on aging the alloy.

2. Changing the solid solution heat treatment temperature affects the stress-corrosion susceptibility of the alloy in a complex manner through the effect on the grain boundary composition and the metallurgical microstructure. Localized enrichment of magnesium, silicon, zinc, copper, and iron occurs at the grain boundaries.

The aluminum alloys do not form protective oxide films as does pure aluminum. Therefore, high-strength alloys are given the protection of pure aluminum by cladding them with thin layers of aluminum. High-strength, clad aluminum alloy sheets are subject to exfoliation where the interior alloy is exposed to the environment, e.g., rivet holes or cut edges. See par. 2-2.5.1 for a discussion of exfoliation.

Heating series 300 stainless steel (18% chromium, 8% nickel) in the 427° to 760° C (800° to 1400° F) range forms chromium carbide. These alloys contain 0.08 to 0.15% carbon. The formation of chromium carbide is called sensitization. During short exposures at the sensitizing temperature, e.g., welding, chromium carbide forms only at the grain boundary. The chromium that is tied up as carbide is no longer available to prevent corrosion at the denuded zones adjacent to grain boundaries. Intergranular attack results and failure can be rapid. See par. 2-2.5.2 for a discussion of weld decay.

Age-hardenable alloys are soft in the as-quenched condition. In contrast, steels quenched from the so-called austenite region form a hard, nonequilibrium phase before reaching room temperature. This phase is called martensite. Martensitic steel is exceptionally hard but is also extremely brittle. The martensite structure, however, can be softened by reheating to some intermediate temperature. This tempering process decreases brittleness and improves ductility, although total strength is lowered. Steels are usually tempered following quenching to obtain the best combination of strength and toughness for particular applications.

Generally, heat treating steel to increase strength and hardness is accompanied by a lowered resistance to corrosion. These operations during fabrication of a metallic assembly can affect the following metal characteristics, which in turn influence the corrosion processes that are initiated at the exposed surfaces:

1. Nature and distribution of induced stress
2. Grain structure and orientation
3. Chemical composition and distribution within the grain and across the dimensions of the metal piece.

It is important to consider how the various process and fabrication operations influence these characteristics so that if potential corrosion problems exist, they can be avoided or mitigated.

## 3-5 INHIBITORS

The definition of an inhibitor favored by the National Association of Corrosion Engineers (NACE) is "a substance which retards corrosion when added to an environment in small concentrations" (Ref. 7). Inhibitors function by one or more of these mechanisms (Ref. 8):

1. By adsorption as a thin film on the surface of a corroding material
2. By inducing formation of a thick corrosion product
3. By forming a passive film on the metal surface
4. By changing characteristics of the environment either by producing protective precipitates or by removing or inactivating an aggressive constituent.

If corrosion is viewed as the consequence of an electrochemical cell composed of anode, cathode, electrolyte, and electronic conductor, inhibitors retard corrosion by

1. Increased polarization of the anode
2. Increased polarization of the cathode
3. Increased electrical resistance of the electrolyte circuit resulting from the formation of a deposit on the surface of the metal.

See par. 2-1.4 for a discussion of polarization. Polarization renders a cathode more anodic and an anode more cathodic. The manner in which polarization influences corrosion is illustrated in Fig. 3-23. Fig. 3-23(A) shows a polarization curve for a freely corroding metal. The corrosion current  $i_{corr}$  corresponds to Point D, at which the cathode and anode potentials are equal. Fig. 3-23(B) illustrates the relation of metallic corrosion D, protection F and G, and inhibition P. Anodic inhibitors give anodic control  $E_aF$ , whereas cathodic control is  $E_cG$ . Mixed anodic-cathodic control is  $E_a-E_cP$  if an inhibitor controls both anodic and cathodic reactions. Anodic control reduces the corrosion current by  $\Delta i_1$ , cathodic control reduces the corrosion current by  $\Delta i_2$ , and mixed anodic-cathodic control reduces the corrosion current by  $\Delta i_3$ .

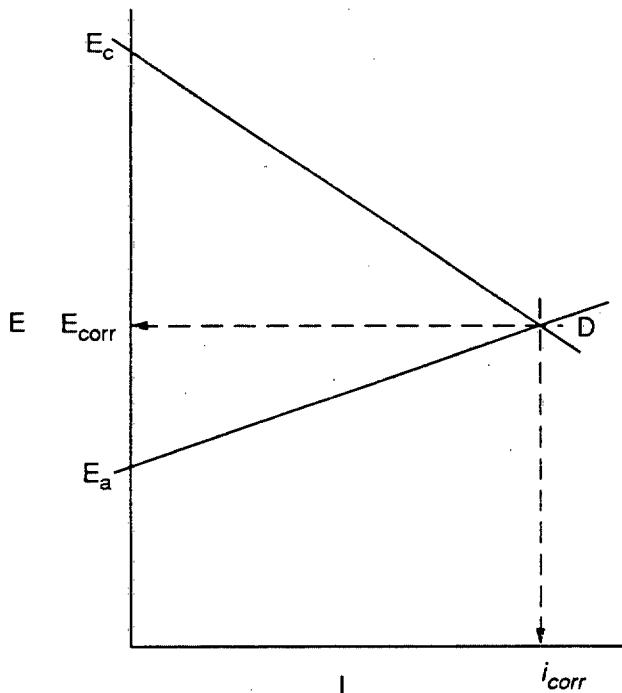
Inhibitors fall into several classes. The most important are passivating, cathodic, organic, precipitate-inducing, and vapor-phase inhibitors.

## 3-5.1 PASSIVATING INHIBITORS

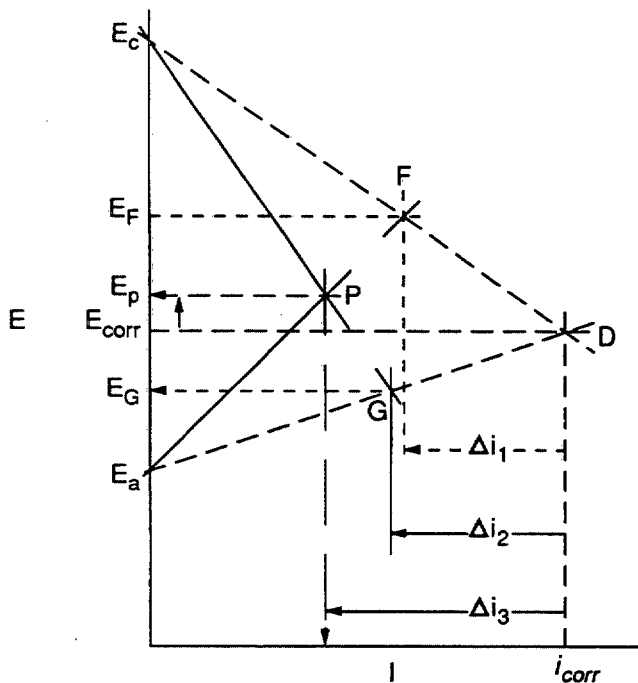
Passivating inhibitors are frequently used because, with careful control of the dosage, they are very effective in reducing corrosion. They are also referred to as "dangerous" inhibitors because they can cause pitting and sometimes an increase in corrosion rate if used in insufficient concentrations. There are two types of passivating inhibitors (Ref. 8):

1. Oxidizing anions, such as chromate, nitrite, and nitrate, can passivate steel in the absence of oxygen.
2. Nonoxidizing ions, such as phosphate, tungstate, and molybdate, can passivate steel only in the presence of oxygen.

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(A) Significant Terms for Freely Corroding Metal



(B) Schematic Showing Relation of Metallic Corrosion, Protection, and Inhibition

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**Figure 3-23. Anodic and Cathodic Polarization Curves (Ref. 9)**

Steel can be passivated in any solution except one containing readily oxidized substances in solution or high concentrations of chloride ions.

### 3-5.2 CATHODIC INHIBITORS

Cathodic inhibitors polarize the cathodic reaction and thereby retard the corrosion process. Three categories of cathodic inhibitors are cathode poisons, cathode precipitates, and scavengers (Ref. 8). Cathode poisons interfere with the formation of hydrogen atoms and the recombination of hydrogen atoms to molecular hydrogen at the surface of the corroding metal. Some cathode poisons, such as sulfides and selenides, are adsorbed on the metal. Compounds of arsenic, bismuth, and antimony are reduced at the cathode and deposit a metallic layer in the process. Because cathodic inhibitors interfere with the recombination of hydrogen atoms, a greater fraction of the hydrogen produced is absorbed by the metal. This absorption results in blistering and sometimes in hydrogen embrittlement.

Some dissolved compounds of calcium, magnesium, and zinc can be made to precipitate on cathodic areas by adjusting the pH and are widely used cathode precipitation-type inhibitors. At the correct pH a hard, smooth eggshell-like protective deposit of calcium carbonate can be formed. Zinc sulfate precipitates as zinc hydroxide on cathodic areas, so it also is a cathode precipitation-type inhibitor. Many metal ions form insoluble hydroxides, but only a few are useful corrosion inhibitors.

Corrosion can be retarded if oxygen is removed from solution. Sodium sulfite and sulfur dioxide are the most common oxygen scavengers used in water at normal ambient temperatures. Cobalt or manganese is generally used as a catalyst to speed the rate of reaction of sulfites with oxygen. Hydrazine is the preferred oxygen scavenger in high-pressure boilers, it does not increase the salt concentration of the water, and it is convenient to use. The by-products of the reaction of hydrazine with oxygen are gases.

### 3-5.3 ORGANIC INHIBITORS

Organic molecules inhibit corrosion by adsorbing at the metal-solution interface. The number of organic chemical inhibitors is very large. The adsorption phenomena involve (Ref. 9)

1. Proton acceptors that accept the hydrogen ion and attach at a point on the metal that would otherwise favor the cathodic reaction. Thus proton acceptors impede the cathodic reaction. This class includes basic organic molecules containing nitrogen, such as anilines, quinolines, ureas, and aliphatic amines.

2. Electron acceptors that attach at a point that would normally experience anodic attack. They accept electrons and are most effective for corrosion reactions under anodic control. This class includes organic perox-

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ides, sulfur as thiols, and selenols. In addition to anodic inhibitors, passivating inhibitors are in this category. The inorganic chromates and nitrates are also electron acceptors.

3. Mixed molecules that contain more than one orienting group. This class includes organic molecules containing groups of both the previous two types, e.g., sulfur and nitrogen.

Although theory provides guidelines for selecting organic inhibitors, the effectiveness of any organic molecule for inhibiting corrosion can be determined only by testing. Inhibition may be obtained by some organic compounds not directly but from a secondary product involving the organic compound. Certain halogen ions improve the efficiency of organic amines as corrosion inhibitors. Some halogen ions alone, e.g., iodide, bromide, and chloride, have inhibitive powers, but a combination of an amine inhibitor and iodide may be more inhibitive than either alone. There are a wide variety and a great number of proprietary inhibitor formulations.

The effectiveness of a soluble organic corrosion inhibitor increases with concentration up to a certain point. This fact suggests that inhibition is the result of adsorption of the inhibitor, i.e., a film only a few molecules thick forms on the metal surface. Thus if an inhibitor forms a strong adsorption bond, less inhibitor is required to saturate a surface. Surface saturation usually requires some equilibrium concentration of inhibitor in the solution; therefore, the concentration of inhibitor must be maintained at an effective inhibiting level. If an insoluble inhibitor is added by dispersion as fine droplets, a film several thousandths of a cm (in.) thick may form. Such films continue to inhibit corrosion beyond the time the concentration falls below the equilibrium level.

### 3-5.4 PRECIPITATION-INDUCING INHIBITORS

Precipitation-inducing inhibitors form a film over the metal surface that interferes with both anodic and cathodic areas. Silicates and phosphates form deposits on steel that result in a combination of both anodic and cathodic effects, as illustrated in Fig. 3-23(B), but they are not as effective as chromates and nitrites. They, however, can be used where nontoxic additives are required.

### 3-5.5 VAPOR-PHASE INHIBITORS

Vapor-phase corrosion inhibitors (also referred to as volatile corrosion inhibitors (VCI)) deposit from a vapor phase on the metal surface to be protected. Therefore, they are protective as long as there is sufficient inhibitor in the vapor phase surrounding the metal to maintain a condensed phase on the surface. The vapor phase acts only as a transport medium from a source to the corrosion site. The vapor-phase corrosion inhibitor should be volatile enough so that all surfaces to be protected are

readily reached but not so volatile that it is rapidly depleted through leaks in the containment vessel in which it is used.

Formulations have been developed that protect ferrous and nonferrous metals. Vapor-phase inhibitors for ferrous metals are volatile amines, such as the nitrite, carbonate, and benzoate salts of dicyclohexylamine, cyclohexylamine, and hexamethyleneimine and other polar substances. It appears that the organic portion of the molecules only provides volatility. Inhibitors for nonferrous metals with vapor space enclosures provide some protection, but they are not as effective as inhibitors used with ferrous metals. Vapor-phase inhibitors are used to impregnate wrapping paper or are placed loosely inside a closed container. They are widely used for corrosion protection within packaging. Specifications for volatile corrosion inhibitors are listed in Table 3-1.

### 3-5.6 INHIBITED ANTIFREEZE

An important application of corrosion inhibitors is in antifreeze solutions for vehicle coolant systems. Because of the many different metals in these systems and because of the different service conditions that are encountered, a single chemical inhibitor cannot provide complete protection. (Ref. 10). For example, a formulated antifreeze product developed by General Motors\* contains the following components by weight % in the antifreeze concentrate (Ref 11):

1. 0.21 of  $\text{NaNO}_3$  for protection of aluminum and solder
2. 0.98 of  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  for its buffering action, reserve alkalinity, and protection of ferrous metals
3. 0.17 of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  for protection of all metals
4. 0.43 of  $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$  for protection of ferrous metals and aluminum and for its buffering action
5. 0.55 of a 50% water solution of mercaptobenzothiazole for protection of copper and brass
6. 0.19 NaOH for additional reserve alkalinity. The ethylene glycol antifreeze solution is mixed with water to give the desired degree of antifreeze protection.

An antifreeze for military use is Type I from Federal Specification O-A-548 (Ref. 12). This antifreeze contains 2.5 weight % borax in the concentrate. It is recommended that other inhibitors be added from a second package, Federal Specification O-I-00490 (Ref. 13). A 170-g (6-oz) package contains approximately 26 g (0.92 oz) of mercaptobenzothiazole, 65 g (2.3 oz) of anhydrous  $\text{Na}_2\text{B}_4\text{O}_7$ , and 16 g (0.56 oz) anhydrous  $\text{Na}_2\text{HPO}_4$ . This inhibitor is added to either water or a Type I antifreeze-water system at a concentration of 28 g (1 oz) inhibitor to 1.8 kg (2 qts) of water. An antifreeze compound that includes all of

\*The discussion of this product is for example only. This discussion does not constitute an endorsement of this product by the US Government.



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TABLE 3-1. SPECIFICATIONS FOR VOLATILE CORROSION INHIBITORS

| SPECIFICATION NUMBER | TITLE  |
|----------------------|--|
| MIL-P-3420           | Packaging Materials, Volatile Corrosion Inhibitor Treated, Opaque                        |
| MIL-I-8574           | Inhibitors, Corrosion, Volatile, Utilization of  |
| MIL-B-22019          | Barrier Materials, Transparent, Flexible, Sealable, Volatile Corrosion Inhibitor Treated |
| MIL-B-22020          | Bag, Transparent, Flexible, Sealable, Volatile Corrosion Inhibitor Treated               |
| MIL-I-22110          | Inhibitor, Corrosion, Volatile, Crystalline Powder                                       |
| MIL-I-23310          | Inhibitor, Corrosion, Volatile, Oil-Type   |
| MIL-P-46002          | Preservative Oil, Contact and Volatile Corrosion Inhibited                               |

these inhibitors in a single package is described in MIL-A-46153 (Ref. 14).

Levy investigated the anodic and cathodic behaviors of steel in inhibited 30% ethylene glycol-water solution by applying an external electromotive force to a copper steel couple (Ref. 15). He found that borax, sodium nitrite, sodium chromate, sodium silicate, sodium benzoate, and triethanolamine function as anodic polarizers.

### 3-6 SURFACE TREATMENTS

Surface treatment is an application of a chemical reaction or physical process that changes the nature of a metal surface and affects the corrosion characteristics of the metal in one or more of the following ways. Surface treatment

1. Achieves some degree of corrosion resistance
2. Facilitates the application of protective paint
3. Retains corrosion protective or inhibitive oils and waxes.

An inhibitor may adsorb on a metal surface, and a metal coating may achieve a metallurgical bond with a surface. For the purpose of this discussion, however, inhibitors and coatings are not considered to be surface treatments. Surface treatments are often an intermediate process in providing an effective corrosion protection system. They are often specified because treated surfaces provide better adherence of coatings than the untreated metal. Many conversion coatings, however, do not by themselves provide adequate corrosion protection to the substrate metal.

#### 3-6.1 CHEMICAL CONVERSION COATINGS

Chemical conversion coatings are formed in situ by chemical reaction with the metal surface. In this way a metal surface is converted to nonmetallic compounds, such as oxides, phosphates, chromates, or complex

products of reactions between the metal and constituents of the treatment agent.

##### 3-6.1.1 Aluminum and Aluminum Alloys

Materials and processes are available to produce chemical conversion and anodic coatings on aluminum and aluminum alloys. Table 3-2 lists the surface treatments and finishes that are covered by specifications and that are required by MIL-STD-171 (Ref. 16).

Materials qualified under MIL-C-81706 (Ref. 17) produce coatings that range in color from clear to iridescent yellow or brown. These coatings, however, are not required by MIL-STD-171 (Ref. 16). Class 1A chemical conversion coatings, (MIL-C-5541, Ref. 18) are intended to prevent corrosion when the surface is left unpainted and to improve adhesion of paint finish systems to aluminum and aluminum alloys. For example, coatings of this type may be used for all surface treatments of tanks, tubings, and component structures for which paint finishes are not required on the interior surfaces but are required on the exterior surfaces. Class 3 chemical conversion coatings are intended to be a corrosion-preventive film for electrical and electronic applications for which low contact resistance is required. Chromate conversion coatings on unpainted surfaces lose their corrosion resistance properties if exposed to temperatures of 60°C (140°F) or above during drying or subsequent fabrication or service.

Coatings are produced on aluminum and aluminum alloys by electrolytic processes in sulfuric or chromic acid electrolytes (MIL-A-8625, Ref. 19). Type I coatings are produced by treating aluminum and aluminum alloys anodically in an electrolyte bath containing chromic acid to produce an inert aluminum oxide coating on the metal surface. Type I coatings should not be applied to aluminum alloys having a nominal copper content greater than

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TABLE 3-2. SURFACE TREATMENTS AND FINISHES FOR ALUMINUM (Ref. 16)

---

|   |
|---|
| Anodic film, chromic acid, MIL-A-8625, Type I   |
| Class 1, nondyed  |
| Class 2, dyed, color to be specified  |
| Anodic film, chromic acid, MIL-A-8625, Type IB (10 W voltage process, 20V)            |
| Anodic film, sulfuric acid, MIL-A-8625, Type II                                       |
| Class 1, nondyed  |
| Class 2, dyed, color to be specified  |
| Chemical film, chromate, MIL-C-5541   |
| Class 1A, for maximum protection against corrosion, painted or unpainted              |
| Class 3, for protection against corrosion where low electrical resistance is required |
| Hard anodic coating, MIL-A-8625, Type III, thickness ( $50.8 \pm 5 \mu\text{m}$ )     |
| $0.002 \pm 0.0002$ in. unless otherwise specified                                     |
| Class 1, nondyed  |
| Class 2, dyed, color to be specified  |

---

5.0%, a nominal silicon content greater than 7.0%, or having a total nominal alloying element content greater than 7.5%. Type II coatings result from treating aluminum and aluminum alloys in an electrolyte containing sulfuric acid to produce an inert aluminum oxide coating on the metal surface. Class I anodic coatings should not be dyed or pigmented, but colors that are characteristic to the coating or sealing process are produced. Class 2 anodic coatings are uniformly dyed or pigmented. Type I and Type II coatings provide better corrosion protection but are more costly than the chromate conversion systems (MIL-C-5541, Ref. 18).

Minute pores are formed in anodic-oxide coatings produced in electrolytes that have a solvent action on the oxide. The growth process of anodic coatings on aluminum is inward toward the metal. New growth takes place near the metal surface and forces the old growth outward. Because the outer surface of the anodic coating is subjected to the electrolyte for the longest period of time, its structure is more porous than that of the inner coating. Sulfuric acid electrolytes produce pores that are smaller than those produced by chromic acid electrolytes. These pores must be sealed to attain maximum corrosion resistance and color fastness for dyed surfaces. Sealing for Class I coatings of both Types I and II is accomplished by immersion in a 5% aqueous solution of sodium dichromate (pH 5.9 to 6.5) for 15 min at 81° to 100°C (178° to 212°F). Sealing of Class 2 coatings of both Types I and II is accomplished by immersion in a hot aqueous solution of cobalt or nickel acetate, boiling deionized water, or other suitable solution.

The thickest anodic coatings on aluminum are produced by hard anodic coating techniques, Type III. The aluminum oxide of the hard anodic coating is no harder than that of conventional anodic coatings. The difference is that the electrolyte and other conditions are such that the thick aluminum oxide coating produced, nominally 51  $\mu\text{m}$  (2 mil), has a dense structure and therefore resists abrasion

and erosion better than the conventional anodic coating. Unless specified to be otherwise, hard anodic coatings are unsealed. Type III anodic coatings are not normally applied to aluminum alloys with a nominal copper content in excess of 3.0% or a nominal silicon content in excess of 7.0%. If the electrolyte is entirely sulfuric acid, however, the copper and silicon content limits should not apply. Type III anodic coatings are usually furnished unsealed as Class I only; however, Class 2 dyed black coatings are sometimes specified.

Wash primers are used to obtain good adhesion of paint, primer, and topcoat on aluminum. The wash primer does not replace conventional organic primers nor should it be used if other surface treatments, such as chemical conversion or anodizing, are used. A typical two-package system (MIL-P-15328, Ref. 20) consists of basic zinc chromate dispersed in a solution of polyvinyl butyral resin, to which a thinner solution containing isopropyl alcohol, water, and phosphoric acid is added just before application. A coating consisting of zinc phosphate, trivalent chromium, and an oxidation product of the polyvinyl butyral is formed on the aluminum surface.

### 3-6.1.2 Copper Alloys

A black chemical finish can be formed on copper alloy surfaces by using proprietary chemical or electrochemical processes (MIL-F-495, Ref. 21). This finish may serve decorative or corrosion-retardant purposes, or it may be used as a base for subsequent coatings, such as lacquer, varnish, oil, and wax. The finish should not be used on food service and water supply items.

Copper surfaces should be acid etched with phosphoric acid conditioner (MIL-M-10578, Ref. 22) prior to painting.

Chromate conversion films may be applied by dipping in a proprietary bath formulation based on acid solutions containing hexavalent chromium.

**MIL-HDBK-735(MR)****3-6.1.3 Ferrous Alloys**

Table 3-3 contains a listing of surface treatments and finishes currently recommended for iron and steel in MIL-STD-171 (Ref. 16).

Phosphate coatings are formed on carbon and low-alloy steels by reaction with solutions of zinc phosphate or manganese phosphate in phosphoric acid. Specifications for the phosphating compounds are contained in MIL-P-50002 (Ref. 23). The reaction produces a network of porous iron, zinc, or manganese phosphates integral with and tightly adherent to the base metal. Also nitrate ion is added to some phosphating compounds to accelerate the reaction.

Manganese-base phosphate coating, Type M, described in DOD-P-16232 (Ref. 24), ranges in color from gray to black and is used on iron and steel. It is suitable for application to parts expected to contact alkaline materials. Although the manganese-base phosphate coating is more resistant to heat than the zinc-base phosphate coating, the manganese-base phosphate coating decomposes between 135° and 218°C (275° and 425°F). It has moderately good corrosion resistance in ambient atmospheres and is used on weapons going into long-term storage and on those to be reissued, e.g., rifle barrels and

breech mechanisms. This coating may be applied to all clean ferrous metal parts with the exception of stainless steels, springs having a wire diameter less than 3.18 mm (0.125 in.), some case-hardened parts, and barrel bores. The coating is also for use with a suitable supplementary petroleum-base finish and alone for special-purpose applications.

Zinc-base phosphate coating, Type Z, described in DOD-P-16232 (Ref. 24), ranges in color from gray to black and is used on iron and steel. It is suitable for application to parts not expected to contact alkaline materials or to be exposed to temperature in excess of 107°C (225°F). This coating is specifically required for parts for which rustproofing is a factor, e.g., cartridge clips and links, bolts and screws, gear housings, and small arms parts. It is also for use with a suitable supplementary petroleum-base finish, or it may be used alone for special-purpose applications.

Phosphate coating for paint base, Type I, described in TT-C-490 (Ref. 25), is a uniform, adherent, crystalline phosphate coating on iron and steel. It is gray to black in color, it inhibits corrosion, and it retards the progress of filiform and underfilm corrosion. This coating increases the adhesion of paint and results in greater durability of

**TABLE 3-3. SURFACE TREATMENTS AND FINISHES FOR IRON AND STEEL  
(INCLUDING CORROSION-RESISTANT STEEL) (Ref. 16)**

**FINISHES FOR IRON AND LOW-ALLOY STEELS**

Light phosphate paint base coatings

Zinc phosphate base, TT-C-490, Type I

Iron phosphate base, TT-C-490, Type II or IV

Pretreatment coating, TT-C-490, Type III (wash primer)

Heavy phosphate coatings

Manganese phosphate base, DOD-P-16232, Type M

Class 1, supplementary preservative treatment or coating, as specified

Class 2, supplementary treatment with lubricating oil conforming to MIL-L-3150

Class 3, with no supplementary treatment

Class 4, chemically converted (may be dyed to color as specified) with no supplementary coating or supplementary coating as specified

Zinc phosphate base, DOD-P-16232, Type Z

Class 1, supplementary preservative treatment or coating, as specified

Class 2, supplementary treatment with preservative conforming to MIL-C-16173, grade 3 or MIL-L-3150 (as alternate for very small parts)

Class 3, with no supplementary treatment

Class 4, chemically converted (may be dyed to color as specified) with no supplementary coating or supplementary coating as specified

**FINISHES FOR CORROSION-RESISTANT STEELS**

Corrosion-resistant steel not to be painted

Clean and passivate, QQ-P-35 (clean ASTM A380)

Corrosion-resistant steel to be painted

Cleaning, passivation, and pretreatment coating

Clean and passivate, QQ-P-35 (clean ASTM A380)

Surfaces to be painted shall be treated with a wash primer conforming to DOD-P-15328

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applied paint finishes. Filiform corrosion is described in par. 2-2.4.6.

Metal surfaces must be completely free of dust, grit, grease, oil, acid, alkaline residues, rust, and other contaminants when the phosphate coating is applied.

Table 3-4 lists black oxide finishes that may be applied to iron and steel and to copper alloys.

Black oxide coatings (MIL-C-13924, Ref. 26) applied to ferrous metals—wrought iron, carbon, low-alloy, and corrosion-resistant steels—are particularly suited for moving parts that cannot tolerate the dimensional build-up of a more corrosion-resistant finish. Black oxide coatings, with or without supplementary preservative treatment, may be used where a black surface is required. Only very limited corrosion protection under mildly corrosive conditions is obtained by using black oxide coating. Black oxide coatings are not recommended for parts going into long-term storage. Therefore, if long-term storage is required, a protective preservative fluid is recommended or a moisture-free package is used. A supplementary water-displacing preservative coating, such as is described in MIL-C-16173 (Ref. 27), Grade 3 or VV-L-800 (Ref. 28), may be specified.

Class 1 black oxide coatings are produced on wrought iron, cast and malleable irons, plain carbon, and low-alloy steels using an alkaline oxidizing process. The alkaline coating compound is specified in MIL-C-46110 (Ref. 29). Class 2 coatings are produced on corrosion-resistant steel alloys, which are tempered at 482°C (900°F) or higher, by using a fused oxidizing salt process—sodium dichromate and/or potassium dichromate. Class 4 coatings are produced on 300 series corrosion-resistant steel alloys only by using a proprietary alkaline oxidizing process.

MIL-HDBK-205 (Ref. 30) discusses black oxide coating and phosphatizing technology and provides detailed instructions for performing phosphatizing technology.

The noble metal-like behavior of corrosion-resistant or stainless steel is the result of the formation of a passive oxide film. Reliable and effective passive films can be formed on corrosion-resistant steels by passivation treatments with solutions containing nitric acid and/or sodium

dichromate. Specific passivating conditions apply to the different grades of corrosion-resistant steels (QQ-P-35B, Ref. 31) and their sulfur or selenium contents.

A particular form of chemical conversion coating is illustrated by weathering steels, which are low-alloy steels that develop a high degree of corrosion resistance by forming a dark-colored, firmly adherent, fine-textured rust upon exposure to the atmosphere. Self-weathering steels contain small additions of copper, chromium, nickel, and/or phosphorus. Additional benefit may occur from the presence of silicon and/or manganese, and sometimes small amounts of molybdenum, vanadium, tantalum, or zirconium are added. Of the latter group, molybdenum appears to have the most beneficial effect. A definite quantity of steel has to corrode to develop the protective rust; in an industrial environment a 25- to 51- $\mu\text{m}$  (1- to 2-mil) penetration is typical. This depth usually requires 1 to 2 years to achieve. In a marine environment an extra year is required, and the rust coat is likely to be less protective than one developed in an industrial environment (Ref. 32).

### 3-6.1.4 Magnesium Alloys

Magnesium alloys are not recommended for use in components of Army materiel, subassemblies or assemblies unless sufficient justification exists and approval is obtained from the procuring activity prior to design incorporation (Ref. 33). When magnesium alloys are used, a protective system must be incorporated that will insure long-term deterioration prevention.

Magnesium has the highest galvanic anodic potential in seawater of any of the commonly used metals. Chemically pure magnesium prepared by distillation has a corrosion rate in seawater of only 0.254 mm/yr (10 mpy). The impurities that are found in commercially pure magnesium are responsible for corrosion rates that are 100 to 500 times those of magnesium prepared by distillation.

Magnesium reacts with saltwater to evolve hydrogen gas. In pure water, magnesium reacts to form magnesium hydroxide, which is alkaline and partially soluble. Accordingly, formation of magnesium hydroxide might loosen organic paint coatings. Several chemical conversion and

**TABLE 3-4. INORGANIC FINISHES, BLACK OXIDE (Ref. 16)**

Black oxide for copper alloys, MIL-F-495

Black oxide for iron and steel, MIL-C-13924

Class 1, alkaline oxidizing process (for wrought iron, plain carbon, low-alloy steels)

Class 1, with MIL-C-16173, Grade 3 supplementary oil treatment

Class 2, alkaline-chromate oxidizing process

Class 2 with MIL-C-16173, Grade 3 supplementary oil treatment

Class 3, fused salt oxidizing process

Class 3 with MIL-C-16173, Grade 3 supplementary oil treatment

Class 4, alkaline oxidizing process

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anodizing processes have been developed to treat magnesium-base alloys in order to increase corrosion resistance and produce surfaces suitable for effective bonding of organic paint finishes.

Table 3-5 lists the magnesium surface treatment types and their correlation to military specifications. Table 3-6 lists the surface treatments currently acceptable for magnesium alloys according to MIL-STD-171 (Ref. 16).

Four chemical conversion coatings (Types I, III, VI, and VIII) and two anodic coatings (Types IV and VII) are detailed in MIL-M-3171 (Ref. 34).

Type I (chrome pickle treatment) is used for temporary storage, domestic shipment, electrical bonding, touching up of previously treated work, and brush-on application when permitted. It is applicable to all alloys when close tolerances are not required. Parts processed by this treatment are not to be subjected to temperatures above 232°C (450°F).

Type III (dichromate treatment) is for general, long-time protection of all alloys except those listed in MIL-M-3171 (Ref. 34), and it is applicable to parts for which close dimensional tolerances are required. Parts processed by

**TABLE 3-5. MAGNESIUM CHEMICAL CONVERSION AND ANODIZING PROCESSES**

| COMMERCIAL DESIGNATION      | TREATMENT TYPE                   | MILITARY SPECIFICATION                        |
|-----------------------------|----------------------------------|---|
| Dow No. 1<br>MACroMag 101   | Chrome pickle                    | MIL-M-3171 Type I                             |
| Dow No. 7<br>MACroMag D-7   | Dichromate                       | MIL-M-3171 Type III                           |
| Dow No. 9<br>MACroMag D-9   | Galvanic anodizing               | MIL-M-3171 Type IV                            |
| Dow No. 19<br>MACroMag D-19 | Chromic acid<br>brush-on         | MIL-M-3171 Type VI                            |
| Magnesium Electron          | Fluoride anodizing               | MIL-M-3171 Type VII                           |
| Iridite No. 15              | Chromate                         | MIL-M-3171 Type VIII                          |
| Dow 17                      | Anodize: light<br>Anodize: heavy | MIL-M-45202 Type I Class C<br>Type II Class D |
| HAE                         | Anodize: light<br>Anodize: heavy | MIL-M-45202 Type I Class A<br>Type II Class A |
| Manodyz                     | Anodize                          |   |

**TABLE 3-6. SURFACE TREATMENTS FOR MAGNESIUM ALLOYS (Ref. 16)**

Anodic treatments, MIL-M-45202

Type I, Class C, light coating

Type II, heavy coating

Class A, Grade 3

Class D

Chrome pickle, MIL-M-3171, Type I

Dichromate treatment, MIL-M-3171, Type III

Galvanic anodizing, MIL-M-3171, Type IV

Chromic acid brush-on treatment, MIL-M-3171, Type VI

Pretreatment coating, DOD-P-15328 with 50% of specified phosphoric acid

Fluoride anodizing process plus corrosion-preventive treatment (for castings), MIL-M-3171, Type VII

Chromate treatment, MIL-M-3171, Type VIII

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this treatment are not to be subjected to temperatures above 288°C (550°F).

Type VI (chromic acid brush-on treatment) is for temporary storage, protective touch up of previously treated metal, and brush-on application to the metal if parts and assemblies are too large to be immersed. Parts processed by this treatment are not to be subjected to temperatures above 232°C (450°F).

Type VIII (chromate treatment) is for general, long-time protection of all alloys when close dimensional tolerances are required. Parts processed by this treatment are not to be subjected to temperatures above 288°C (550°F).

Type IV (galvanic anodizing treatment) may be applied to all alloys, but specifically it is used for those alloys that do not react to produce a protective film with Type III treatment. It causes no dimensional change and may be applied after machining operations. Parts processed by this treatment cannot be subjected to temperatures above 288°C (550°F). The anodizing solution contains ammonium sulfate, sodium dichromate, and ammonium hydroxide in aqueous solution.

Type VII (fluoride anodizing treatment) is essentially an anodic treatment followed by a stripping operation to remove the fluoride coating. The alloy is then treated with a corrosion preventive to provide optimum protection. The anodizing and stripping portions of the treatment are applicable to all alloys and forms, and they form a good base for other types of treatments, such as Type III.

The Dow 17 and HAE anodic coatings are covered by MIL-M-45202 (Ref. 35). The Manodysz process is an extensively used anodic treatment for magnesium (Ref. 36).

Dow 17 coatings range from thin, clear to light gray-green to thick, dark green coatings, depending on their intended use. The clear coatings are used as a base for clear lacquers or paints to produce a final appearance similar to clear anodizing on aluminum. The light gray-green coatings are used in most applications that are to be painted. The thick, dark green coating offers the best combination of abrasion resistance, protection, and paint base characteristics. The coating has good corrosion resistance, abrasion resistance, and paint base quality. It is uniform, has high dielectric strength, and resists very high temperatures. The dimensional buildup varies from 0.5 to 25  $\mu\text{m}$  (0.02 to 1 mil). The Dow 17 treatment is covered by MIL-M-45202 (Ref. 35), Type I, Class C for light coatings and Type II, Class D or E for heavy coatings.

The HAE process deposits a brown ceramic coating, ranging from tan-colored light films to dark brown, heavy coatings. The low-voltage HAE process produces a smooth, olive-drab, hard coating varying from 3.8 to 10  $\mu\text{m}$  (0.15 to 0.40 mil), depending on the length of treatment. The high-voltage HAE process produces a heavy, dark brown, lusterless coating 25 to 33  $\mu\text{m}$  (1 to 1.3

mil) thick. The coating has good temperature resistance up to 1371°C (2500°F) and has high dielectric strength. The HAE treatment is covered by MIL-M-45202 (Ref. 35) and has these classifications:

1. Type I - Light Coating

Class A - Tan coating (HAE)

Grade 1 - Without posttreatment (dyed)

Grade 2 - With bifluoride-dichromate posttreatment

2. Type II - Heavy Coating

Class A - Hard brown coating (HAE)

Grade 1 - Without posttreatment

Grade 3 - With bifluoride-dichromate posttreatment

Grade 4 - With bifluoride-dichromate posttreatment including moist heat aging

Grade 5 - With double application of bifluoride-dichromate posttreatment including moist heat aging.

The Manodysz process applies a coating during a strong alkaline bath in which the magnesium part is one of the electrodes when using alternating current or the anode when using direct current (Ref. 36). The alternating current process is preferred for thin gauge, wrought alloy parts. The coating is gray in color and approximately 10  $\mu\text{m}$  (0.4 mil) thick. With direct current the coating is light green and up to 20  $\mu\text{m}$  (0.8 mil) thick. Direct current is preferred for heavier gauge wrought alloy and coatings. This coating is considerably more resistant to corrosion than the dichromate conversion coating (MIL-M-3171, Type III, Ref. 34). It is also harder and more wear resistant than most of the chemical conversion coatings for magnesium.

MIL-STD-186 (Ref. 37) specifies that all magnesium alloys shall receive an anodic coating in accordance with MIL-M-45202, Type I or Type II, Class A (Ref. 35). These coatings are to be used in parts subject to abrasion, erosion, or wear. MIL-M-3171 (Ref. 34) treatments are to be used only for temporary protection or as a paint base. Surfaces that have the anodic coating removed or damaged are to be touched up using either the Type I or Type IV process of MIL-M-3171 (Ref. 34). Damaged or touched up magnesium surfaces that were previously anodically coated in accordance with MIL-M-45202 (Ref. 35) may be reanodized.

Voids in magnesium castings should be filled before or after anodizing, preferably before, and varnishes or heat-reactive resins may be used. If the anodized magnesium component is to serve as a bearing surface, however, high molecular weight waxes or lubricating resins are recommended for sealing the anodic coating.

### 3-6.1.5 Zinc and Zinc Alloys, and Cadmium

Coatings can be applied to zinc surfaces by electrochemical anodizing and by chemical conversion. The anodized coatings are thicker, harder, and more corrosion

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resistant than chromate or phosphate corrosion coatings. Table 3-7 lists surface treatments available for zinc and cadmium.

Anodic coatings are produced on zinc surfaces to provide high-quality finishes with corrosion resistance and the decorative advantage of color (MIL-A-81801, Ref. 38). The type of electrolyte used determines the color of the finish. The anodizing can be applied to wrought or die-cast zinc and zinc-base alloy parts as well as to coatings formed from electrodeposited, mechanically deposited, and hot-dipped zinc on steel or thermal-sprayed zinc.

Zinc anodizing produces a barrier-type film consisting of a porous structure overlaying an initial barrier layer. During the anodizing of zinc, a complex fritted compound (of fused particles) is formed by anodic spark discharge beginning at about 65 to 70 V. The coating is hard, porous, and absorbent and has excellent masking properties. Because the anodized coatings are porous and absorbent, they form an excellent base for paints, enamels, lacquers, etc. After painting, further treatments are not generally needed because the anodizing restricts moisture penetration and prevents underfilm corrosion.

Zinc chromate conversion coatings retard or prevent the formation of white corrosion products on zinc alloy castings and hot-dipped galvanized surfaces exposed to stagnant water, high-humidity atmospheres, saltwater, marine atmospheres, and exposure to cyclic condensation and drying (MIL-C-17711, Ref. 39). Some types of zinc chromate coatings are a satisfactory base for paint. Requirements for chromate coatings for zinc-plated surfaces are specified in ASTM B633 (Ref. 40). Zinc phosphate conversion coatings may be used as a base for painting (MIL-T-12879, Ref. 41, and DOD-P-16232, Ref. 24).

**3-6.2 ION IMPLANTATION**

Ion implantation uses an energetic beam of ions to introduce atoms of specified elements into the surface layer of materials. This influences the composition and structure of the surface layer within about 1  $\mu\text{m}$  (0.04 mil) of the surface. This modification of the surface layer affects several material characteristics that are exhibited

**TABLE 3-7. SURFACE TREATMENTS FOR ZINC AND CADMIUM (Ref. 16)**

|  |
|--|
| Phosphate and chromate treatments, MIL-T-12879 |
| Type I, repaint treatment                      |
| Class 1, phosphate                             |
| Class 2, chromate                              |
| Type II, chromate final finish                 |
| Phosphoric acid conditioner, MIL-M-10578       |
| Type I, wash-off                               |
| Type II, wipe-off                              |

at the surface interface. These characteristics are friction, wear, hardening, corrosion resistance, electrochemistry, catalysis, bonding, lubrication, and adhesion (Ref. 42).

The process of ion implantation has been adapted from the manufacture of semiconductor devices. Ion implantation equipment and processes that must meet the needs of the semiconductor industry have become highly developed. Requirements for precise doping control are stringent in producing semiconductor devices. However, the geometry of semiconductor devices is simple, the areas to be treated are small, and solving the ion source problem is relatively easy.

To treat engineering materials, however, intense ion beams are required. The components to be treated differ greatly in size, shape, and complexity, and ion implantation treatment for corrosion control requires a variety of ion species. Therefore, the question of economic justification of production scale equipment is very important. As long as the cost is high and equipment of relatively low capability is being used, ion implantation treatment for corrosion control will involve small critical parts and components.

Table 3-8 lists the general advantages and disadvantages of ion implantation processes.

**TABLE 3-8. ADVANTAGES AND DISADVANTAGES OF ION IMPLANTATION (Ref. 42)**

| ADVANTAGES   |
|--|
| Versatility (regarding ion species and the substrate)                    |
| Controllability (regarding ion energy, ion concentration, and area)      |
| Low-temperature process  |
| No buildup, hence no dimensional change                                  |
| Clean vacuum process   |
| Applied to finished components   |
| Monitored electrically throughout  |
| Low power consumption  |
| Conserves material   |
| No environmental contamination   |
| No changes in bulk substrate properties                                  |
| Solid solubility limit can be exceeded in treated zone                   |
| No sharp interface, thus no coating adhesion problems                    |
| Composition may be changed without affecting grain size                  |
| DISADVANTAGES  |
| High capital cost  |
| Relatively shallow treatment region                                      |
| Line of sight process  |
| Commercially scaled ion sources need development                         |
| Unfamiliar process for most metalworking surface or treatment operations |
| Requires manipulation in a vacuum  |

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Ions of a given element can be directly implanted into a substrate surface. However, achieving appreciable quantities of a metallic or metalloid species in a material surface by using this approach would be too expensive relative to alternative means of corrosion prevention.

Energetic ion beams can result in intermixing a thin coating and its substrate. Repeated collisions between the ion beam species and the coating material eventually distribute the coating material throughout a surface depth corresponding to the ion penetration range. In any process involving intermixing of a coating and substrate through the action of an ion beam, there may be chemical interaction between the ion beam species and the coating or substrate.

Ion implantation can produce novel, metastable, single-phase surface alloy layers with compositions and structures that cannot be created by conventional metallurgical processes. This capability provides considerable opportunity for developing new, corrosion-resistant coatings. Practical applications of ion implantation are improving the general resistance of materials that already exhibit good corrosion resistance in applications. Improved resistance to specific forms of localized corrosion can be advised, and ion implantation can create surfaces that impede the diffusion of reacting species in high-temperature applications. In addition, elements can be implanted in surfaces to improve the mechanical properties of the scale that forms at high temperatures (Ref. 43).

### 3-6.3 DRY FILM LUBRICANTS

Dry film lubricants could be specifically formulated to act as a corrosion-preventive film. However, the standard dry film lubricants containing lubricant pigments, such as graphite, heavy metal powders, and/or uninhibited molybdenum disulfide, can create corrosion problems. For example, molybdenum disulfide reacts in water to form acidic sulfur compounds, such as hydrogen sulfide or sulfur dioxide. In the presence of this acidic sulfurous electrolyte, galvanic corrosion occurs between the graphite or heavy metal powder and the base metal surface, on which the dry lubricant was applied. For example, MIL-L-81329 (Ref. 44) does not prohibit the use of graphite or heavy metal powders, whereas MIL-L-46010 (Ref. 45) and MIL-L-45983 (Ref. 46) do prohibit the use of graphite and heavy metal powders. In addition, these last two specifications require that the film meet stringent salt-fog tests. Products that meet these specifications are classified as "corrosion inhibiting". If molybdenum disulfide is used in a corrosion-inhibiting dry film lubricant, acid-accepting inhibitors should be included to combine with the acidic hydrolysis products of molybdenum disulfide.

Initially, dry film lubricants were used to replace petroleum-base lubricants on exposed surfaces because "greasy" lubricants can pick up and retain nuclear,

biological, and chemical (NBC) warfare agents. Dry film lubricants, however, proved to be long-lasting and very effective. They are used where access to a lubricated part is limited, and they are even used to treat surfaces that will also be lubricated by greases or oils. Examples of uses of dry film lubricants are the M-16 rifle, M-16 magazines, and vane-type pumps used in automotive power steering.

### 3-6.4 SHOT PEENING

Surfaces that are under compressive stress are less likely to experience corrosion fatigue and stress-corrosion cracking. Shot peening directs a high-velocity flow of metallic shot or glass beads against a metal surface to induce compressive stresses in the surface layer (MIL-P-81985 (Ref. 47) and MIL-S-13165 (Ref. 48)). Accordingly, peening is applied on metal parts, such as axles, springs (helical, torsional, and leaf), gears, shafting, aircraft landing gear assemblies, wing structures, jet engine support members, and helicopter rotor hub assemblies, that are subjected to repeated applications of a load pattern.

Metallic shot peening is also used to close porosity in castings and to straighten or form parts. Peening with glass beads is used primarily where contamination from metal shot presents a special problem, where a fine surface finish is required, or where peening in a very sharp radius, such as a thread root, is required.

Peening metals with portable, bonded shot, rotary flap wheels accomplishes the same purpose, i.e., to induce compressive stresses in a metal surface. In some applications it is more convenient than conventional shot-peening processes. Peening with metal carbide bonded shot flaps should be used where iron contamination of nonferrous parts or a fine surface finish is particularly important.

## 3-7 COATINGS

Coatings prevent or retard corrosion by acting as a barrier between the base metal and the environment, and they can be described in the following terms:

1. The substance or class of substance that comprises the coatings
2. The method of applying or generating the coating onto a metal surface
3. The mechanism or process by which a coating mitigates corrosion.

On the basis of classes of materials used as coatings, they can be classified as metallic, inorganic, and organic.

### 3-7.1 METALLIC COATINGS

Metallic coatings are classified in terms of whether they are anodic or cathodic to the base metal in the environment of interest. For example, copper or nickel coatings are normally cathodic on steel. Zinc and aluminum are



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normally anodic on steel. Cathodic coatings are referred to as "noble", and anodic coatings are "sacrificial".

The objective of a noble metal coating is to obtain the corrosion resistance and appearance of the noble metal while retaining the mechanical properties and low cost of the base metal. This presents a problem if there are pinholes or cracks in the coating. Because the base metal is anodic to the coating, it will corrode preferentially, and because the area of the anodic pinhole or crack is small relative to the area of the cathodic coating, the intensity of corrosion at the defect will be great.

In contrast, a sacrificial coating, such as aluminum or zinc, will protect steel exposed at a defect or gap in the coating. A sacrificial coating corrodes preferentially to the base metal. The protection afforded by a sacrificial coating depends on the aggressiveness of the environment, the thickness of the coating, and the size of coating defect.

Metallic coatings are created on a base metal by several processes. Some of the processes are

1. Hot dipping consists of immersing the base metal in a molten bath of the coating metal.

2. The article to be coated can be made the cathode, by an impressed current, in a bath containing a compound of the metal to be deposited as a coating. This process is called electroplating.

3. Tiny droplets of molten metal can be sprayed on the metal to be coated. Metal spraying processes use a gun in which metal powder or wire is melted and propelled as tiny droplets toward the article being coated.

4. Metal wire or rods can be melted onto a small area of the surface being coated with a torch, electric arc, or laser in a manner similar to welding. Large areas can be covered by this process, but only a small area can be worked on at any one time.

5. Metal can be deposited from the vapor state onto the article being coated. In this vacuum-metallizing process the article is placed in a vacuum in which the coating metal is vaporized. In the ion vapor deposition of aluminum, the vaporized aluminum is ionized and

attracted to the negatively charged part to be coated. This process results in a thick, dense, adherent coating of aluminum.

6. Cementation coatings are formed by diffusing the coating metal into the surface of the base metal. This is accomplished by heating the article to be coated in a powdered mass of the coating metal.

7. Electroless deposition does not use the applied electromotive force of electroplating. Instead a metal coating is deposited from a solution containing a salt of the coating metal and a suitable reducing agent.

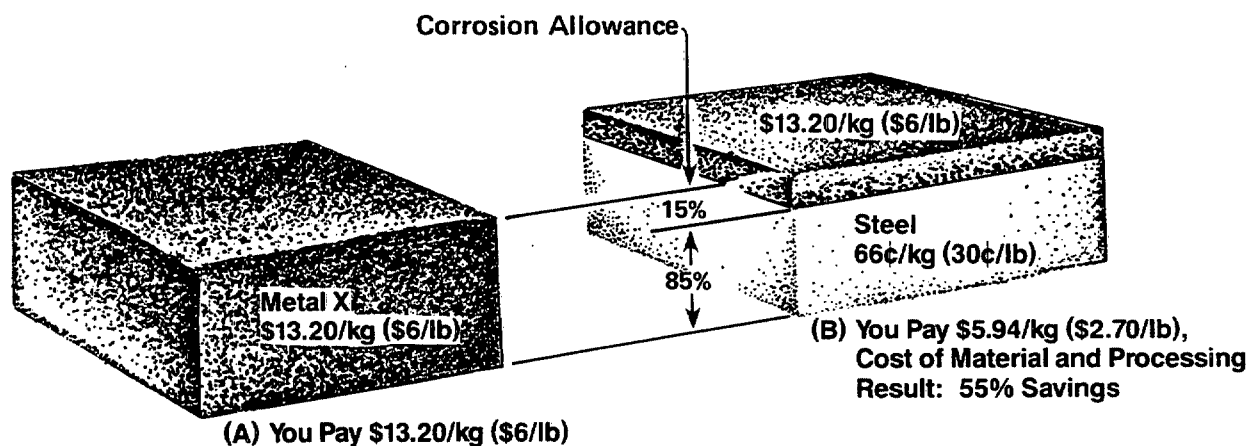
8. Cladding usually refers to a relatively thick coating of a corrosion-resistant metal on a base metal. As such, cladding may be applied by any of the previously discussed methods that can produce a relatively thick layer of metal coating. Usually, however, cladding is applied by rolling a composite billet to the required thickness of sheet, by explosive bonding, or by mechanically fixing the clad to the substrate metal. Fig. 3-24 illustrates the potential economic saving of using a clad metal, and Fig. 3-25 illustrates the explosion cladding process and the unique wavy bonding zone created.

9. In addition to the processes described, many processes are available for applying metallic coatings. These processes use various electrical, chemical, and mechanical means to deposit metals or metal compounds on a metallic surface. For example, metal-containing particles may be attracted to a surface by electrophoresis or by simple immersion in a slurry containing the suspended particles.

Zinc, nickel, tin, and cadmium, in that order, are applied on the largest tonnage basis. Gold, silver, and platinum plates are common.

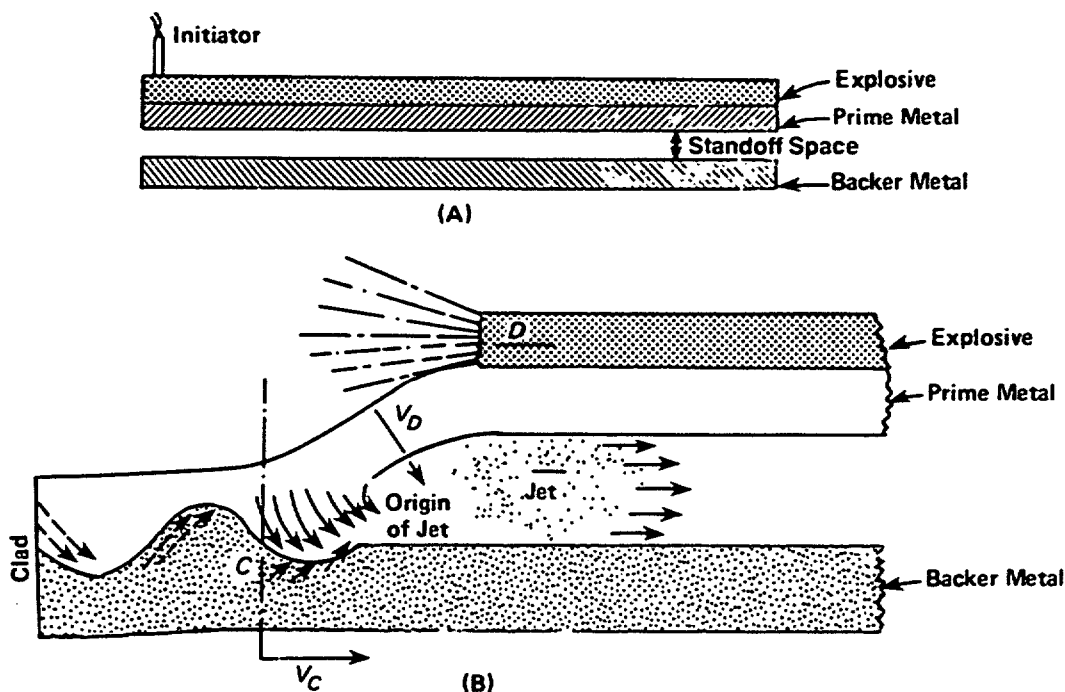
Because of the possible problem of hydrogen cracking that can result from hydrogen generated during electroplating, steel parts having a tensile strength of 1655 MPa (240,000 psi) or greater shall be coated (MIL-5-5002, Ref.

1. With cadmium by vacuum deposition in accor-



**Figure 3-24. Economic Savings of a Clad Material**

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Parallel arrangement for explosion cladding and subsequent collision between the prime and backer metals that leads to jetting and formation of wavy bond zone.

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### Figure 3-25. Explosion Cladding Process (Ref. 49)

dance with MIL-C-8837 (Ref. 51)

2. With aluminum by vacuum deposition in accordance with MIL-C-23217 (Ref. 52)

3. With cadmium or zinc by mechanical deposition in accordance with MIL-C-81562 (Ref. 53)

4. With aluminum and aluminum alloys by metallic compound decomposition in accordance with MIL-C-81740 (Ref. 54)

5. With zinc, aluminum, or other metals by thermal spraying (preferably flame spraying) in accordance with MIL-M-6874 (Ref. 55)

6. With aluminum (metallic ceramic) in accordance with MIL-C-81751 (Ref. 56) or MIL-C-81797 (Ref. 57).

Various metallic coatings are listed Table 3-9 with the corresponding specifications.

**MIL-HDBK-735(MR)****TABLE 3-9. METALLIC COATINGS (Ref. 16)****ALUMINUM COATINGS**

Hot-dip aluminum, Data to be specified on drawing or in contract  
 Vacuum-deposited aluminum, MIL-C-23217

**CADMIUM COATINGS**

Plating, QQ-P-416, Type I, without supplementary treatment

Class 1, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 2, 7.6  $\mu\text{m}$  (0.0003 in.) thick

Class 3, 5.1  $\mu\text{m}$  (0.0002 in.) thick

Plating, QQ-P-416, Type II, with supplementary chromate treatment; normal color; not bleached or clear

Class 1, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 2, 7.6  $\mu\text{m}$  (0.0003 in.) thick

Class 3, 5.1  $\mu\text{m}$  (0.0002 in.) thick

Plating, QQ-P-416, Type III, with supplementary phosphate treatment

Class 1, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 2, 7.6  $\mu\text{m}$  (0.0003 in.) thick

Class 3, 5.1  $\mu\text{m}$  (0.0002 in.) thick

Cadmium coating (vacuum-deposited), MIL-C-8837, Type I without supplementary treatment

Class 1, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 2, 7.6  $\mu\text{m}$  (0.0003 in.) thick

Class 3, 5.1  $\mu\text{m}$  (0.0002 in.) thick

Cadmium coating (vacuum-deposited), MIL-C-8837, Type II, with supplementary chromate treatment, normal color, not bleached or clear

Class 1, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 2, 7.6  $\mu\text{m}$  (0.0003 in.) thick

Class 3, 5.1  $\mu\text{m}$  (0.0002 in.) thick

Cadmium coating (vacuum-deposited), MIL-C-8837, Type III, with supplementary phosphate treatment

Class 1, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 2, 7.6  $\mu\text{m}$  (0.0003 in.) thick

Class 3, 5.1  $\mu\text{m}$  (0.0002 in.) thick

Cadmium coating, mechanically deposited, MIL-C-81562, thickness and supplementary treatment as specified

**CHROMIUM COATINGS**

Decorative plating, QQ-C-320, Class 1

Type I, bright

Type II, satin

Engineering plating, QQ-C-320, Class 2; thickness and undercoating, if necessary, as specified

Class 2a

Class 2b

Class 2c

Class 2d

Class 2e

Black, MIL-P-14538

Porous chromium plating, MIL-C-20218

**COPPER COATING**

Electrodeposited, MIL-C-14550

Class 1, 25  $\mu\text{m}$  (0.0010 in.) thick

Class 2, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 3, 5.1  $\mu\text{m}$  (0.0002 in.) thick

Class 4, 2.5  $\mu\text{m}$  (0.0001 in.) thick

(cont'd on next page)

**MIL-HDBK-735(MR)****TABLE 3-9. (Cont'd)****GOLD COATING****Electrodeposited, MIL-G-45204**

**Type I, 99.7% gold, minimum; hardness shall be specified**

Class 1, 1.3  $\mu\text{m}$  (0.00005 in.) thick, minimum

Class 2, 2.5  $\mu\text{m}$  (0.00010 in.) thick, minimum

Class 3, 5.1  $\mu\text{m}$  (0.00020 in.) thick, minimum

Class 4, 7.6  $\mu\text{m}$  (0.00030 in.) thick, minimum

Class 5, 13  $\mu\text{m}$  (0.00050 in.) thick, minimum

Class 6, 38  $\mu\text{m}$  (0.00150 in.) thick, minimum

Class 0, 0.76  $\mu\text{m}$  (0.00003 in.) thick, minimum

Class 00, 0.51  $\mu\text{m}$  (0.00002 in.) thick, minimum

**Type II, 99.0% gold, minimum; hardness shall be specified**

Class 1, 1.3  $\mu\text{m}$  (0.00005 in.) thick, minimum

Class 2, 2.5  $\mu\text{m}$  (0.00010 in.) thick, minimum

Class 3, 5.1  $\mu\text{m}$  (0.00020 in.) thick, minimum

Class 4, 7.6  $\mu\text{m}$  (0.00030 in.) thick, minimum

Class 5, 13  $\mu\text{m}$  (0.00050 in.) thick, minimum

Class 6, 38  $\mu\text{m}$  (0.00150 in.) thick, minimum

Class 0, 0.76  $\mu\text{m}$  (0.00003 in.) thick, minimum

Class 00, 0.51  $\mu\text{m}$  (0.00002 in.) thick, minimum

**Type III, 99.9% gold, minimum; hardness shall be specified**

Class 1, 1.3  $\mu\text{m}$  (0.00005 in.) thick, minimum

Class 2, 2.5  $\mu\text{m}$  (0.00010 in.) thick, minimum

Class 3, 5.1  $\mu\text{m}$  (0.00020 in.) thick, minimum

Class 4, 7.6  $\mu\text{m}$  (0.00030 in.) thick, minimum

Class 5, 13  $\mu\text{m}$  (0.00050 in.) thick, minimum

Class 6, 38  $\mu\text{m}$  (0.00150 in.) thick, minimum

Class 0, 0.76  $\mu\text{m}$  (0.00003 in.) thick, minimum

Class 00, 0.51  $\mu\text{m}$  (0.00002 in.) thick, minimum

**LEAD COATINGS****Electrodeposited lead, MIL-L-13808, Type I, without preliminary copper coatings**

Class 1, 25  $\mu\text{m}$  (0.001 in.) thick

Class 2, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 3, 6.4  $\mu\text{m}$  (0.00025 in.) thick

38  $\mu\text{m}$  (0.0015 in.) thick

**Electrodeposited lead, MIL-L-13808, Type II, with preliminary copper plating 0.38  $\mu\text{m}$  (0.000015 in.) thick**

Class 1, 25  $\mu\text{m}$  (0.001 in.) thick

Class 2, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 3, 6.4  $\mu\text{m}$  (0.00025 in.) thick

38  $\mu\text{m}$  (0.0015 in.) thick

**Hot-dip lead coating, MIL-L-13762**

Type I (low tin content)

Type II (medium tin content)

Type III (high tin content)

**NICKEL COATINGS****Decorative plating, QQ-N-290, class 1; bright or dull finish as specified on drawing**

Grade C, 25  $\mu\text{m}$  (0.0010 in.) thick

Grade E, 15  $\mu\text{m}$  (0.0006 in.) thick

Grade F, 10  $\mu\text{m}$  (0.0004 in.) thick

Grade G, 5  $\mu\text{m}$  (0.0002 in.) thick

Grade A, 40  $\mu\text{m}$  (0.0016 in.) thick

(cont'd on next page)

**MIL-HDBK-735(MR)****TABLE 3-9. (Cont'd)**


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Grade B, 30  $\mu\text{m}$  (0.0012 in.) thick

Grade D, 20  $\mu\text{m}$  (0.0008 in.) thick

Engineering plating, QQ-N-290, Class 2, thickness as specified

Electroless nickel coating, MIL-C-26074

Class 1, as coated, no subsequent heat treatment

Class 2, steel, copper, nickel, cobalt, titanium-based alloys, and any base metal not adversely affected by heating as specified for improved hardness

Class 3, aluminum alloys non-heat-treatable, and beryllium alloys processed to improve adhesion of the nickel deposit

Class 4, aluminum alloys, heat-treatable, process to improve adhesion of the nickel deposit

Black nickel coating, MIL-P-18317 (undercoat as specified)

**PALLADIUM COATING**

Electrodeposited palladium, MIL-P-45209, thickness as specified

**RHODIUM COATING**

Electrodeposited rhodium, MIL-R-46085

Class 1, 0.05  $\mu\text{m}$  (0.000002 in.) thick

Class 2, 0.25  $\mu\text{m}$  (0.000010 in.) thick

Class 3, 0.51  $\mu\text{m}$  (0.000020 in.) thick

Class 4, 2.5  $\mu\text{m}$  (0.000100 in.) thick

Class 5, 6.4  $\mu\text{m}$  (0.000250 in.) thick

**SILVER COATING, QQ-S-365**

Type I, Grade B, matte

Type II, Grade B, semibright

Type III, Grade B, bright

Type I, Grade A (supplementary treatment), matte

Type II, Grade A (supplementary treatment), semibright

Type III, Grade A (supplementary treatment), bright

**TIN COATINGS**

Electrodeposited, MIL-T-10727, specifies ASTM B545 for Type I, thickness as specified

Hot-dipped, MIL-T-10727, Type II, thickness as specified

**ZINC COATINGS**

Electrodeposited zinc, ASTM B633, Type I, as plated without supplementary treatment

Class 1, 25  $\mu\text{m}$  (0.0010 in.) thick

Class 2, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 3, 5.1  $\mu\text{m}$  (0.0002 in.) thick

Electrodeposited zinc, ASTM B633, Type II, with supplementary chromate treatment; normal color; not bleached or clear

Class 1, 25  $\mu\text{m}$  (0.0010 in.) thick

Class 2, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 3, 5.1  $\mu\text{m}$  (0.0002 in.) thick

Electrodeposited zinc, ASTM B633, Type IV with supplementary phosphate treatment

Class 1, 25  $\mu\text{m}$  (0.0010 in.) thick

Class 2, 13  $\mu\text{m}$  (0.0005 in.) thick

Class 3, 5.1  $\mu\text{m}$  (0.0002 in.) thick

Zinc, hot-dip galvanizing, ASTM A153 (for hardware)

With chromate treatment, finish 6.1.1.2

With phosphate treatment, finish 6.1.1.1

Zinc coating, mechanically deposited, MIL-C-81562, thickness and supplementary treatment as specified

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## MIL-HDBK-735(MR)

### 3-7.1.1 Aluminum Coatings

Aluminum coatings are commonly applied by immersing steel sheets and shapes of uniform cross section into molten baths of aluminum, by spraying molten aluminum on steel assemblies, or by depositing aluminum from a vapor in a vacuum (MIL-C-23217, Ref. 52). Aluminum coatings are also applied by the ion vapor deposition process. In this process ionized aluminum vapor is attracted to the negative charge applied to the part to be coated. In most environments aluminum does not provide sacrificial protection to the surfaces to which it is applied, except at the onset of exposure. Aluminum forms an oxide layer, which stifles the anodic reaction. In addition, aluminum reaction compounds fill any pores and thereby provide mechanical exclusion to the environment. Thus aluminum coatings provide high resistance to atmospheric corrodents and hot gases. Aluminum coatings are often sealed with topcoats compatible with the coating and the environment. Porous aluminum coatings are especially effective with the topcoat seal.

Aluminum coatings can be formed by the decomposition of complex aluminum-organic compounds or aluminum in conjunction with other elements (MIL-C-81740, Ref. 54). Aluminum and aluminum alloy coatings produced by this method protect steel used at temperatures in excess of 232° C (450° F). The degree of corrosion resistance varies with the thickness of the coating, i.e., 3  $\mu$ m (0.1 mil) for general usage to 13  $\mu$ m (0.5 mil) for severe chemical corrosion. A chromate chemical conversion finish of the aluminum coating (MIL-C-5541, Ref. 18) provides a corrosion-preventive film when left unpainted; it also provides improved adhesion of paint finish systems to the coating. An anodizing treatment (MIL-A-8625, Ref. 19) improves corrosion protection under severe conditions, or it provides a base for paint finish systems. See Table 3-2 for a list of surface treatments and finishes for aluminum.

Inorganically bonded aluminum coatings can also be formed by electrophoresis (MIL-C-81797, Ref. 57). An inorganically bonded aluminum coating from two or more deposition applications and curing is used to prevent heat scaling, oxidation, and saltwater corrosion and to protect from other corrosive environments. A coating cured at 343° ± 14° C (650° ± 25° F) (Class 1) provides oxidation corrosion protection up to 649° C (1200° F) and marine atmosphere corrosion protection where the parts are operated at elevated temperatures that convert the coating to Class 2. Class 2 coatings are created by curing at temperatures from 510° to 593° C (950° to 1100° F) for specified times. This coating provides oxidation corrosion protection, galvanic corrosion protection, and marine atmosphere corrosion protection of ferrous alloys, titanium, titanium alloys, and other metallic substrates. The coating also has current-carrying capacity for static charges.

Aluminum diffusion coatings can be applied by pack cementation of aluminum powder.

Relatively thick aluminum cladding does not exhibit the porosity of thin coatings. High-strength aluminum alloys, which are subject to intergranular attack, are commonly clad with pure aluminum to obtain its inherently good corrosion resistance. However, corrosion attack can occur where the high-strength alloy is exposed, such as sheet edges and drilled holes.

Wire-sprayed aluminum coatings are widely used to protect exposed steel surfaces of naval vessels.

### 3-7.1.2 Cadmium Coatings

Cadmium is not as strongly anodic to iron as is zinc, but cadmium coatings retain a bright metallic appearance longer than zinc coatings. They are also superior to zinc coatings on articles exposed to conditions of high humidity and high temperature, even though cadmium is less protective than zinc in industrial atmospheres. Cadmium is relatively easy to solder. It resists attack by strong alkalis, whereas zinc is attacked. Cadmium is more expensive than zinc. Because cadmium salts are toxic, cadmium-plated items should not be used in contact with food or in any applications in which cadmium may be ingested. Most cadmium coatings are produced by electrodeposition. Care should be exercised when welding cadmium-coated parts because toxic gas can be generated.

Cadmium coatings, whether electrodeposited (QQ-P-416, Ref. 58) or vapor deposited (MIL-C-8837, Ref. 51), are intended for use as corrosion-protective coatings on ferrous parts. Cadmium deposition by electrodeposition is not recommended for steel heat treated to an ultimate strength greater than 1655 MPa (240,000 psi) because of the possibility of hydrogen embrittlement. Vapor-deposited cadmium coatings rather than electrodeposited coatings are recommended on high-strength steels. Chromate finishes on cadmium coatings retard or prevent the formation of white corrosion products on surfaces exposed to stagnant water, high-humidity atmospheres, saltwater, marine atmospheres, or cyclic condensation and drying. Some types of chromate coatings are satisfactory as a base for paints. Although temperatures greater than 75° C (167° F) destroy the effectiveness of chromate films, paint coatings on the chromate films protect the film from heat damage. Phosphate finishes, however, form a better paint base.

Cadmium plating and coating shall not be used (MIL-S-5002, Ref. 50)

1. On parts of hydraulic equipment that may be in contact with hydraulic fluids and fuels
2. On parts in frictional contact if gouging or binding may be a detrimental factor
3. In confined spaces containing organic materials that give off corrosive and damaging vapors
4. On titanium or in contact with titanium or on high-tensile-strength steels (above 1655 MPA (240,000

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psi)) if high levels of sustained stress are imposed

5. On parts that will be subsequently soldered
6. On parts whose service temperatures exceed 232°C (450°F).

### 3-7.1.3 Chromium Coatings

Class 1 (corrosion-protective) electrodeposited chromium plating (QQ-C-320, Ref. 59) is applied as a decorative finish, usually over nickel or over copper and nickel. It is also used as a finish for base metals, such as iron, steel, copper and copper-base alloys, and zinc and zinc-base die castings, to protect the base metal from corrosion and wear and to provide a pleasing appearance. The function of the underlayers of nickel is to provide a pore-free, continuous underplate for the chromium outer layer. Generally, the thicker the underlying nickel layer, the better the corrosion resistance.

Class 2 (engineering) chromium plating—also known as industrial chromium or hard chromium—is used to provide wear resistance, abrasion resistance, and such incidental corrosion protection of parts as the plating may afford.

Engineering chromium plating is usually applied directly to the base metal and is finished by grinding to the specified dimension. Heavy deposits of Class 2 plating may be used to build up worn or undersized parts, to provide protection against corrosive chemical environments, or for salvage purposes.

Porous electrodeposited chromium plating (MIL-C-20218, Ref. 60) is applied to the cylinder bores of internal combustion engines to provide wear resistance and to aid in retention of the lubricant film.

Black chromium plate (MIL-C-14538, Ref. 61) is hard, adherent, heat resistant, and free of light reflection. Therefore, it is suitable for military applications in which a nonreflecting black coating is desirable. This coating provides limited corrosion protection, but added protection can be obtained by specifying a corrosion-resistant underplate, such as nickel.

The chromizing process deposits a chromium-rich surface layer on iron or steel by diffusion. The deposit provides a heat-, abrasion-, and wear-resistant surface. Parts to be treated are packed in a powder containing 55 parts of chromium powder and 45 parts of alumina by weight. The parts in powder are then heated in a vacuum, an inert gas, or a hydrogen atmosphere to 1300°-1400°C (2370°-2550°F) for 3 to 4 h. The depth of penetration by diffusion is a function of time and temperature.

A gaseous method of chromizing produces a layer that may contain 50% chromium on the surface of a low-carbon steel. At temperatures of 1000°-1050°C (1830°-1920°F) chromium halide decomposes on the steel surface and diffuses into the base metal. (Chromium halide is formed by reaction of an ammonium halide with powdered chromium or ferrochrome.)

### 3-7.1.4 Copper Coatings

Copper coatings are not widely used directly for corrosion protection. The various classes of electrodeposited copper plating (MIL-C-14550, Ref. 62) are intended to perform the following functions:

1. *Class 0.* 25.4 to 127.0  $\mu\text{m}$  (1.0-5.0 mil) for heat treatment stop-off shield
2. *Class 1.* 25.4  $\mu\text{m}$  (1.0 mil) for carburizing shield, decarburizing shield, and printed circuit board plated through holes or as specified. It is also used as a nitriding shield.
3. *Class 2.* 13.0  $\mu\text{m}$  (0.5 mil) as undercoating for nickel and other metals
4. *Class 3.* 5.1  $\mu\text{m}$  (0.2 mil) and *Class 4.* 2.5  $\mu\text{m}$  (0.1 mil) to prevent base metal migration into tin layer to poison solderability.

Bright alloy is used as a plating over copper and copper alloys as base materials. Bright alloy is 50 to 60% copper, 25 to 30% tin, and 14 to 20% zinc. Bright alloy electroplate is to be used if corrosion protection or solderability is required on metal parts. It is particularly applicable to parts with irregular surfaces or cavities because of its high throwing power. The base metal is given a copper flash, and following the copper flash, an undercoat of nickel, silver, or other suitable deposit may precede the final bright alloy plate.

### 3-7.1.5 Lead Coatings

Lead coatings are formed on steel either by hot dipping or by electrodeposition. Molten lead will not form a coating on steel unless a few percent of tin are incorporated (Ref. 2). Steel coated with lead containing 15% to 25% tin is calledterneplate. Lead or lead-tin coatings are resistant to atmospheric corrosion because the pores tend to fill with rust and thereby stifle further corrosion. Terneplate is used for roofing and in drums and cans used to store paint and hydrocarbon fuels.

Electrodeposited lead coatings (MIL-L-13808, Ref. 63) are used to prevent corrosion, to prevent galling of metal parts, to improve the performance of bearings, and to facilitate soldering. Lead may be plated directly on copper, brass, or copper-rich alloy surfaces. For steel surfaces, however, a preliminary copper coating should be used to obtain adequate adhesion and corrosion resistance.

Electrodeposited lead-tin alloy coatings (MIL-L-46064, Ref. 64) are used for bearing purposes. Hot-dipped lead-tin alloy coatings are intended for corrosion protection and soldering (MIL-L-13762, Ref. 65). Addition of tin to lead improves the bond of the lead coating to steel. It also improves wear and abrasion resistance without materially reducing corrosion resistance. Type I hot-dipped lead-tin alloy coating contains a minimum of 5.0% tin, Type II contains 6.5 to 8.5% tin, and Type III contains a minimum of 30% tin.

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### 3-7.1.6 Nickel Coatings

"Chromium plating", which is widely used on automobiles and other consumer items, is a bright nickel deposit covered with a thinner chromium coating. The nickel protects the steel or brass against corrosion while the chromium protects the nickel from fogging. (Fogging is the formation of a corrosion film that dulls the luster of the nickel.)

The nickel is sometimes plated over an intermediate, thin coating of copper. This copper coating facilitates buffing of the surface on which the nickel is plated, reduces the thickness of nickel required to obtain a coating of minimum porosity, and improves the bond between the nickel and steel. Nickel is noble to iron; therefore, the absence of porosity in the coating is important in providing corrosion protection. To achieve adequate life and appearance, a certain minimum coating thickness is necessary, which depends upon exposure conditions. The range of coating thickness for most environmental exposures is 19 to 38  $\mu\text{m}$  (0.75 to 1.5 mil).

Federal specification QQ-N-290 (Ref. 66) covers electro-deposited nickel plating on steel, copper and copper alloys, and zinc and zinc alloys. If a copper underplate is used, the thickness of the underplate does not substitute for any part of the specified nickel thickness. Class 1 (corrosion-protective) plating is used to protect iron, copper, or zinc alloys against corrosion attack in rural, industrial, or marine atmospheres, or it is used as an undercoat for chromium or one of the precious metals. Class 1 plating is also used for decorative purposes. Class 2 (engineering) plating is used to obtain wear resistance, abrasion resistance, and such incidental corrosion protection of parts as the specified thickness of the nickel plating may afford. Heavy deposits of Class 2 plating may be used to build up worn or undersized parts, to protect against corrosive chemical environments, and for salvage purposes.

Black nickel plating (MIL-P-18317, Ref. 67) is intended primarily for use on brass, bronze, or steel instrument parts to produce black, nonreflective surfaces. Black nickel plating, however, has little protective value.

With a double-layer nickel deposition as the undercoat and with other metals as electrodeposited topcoats, the nickel immediately beneath the topcoat is bright nickel that contains sulfur. The bottom layer is semibright nickel and is essentially free of sulfur. The bright nickel is anodic to the semibright nickel. If corrosion locally penetrates the outer coat, the galvanic action between the two kinds of nickel plating causes the microscopic pit to spread laterally in the outer nickel layer. This action prevents the corrosion pit from burrowing deeper into the inner layer of nickel.

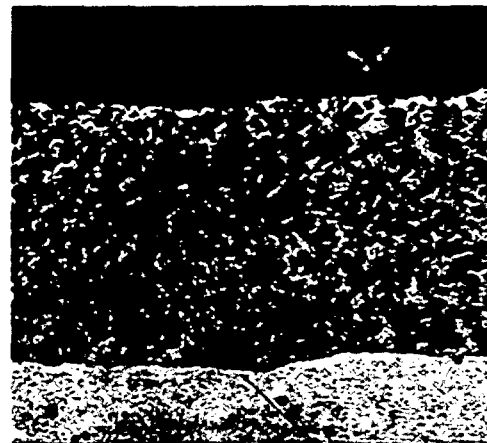
Nickel can also be deposited on a surface from a chemical solution. These deposits are called electroless nickel coatings. Articles immersed in a bath containing a

nickel salt and sodium hypophosphite become coated with a nickel-phosphorous alloy. The phosphorous content in a coating of this kind is 7 to 9%. Various metal surfaces including nickel act as catalysts for the reaction; therefore, relatively thick layers can be deposited. The coating will not deposit on lead, tin, or solder.

According to MIL-C-26074 (Ref. 68), electroless nickel coatings are intended to be used when hard and smooth surfaces are required on coated parts. These coatings produce excellent uniform deposits on irregular parts. Coated parts, such as those used in air compressors, missile fuel injector plates, pumps, reciprocating surfaces, etc., are protected from oxidation, corrosion, and wear. With aluminum electronic devices, not only does the coating prevent product contamination, but it also facilitates soldering. These coatings on stainless steel similarly facilitate brazing. Electroless nickel coatings are used on iron, copper, aluminum, nickel, cobalt, beryllium, and titanium-base alloys. However, if the electroless nickel coating is porous or if it develops cracks or is damaged, severe galvanic corrosion of an anodic underlying metal, such as aluminum, can take place.

Electroless nickel coating processes have been developed that codeposit micron-sized particles with the nickel coating. Coatings enhanced with silicon carbide particles have improved wear resistance, but the corrosion resistance is a result of the nickel coating. Fig. 3-26 illustrates the microstructure of the composite coating. Other inorganic and organic particles can also be codeposited with electroless nickel.

Nickel deposits may be formed on steel surfaces by displacement nickel plating. The steel article is immersed in a bath of nickel sulfate or nickel chloride having a pH



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**Figure 3-26. Photomicrograph of Composite  
Coating (Ref. 69)**



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of 3 to 4 and a temperature of 70°C (160°F). Because iron has a higher solution potential, it is displaced at the surface by nickel and the iron passes into solution. The reaction continues only as long as iron is exposed at the surface. Even though the coating thickness that may be formed is limited, the thin coatings of less than 1.25  $\mu\text{m}$  (0.05 mil) thick improve the adhesion of enamel to steel.

### 3-7.1.7 Tin Coatings

The principal user of tin coatings is the food and beverage canning industry. Tin coatings can be applied by dipping, but most are electroplated. Tin coatings are commonly produced by electroplating steel strip in a continuous process. The dull matte appearance of electroplated tin is converted to the bright appearance of hot-dipped tin by momentarily melting the coating immediately after plating. This also improves the solderability. Following this momentary melting, electroplated tin is usually given a passivating treatment. A protective film forms that prevents discoloration of the surface and improves the adhesion of lacquer coats.

In fruit juice, which is probably the most corrosive substance preserved in cans, iron is generally cathodic to tin. Therefore, intense attack at exposed steel does not occur. Hydrogen generated at the cathode, however, may distend the can. In addition to preventing corrosion, the tin coating permits the can to be readily produced by soldering. The interior surfaces of food cans are also coated with lacquer, which aids in preventing corrosion and the generation of hydrogen.

Electrodeposited and hot-dipped tin coatings (MIL-T-10727, Ref. 70) in various thicknesses are used in the following applications:

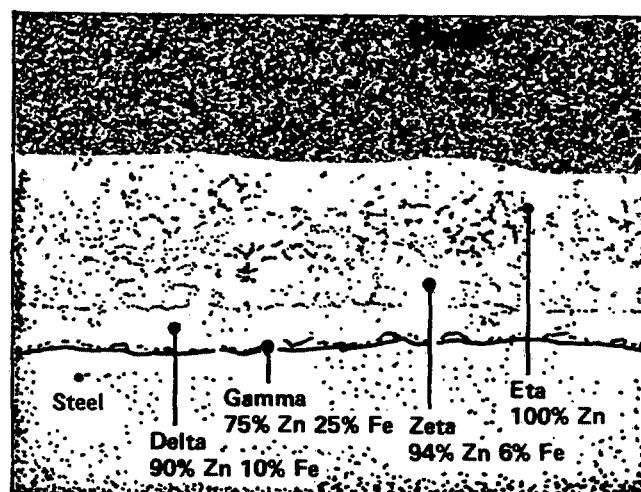
1. 2.5 to 6.4  $\mu\text{m}$  (0.1 to 0.25 mil) for "tin flashing" of articles to be soldered
2. 5.1 to 10  $\mu\text{m}$  (0.2 to 0.4 mil) for articles plated to prevent galling or seizing
3. 7.6  $\mu\text{m}$  (0.3 mil) minimum for articles plated to prevent corrosion of base metals
4. 5.1 to 15  $\mu\text{m}$  (0.2 to 0.6 mil) for articles plated to prevent formation of case during hardening. In case hardening, a metal article is located so that the surface layer is harder than the interior. Tin is applied to those areas of the metal surface that are not to be hardened.

### 3-7.1.8 Zinc Coatings

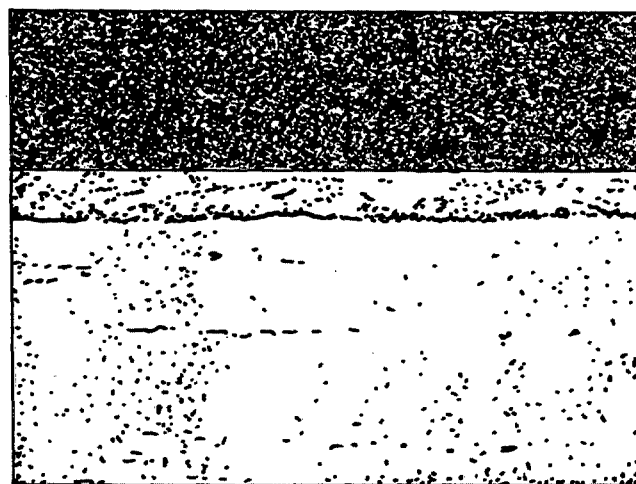
The most commonly used sacrificial metallic coating is zinc. In the hot-dip galvanizing process, a layer of zinc is applied by dipping a ferrous article, which has been cleaned and pickled, into molten zinc. The molten zinc reacts with the base metal, and a series of zinc-iron alloy layers is formed. The top layer is normally of solidified zinc. For most hot-rolled steels the zinc-iron alloy portion of the coating represents 50 to 70% of the total coating thickness. Fig. 3-27A is a photomicrograph of a section

through a typical hot-dip galvanizing coating showing the alloy layers. The zinc-iron alloy zone is also protective. Fig. 3-27B indicates the uniform coating that may be obtained by adding aluminum to the galvanizing bath. Greater than 0.15% aluminum in the galvanizing bath suppresses the development of the zinc-iron alloy. A much lighter coating is achieved, but the product has superior formability characteristics.

Hot-dip galvanizing has long been used to protect steel sheet, wire, pipes, tanks, castings, and other items (ASTM



(A) Photomicrograph of a Section Through a Typical Hot-Dip Galvanizing Coating Showing Alloy Layers  
(250X Magnification)



(B) Photomicrograph of Continuous Galvanized Coating Cross Section. Aluminum Addition Minimizes Alloy Layers, Provides Uniform Coating.  
(250X Magnification)

Figure 3-27. Photomicrographs of Galvanized Coating (Ref. 72)

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A153 for hardware, Ref. 71). Zinc is anodic to steel; therefore, it provides protection at scratches and other places where steel is exposed. Because zinc is destroyed while providing protection, the protection conferred by zinc coatings is a function of its thickness.

Mechanical plating deposits a uniform thickness of zinc on a metallic surface, even in threaded areas. Parts plated by this process do not encounter hydrogen embrittlement, which is a potential problem in electroplating. Small parts are plated by tumbling with glass beads, zinc powder, and a catalyst. The zinc deposit is "cold-welded" to the surface by the peening action of the glass beads.

Zinc may also be deposited by the ion vapor deposition process. Thermosprayed zinc coatings are applied as molten metal. Spray guns may be fed powdered zinc or zinc wire, and the heat may be supplied by gas combustion or electricity. The sprayed zinc coating is slightly rough and slightly porous.

Electrodeposited coatings of zinc (ASTM B 633, Ref. 40) are used as protective coatings on ferrous parts, as are the hot-dip, mechanical plating, and sprayed coatings. Chromate treatment of zinc coatings (Type II treatment) retards or prevents formation of white corrosion products on surfaces exposed to stagnant water, high-humidity atmospheres, saltwater, or marine atmospheres or to cyclic condensation and drying. The surface of zinc plate is converted by supplementary chromate treatment, which diminishes the amount of metallic zinc present. Therefore,

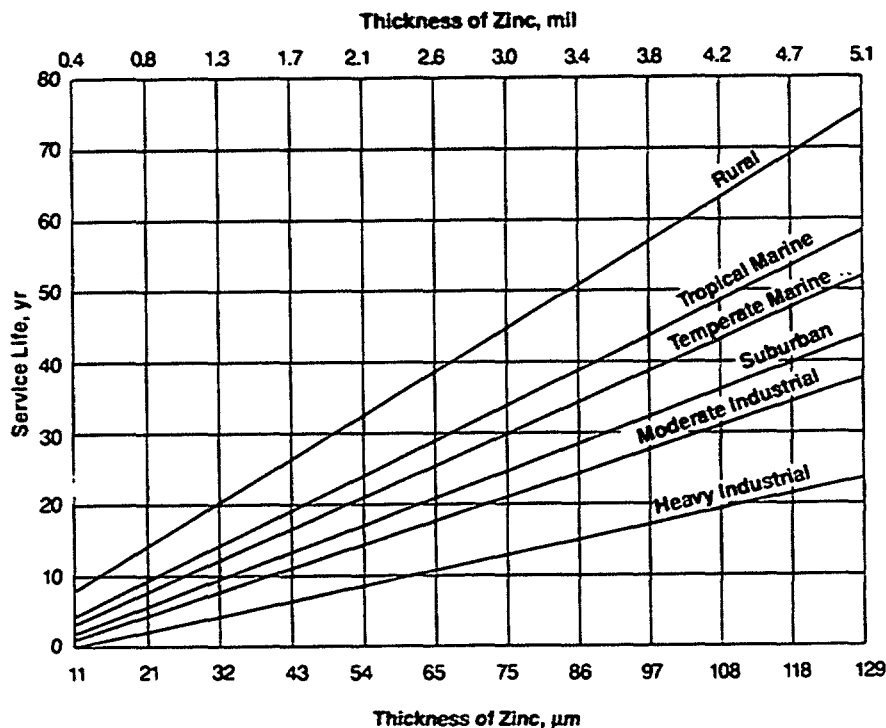
additional thickness of zinc plating must be applied to insure that sufficient zinc plate thickness remains after the chromate treatment. The primary purpose of phosphate finishes (Type III treatment) is to form a good paint base. See par. 3-6.1.5 for discussion of zinc surface treatments. Fig. 3-28 indicates the expected service life of various thicknesses of zinc coatings in different exposure environments.

Zinc plating and coating shall not be used (MIL-S-5002, Ref. 50)

1. On parts for aerospace and missile systems
2. On parts in contact with structured fabric surfaces
3. On parts in contact where corrosion products might interfere with normal functioning
4. On grounding contacts for which the increased electrical resistance of zinc-plated surfaces would be objectionable
5. On parts whose service temperatures will exceed 260°C (500°F).

### 3-7.1.9 Noble Metal Coatings

The outstanding chemical resistance of the noble metals (gold, silver, palladium, and rhodium) would appear to make them desirable as corrosion-resistant coatings. However, the noble metals are strongly cathodic to iron. Therefore, at any discontinuity in the coating, intensified attack of the anodic iron would occur. Thick coatings of the noble metals, which are free from dis-



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Figure 3-28. Expected Service Life of Zinc Coatings (Ref. 73)

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continuities, can be obtained by mechanical means if the high cost can be justified.

Electrodeposited gold plating (MIL-G-45204, Ref. 74) is intended for electrical application, good corrosion resistance, and good solderability. In the plating process a strike of copper, nickel, copper-plus-nickel, or copper-plus-silver may be used; the choice depends on the application and the environment. A nickel strike is preferred, however, because copper and silver may migrate through the gold. A "strike" is an application of any plated material  $0.25\ \mu\text{m}$  ( $10\ \mu\text{in.}$ ) or less in thickness. An "underplate" is a deposit of greater thickness than a strike, and it will impart some characteristic to the finished plated surface that the overplate would not otherwise impart.

Electrodeposited silver plating of various thickness (QQ-S-365, Ref. 75) is used in the following applications:

1.  $8\ \mu\text{m}$  (0.3 mil) for articles, such as terminals, that are to be soldered
2.  $13\ \mu\text{m}$  (0.5 mil) for corrosion protection of nonferrous base metal
3.  $13\text{-}25\ \mu\text{m}$  (0.5-1.0 mil) for electrical contacts, but the choice depends on pressure, friction, and electrical load.
4.  $13\ \mu\text{m}$  (0.5 mil) for increasing the electrical conductivity of base metals.

For applications in which corrosion protection is important, use of an electrodeposited nickel undercoat is advantageous. For example, copper forms a eutectic with silver. Therefore, silver plating on a copper underlayment or copper base metal should not be used for continuous service at a temperature greater than  $149^\circ\text{C}$  ( $300^\circ\text{F}$ ). At that temperature and above, the eutectic is formed by diffusion at the copper-silver interface. Silver plating with a tarnish-resistant coating produced using chromate treatments (Grade A) has a low contact resistance of approximately  $0.5$  to  $0.6$  microhms/ $\text{mm}^2$  ( $300$  to  $400$  microhms/ $\text{in.}^2$ ). These chromate-produced silver-plated items are readily soldered with rosin-cored solder.

Electrodeposited palladium plating (MIL-P-45209, Ref. 76) is used for electrical applications requiring freedom from oxidation and to prevent tarnishing of silver items. Electrodeposited rhodium plating (MIL-R-46085, Ref. 77) protects articles from corrosion, prevents galling of electrical contacts, furnishes a highly decorative finish, and provides a mirror surface that is highly reflective and nontarnishing.

### 3-7.2 INORGANIC COATINGS

#### 3-7.2.1 Glassy Coatings

Vitreous enamels, glass linings, and porcelain are all glassy, i.e., noncrystalline, coatings fused onto metals. Such glassy coatings are used mostly on steel and cast irons, but they may also be applied successfully to copper, brass, and aluminum (Ref. 2). Powdered glass of the

desired composition, often suspended in water or some volatile liquid, is applied to the pickled metal surface. After being dried in warm air the metal is heated to a temperature high enough to fuse the glass; this fusion creates a coherent coating over the surface.

The glassy coatings must possess suitable coefficients of expansion, must adhere tightly to the metal, and must resist the corrosive and erosive conditions of the service environment. In practice, several coats are applied. The initial coat is chosen for adhesion, and the other coats are chosen for corrosion and erosion resistance. The domestic glass-lined water heater is an example of this type of coating.

The composition of the coating for general purposes is a borosilicate glass containing fluoride and often lead. It is generally made from borax, feldspar, quartz, and cryolite. The amount of silica is increased and titania is introduced for acid resistance. The initial coat usually contains compounds of cobalt or nickel to improve adhesion to iron. Because the coefficient of expansion of acid-proof enamels is considerably lower than that of iron, enamels with a high coefficient of expansion are chosen for the initial coat. Additional successive coats to increase acid resistance and decrease the coefficient of expansion are then applied.

#### 3-7.2.2 Metallic-Ceramic Coatings

Inorganic metallic-ceramic coatings, i.e., of metal plus inorganic compounds, ceramic oxides, or glass frits (MIL-C-81751, Ref. 56), may be applied to provide oxidation and corrosion resistance to base metals under various conditions. SermeTel<sup>®</sup> W and SermaLoy<sup>®</sup> J are proprietary examples of this class of coatings. Table 3-10 shows the composition of three formulations of coating material. The ingredients for a Type I coating form an acidic, aqueous slurry containing aluminum powder and a homogeneous solution of binder solids. The ingredients for a Type II coating form an aqueous slurry of metal powders and ceramic binder solids. The ingredients for a Type III coating make up a dry blend of sprayable metal and ceramic powder. The material is applied and cured at the temperatures indicated in Table 3-11.

The Type I metallic-ceramic coating, accomplished by two or more spraying applications and curing, is intended to prevent heat scaling, oxidation, and saltwater corrosion and to protect against corrosion due to other corrosive environments. The coating material may be applied to jet engine parts, but there may be an unfavorable effect upon the fatigue strength of base materials beginning at about  $538^\circ\text{C}$  ( $1000^\circ\text{F}$ ). This effect is due to diffusion of the Type I coating into the base metals. Type II and Type III coatings are intended for general prevention of oxidation and corrosion of base metals in marine, aboveground, and underground applications. The Type II coating may be used with any base metal capable of withstanding the

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**TABLE 3-10. METALLIC-CERAMIC COATINGS  
(COMPOSITION: PERCENT BY WEIGHT) (Ref. 56)**

| MATERIAL                      | TYPE I   | TYPE II  | TYPE III |
|-------------------------------|----------|----------|----------|
| Solvent contents (water)      | 38 to 44 | 30 to 40 | —        |
| Nonvolatile contents (solids) | 56 to 62 | 60 to 70 | 100      |
| Nonvolatile contents          |          |          |          |
| Metal or pigment contents     | 60 to 64 | 30 to 60 | 40 to 60 |
| Binder contents               | 36 to 40 | 40 to 70 | 40 to 60 |

**TABLE 3-11. CLASSIFICATION OF METALLIC-CERAMIC COATINGS (Ref. 56)**

|                    |   |
|--------------------|---|
| Type I, Class 1:   | Coating cured at $343^{\circ} \pm 14^{\circ} \text{C}$ ( $650^{\circ} \pm 25^{\circ} \text{F}$ )  |
| Class 2:           | Coating cured at $343^{\circ} \pm 14^{\circ} \text{C}$ ( $650^{\circ} \pm 25^{\circ} \text{F}$ ) and posttreated at elevated temperature  |
| Class 3:           | Initial coat(s) cured at $343^{\circ} \pm 14^{\circ} \text{C}$ ( $650^{\circ} \pm 25^{\circ} \text{F}$ ) and burnished prior to applying topcoat, which is cured at $343^{\circ} \pm 14^{\circ} \text{C}$ ( $650^{\circ} \pm 25^{\circ} \text{F}$ ) |
| Class 4:           | Coating cured at $343^{\circ} \pm 14^{\circ} \text{C}$ ( $650^{\circ} \pm 25^{\circ} \text{F}$ ) and posttreated by burnishing  |
| Type II, Class 1:  | Coating fused at $807^{\circ} \pm 19^{\circ} \text{C}$ ( $1485^{\circ} \pm 35^{\circ} \text{F}$ )   |
| Class 2:           | Coating fused at $807^{\circ} \pm 19^{\circ} \text{C}$ ( $1485^{\circ} \pm 35^{\circ} \text{F}$ ) and posttreated by burnishing   |
| Type III, Class 1: | Coating deposited by thermal spraying   |
| Class 2:           | Coating deposited by thermal spraying and posttreated by burnishing   |

elevated fusion temperatures of  $788^{\circ}$  to  $827^{\circ} \text{C}$  ( $1450^{\circ}$  to  $1520^{\circ} \text{F}$ ). As with Type I coating, there may be an unfavorable effect upon the physical properties of the base metals due to diffusion of the coating materials. The Type III coating should be used primarily on base metals not capable of withstanding processing temperatures above  $177^{\circ} \text{C}$  ( $350^{\circ} \text{F}$ ), with metal parts that may be prone to distortion at temperatures above  $177^{\circ} \text{C}$  ( $350^{\circ} \text{F}$ ), or for parts that are too large for the furnace capacity of a Type II application. The Type III coating is compatible in terms of corrosion with the Type II coating and may be used to protect the weldments of parts welded after having been coated with Type II material.

Important metallic-ceramic coatings are those applied to gas turbine blades and vanes. Development of superalloys has at times emphasized high-temperature mechanical properties and castability at the expense of oxidation and hot corrosion caused by sulfate-chloride deposition. As a result, high-temperature coatings are relied upon to provide corrosion resistance for nickel-base and cobalt-base superalloys. The protective mechanism for all coatings intended for use above  $871^{\circ} \text{C}$  ( $1600^{\circ} \text{F}$ ) is the formation by oxidation of aluminum oxide (alumina) scales. This is achieved by raising the aluminum and/or chromium concentrations on the surface of the alloy.

Surface coatings used in gas turbine hot components are either diffusion type or overlay type. Diffusion aluminide coatings are formed by slurry-fusion or pack-cementation processes in which aluminum is diffused into

the base alloy. Good oxidation results from the protective alumina scales that result from the very high aluminum content of the inward diffusing aluminide coatings. Hot corrosion resistance, however, is limited because these coatings have insufficient chromium concentrations.

Platinum-modified diffusion aluminide coatings have enhanced oxidation and corrosion resistance compared to simple aluminide coatings (Ref. 78). Platinum overlays on MCrAlY (M is Co or Ni or both) coatings have been found to be very effective in inhibiting the hot corrosion attack caused by sulfate-chloride deposition (Ref. 79).

Compared to diffusion aluminides, overlay protective coatings for gas turbine airfoil surfaces provide significant improvements in hot corrosion resistance and in oxidation resistance. Chromium levels may be high (18-25%) at moderate aluminum concentrations (10-15%). Rare earth elements such as yttrium are added to improve alumina scale adhesion. A number of fabrication methods may be used to produce this type of MCrAlY overlay coating, including electron beam physical vapor deposition and plasma spraying.

The electron beam physical vapor deposition process is conducted in a vacuum. The material to be deposited is contained in a crucible, and an electron beam is directed onto the surface. The material is heated, melted, and evaporated to produce a vapor of the coating metals. The parts to be coated are positioned above the material in the crucible and are rotated during coating to achieve complete coverage because the vapor travels in a line of sight.

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Plasma spraying is conducted in an inert atmosphere. A high-velocity plasma stream (Mach 2-3) is created into which the coating particles are injected. The stream of molten particles impinges upon the specimen to be coated. Tests of NiCoCrAlY-base coating systems used to protect a single crystal nickel-base superalloy and of CoCrAlY-base coating systems used to protect a conventionally cast B 1900 + Hf alloy indicated that plasma spraying produces a more protective coating than electron beam physical vapor deposition (Ref. 80). A plasma spraying system using a low-pressure chamber produced a more protective coating than an argon atmospheric pressure plasma spraying system.

Some of the components of a gas turbine engine require air cooling to keep the metal temperature sufficiently low to provide an adequate service life span. Ceramic thermal barrier coatings were devised to provide thermal insulation for the metal component. Thermal insulation allows the component to run cooler (and thereby last longer) or to maintain the same temperature but at reduced cooling airflows. Reducing the cooling airflow results in a more efficient gas turbine engine.

Ceramic thermal barrier coatings rely on a certain degree of porosity to achieve resistance to thermal transients and to thermal expansion differences between the coating and the substrate alloy. Therefore, porous ceramic thermal barrier coatings alone cannot provide protection to the base metal. An underlay coating of the MCrAlY type is provided between the substrate alloy and the ceramic thermal barrier. Oxidation resistance and corrosion resistance are provided by this thin, relatively ductile MCrAlY metal applied to the substrate alloy. A thicker ceramic coating is applied by plasma spraying on top of the underlay coating. The primary function of the ceramic coating is to provide thermal insulation. Plasma-sprayed zirconia on an MCrAlY bond coating remains the best ceramic coating candidate (Ref. 81). Coarse-grained zirconia with 8 weight % yttria has undergone the most extensive development. Other ceramic thermal barrier coatings that have received attention include  $\text{CaO}\cdot\text{TiO}_2$ ,  $2 \text{CaO}\cdot\text{SiO}_2$ , and  $\text{MgO}\cdot\text{Al}_2\text{O}_3$ . Complex graded and multilayered structures have also been studied, but when they are optimized to operating conditions, the duplex coatings are superior (Ref. 82).

Although contemporary thermal barrier coatings can operate adequately in clean oxidizing environments, their adequacy in contaminated combustion products (Na, V, S) is at best marginal. The porosity required to give ceramic coatings thermal stress resistance makes them subject to failure by corrosive combustion products. Sodium sulfate is particularly detrimental. Failure is attributed to internal mechanical stresses that occur during thermal cycling.

Dense overcoats that retard penetration of contaminants to the interiors of coatings can significantly increase

the life spans of porous ceramic coatings. The best overcoats for plasma-sprayed, coarse particle, zirconia-base coats are (1) plasma-sprayed, fine-particle zirconia and (2) plasma-sprayed, fine-particle zirconia containing 20-25% of certain glasses (Ref. 81). The thermal cycling life spans of ceramic thermal barrier coatings can be improved by incorporating a metal wire screen between the ceramic and the metal bond coatings. The screen functions as a mechanical lock for the ceramic and retards crack propagation.

The corrosiveness of contaminated combustion products may be related to the formation of condensates at the bond coat-ceramic coat interface. The durability of a 0.13-mm (5-mil) thermal barrier coating is better than that of a 0.38-mm (15-mil) coating (Ref. 83). If the temperatures within the ceramic coating or at the bond coat-ceramic coat interface are higher than the dew points of the condensates ( $904^\circ\text{C}$  ( $1659^\circ\text{F}$ ) for  $\text{Na}_2\text{SO}_4$ ,  $1210^\circ\text{C}$  ( $2210^\circ\text{F}$ ) for  $\text{V}_2\text{O}_5$ , and  $1155^\circ\text{C}$  ( $2111^\circ\text{F}$ ) for  $\text{Na}_2\text{V}_2\text{O}_6$ ), no condensate can form at the interface.

Tantalum and columbium (niobium) alloys are candidate materials for components of advanced gas turbine engines. These engines would have turbine inlet temperatures between  $1260^\circ$  and  $1650^\circ\text{C}$  ( $2300^\circ$  and  $3000^\circ\text{F}$ ). Tantalum and columbium alloys, however, require coatings to protect against high-temperature oxidation. Complex disilicide coatings can provide complete protection to a 90 tantalum-10 tungsten alloy against static oxidation at temperatures between  $927^\circ$  and  $1482^\circ\text{C}$  ( $1700^\circ$  and  $2700^\circ\text{F}$ ) for at least 200 h (Refs. 84 and 85). The protective layer consists mainly of silica, although there is some titanium, vanadium, and tungsten in solution and a second dispersed phase of titania. Disilicides, however, do not afford protection in the intermediate range of  $760^\circ$  to  $871^\circ\text{C}$  ( $1400^\circ$  to  $1600^\circ\text{F}$ ) because of a deterioration process, "pestring". If the protective coating is preoxidized at  $1149^\circ\text{C}$  ( $2100^\circ\text{F}$ ), a glassy protective layer is formed. To accomplish preoxidation at this temperature and to avoid pestring, the rate of temperature rise through the pestring range must exceed  $10 \text{ deg C}$  ( $18 \text{ deg F}$ ) per min.

### 3-7.2.3 Portland Cement Coatings

Portland cement coatings are inexpensive, they have a coefficient of expansion approximating that of steel, and they are easy to apply (Ref. 2). Cement layers can be cast in contact with metal. Coatings may be applied by centrifugal casting (to the interior of piping), by troweling, and by spraying. Portland cement coatings are sensitive to damage by mechanical or thermal shock.

These coatings are used to protect iron and steel water pipes on either or both sides, hot- or cold-water tanks, and chemical storage tanks. They also protect against seawater and wastewaters.

**MIL-HDBK-735(MR)****3-7.3 ORGANIC COATINGS**

The formulas of organic coatings include naturally occurring and synthetic organic materials, such as solvents and film-forming materials. In a manner analogous to inorganic and metal coatings, organic coatings act as a barrier between a metal surface and the environment to prevent or retard corrosion. Organic coatings are generally applied as a liquid and form a film upon "drying". Some materials, however, are applied as a powder that fuses to a hot surface. These dry powder films can be highly moisture resistant.

Usually organic coatings are composed of both volatile and nonvolatile components. Volatile components act as a thinning agent and consist of solvents and diluents, whereas nonvolatile components are the film-forming materials. These components may be resins, oils, or waxes and may incorporate both pigments and plasticizers. The degree of protection offered by an organic coating depends upon

1. The extent and uniformity of coverage
2. The degree of impermeability to the environment
3. The degree of adhesion to the substrate
4. The coherence of the protective film
5. The resistance to mechanical wear and damage
6. The chemical inertness to the environment.

Pigments are solid particles in a paint, which consist of fine powders of various compositions and colors. The types and amounts of each pigment in a paint affect the properties of the paint. A function of the pigments is either to retard moisture penetration of the film or to reduce the corrosiveness of penetrating moisture. Pigments protect the paint binder (the film-forming components) from weathering and abrasion, they provide color and create hiding power, they provide mechanical strength, they add body for ease of application, and they influence the gloss of the finish. Plasticizers are added to some paint formulations to prevent the film from becoming brittle during application or service.

An organic coating is selected on the basis of the service conditions, the metal to be protected, the degree or duration of protection desired, and the cost. In general, the useful life of a coating depends on two major factors:

1. The durability of the organic coating itself
2. The adherence of the film to the surface to be protected.

These factors are influenced by the characteristics of the base metal, the type and formation of the finish, the surface preparation, and the nature of the service environment. Proper surface preparation is particularly important to insure a stable, nonreactive coating. The metal surface to be coated should be free of dirt, oil, grease, mill scale, and any corrosion products. Furthermore, the method chosen to prepare the metal should reduce the activity of the metal surface to prevent corrosion at the coating-metal interface.

Organic coatings offer certain advantages over metallic coatings in preventing corrosion. They are less expensive, more easily applied, can be readily applied to complex geometries, can be applied over metallic and chemical conversion coatings, can be produced in a wide range of colors and glosses, and can be formulated to have a wide range of physical characteristics. In addition, certain formulations can exhibit a degree of anodic protection. Most organic coatings, however, are less durable and are restricted to lower service temperatures than metallic coatings.

There are several ways to describe and classify organic coatings, i.e., according to what they contain, how they are applied, how they function, and what they accomplish. The general distinctions usually made among organic coatings include paint, enamel, varnish, lacquer, and corrosion- or rust-preventive compounds.

**3-7.3.1 Paint, Enamel, Varnish, and Lacquer**

Paint is a pigmented composition of liquid consistency, which, after application as a thin layer, is converted to a solid, adherent, and tough film. An oil-base paint contains drying oil or oil varnish as the basic film-forming vehicle, whereas a water-base paint contains a water emulsion or dispersion as the basic ingredient. An enamel is a paint that is characterized by an especially hard surface film. Varnish is a liquid composition, which, after application as a thin layer, is converted to a transparent or translucent solid film. Varnish is generally a clear liquid combining a drying oil and a fortifying resin that air dries by oxidation of the oil and polymerization of the resin. Lacquer is a film-forming liquid composition containing polymeric resins and plasticizers as the basic film-forming ingredients in a volatile solvent. Lacquers, which sometimes contain pigments, dry by evaporation of the solvent.

Paint and other organic coatings generally require more than one coat to attain a certain minimum thickness and to form a pore-free film. The thickness required depends upon the physical characteristics of the film and the particular environment in which it is used. In a paint system consisting of primer and topcoat, the primer is crucial to achieving a satisfactory corrosion-preventive coating. The primer is usually applied as a surface treatment achieved by chemical conversion or anodic treatment of the metal surface. The fact that specifications may call for two coats of corrosion-inhibiting primer covered by a single finishing topcoat emphasizes the importance of the primer.

A great many pigments are used in paints, but only a small number have corrosion-inhibiting properties. Typical pigments used in metal-priming paints include red lead, lead-silico chromate, zinc chromate, strontium chromate, and zinc dust. These pigments are particularly effective in inhibiting corrosion on steel, and they are effective on some other metals as well. Red lead and zinc

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chromate pigments in primers inhibit corrosion by passivating steel base metal. An overwhelming portion of metallic surfaces that are painted are steel (iron) or aluminum and magnesium and their alloys. Lead pigments, however, may accelerate corrosion on some aluminum, magnesium, or zinc alloys; therefore, zinc chromate and strontium chromate are commonly used as inhibiting pigments in priming coats for these alloys. Zinc chromate and basic lead chromate are commonly used as inhibiting pigments in priming coats on various metals. Zinc oxide, metallic zinc dust, and iron oxide are also used as inhibiting primers. Primers that are heavily loaded with zinc dust can provide a degree of anodic protection to the base metal. Iron oxide pigments act primarily as barriers in primers.

The topcoat complements the primer by forming a complete paint system. Topcoats perform different functions than a primer. They form the outer barrier film, and they furnish the color of the metal finish. The nature of this outer film is important in resisting contamination by toxic (nuclear, biological, and chemical (NBC)) warfare agents and in providing a surface that can be readily decontaminated. The color, gloss, and texture of the finish create the visual and infrared hiding power of camouflage. In other situations the topcoat provides markings for visual identification and warnings. Pigments such as titanium dioxide, molybdates, aluminum, graphite and other forms of carbon are used primarily in topcoats rather than in primers. Carbon pigments in primers can stimulate attack on steels and should be avoided. Aluminum powder is used because of its metallic color, and in the form of flat flakes aluminum powder forms a film upon drying in which the flat flakes overlap one another and create a continuous metallic barrier.

The vehicle is the liquid portion of a paint and includes anything that is in solution or in an emulsion, but it does not include solid material in suspension (the pigment). It may consist of one or more of the following materials: drying oils, driers, thinners, solvents, plasticizers, resins, catalysts, and other materials. The vehicle consists of a nonvolatile portion and a volatile portion. The nonvolatile portion forms the binder for the pigment and remains in the dry film, whereas the volatile portion, i.e., thinners and solvents, completely evaporates eventually.

When selecting a paint finish, it is important that all of the components of the paint be inert to the base material. Otherwise corrosion will result. For example, acid-catalyzed primers and topcoats should not be used on high-strength steel parts (Rockwell C48 and higher) (MIL-STD-171, Ref. 16) without approval of the procuring activity.

A wide variety of synthetic resins are currently used in paints. These include alkyd, phenolic, vinyl, silicone, epoxy, acrylic, styrenebutadiene, and polyurethane resins. Synthetic resins have individual characteristics that deter-

mine their advantages in specific applications, and they may cure, as a result of special catalysts in their formulation, with oxygen in the air, with water vapor, or by the application of heat.

Environmental and occupational safety concerns have influenced the direction of development of corrosion-resistant paints. The goal of environmental regulations is to limit the use of toxic pigments and inhibitors such as lead and chromates and to limit the hydrocarbon solvent and hazardous vapor emissions of air-drying paints. Responding to these concerns has stimulated development of paint coatings that are equal to or better than the products they have replaced (Ref. 86).

Paint coatings may be applied by any method that achieves satisfactory results, i.e., a smooth, uniform, continuous film free from dried overspray, runs, sags, blisters, orange peel, or other imperfections. Brushes are useful for small areas and areas that cannot conveniently be reached by other means or for building up additional thickness on specific areas, such as bolts, rivet heads, or sharp edges. Paint rollers are useful for large areas and rough or perforated surfaces. Spraying systems can produce high-quality coatings at rapid rates. Air sprayers use compressed air to atomize and propel paint droplets onto a surface, and airless sprayers eject the coating under high pressure so that it is atomized into droplets and propelled against the surface to be coated. Airless sprayers produce less overspray than air sprayers and can produce thicker coats in one pass.

In electrostatic spraying systems the surface to be coated is given the opposite electrical polarity of the atomizing gun. In this system objects tend to be coated both front and back with little overspray.

Electrodeposited coatings are applied in large volume to complex objects. In electrodeposited coating processes finely divided particles of the coating are suspended in a water bath into which the object to be coated is immersed. The walls of the coating tank are made electrically negative, and the object to be coated is made electrically positive. Under the impetus of electrical current paint particles become charged and are propelled against the surface to be coated, where they coalesce. Relatively thick, uniform coatings can be deposited in a short time onto irregular surfaces. This process is described as anaphoretic deposition. Most automobile manufacturers have converted to a process in which the object to be painted is negatively charged. This process is termed cathaphoretic deposition and is applied to the primer coat. Cathaphoresis offers several advantages over anaphoresis:

1. There is no bare metal attack.
2. Phosphate coatings are not dissolved.
3. There are no metallic salts in the deposited films.
4. There is improved corrosion protection with less film thickness.

Articles can be coated with finely powdered thermo-

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plastic and thermosetting material. This system maintains a bed of finely powdered material in a fluid-like state by flowing air. When heated articles are dipped into the powder, the plastic melts and adheres to their surfaces. Powdered thermoplastic and thermosetting material may also be sprayed onto a heated article, where it melts and coalesces into a continuous film. Thermoplastic material coating may be melted in a spray gun and impelled against the surface to be coated in a manner analogous to metal spraying.

Coatings may be applied by dipping articles into a bath that contains the coating in a liquid form and allowing it to cure in heated air.

Certain coatings are available in aerosol spray cans for painting small areas and touching up damaged spots.

Painting systems are described in par. 3-7.3.5.

**3-7.3.2 Adhesives, Sealants, Encapsulants, and Bonding and Potting Compounds**

This class of organic coatings performs specific functions with respect to metal surfaces as indicated by their descriptive nomenclature. In addition to their specialized functions, they are intended to prevent corrosion. While performing these functions, the compounds may harden or maintain some degree of plasticity, they may take a certain set or flow under certain conditions, and they may adhere to a surface or not form a lasting bond. One property they have in common, however, is a degree of impermeability to moisture and other corrosive environmental components.

Sealing and bonding compounds are listed in Table 3-12 with their applications and specifications. Table 3-13 lists encapsulants and potting compounds and indicates their applications and specifications. Table 3-14 lists miscellaneous organic-base finishes not otherwise classified.

**TABLE 3-12. SEALING AND BONDING COMPOUNDS (Ref. 37)**

| MILITARY SPECIFICATION | DESCRIPTION                                      | APPLICATION  |
|------------------------|--|--|
| MIL-S-22473            | Single-component retaining compound              | Specify grade and primer on drawing                            |
| MIL-S-8802             | Polysulfide-type sealing compound                | Delineate class and dark number on drawing                     |
| TT-P-1757              | Unthinned zinc chromate primer                   | Apply wet for sealing threaded areas and interface capillaries |
| MIL-P-8116             | Zinc chromate paste                              | Sealing in the threaded, adjustable parts                      |
| MIL-STD-276, Method B  | Impregnation compound                            | Aluminum alloy and magnesium alloy castings                    |
| MIL-S-23586            | Two-component, silicone sealant                  | Specify type, class, and grade on drawing                      |
| MIL-T-23142            | Tape   | Dissimilar metal protection                                    |
| MIL-S-11030            | Noncuring polysulfide sealant                    | For helicoils and steel inserts, specify type on drawing       |
| MIL-S-11031            | Two-component polysulfide sealant                | Adhesive and sealant   |
| MIL-S-45180, Type II   | Hydrocarbon and water-resisting sealing compound | Sealing gaskets  |
| MIL-A-3920             | Optical, thermosetting adhesive                  | Bonding glass-to-glass   |
| MIL-A-8576             | Acrylic-base adhesive                            | For acrylic plastics, delineate type on drawing                |

(cont'd on next page)



**MIL-HDBK-735(MR)****TABLE 3-12. (Cont'd)**

| MILITARY SPECIFICATION | DESCRIPTION                                      | APPLICATION  |
|------------------------|--|--|
| MMM-A-134              | Epoxy resin adhesive                             | For metal-to-metal structural bonding, specify type on drawing                   |
| MMM-A-132              | Heat-resistant adhesive                          | For airframe, structural, and metal-to-metal, specify type and class on drawing  |
| MIL-A-81236            | Epoxy resin adhesive with polyamide curing agent | Type I or II as applicable   |
| MIL-A-25463            | Adhesive   | For metallic structural sandwich construction, specify type and class on drawing |
| MMM-A-121              | Bonding adhesive                                 | Vulcanizing synthetic rubber to steel  |
| MMM-A-1617             | General-purpose rubber adhesive                  | Specify type on drawing  |
| MIL-A-5540             | Polychloroprene rubber adhesive                  | Specify class on drawing   |
| MIL-S-81733            | Polysulfide sealing and coating compound         | Delineate type and dash number on the drawing                                    |

**TABLE 3-13. ENCAPSULANTS AND  
POTTING COMPOUNDS  
(Adapted from Ref. 37)**

| COATING  |
|--|
| Insulating compound electrical, embedding, MIL-I-16923   |
| Molding and potting compound, chemically cured, polyurethane, MIL-M-24041                                    |
| Insulating compound, electrical (for coating printed circuit assemblies), Type ER, Epoxy, MIL-I-46058        |
| Insulating compound, electrical (for coating printed circuit assemblies), Type UR, Polyurethane, MIL-I-46058 |
| Insulating Compound, electrical (for coating printed circuit assemblies), Type SR, Silicone, MIL-I-46058     |
| Insulating compound, electrical (for coating printed circuit assemblies), Type XY, Paraxylylene, MIL-I-46058 |

**TABLE 3-14. MISCELLANEOUS FINISHES  
(Ref. 16)**

|   |
|---|
| Filler, graduation, TT-F-325  |
| Type I, crayon type; color as specified; black, deep red, white, translucent white                              |
| Type II, paste type: color as specified, black, deep red, white, translucent white                              |
| *Nonskid coating, 0.794- to 1.59-mm (0.0313- to 0.0625-in.) dry film thickness, DOD-C-24667, color as specified |
| *Walkway coating and matting, nonslip, MIL-W-5044, type and color as specified                                  |
| Coating, luminescent, fluorescent and phosphorescent  |
| Luminescent material, fluorescent, Type I, MIL-L-25142  |
| Luminescent material, phosphorescent, Type P, form 1, MIL-L-3891  |
| Luminescent material, fluorescent, Type F, form 1, MIL-L-3891, color as specified                               |
| MIL-V-173; applied in accordance with MIL-T-152.  |
| For moisture and fungus proofing of electronic and associated equipment.  |

\*When nonskid (DOD-C-24667) or walkway coating and matting, nonslip (MIL-W-5044) are required for chemical-agent-resistant coating (CARC) environments, the sequence of application shall be:  
CARC primer followed by DOD-C-24667 or MIL-W-5044 followed by CARC top coat

**MIL-HDBK-735(MR)****3-7.3.3 Rust-Preventive Compounds**

Rust-preventive compounds are a class of relatively inexpensive organic coatings that are applied to metal surfaces to improve corrosion resistance through barrier action. They are also referred to as preservatives.

These compounds are composed mainly of petroleum or coal-tar-base oils, greases, and waxes, and they may contain corrosion inhibitors. The films may be oily, greasy, waxy, soft, or hard. They may have lubricating properties. The films may be applied dissolved in a solvent, dispersed in a water emulsion, or undiluted. Rust-preventive compounds may be heated to improve their flow properties during application. Application to the materiel components may be achieved by dipping, spraying, swabbing, or brushing.

The various methods of preservation are covered in MIL-P-116 (Ref. 87). The following descriptions illustrate the range of products available:

1. Petroleum compounds that are applied in the molten state by dipping, brushing, swabbing, etc. (MIL-C-11796, Ref. 88). The films may range from hard to soft, and they have a wide range of applications to military materiel.

2. Petroleum-base compounds whose application properties are achieved by solvent cutback (MIL-C-16173, Ref. 27). As the solvent evaporates, these compounds form films that range from hard to soft and oily to waxy. The films may be miscible with lubricating oil and not require removal before use, or they may be immiscible.

3. Rust-preventive lubricating oils (VV-L-800, Ref. 28) that do not require removal before use

4. Water-displacing types that may be applied to a wet surface and leave a thin, transparent film (MIL-C-81309, Ref. 89)

5. Fingerprint-removing corrosion preventives (MIL-C-15074, Ref. 90). The residue of fingerprints can result in corrosion of metal that has been handled during fabrication; it must be removed before the final protective finish is applied.

6. Water-emulsifiable types that are fire resistant (MIL-C-40084, Ref. 91).

7. Wax emulsions for general weatherproofing (MIL-W-3688, Ref. 92)

8. A petrolatum-base, solvent-diluted type that is of suitable purity to spray on food-handling machinery and equipment (MIL-C-10382, Ref. 93)

9. Formulation for rustproofing sheet metal areas and structural members of new (MIL-C-83933, Ref. 94) and fielded (MIL-C-62218, Ref. 95) vehicles.

Rust-preventive compounds are used in a wide variety of applications in military materiel to protect metals during transportation and storage. They minimize the time required to prepare stored materiel for use; they also protect materiel in the field and prevent breakdowns and failures in service.

These compounds are used to protect dies, molds, gages, fabricating equipment, gears, armatures, bearings, tools of all kinds, repair parts, and stored machinery. Finished mill products such as sheets, strips, bar stock, piping, rods, wires, contoured parts, and plates are protected during handling, shipping, and storage by preservative compounds. Small arms, ammunition clips, links, etc., are protected and lubricated in the field by using rust-preventive compounds.

A specific form of rustproofing compound is widely used to prevent corrosion in vehicles. This form is used on underbody parts, on the interior surfaces of doors, and on other boxed-in areas. Rustproofing compounds may be applied to new vehicles and to fielded vehicles.

These petroleum-base rustproofing compounds are susceptible to sorption of toxic chemical agents. Furthermore, rustproofing compounds are applied to a minimum thickness of 127  $\mu\text{m}$  (5 mil). Therefore, they can absorb considerable quantities of toxic chemical agents. The undercarriage of a vehicle is particularly susceptible to attracting toxic chemical agents as the vehicle traverses contaminated areas.

In addition to the potential contamination problem, vehicles protected with petroleum-base rustproofing compounds do not meet the contamination survivability requirements for decontaminability and hardness. Decontaminability is the ability to be rapidly and thoroughly decontaminated. Hardness is the ability to withstand both the damaging effects of contamination and the damaging effects of decontamination agents and procedures. Decontamination with detergents, high-pressure water sprays, or steam removes petroleum-base rustproofing compounds. Of course, if the rustproofing compound has physically absorbed the toxic agent, the only way to decontaminate is to remove the rustproofing compound.

A chemical-agent-resistant coating (CARC) system consists of a polyurethane coating (MIL-C-46168, Ref. 96) over epoxy primers (MIL-P-23377, Ref. 97 on aluminum and MIL-P-53022, Ref. 98 on steel). This coating system does not appear to be a satisfactory alternative to the use of petroleum-base rustproofing compounds in terms of corrosion protection. Because of the abuse that the underbody of a vehicle takes, the polyurethane or epoxy coating could crack and expose the substrate to corrosion much more readily than the thick and relatively flexible petroleum-base rustproofing compound. A possible solution is the use of galvanizing to protect the surface from corrosion even if the polyurethane-epoxy coating were damaged.

The process of applying polyurethane and epoxy finishes generates both workplace and environmental hazards. Formulation and application processes are being developed that satisfy Occupational Safety and Health Administration (OSHA) and Environmental Pro-

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tection Agency (EPA) regulations.

Table 3-15 lists some lubrication and preservation treatments.

**TABLE 3-15. LUBRICATION AND PRESERVATION TREATMENTS  
(Adapted from Ref. 37)**

---

|   |
|---|
| Corrosion-preventive compound, MIL-C-16173, Grade 1 (hard film)                         |
| Corrosion-preventive compound, MIL-C-16173, Grade 2 (soft film)                         |
| Medium preservative lubricating oil, MIL-L-3150   |
| Lubricating oil, general-purpose, VV-L-800, water displacing, low temperature           |
| Corrosion-preventive compound, MIL-C-81309, water displacing, ultra-thin                |
| Lubricating grease, MIL-G-10924   |
| Lubricant, dry film, MIL-L-46010, bake-type   |
| Lubricant, dry film, MIL-L-46147, air-drying  |
| Lubricating oil, VCI, MIL-L-46002. Specify grade on the drawing                         |
| Solid, VCI corrosion inhibitor, MIL-I-22110, per MIL-I-8574, Type I or II as applicable |
| Preservative coating, rubber for rubber surfaces, MIL-P-11520                           |

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### 3-7.3.4 Metal Cleaning Processes

The general cleaning requirement is that before any plating, metal conversion, or painting, all surfaces should be free from soils and corrosion including grease, oil, solder flux, welding flux, weld spatter, sand, rust scale, and all other contaminants that might interfere with the intimate application of the finish. Cleaning should be done immediately before the finishing operations, or suitable precautions should be taken to insure that the surfaces remain clean until they are finished. Precautions should also be taken to insure that all residual products from the cleaning process are removed. The various cleaning methods for metals are listed in Table 3-16.

As the first step in any metal finishing process, the metal surface should be bare and free from substances that may interfere with a subsequent treatment or operation. These contaminants may be greasy substances, foreign particles and compounds, or oxides of the base metal itself.

Selecting a process for cleaning a surface involves consideration of the factors that follow:

1. Nature and type of surface dirt
2. Type of base metal
3. Geometrical and mechanical characteristics of the part and its surfaces
4. The degree of cleanliness required
5. The operations that are to follow the cleaning process

**TABLE 3-16. METAL CLEANING METHODS\* (Ref. 16)**

---

|  |
|--|
| Abrasive blasting  |
| Hot alkaline cleaning  |
| Solvent cleaning (immersion or spray)  |
| Phosphoric acid cleaning (alcoholic, detergent, or solvent type with detergent) MIL-C-10578  |
| Emulsion cleaning  |
| Alkaline derusting (MIL-C-46156 or MIL-C-14460)  |
| Acid pickling  |
| Sulfuric acid pickling. Immerse the part in a solution consisting of 5 volumes of sulfuric acid (66 Baumé or 1.84 Sp Gr), 95 volumes of water, and nonfoaming liquid inhibitor, 0-1-501, Type B, class A, as directed by manufacturer of inhibitor, at a temperature of 77° to 82° C (170° to 180° F). After removal of scale (indicated by a uniform gray color), remove part from solution, allow to drain, and then rinse in fresh circulating water at 77° to 82° C (170° to 180° F). Immerse for 2 to 5 min in solution of 28 g (1 oz) sodium dichromate and 21 g (0.75 oz) phosphoric acid (75% grade) per 3.8 ℓ (1 gal) water, at 88° to 96° C (190° to 205° F). Discard rinsing bath when combined sulfuric acid and iron sulfate reaches 0.5 g/ℓ (0.08 oz/gal). After surfaces are thoroughly dry, treat and/or paint as soon as possible. (Note: Where the steel parts will be used under stress, cleaning by acid pickling is not recommended because of hydrogen embrittlement. Acid pickling is also not recommended prior to phosphating.) |
| Other methods as specified in detail on drawing or in contract   |
| Hot alkaline cleaning, nonetching, for nonferrous (and ferrous) metals. Use P-C-436 material in accordance with specification  |
| Vapor degreasing, using solvent conforming to O-T-634, Type II, or MIL-T-81533   |

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\*Additional details on cleaning methods and procedures may be found in MIL-HDBK-132, MIL-HDBK-205, MIL-P-116, and TT-C-490.

6. Special precautions such as preserving dimensional tolerances or not introducing hydrogen into the metal
7. The efficiency with which a cleaning process achieves the degree of cleanliness required
8. The cost
9. The type of cleaning compounds available.

Cleaning methods may be characterized as mechanical, chemical, and electrochemical. Mechanical cleaning methods include grinding, brushing, abrasive blasting, steam or flame, laser, jet cleaning, tumbling, polishing, and buffing. Chemical cleaning methods include solvent, alkaline, and acid cleaning; pickling; descaling with sodium hydride; and paint stripping. Electrochemical

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cleaning methods include electropolishing, electrolytic alkaline cleaning, and electrolytic pickling.

Grinding cleans by wearing away the dirt and usually takes part of the base metal with it; grinding is accomplished with abrasive particles bonded together in various shapes, such as a wheel or disc. Wire brushing is an abrasive operation usually done with a wire or fiber brush; sometimes an abrasive or polishing compound is used. Wire brushing is used to remove tenacious scale, embedded sand, and paint, but it contaminates the base metal with the wire material. This contamination should always be considered; for example, never use a copper brush on aluminum.

Abrasive blasting bombards a surface with an abrasive material, which may be carried by compressed air or a high-velocity water stream or it may be propelled by centrifugal force. Jets of steam or flame can remove loose scale on ferrous metals. During tumble cleaning parts are tumbled in a rotating drum either alone or with abrasives and lubricating liquids. Polishing and buffing are accomplished with motor-driven wheels and abrasives. Proceeding from grinding to polishing to buffing, the abrasive wheel becomes more resilient, the abrasive becomes finer, and the amount of metal removed decreases.

Solvent cleaning exposes a metal surface to solvents such as hydrocarbons and chlorinated hydrocarbons. The solvents may be used directly, as emulsions, or in diphasic systems. In diphasic systems a solvent phase floats on top of an aqueous phase. The solvent may be applied to the surface by immersing the article in a tank, by spraying the solvent onto the surface, or by suspending the article in solvent vapors so that condensation occurs on the surface. The tank cleaning method may be augmented with ultrasonic energy.

Alkaline compounds in aqueous solution are extremely effective for removal of organic and water-soluble soils, vegetable and animal greases, and solid dirt that may be embedded in a surface. Alkaline cleaners displace dirt from the surface and suspend it in solution. Fatty acids are converted into soluble soaps.

Acid cleaners, which are usually water solutions of phosphoric acid, organic solvents, or acid-stable detergents and wetting agents, are used where light soil and rust are encountered. Pickling is an acidic treatment to remove surface oxide, scale, and dirt from a metal by a chemical process. Wide variations are possible in the type, strength, and temperatures of the acid solutions used.

The sodium hydride process is a metal-descaling process suitable for ferrous metals, copper, nickel, and titanium. The metal to be descaled is immersed in a bath consisting of fused sodium hydroxide at approximately 371°C (700°F) and containing approximately 2% sodium hydride.

Paint stripping is accomplished by a combination of chemical strippers and mechanical action. Strong,

aqueous alkali solutions are used for paints based on drying oils and polymerized resins; however, alkali solutions are not used on aluminum. In other cases, a mixture of organic solvents works well.

The principle of electropolishing action is rapid attack on elevated spots or asperities in the rough finish and minimum attack on depressed spots. Electropolishing processes represent a wide variety of electrolytes and operating details. Electrolytic alkaline cleaning speeds up alkaline cleaning by generating gas to assist agitation and soil removal. The alkaline solution is the electrolyte, the metal to be cleaned is one electrode, and the tank or a steel plate is the other electrode. The advantage of applying an electric current to pickling is similar to that for alkaline cleaning, i.e., gas is liberated and mechanically loosens the scale and speeds up the process. In electrolytic pickling the bath may be either acid or alkaline.

Porous castings may require sealing to assure that they are leakproof and to prevent bleeding out of treating chemicals, which would cause staining or corrosion of the metal surface and damage to the finishing system. Sealing of castings should be accomplished after surface cleaning and after machining. MIL-I-13857 (Ref. 99) covers the requirements for the impregnation of castings that contain micropores but not visible blowholes or other major defects.

**3-7.3.4.1 Ferrous Metal Cleaning**

Typically, ferrous metal surfaces are cleaned using the following procedure:

1. Degrease to insure that the surface is free from all oil and grease.
2. Remove mill scale, products of corrosion, dirt, casting sand, slag, and other foreign substances by an abrasive blast. Blasting should not be used on surfaces that could be damaged, such as machined parts and thin sheet metal. Blast-cleaned surfaces should be given a primer coat no longer than 4 h after cleaning.
3. Oil and grease contamination resulting from fabrication, machining, or handling subsequent to cleaning should be removed with solvent, hot alkaline cleaning, or phosphoric acid cleaning. High-strength steel (Rockwell C48 or higher) should not be cleaned or pickled with acid-containing materials.

**3-7.3.4.2 Aluminum Cleaning**

Typically, aluminum and aluminum alloys are cleaned using the following procedure:

1. Vapor degreasing
2. Nonetching hot alkaline cleaning
3. After removing all traces of oil, grease, dirt, and other foreign substances, aluminum and aluminum alloys are treated by immersion in or pressurized spraying of a hot 10% solution of chromic acid.
4. The surfaces are rinsed with clean, warm water to

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remove excess chromic acid from cavities, joints, and recesses.

**3-7.3.4.3 Magnesium Cleaning**

Magnesium alloys are first cleaned with solvents. This initial cleaning may be followed by fluoride anodizing and a hot water rinse or by mechanical cleaning followed by nonetching alkaline cleaning and a cold water rinse. The nonetching alkaline cleaning and cold water rinse may, in some cases, be followed by chromic acid pickling and a cold water rinse.

**3-7.3.5 Painting Systems**

A painting system for a cleaned metal surface consists of the pretreatment, the primer coating, and the topcoat. Tables 3-17, 3-18, and 3-19 list specifications for most of the paint finishes for metals necessary for a wide variety of military equipment. These tables provide specifically for steel (iron), aluminum, and magnesium, and their alloys. The finishes are, however, also suitable for zinc, cadmium, copper, tin, terneplate, and titanium provided these metals have been appropriately pretreated. A common pretreatment is the so-called "wash primer" (DOD-P-15328, Ref. 20).

Aluminum and magnesium and their alloys require special primers in many of the finishes listed. Primers meeting TT-P-1757 (Ref. 100), zinc chromate; MIL-P-15930 (Ref. 101), vinyl-zinc chromate; or MIL-P-23377 (Ref. 97), epoxy polyamid are listed in Tables 3-17, 3-18, and 3-19 in lieu of TT-E-485 (Ref. 102), semigloss enamel; TT-P-664 (Ref. 103), synthetic primer; and MIL-P-11414 (Ref. 104), lacquer primer to prime aluminum. Two coats of vinyl-zinc chromate primer meeting MIL-P-15930 (Ref. 101) or one coat of epoxy primer meeting MIL-P-23377 (Ref. 97) are listed in Tables 3-17, 3-18, 3-19 in lieu of TT-E-485 (Ref. 102), TT-P-664 (Ref. 103), and MIL-P-11414 (Ref. 104) to prime magnesium.

The primer coat of paint is applied as promptly as possible after the metal surface has been pretreated. Each coat of paint should be dry before applying a succeeding coat. For example, under ideal conditions 24 h is sufficient for an air drying paint, i.e., one that conforms to TT-E-485 (Ref. 102), or TT-E-529 (Ref. 105), 15 min for lusterless enamel that conforms to TT-E-516 (Ref. 106), and 10 min for lacquer that conforms to MIL-L-11195 (Ref. 107). When surfaces to be painted are not readily accessible after assembly, primers and intermediate coats may be applied to unassembled parts of an assembly; the final coat is applied after assembly.

**TABLE 3-17. LUSTRELESS PAINT FINISHES FOR METAL SURFACES  
(Adapted from Ref. 16)**

| PRIMER COAT                  | TOPCOAT(S)                             | REMARKS   |
|------------------------------|--|---|
|                              | TT-E-516 or MIL-E-52891<br>MIL-L-11195 | One-coat finish for projectiles, grenades, etc.   |
| MIL-P-11414* or TT-P-664     | MIL-L-11195                            | Two-coat lacquer finish for automotive and general use  |
| TT-P-664* or MIL-P-11414     | MIL-E-52891 (for<br>ammunition use)    | Two-coat lustreless alkyd finish for general use except<br>poor gasoline resistance<br>Determine where finish is to be used and accordingly<br>substitute the previous finish or one of the following<br>two finishes |
| TT-P-664*                    | TT-E-527                               | Two-coat alkyd finish for general use   |
| TT-P-664*                    | TT-E-515                               | Quick drying two-coat alkyd finish for general use  |
| MIL-P-11414* or TT-P-664     | TT-P-662 plus MIL-L-11195              | Three-coat lacquer finish for automotive and general<br>use   |
| MIL-P-53022<br>MIL-P-53030** | MIL-C-46168 or<br>MIL-C-53039          | Chemical-agent-resistant camouflage   |

\*When these finishes are specified for aluminum or magnesium, the primers shall be as indicated in par. 3-7.3.5

\*\*MIL-P-23377 (Type I) or MIL-P-85582 may be used on aluminum and non-ferrous metals or when both ferrous and non-ferrous metals are present.

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**TABLE 3-18. SEMIGLOSS PAINT FINISHES FOR METAL SURFACES**  
(Adapted from Ref. 16)

| PRIMER COAT  | TOPCOAT(S)                               | REMARKS   |
|--|--|---|
|  | TT-E-485                                 | One-coat finish for ammunition containers, gasoline drums, etc. |
| TT-P-664   | TT-E-529                                 | Two-coat alkyd finish for general use                           |
| TT-E-485*  | TT-E-485                                 | Two-coat alkyd finish for general use                           |
| TT-P-664   | TT-E-529 (2 coats)                       | Three-coat alkyd finish for general use                         |
| MIL-P-11414*<br>or TT-P-664                                      | MIL-L-52043                              | Two-coat lacquer finish<br>for automotive materials             |
| MIL-P-11414*<br>or TT-P-664                                      | TT-P-662 plus<br>MIL-L-52043             | Three-coat lacquer finishes<br>for automotive materials         |
| MIL-P-11414*<br>or TT-P-664                                      | MIL-L-52043<br>(2 coats)                 |   |
| TT-P-1757  | TT-E-485 (2 coats)                       | Three-coat finish for general use                               |
| MIL-P-14553<br>(dip and bake)<br>or TT-P-664<br>(spray and bake) | TT-E-485<br>or TT-E-529<br>(baking type) | Two-coat baking finish for automotive equipment                 |

\*When these finishes are specified for aluminum or magnesium, different primers are required as indicated in par. 3-7.3.5.

**TABLE 3-19. FULL GLOSS PAINT FINISHES FOR METAL SURFACES**  
(Adapted from Ref. 16)

| PRIMER COAT   | TOPCOAT(S)                               | REMARKS   |
|---|--|---|
| TT-P-664  | TT-E-489                                 | Two-coat alkyd finish for general use   |
| MIL-P-14553<br>(dip and bake)<br>or TT-P-664<br>(spray) | TT-E-489<br>(air-dry,<br>VOC compliance) | Two-coat alkyd enamel finish  |
| TT-P-664  | TT-E-1593                                | Two-coat silicone-alkyd finish for general exterior use.<br>Outstanding gloss and color retention |

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The film thicknesses of single dry coats of finishes, as designated by the specifications, are listed in Table 3-20. Multiple coats proportionately increase the dry film thickness. One coat is applied by a minimum of one double or cross pass of the spray gun. One coat, however, is not to be construed as one pass of a spray gun. If camouflage topcoats are used, a minimum dry film thickness of 46  $\mu\text{m}$  (1.8 mil) is applied. Normally two sprayed coats will obtain this minimum film thickness. Camouflage paint systems are listed in Table 3-21.

By specifying finishes, military handbooks are supplementing standards and specifications in providing general guidance and a working knowledge.

When specifying a finishing system for metals, the following items must be listed: cleaning of the surface, surface pretreatment, primer, topcoat, and color. Each of these is assigned codes in standards such as MIL-STD-186 (Ref. 37). A full finish would be listed as cleaning code/pretreatment code/primer code/topcoat code/color code, and standard listing, e.g., "Finishing Codes

**TABLE 3-20. FILM THICKNESS OF SINGLE DRY COATS (Adapted from Ref. 16)**

| SPECIFICATION                              | THICKNESS     |         |
|--|---------------|---------|
|  | $\mu\text{m}$ | mil     |
| Pretreatment coating:<br>DOD-P-15328       | 8-13          | 0.3-0.5 |
| Primers:                                   |               |         |
| TT-E-485                                   | 20-30         | 0.8-1.2 |
| TT-P-664                                   | 25-38         | 1.0-1.5 |
| TT-P-1757                                  | 10-15         | 0.4-0.6 |
| MIL-P-11414                                | 15-20         | 0.6-0.8 |
| MIL-P-14553                                | 10-15         | 0.4-0.6 |
| MIL-P-15930                                | 10-15         | 0.4-0.6 |
| MIL-P-23377*                               | 20-30         | 0.8-1.2 |
| MIL-P-46105                                | 51-76         | 2.0-3.0 |
| MIL-P-53022                                | 25-38         | 1.0-1.5 |
| MIL-P-53030                                | 25-38         | 1.0-1.5 |
| MIL-P-85582                                | 20-30         | 0.8-1.2 |
| Primer surfacers:                          |               |         |
| TT-P-662                                   | 20-30         | 0.8-1.2 |
| Other primers (unless otherwise specified) | 20-30         | 0.8-1.2 |
| Top coats:                                 |               |         |
| MIL-C-22750                                | 33-43         | 1.3-1.7 |
| MIL-C-46168                                | 46 min        | 1.8 min |
| MIL-C-53039                                | 46 min        | 1.8 min |
| All other top coats, clear or opaque       | 20-30         | 0.8-1.2 |

\*Except for aircraft, film thickness shall be 15-23  $\mu\text{m}$  (0.6-0.9 mil).

NOTE: Where multiple coats are designated in the tables for finishes the dry film thickness shall be multiplied proportionally. One coat shall be applied by a minimum of one double or cross pass of spray gun. One coat shall not be construed as one pass of the spray gun.

**TABLE 3-21. CAMOUFLAGE PAINT SYSTEMS (Adapted from Ref. 108)**

| TOPCOAT     | PRIMER COAT |                            |
|-------------|-------------|----------------------------|
|             | ALUMINUM    | STEEL                      |
| MIL-C-46168 | TT-P-1757   | TT-P-664                   |
|             | MIL-P-23377 | MIL-E-52891                |
|             | MIL-P-53030 | MIL-P-53022<br>MIL-P-53030 |
| MIL-C-53039 | MIL-P-53022 | MIL-P-53022                |
|             | MIL-P-53030 | MIL-P-53030                |

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106/401/402/425, black 27038, in accordance with MIL-STD-186" (Ref. 37). Other information, such as the following, is either described in the standard or specification or is left to the user's judgment based upon his experience:

1. Proper preparation of surface
2. Proper mixing and thinning
3. Thickness of coat
4. Suitable drying time between coats
5. Proper handling of painted surface.

The specification or standard may list a series of methods or a series of types, and which of these is to apply should be designated.

A different arrangement of finish codes is used in MIL-STD-171 (Ref. 16) than in MIL-STD-186 (Ref. 37). Appendix A of MIL-STD-171 provides guidance on finish selection for classes of parts, the conditions affecting the selection of the finish, and the type of exposure of the particular surface.

**3-8 PACKAGING**

To prevent deterioration from environmental exposure during the interval between when materiel leaves the producer's facility and when it is placed in use in the field, packaging is applied to Army materiel. During this period materiel may experience a variety of environments and several different transportation modes. Packaging therefore achieves several goals. In preventing material deterioration, packaging protects from induced environments produced by mechanical and physical forces, and it provides protection from those natural environmental factors, such as rain, salt, dust, and heat. Physical damage is usually prevented through the use of physical shielding, cushioning, blocking, and bracing. Chemical and biological attacks are prevented through the use of preservative treatments, environmental control provided by liquid and vapor barriers, vapor-phase corrosion inhibitors, desiccants, and inert gas blankets. It is important that

materials used in packaging are compatible with the enclosed materiel. Similarly, it is important that the various materials comprising a materiel system do not, when packaged, interact to result in deterioration.

Packaging is a concern of the materiel designer as well as of the packaging engineer. The boundaries of these people's concerns overlap. The packaging engineering procedure follows a sequence of steps shown in Table 3-22.

The term "packaging" includes preservation packaging, packing, preparation of unit loads, and marking of packages, packs, and unit loads (Ref. 109). Preservation packaging is the application or use of protective measures, which include appropriate cleaning and drying methods, preservatives, protective wrappings, cushioning and containers, and complete package identification marking. "Packing", however, is the assembly of packaged or unpackaged items in a bale, bundle, container, or similar structure together with necessary blocking, bracing, cushioning, and weatherproofing in addition to exterior strapping or reinforcing and marking. The unit, packaged and packed as described, can be stored and transported without additional protection. It is known as a "pack".

The requirements for packaging military materiel are significantly different from those for items in commercial trade. The most important of these differences is that many items of military materiel are in long-term, static storage until used, and when removed from storage, these items must perform instantly with complete reliability, e.g., an antitank rocket stored in its launch tube. The whole assembly is packaged for shipment and storage. At the time of use, the warhead, propulsion, and guidance systems must not have deteriorated as a result of their confinement in the launch tube. Furthermore, the launch tube and those components external to the launch tube must also not have deteriorated as a result of exposure to the package environment or to any ambient environments to which the package may have been exposed.

**TABLE 3-22. PACKAGING ENGINEERING SEQUENCE PROCEDURE (Ref. 110)**

1. Obtain item drawings, specifications, procurement documents, and the actual hardware item whenever possible.
2. Determine item characteristics, i.e., size, weight, configuration, chemical characteristics, etc.
3. Determine level of protection required. The level of protection cannot be determined until the procurement purpose or destination is known. If these are unknown, the worst case is mandated.
4. Determine unit package quantities and intermediate package quantities. The user's requirements for accessibility, protection until use, and distribution weigh heavily in determining unit package quantities and intermediate package quantities. Mass or bulk shipping modes also affect the use and consolidation configurations.
5. Establish method of preservation.
6. Establish method of cleaning, drying, and applying preservative.
7. Select unit and intermediate packaging materials.
8. Determine barrier and cushioning requirements.
9. Select an exterior container; design special container or pallets when required.
10. Establish marking requirements.
11. Prepare packaging documents, which describe the above requirements and special bracing, cushioning, or container design.



**MIL-HDBK-735(MR)****3-8.1 PACKAGING LEVELS**

There are three basic levels of protection. Level A is the degree required to protect against the most severe conditions known or anticipated to be encountered during shipping, handling, and storage. Level A preservation packaging and Level A packing are designed for direct exposure to all extremes of climate, terrain, and operational and transportation environments without protection other than that provided by the package and pack. In general, the following criteria determine the requirements for Level A design:

1. Multiple rough handling during transportation and in-transit storage from manufacturer to ultimate user
2. Shock, vibration, and static loading during shipment, including dock-to-ship loading and offshore or over-the-beach discharge to the ultimate user
3. Natural environmental exposure during transit if port and warehouse facilities are limited or nonexistent
4. Extended unimproved open storage in all climatic zones, particularly while under static loads imposed by stacking
5. Special package and pack features for field and combat operations (handling and utility)
6. Special features as required by combat development agencies.

Level B is the degree of protection required under conditions known to be less severe than those requiring Level A but more severe than those for which Level C is adequate. Level B preservation packaging and Level B packing are designed to protect items from physical and environmental damage during shipment, handling, and storage under conditions other than those identified for Levels A and C. In general, the following criteria determine the requirements of Level B design:

1. Multiple handling during transportation and in-transit storage
2. Shock, vibration, and static loading of shipment worldwide by truck, rail, aircraft, or ocean transport
3. Favorable warehouse environment for extended periods
4. Effects of environmental exposure during shipment and in-transit transfers, excluding deck loading and offshore cargo discharge
5. Stacking and supporting superimposed loads during shipment and extended storage
6. Special features as required by military and technical characteristics and logistic considerations.

Level C is the degree of protection required under the most favorable conditions during shipment, handling, and limited tenure of storage. Level C preservation packaging and Level C packing are designed to protect items against physical and environmental damage during conditions of shipment, handling, and storage known to be favorable. In general, the following criteria determine the requirements of Level C design:

1. Limited and careful handling during transportation and in-transit storage
2. Minimal shock, vibration, and static loading during the limited transportation cycle
3. Controlled warehouse environment for temporary periods
4. Effects of environmental exposure during shipment and in-transit delays
5. Limited stacking and supporting superimposed loads during limited shipment and temporary storage.

The key step in protecting against chemical or biological deterioration is to select the method of preservation and determine barrier requirements. Preservation methods and packaging designs should be of minimum cost consistent with required performance. Unit and intermediate packages and packs should be designed to conserve weight and cube (volume) without reducing the protection required to insure the materiel arrives undamaged at the destination, which could be the point of use. The preservation and packaging methods selected should insure protection of end-items, repair parts, and kits against anticipated natural and induced environments. Prerequisites to selecting preservation and package designs and materials are analyses of the environments to which the item may be subjected during its life. Such analyses should include, but not be limited to, item characteristics related to the need for protection, induced forces produced in transportation and handling, and climatic environments.

Level A preservation and packaging are accomplished in accordance with MIL-P-116 (Ref. 87). The preservation methods described in this specification establish the basic packaging strategy. There are three basic methods of preservation and several submethod variations; they are listed in Table 3-23.

The use of Level B preservation and packaging must be based on firmly established knowledge of the shipment and storage conditions to be encountered and a determination that monetary savings will result.

Unless otherwise specified, items should be preserved and packaged to prevent deterioration and damage during shipment from the supply source to the first receiving activity. This degree of protection is Level C, and this type of packaging is not meant for overseas shipment or uncontrolled long-term storage.

Preservation and packaging requirements are specified in a coded sequence, which can be entered into a computer system. Information reflecting the packaging engineer's decisions are entered into the Packaging Requirements worksheet, Fig. 1 of Appendix D to MIL-STD-2073/1 (Ref. 109). The actual packaging requirements code is detailed in MIL-STD-2073/2 (Ref. 111). The minimum essential elements that must be specified to define packaging requirements follow:

1. Method of preservation

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2. Quantity per unit pack
3. Cleaning and drying procedures
4. Preservative material
5. Wraps, cushioning, and dunnage
6. Unit container
7. Intermediate container quantity
8. Intermediate container
9. Level of preservation.

In addition to the basic packaging information, codes are provided for including the following items of logistic information:

1. Level A packing requirements
2. Level B packing requirements
3. Level C packing requirements
5. Special markings.

**TABLE 3-23. PACKAGING AND SUBMETHODS (Ref. 87)**

| I  | IA   | IC  | II   | III                                     |
|--|--|---|--|---|
| Preservative coating (with greaseproof wrap as required) | Water-vaporproof enclosure (with preservatives as required)              | Waterproof or water-proof and greaseproof enclosure (with preservative as required)                   | Water-vaporproof enclosure with desiccant and preservative as required | Physical and mechanical protection only |
|  | IA-5<br>Rigid metal container sealed                                     | IC-1<br>Greaseproof, waterproof bag, sealed   | IIa<br>Floating bag, heat sealed*,**                                   |   |
|  | IA-6<br>Rigid container (items immersed in oil-type preservative) sealed | IC-2<br>Container, waterproof bag, sealed   | IIb<br>Container bag, heat sealed, container*,**                       |   |
|  | IA-8<br>Bag sealed*,**   | IC-3<br>Waterproof bag, sealed  | IIc<br>Bag, heat sealed*,**  |   |
|  | IA-13<br>Rigid container other than all metal, sealed                    | IC-4<br>Rigid container other than all metal, sealed  | II d<br>Rigid metal container, sealed                                  |   |
|  | IA-14<br>Container, bag, heat sealed, container*,**                      | IC-7<br>Blister pack, greaseproof and waterproof, single or multiple compartment, individually sealed | IIe<br>Container, bag, heat sealed                                     |   |
|  | IA-15<br>Container, bag, heat sealed*,**                                 | IC-9<br>Skin pack, greaseproof, waterproof, vacuum formed, sealed                                     | II f<br>Rigid container, other than all metal, sealed                  |   |
|  | IA-16<br>Floating bag, heat sealed*,**                                   | IC-10<br>Skin package, waterproof, vacuum formed  |  |   |

\*When specified, Class F of MIL-B-117 shall be used.

\*\*When specified, Class G of MIL-B-117 shall be used.

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## 3-8.2 VOLATILE CORROSION INHIBITORS

Volatile corrosion inhibitors are often used in conjunction with packaging to protect metal items. Volatile corrosion inhibitors have a low but significant vapor pressure. Therefore, they will penetrate most recesses of an item to be protected, but in a nonhermetic enclosure a volatile corrosion inhibitor will have a limited effective lifetime. Volatile corrosion inhibitors are discussed in par. 3-5.5. Caution should be exercised in applications involving energetic materials.

## 3-8.3 DESICCANTS

Many materials are available as desiccants for moisture control. A very commonly used desiccant is silica gel, which is an amorphous form of silicon dioxide (sand). Packaging employing desiccants often contains an indicator of desiccant saturation that is visible from outside the package. Most desiccants can be reactivated by heating to a temperature sufficiently high to evaporate the accumulated moisture.

Humidity can be controlled in bulk storage facilities by dehumidification machines employing desiccant beds, and machines based on refrigeration dehumidification.

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## CHAPTER 4

# METAL CORROSION AND PREVENTION

*This chapter examines the corrosion characteristics of specific metals and alloys. The organization of the chapter is alphabetical according to the primary chemical element constituting a metal or alloy. Carbon is considered because it enters into electrochemical reactions with metals. Metal matrix composites are considered in a separate category. The metals and alloys that are included are those having widespread use as well as those having specific application in Army materiel.*

*Alloys are discussed within the context of the primary chemical element contained in the alloy. Where appropriate, however, major classes of alloys are discussed as separate entities. The rationale behind the alloy classification is given in terms of metallurgical, mechanical, and/or corrosion characteristics. In many cases minor amounts of alloying elements are used to modify incrementally mechanical properties or corrosion characteristics. In these cases separate discussion as an alloy class is not warranted.*

*The amount and scope of information available on specific metals and alloys vary widely. Usually the amount of information corresponds to the relative importance of specific metals to widespread applications. In some cases, however, metals and alloys have been systematically investigated because of potential applications that have not been realized.*

*Chapters 2 and 3 discuss the general types of corrosion and methods for preventing corrosion, respectively. This chapter focuses on specific metals and alloys and the types of applications for which they are used or for which they may have potential use. Therefore, the types of corrosion discussed include the general types mentioned in Chapter 2 as well as those that may be experienced in specific environments or media. The effect of the characteristics of the environment and the condition of the metal in that environment are considered.*

*Some of the metals and alloys are highly corrosion resistant in specific applications, whereas in other applications a metal may be used because of desirable mechanical properties or cost constraints. In these cases corrosion prevention measures may be required. Some of the metals and alloys are used as corrosion-resistant coatings on other less resistant metals. Corrosion prevention methods specific to metals in specific applications are discussed in this chapter.*

*In specific applications metals and alloys are interfaced or joined with other materials, both metallic and nonmetallic. In some applications the corrosion action itself creates an interface between the underlying metal and the corrosion products. Some interfaces result in specific corrosion types, such as galvanic corrosion. The discussion of metal-to-metal and metal-to-nonmetal interfaces in this chapter emphasizes the unique problems arising from the nature of the metal and the environment in specific applications.*

*Examples of corrosion problems that have arisen in the application of specific metals and alloys to specific items of Army materiel are discussed.*

*Throughout this chapter numerous alloys are discussed. Some of these alloys are proprietary, and their designations are registered trademarks. Mention of the registered trademark of a proprietary alloy in no way constitutes an endorsement by the US Government.*

### 4-1 INTRODUCTION

A modern military force uses a tremendous array of materiel items that perform a wide range of functions. The materiel design processes select appropriate materials for specific applications. Each metal and alloy used in Army materiel is chosen because of its particular properties.

Properties of metals and alloys may be characterized as physical properties, chemical and electrochemical characteristics, mechanical properties, fabrication characteristics, and economic costs and availability. The

properties of metals can be described by a wide range of attributes, and these attributes must fall within certain limits if they are to impart utility in an item of materiel. Table 4-1 lists some chemical and electrochemical characteristics, and Table 4-2 some of the economic and availability considerations in the application of a specific alloy.

The generalized material design process proceeds from statements of mission requirements through many steps, as outlined in Fig. 4-1. A statement of mission requirements might address some of the characteristics listed in Table 4-3. At each stage of the design process, the

**MIL-HDBK-735(MR)****TABLE 4-1. SELECTED CHEMICAL AND ELECTROCHEMICAL CHARACTERISTICS OF METALS AND ALLOYS**


---

|  |
|--|
| Chemical composition of bulk metal   |
| Chemical composition of microstructural phases and zones   |
| Thermodynamic reaction tendencies, i.e., relative position in electromotive force or galvanic series |
| Reaction kinetics-polarization tendencies, i.e., exchange currents of reacting systems               |
| Sorption and diffusion characteristics of hydrogen   |
| Physical and chemical characteristics of reaction products   |
| Toxicity of material and reaction products   |
| Tendency to form precipitates from solid solution  |

---

**TABLE 4-2. SELECTED ECONOMIC AND AVAILABILITY CONSIDERATIONS****Availability:**

- Required quantities
- Desired forms
- Coatings and pretreatment desired
- Uniformity
- Freedom from defects
- Delivery period after receipt of order
- Applicable specifications and standards
- Terms and conditions of ordering

**Size limitations in different forms:**

- Gage
- Length and width
- Weight

**Costs of different forms and quantities**

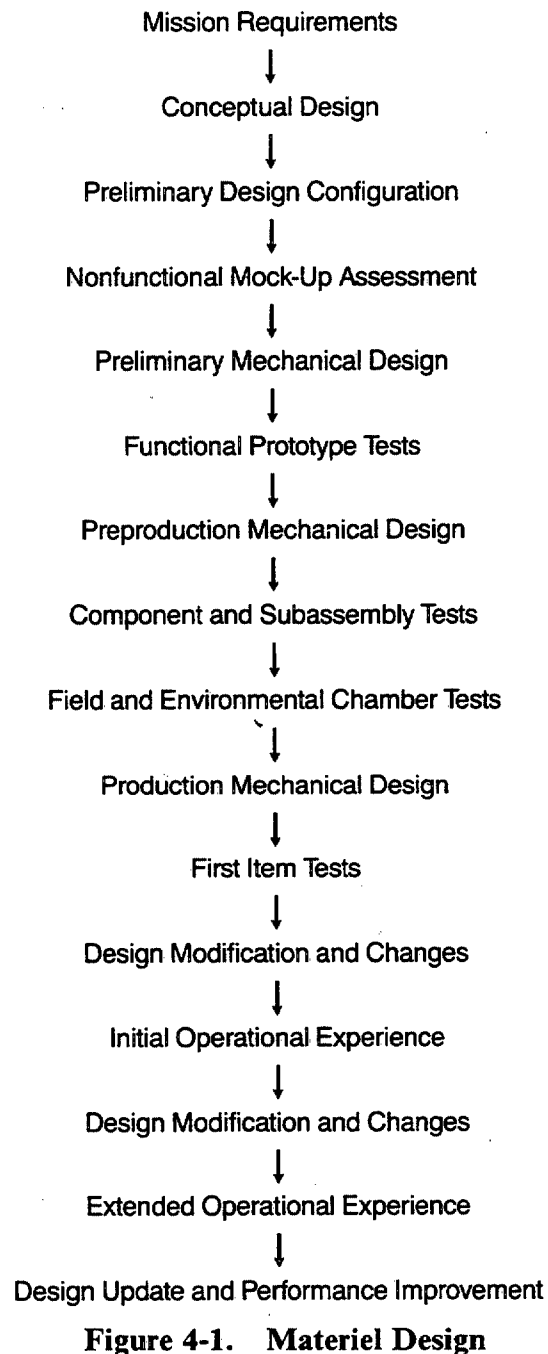
material requirements become more specific and detailed. Also the constraints and limitations of materials become more apparent. The reconciliation of performance with requirements becomes increasingly fixed. To achieve this reconciliation, the designer assesses, balances, and trades material attributes to realize an acceptable design. Fig. 4-2 illustrates limiting material problem areas for different classes of materiel components and subsystems. These are organized according to mission areas. (Ref. 1)

**4-2 ALUMINUM AND ALUMINUM ALLOYS**

The density of elemental aluminum at 20°C (68°F) is 2698.79 kg/m<sup>3</sup> (168.48 lbm/ft<sup>3</sup>). Its melting point is 660°C (1220°F). The metal is soft and malleable and is nonmagnetic.

Aluminum is alloyed to improve its mechanical properties, especially its strength. There are two basic types of alloys: One is strengthened by work hardening and the other is strengthened by heat treating.

Aluminum and aluminum alloys are available in wrought, cast, and powder forms.



4-3

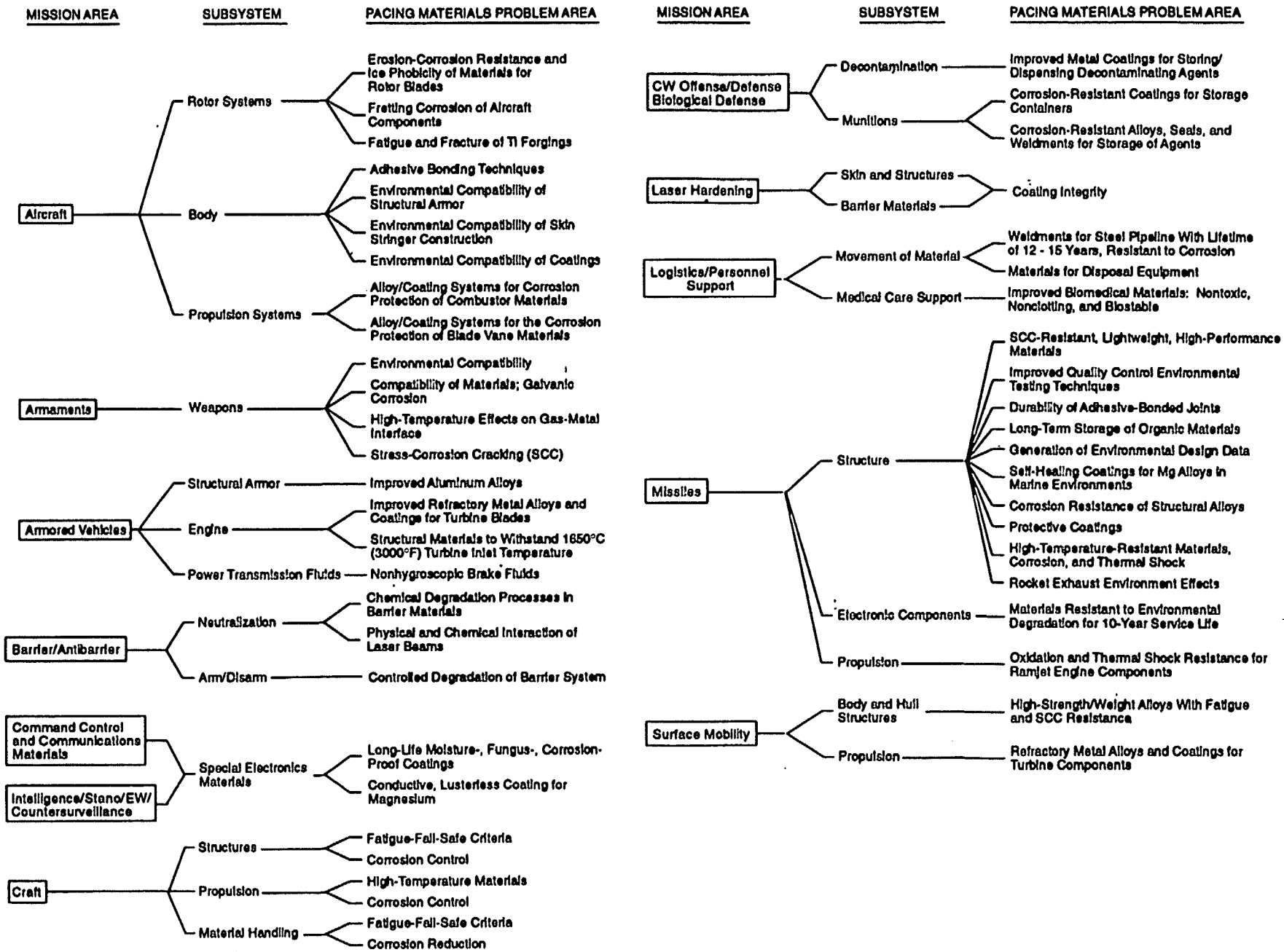


Figure 4-2. Relationship of Corrosion-Susceptible Subsystems to Mission Areas

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**TABLE 4-3. SELECTED DESIGN CONSIDERATIONS FOR A TACTICAL VEHICLE**

---

|   |
|---|
| Empty weight and dimensions                       |
| Minimum cube dimensions for transport and storage |
| Carrying capacities:                              |
| Personnel   |
| Cargo weights and dimensions                      |
| Towed weight                                      |
| Mounted weapons, armor, and equipment             |
| Overload limits                                   |
| Fuel capacity and type                            |
| Performance at nominal capacity:                  |
| Acceleration                                      |
| Speed   |
| Stopping distance                                 |
| Turning radius                                    |
| Grade limits                                      |
| Range   |
| Terrain capabilities:                             |
| Highway   |
| Off-road  |
| Obstacles   |
| Clearances  |
| Operating environments                            |
| Storage environments                              |
| Transportation modes and environments             |
| Camouflage and infrared signature                 |
| Decontamination                                   |
| Service life                                      |
| Maintainability and maintenance                   |
| Life cycle costs                                  |

---

Aluminum alloys are used in Army materiel because of their many desirable qualities:

1. High strength-to-weight ratio
2. Ready availability at a reasonable cost
3. Good corrosion resistance in many environments
4. High thermal and electrical conductivities
5. Readily formed and joined by conventional fabrication processes
6. Amenable to surface treatments that enhance corrosion resistance and impart colors
7. Nontoxic, white or colorless, and nonstaining salts
8. A wide range of properties including high strength achievable by alloying, work hardening, and thermal treatment
9. Application as a surface coating to other metals by a variety of processes.

Some examples of military application of aluminum alloys include aircraft structures; lightweight armor; tactical vehicle bodies and frames; track shoes for tracked

vehicles; road wheels; bulldozer mould boards with steel cutting edges; spades to anchor self-propelled guns when firing; and large bearing races having steel inserts for turrets, cupolas, and machine gun mounts (Ref. 1).

The commonly used designation for wrought aluminum alloys is a four-digit number. The first digit indicates the principal alloying element, as shown in Table 4-4. The other three digits have no specific relationship to alloying elements but do relate to an alloy series. For example, alloy 7175 is the first definable change in the 7075 alloy series. But the final two digits, 75, do not relate to specific alloying components in that series.

A three-digit designation is used for casting alloys. The major alloying element is indicated by the first digit. The major alloying element designation is that used for the wrought alloys and is shown in Table 4-4. Prefix letters are used to distinguish between compositions that differ in impurity or secondary alloying element contents. For example, A356 contains 0.2% iron maximum, whereas 356 does not contain iron.

**TABLE 4-4. ALUMINUM ALLOY NUMBERING SYSTEM FOR WROUGHT PRODUCTS**

---

| ALLOY DESIGNATION | PRINCIPAL ALLOYING ELEMENT |
|-------------------|----------------------------|
| 1XXX              | Commercially pure aluminum |
| 2XXX              | Copper                     |
| 3XXX              | Manganese                  |
| 4XXX              | Silicon                    |
| 5XXX              | Magnesium                  |
| 6XXX              | Magnesium-silicon          |
| 7XXX              | Zinc                       |

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Aluminum powders and particles are identified descriptively. However, aluminum-aluminum oxide alloys made from aluminum are distinguished as XAP or SAP alloys followed by a three-digit number. The XAP alloys are made from flake powder, and the SAP alloys are made from granules. The three-digit numbers are not related to a composition code. Prealloyed powders are used to make powder metallurgy products that cannot be made by conventional means or that do not develop the desired microstructure because of incompatibility of the alloying agents with aluminum. These powders are identified descriptively or by a proprietary designation.

The wrought and cast aluminum alloy designations are followed by an indication of the condition or temper of the alloy. Temper designations for aluminum alloys are described in Table 4-5. Selected wrought and cast aluminum alloys, their nominal chemical compositions, and their mechanical properties are listed in Table 4-6.

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TABLE 4-5. TEMPER DESIGNATIONS FOR ALUMINUM ALLOYS (Ref. 2)

|  |   |  |
|--|---|--|
| <p><b>F</b> As fabricated. Applies to products of shaping processes in which no special control over thermal conditions or strain hardening is employed.</p>   | <p><b>H3</b> Strain hardened and stabilized. Applies to products that are strain hardened and whose mechanical properties are stabilized by a low-temperature thermal treatment, which results in slightly lower tensile strength and improved ductility. This designation is applicable only to those alloys, which, unless stabilized, gradually age soften at room temperature. The number following this designation indicates the degree of strain hardening before the stabilization treatment.</p> | <p>the effects of cold work in flattening or straightening may not be recognized in mechanical property limits.</p>  |
| <p><b>H</b> Strain hardened (wrought products only). Applies to products that have their strength increased by strain hardening, with or without supplementary thermal treatments to produce some reduction in strength.</p>   | <p><b>H311</b> Applies to products that are strain hardened less than the amount required for a controlled H31 temper.</p>  | <p><b>T2</b> Cooled from an elevated temperature shaping process, cold worked and naturally aged to a substantially stable condition. Applies to products that are cold worked to improve strength after cooling from an elevated temperature shaping process or in which the effect of cold work in flattening or straightening is recognized in mechanical property limits.</p>  |
| <p><b>H1</b> Strain hardened only. Applies to products that are strain hardened to obtain the desired strength without supplementary thermal treatment.</p>  | <p><b>H321</b> Applies to products that are strain hardened less than the amount required for a controlled H32 temper.</p>  | <p><b>T3</b> Solution heat treated, cold worked, and naturally aged to a substantially stable condition. Applies to products that are cold worked to improve strength after solution heat treatment or in which the effect of cold work in flattening or straightening is recognized in mechanical property limits.</p>  |
| <p><b>H111</b> Applies to products that are strain hardened less than the amount required for a controlled H11 temper.</p>   | <p><b>H323</b> Applies to products that are specially fabricated to have acceptable resistance to stress-corrosion cracking.</p>  | <p><b>T4</b> Solution heat treated and naturally aged to a substantially stable condition. Applies to products that are not cold worked after solution heat treatment or in which the effect of cold work in flattening or straightening may not be recognized in mechanical property limits. (T42 indicates material is solution heat treated from the O or F temper to demonstrate response to heat treatment and naturally aged to a substantially stable condition).</p> |
| <p><b>H112</b> Applies to products that acquire some temper from shaping processes not having special control over the amount of strain hardening or thermal treatment but for which there are mechanical property limits.</p>   | <p><b>O</b> Annealed. Applies to wrought products that are annealed to obtain the lowest strength temper and to cast products that are annealed to improve ductility and dimensional stability.</p>   | <p><b>T5</b> Cooled from an elevated temperature shaping process and then artificially aged. Applies to products that are not cold worked after cooling from an elevated temperature shaping process or in which the effect of cold work in flattening or straightening may not be</p>   |
| <p><b>H2</b> Strain hardened and partially annealed. Applies to products that are strain hardened more than the desired final amount and then reduced in strength to the desired level by partial annealing. For alloys that age soften at room temperature, the H2 tempers have the same minimum tensile strength as the corresponding H3 tempers. For other alloys the H2 tempers have the same minimum tensile strength as the corresponding H1 tempers and slightly higher elongation. The number following this designation indicates the degree of strain hardening remaining after the product has been partially annealed.</p> | <p><b>T</b> Thermally treated to produce stable tempers other than F, O, or H. Applies to products that are thermally treated, with or without supplementary strain hardening, to produce stable tempers.</p>   |  |
|  | <p><b>T1</b> Cooled from an elevated temperature shaping process and naturally aged to a substantially stable condition. Applies to products that are not cold worked after cooling from an elevated temperature shaping process or in which</p>  |  |

(cont'd on next page)

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TABLE 4-5. (cont'd)

|   |   |   |
|---|---|---|
| cont'd recognized in mechanical property limits.  |   |   |
| <b>T51 Stress relieved by stretching.</b> Applies to the following products when stretched the indicated amounts after solution heat treatment or cooled from an elevated temperature shaping process:<br>Plate ..... 1.5 to 3% permanent set<br>Rod, bar, shaped, extruded tube ..... 1 to 3% permanent set<br>Drawn tube ..... 0.5 to 3% permanent set.<br>Applies directly to plate and rolled or cold-finished rod and bar that receive no further straightening after stretching. Applies to extruded rod, bar, shapes, tubing and to drawn tubing when designated as follows:<br><b>T510</b> Products that receive no further straightening after stretching.<br><b>T511</b> Products that may receive minor straightening after stretching to comply with standard tolerances. | <b>T52 Stress relieved by compressing.</b> Applies to products that are stress relieved by compressing after solution heat treatment or cooled from an elevated temperature shaping process to produce a permanent set of 1 to 5%.<br><b>T54 Stress relieved by combining stretching and compressing.</b> Applies to die forgings that are stress relieved by restriking cold in the finish die.<br><b>T6 Solution heat treated and then artificially aged.</b> Applies to products that are not cold worked after solution heat treatment or in which the effect of cold work in flattening or straightening may not be recognized in mechanical property limits. (T62 indicates material is solution heat treated from the O or F temper to demonstrate response to heat treatment and is artificially aged.)<br><b>T7 Solution heat treated and stabilized.</b> Applies to products that are stabilized after solution heat treatment to carry them beyond | the point of maximum strength to provide control of some special characteristic.<br><b>T8 Solution heat treated, cold worked, and artificially aged.</b> Applies to products that are cold worked to improve strength or in which the effect of cold work in flattening or straightening is recognized in mechanical property limits.<br><b>T9 Solution heat treated, artificially aged, and cold worked.</b> Applies to products that are cold worked to improve strength.<br><b>T10 Cooled from an elevated temperature shaping process, cold worked, and artificially aged.</b> Applies to products that are cold worked to improve strength or in which the effect of cold work in flattening or straightening is recognized in mechanical property limits.<br><b>W Solution heat treated.</b> An unstable temper applicable only to alloys that spontaneously age at room temperature after solution heat treatment. |

**NOTE:** The digits following the designations H1, H2, and H3 indicate the degree of strain hardening. For example, H12 is quarter hard and H18 is full hard. The full hard condition is achieved by approximately a 75% reduction in area.

Additional digits are added to designations T2 through T10 to indicate a variation in treatment that significantly alters the characteristics of the product. This includes tempers of stress-relieved wrought products, tempers that differ in the amount and type of cold work applied after quenching or between quenching and artificial aging, and tempers produced by special practices to control such characteristics as resistance to corrosion or dimensional stability.

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TABLE 4-6. ALUMINUM ALLOYS (Ref. 2)

| AA<br>DESIG-<br>NATION | UNS    | COMPOSITION, %* |          |          |         |         |           |            | MECHANICAL PROPERTIES**         |                                   |                                      |                 |      |
|------------------------|--------|-----------------|----------|----------|---------|---------|-----------|------------|---------------------------------|-----------------------------------|--------------------------------------|-----------------|------|
|                        |        | Cr              | Cu       | Mg       | Mn      | Si      | OTHER     | CONDITION† | YIELD<br>STRENGTH,<br>MPa (ksi) | TENSILE<br>STRENGTH,<br>MPa (ksi) | ELONGATION<br>IN 51 mm<br>(2 in.), % | HARDNESS,<br>HB |      |
| <b>Wrought</b>         |        |                 |          |          |         |         |           |            |                                 |                                   |                                      |                 |      |
| 1060                   | A91060 | —               | —        | —        | —       | —       | —         | 99.6Al min | 0                               | 28 (4.)                           | 69 (10.)                             | 43              | 19   |
| 1100                   | A91100 | —               | 0.05-0.2 | —        | —       | —       | —         | 99.0Al min | 0                               | 34 (5.)                           | 90 (13.)                             | 45              | 23   |
| 2024                   | A92024 | 0.1             | 3.8-4.9  | 1.2-1.8  | 0.3-0.9 | 0.5     | —         | —          | T4                              | 324 (47.)                         | 469 (68.)                            | 19.             | 120. |
| 3003                   | A93003 | —               | 0.05-0.2 | —        | 1.0-1.5 | 0.6     | —         | —          | H14                             | 145 (21.)                         | 152 (22.)                            | 16.             | 40.  |
| 5052                   | A95052 | 0.15-0.35       | 0.1      | 2.2-2.8  | 0.1     | —       | —         | —          | 0                               | 90 (13.)                          | 193 (28.)                            | 30              | 47.  |
| 5083                   | A95083 | 0.05-0.25       | 0.1      | 4.0-4.9  | 0.4-1.0 | 0.4     | —         | —          | 0                               | 145 (21.)                         | —                                    | —               | —    |
| 5086                   | A95086 | 0.05-0.25       | 0.1      | 3.5-4.5  | 0.2-0.7 | 0.4     | —         | —          | 0                               | 117 (17.)                         | 262 (38.)                            | 30.             | —    |
| 5154                   | A95154 | 0.05-0.35       | 0.1      | 3.1-3.9  | 0.1     | 0.25    | —         | —          | 0                               | 117 (17.)                         | 241 (35.)                            | 27              | 58   |
| 6061                   | A96061 | 0.04-0.35       | 0.15-0.4 | 0.8-1.2  | 0.15    | 0.4-0.8 | —         | —          | T6                              | 276 (40.)                         | 310 (45.)                            | 17.             | 95.  |
| 6063                   | A96063 | 0.1             | 0.1      | 0.45-0.9 | 0.1     | 0.2-0.6 | —         | —          | T6                              | 214 (31.)                         | 241 (35.)                            | 18.             | 73.  |
| 7075                   | A97075 | 0.18-0.28       | 1.2-2.0  | 2.1-2.9  | 0.3     | 0.40    | 5.1-6.1Zn | —          | T6                              | 503 (73.)                         | 572 (83.)                            | 11              | 150. |
| <b>Cast</b>            |        |                 |          |          |         |         |           |            |                                 |                                   |                                      |                 |      |
| 242.0                  | A02420 | 0.25            | 3.5-4.5  | 1.2-1.8  | 0.35    | 0.7     | 1.7-2.3Ni | —          | S-T571                          | —                                 | 200 (29.)                            | —               | —    |
| 295.0                  | A02950 | —               | 4.0-5.0  | 0.03     | 0.35    | 0.7-1.5 | —         | —          | S-T4                            | —                                 | 200 (29.)                            | 6.              | —    |
| A332.0                 | A13320 | —               | 0.5-1.5  | 0.7-1.3  | 0.35    | 11.-13. | 2.0-3.0Ni | —          | P-T551                          | —                                 | 214 (31.)                            | —               | —    |
| B443.0                 | A24430 | —               | 0.15     | 0.05     | 0.35    | 4.5-6.0 | —         | —          | S-F                             | —                                 | 117 (17.)                            | 3.              | —    |
| 514.0                  | A05140 | —               | 0.15     | 3.5-4.5  | 0.35    | 0.35    | —         | —          | S-F                             | —                                 | 152 (22.)                            | 6.              | —    |
| 520.0                  | A05200 | —               | 0.25     | 9.5-10.6 | 0.15    | 0.25    | —         | —          | S-T4                            | 152 (22.)                         | 290 (42.)                            | 12.             | —    |

\*Single values are maximum values.

\*\*Typical room temperature properties.

†S = sand cast; P = permanent mold cast; Other = temper designations.

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### 4-2.1 WROUGHT ALUMINUM ALLOYS

The 1XXX, 3XXX, 4XXX, and 5XXX series are nonheat treatable. The heat-treatable alloys are the 2XXX, 6XXX, and 7XXX series.

Commercially pure aluminum alloys (1XXX series) have relatively low strength but good ductility. The 3XXX series (aluminum-manganese and aluminum-manganese-magnesium) have higher strengths than the 1XXX series alloys, which are developed by strain hardening, or stretching. The 5XXX series alloys (aluminum-magnesium) are the strongest of the nonheat-treatable alloys. The 5XXX alloys are readily fabricated without degrading the mechanical properties. They provide higher strength per unit cost than the 1XXX or 3XXX alloys and are widely used in watercraft. Their higher strength is the result of the solid solution hardening effect of magnesium. Additional strength may be developed by strain hardening. The aluminum-silicon alloys (4XXX series) are low-strength alloys and are used for brazing and welding products and as a cladding in architectural products.

The heat-treatable aluminum alloys are the alloys having the highest strength. Strengthening is produced in these alloys by (1) a solution heat treatment at 460° to 565°C (860° to 1050°F) to dissolve soluble alloying elements, (2) quenching, or rapid cooling, to retain them in solid solution, and (3) a precipitation, or aging, treatment. The aging is accomplished either naturally at room temperature or artificially at 116° to 193°C (240° to 380°F). Aging precipitates the alloying elements from the solid solution in an optimum size and distribution. The precipitated phases give the heat-treatable alloys their high strength. The corrosion resistance of the heat-treatable alloys is strongly influenced by the presence of copper in the alloys. The corrosion resistance of the 6XXX series alloys (aluminum-magnesium-silicon), which may contain only impurity amounts of copper, approaches that of the nonheat-treatable alloys. The 2XXX series

alloys (aluminum-copper, aluminum-copper-magnesium, and aluminum-copper-silicon-magnesium) contain copper as the principal alloying element. The 7XXX series alloys (aluminum-zinc-magnesium and aluminum-zinc-magnesium-copper) include both copper-containing and noncopper-containing alloys. The noncopper-containing alloys have high resistance to corrosion, whereas the 2XXX series alloys and the copper-containing alloys of the 7XXX series have significantly lower resistance to corrosion. The high-strength, copper-containing alloys are widely used in aerospace applications, and they are being used increasingly in other applications that benefit from their high strength-to-weight ratios, such as light-weight armor.

The mechanical properties of some wrought aluminum alloys are given in Table 4-7. This list includes the fatigue limit and fracture toughness parameters. A list of typical applications for wrought aluminum alloys is given in Table 4-8.

A relatively recent aluminum alloy development is aluminum-lithium. Substitution of an aluminum-lithium-copper-x alloy with 2.4 to 2.77 weight % lithium in an existing aircraft design could reduce weight by 8 to 10%. Lithium has a density of 530 kg/m<sup>3</sup> (33.1 lbm/ft<sup>3</sup>) compared to 2700 kg/m<sup>3</sup> (168.6 lbm/ft<sup>3</sup>) for aluminum. The solid solubility of lithium in aluminum approaches 3% by weight, or about 10 atom %. Lithium increases the modulus of elasticity, or stiffness, by 6% (Ref. 4). Therefore, new aircraft designs that take advantage of the increased stiffness of the alloy and its decreased density could provide overall weight reductions of 15%.

In commercial production aluminum-lithium alloys will cost 2 to 3 times more than conventional alloys because formation of these alloys is significantly more difficult. However, the added costs for aircraft would be more than offset by decreased fuel consumption and/or increased payload.

TABLE 4-7. TYPICAL MECHANICAL PROPERTIES OF WROUGHT ALUMINUM ALLOYS (Ref. 3)

| ALLOY DESIGNATION |      | TEMPER    | TENSILE STRENGTH, |       | YIELD STRENGTH, |       | FATIGUE LIMIT, |       | ELON-<br>GATION,<br>% | FRACTURE TOUGHNESS  |      |  |      |   |      |
|-------------------|------|-----------|-------------------|-------|-----------------|-------|----------------|-------|-----------------------|---|------|--|------|---|------|
| UNS               | AA   |           | MPa               | (ksi) | MPa             | (ksi) | MPa            | (ksi) |                       | LONGITU-<br>DINAL,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) |      | LONG<br>TRANSVERSE,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) |      | SHORT<br>TRANSVERSE,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) |      |
| A91060            | EC   | O         | 83                | (12)  | 28              | (4)   |                |       | 23                    |   |      |  |      |   |      |
|                   |      | H19       | 186               | (27)  | 165             | (24)  | 48             | (7)   | 1.5                   |   |      |  |      |   |      |
|                   | 1060 | O         | 69                | (10)  | 28              | (4)   | 21             | (3)   | 43                    |   |      |  |      |   |      |
|                   |      | H18       | 131               | (19)  | 124             | (18)  | 45             | (6.5) | 6                     |   |      |  |      |   |      |
| A91100            | 1100 | O         | 90                | (13)  | 34              | (5)   | 34             | (5)   | 35                    |   |      |  |      |   |      |
|                   |      | H18       | 165               | (24)  | 152             | (22)  | 62             | (9)   | 5                     |   |      |  |      |   |      |
| A92011            | 2011 | T3        | 379               | (55)  | 296             | (43)  | 124            | (18)  | 15                    |   |      |  |      |   |      |
| A92014            | 2014 | T8        | 407               | (59)  | 310             | (45)  | 124            | (18)  | 12                    |   |      |  |      |   |      |
|                   |      | T451      | 427               | (62)  | 290             | (42)  | 138            | (20)  | 20                    | 44  | (40) | 42   | (38) | 23  | (21) |
|                   |      | T651      | 483               | (70)  | 414             | (60)  | 124            | (18)  | 13                    | 26  | (24) | 22   | (20) | 20  | (18) |
| A92017            | 2017 | T451      | 427               | (62)  | 276             | (40)  | 124            | (18)  | 22                    |   |      |  |      |   |      |
| A92020            | 2020 | T651      | 579               | (84)  | 531             | (77)  |                |       | 7                     | 23  | (21) | 20   | (18) |   |      |
| A92021            | 2021 | T81       | 503               | (73)  | 434             | (63)  |                |       | 9                     | 30  | (27) | 25   | (23) |   |      |
| A92024            | 2024 | T4, T351  | 469               | (68)  | 324             | (47)  | 138            | (20)  | 20                    | 49  | (45) | 44   | (40) | 23  | (21) |
|                   |      | T81, T851 | 448               | (65)  | 414             | (60)  |                |       | 6                     | 26  | (24) | 21   | (19) | 18  | (16) |
| A92025            | 2025 | T6        | 400               | (58)  | 255             | (37)  | 124            | (18)  | 19                    |   |      |  |      |   |      |
| A92048            | 2048 | T851      | 483               | (70)  | 455             | (66)  |                |       |                       | 37  | (34) | 33   | (30) | 27  | (25) |
| A92117            | 2117 | T4        | 296               | (43)  | 165             | (24)  | 97             | (14)  | 27                    |   |      |  |      |   |      |
| A92124            | 2124 | T851      | 469               | (68)  | 434             | (63)  | 90             | (13)  | 8                     | 30  | (27) | 25   | (23) | 23  | (21) |
| A92214            | 2214 |           |                   |       |                 |       |                |       | 11                    |   |      |  |      |   |      |
| A92218            | 2218 | T72       | 331               | (48)  | 255             | (37)  |                |       | 17                    | 44  | (40) | 44   | (40) |   |      |
| A92219            | 2219 | T351      | 359               | (52)  | 248             | (36)  |                |       | 11                    | 44  | (40) | 37   | (34) | 36  | (33) |
|                   |      | T37       | 393               | (57)  | 317             | (46)  |                |       | 10                    | 44  | (40) | 40   | (36) |   |      |
|                   |      | T62       | 414               | (60)  | 290             | (42)  | 103            | (15)  | 10                    | 44  | (40) | 40   | (36) |   |      |
|                   |      | T851      | 455               | (66)  | 352             | (51)  | 103            | (15)  | 10                    | 38  | (35) | 36   | (33) |   |      |
|                   |      | T87       | 476               | (69)  | 393             | (57)  | 103            | (15)  | 10                    | 33  | (30) | 31   | (28) | 26  | (24) |
| A92419            | 2419 |           |                   |       |                 |       |                |       | 10                    |   |      |  |      |   |      |
| A92618            | 2618 | T6        | 441               | (64)  | 372             | (54)  |                |       | 10                    | 33  | (30) | 29   | (26) | 20  | (18) |
| A93003            | 3003 | O         | 110               | (16)  | 41              | (6)   | 48             | (7)   | 30                    |   |      |  |      |   |      |
|                   |      | H18       | 200               | (29)  | 186             | (27)  | 69             | (10)  | 4                     |   |      |  |      |   |      |
| A93004            | 3004 | O         | 179               | (26)  | 69              | (10)  | 97             | (14)  | 20                    |   |      |  |      |   |      |
|                   |      | H38       | 283               | (41)  | 248             | (36)  | 110            | (16)  | 5                     |   |      |  |      |   |      |

(cont'd on next page)

TABLE 4-7. (cont'd)

| ALLOY DESIGNATION |      | TEMPER  | TENSILE STRENGTH, |       | YIELD STRENGTH, |       | FATIGUE LIMIT, |       | ELON- GATION,<br>% | FRACTURE TOUGHNESS  |  |   |      |    |      |
|-------------------|------|---------|-------------------|-------|-----------------|-------|----------------|-------|--------------------|---|--|---|------|----|------|
| UNS               | AA   |         | MPa               | (ksi) | MPa             | (ksi) | MPa            | (ksi) |                    | LONGITU-<br>DINAL,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) | LONG<br>TRANSVERSE,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) | SHORT<br>TRANSVERSE,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) |      |    |      |
| A93105            | 3105 | O       | 117               | (17)  | 55              | ( 8)  |                |       | 24                 |   |  |   |      |    |      |
|                   |      | H25     | 179               | (26)  | 159             | (23)  |                |       | 8                  |   |  |   |      |    |      |
| A94032            | 4032 | T6      | 379               | (55)  | 317             | (46)  | 110            | (16)  | 9                  |   |  |   |      |    |      |
| A95005            | 5005 | O       | 124               | (18)  | 41              | ( 6)  |                |       | 25                 |   |  |   |      |    |      |
|                   |      | H38     | 200               | (29)  | 186             | (27)  |                |       | 5                  |   |  |   |      |    |      |
| A95050            | 5050 | O       | 145               | (21)  | 55              | ( 8)  | 83             | (12)  | 24                 |   |  |   |      |    |      |
|                   |      | H38     | 221               | (32)  | 200             | (29)  | 97             | (14)  | 6                  |   |  |   |      |    |      |
| A95052            | 5052 | O       | 193               | (28)  | 90              | (13)  | 110            | (16)  | 25                 |   |  |   |      |    |      |
|                   |      | H38     | 290               | (42)  | 255             | (37)  | 138            | (20)  | 7                  |   |  |   |      |    |      |
| A95056            | 5056 | O       | 290               | (42)  | 152             | (22)  | 138            | (20)  | 35                 |   |  |   |      |    |      |
|                   |      | H18     | 434               | (63)  | 407             | (59)  | 152            | (22)  | 10                 |   |  |   |      |    |      |
| A95083            | 5083 | O       | 290               | (42)  | 145             | (21)  |                |       | 22                 | 66  | (60)   | 66  | (60) |    |      |
|                   |      | H321    | 317               | (46)  | 228             | (33)  | 159            | (23)  | 16                 | 49  | (45)   | 43  | (39) | 25 | (23) |
| A95086            | 5086 | O       | 262               | (38)  | 117             | (17)  |                |       | 22                 |   |  |   |      |    |      |
|                   |      | H32     |                   |       |                 |       |                |       |                    |   |  |   |      |    |      |
|                   |      | H116    | 290               | (42)  | 207             | (30)  |                |       | 12                 | 56  | (51)   | 49  | (45) | 29 | (26) |
|                   |      | H117    |                   |       |                 |       |                |       |                    |   |  |   |      |    |      |
| A95154            | 5154 | O       | 241               | (35)  | 117             | (17)  | 117            | (17)  | 27                 |   |  |   |      |    |      |
|                   |      | H38     | 331               | (48)  | 269             | (39)  | 145            | (21)  | 10                 |   |  |   |      |    |      |
| A95252            | 5252 | H25     | 234               | (34)  | 172             | (25)  |                |       | 11                 |   |  |   |      |    |      |
|                   |      | H38,H28 | 283               | (41)  | 241             | (35)  |                |       | 5                  |   |  |   |      |    |      |
| A95254            | 5254 | O       | 241               | (35)  | 117             | (17)  | 117            | (17)  | 27                 |   |  |   |      |    |      |
|                   |      | H38     | 331               | (48)  | 269             | (39)  | 145            | (21)  | 10                 |   |  |   |      |    |      |
| A95454            | 5454 | O       | 241               | (35)  | 117             | (17)  |                |       | 22                 |   |  |   |      |    |      |
|                   |      | H34     | 303               | (44)  | 241             | (35)  |                |       | 10                 |   |  |   |      |    |      |
| A95456            | 5456 | O       | 310               | (45)  | 159             | (23)  |                |       | 24                 |   |  |   |      |    |      |
|                   |      | H321    | 352               | (51)  | 255             | (37)  |                |       | 16                 | 49  | (45)   | 49  | (45) | 34 | (31) |
|                   |      | H343    | 386               | (56)  | 296             | (43)  |                |       | 8                  |   |  |   |      |    |      |
|                   |      | H112    |                   |       |                 |       |                |       |                    | 42  | (38)   | 40  | (36) |    |      |
| A96005            | 6005 | T5      | 310               | (45)  | 276             | (40)  | 97             | (14)  | 12                 |   |  |   |      |    |      |
| A96061            | 6061 | O       | 124               | (18)  | 55              | ( 8)  | 62             | ( 9)  | 25                 |   |  |   |      |    |      |
|                   |      | T4      | 241               | (35)  | 145             | (21)  | 97             | (14)  | 22                 |   |  |   |      |    |      |
|                   |      | T651    | 310               | (45)  | 276             | (40)  | 97             | (14)  | 12                 | 41  | (37)   | 34  | (31) | 23 | (21) |

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(cont'd on next page)

TABLE 4-7. (cont'd)

| ALLOY DESIGNATION |      | TEMPER | TENSILE STRENGTH, |       | YIELD STRENGTH, |       | FATIGUE LIMIT, |       | ELONGATION,<br>% | FRACTURE TOUGHNESS   |      |   |      |  |      |
|-------------------|------|--------|-------------------|-------|-----------------|-------|----------------|-------|------------------|--|------|---|------|--|------|
| UNS               | AA   |        | MPa               | (ksi) | MPa             | (ksi) | MPa            | (ksi) |                  | LONGITUDINAL,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) |      | LONG TRANSVERSE,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) |      | SHORT TRANSVERSE,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) |      |
| A96063            | 6063 | T4     | 172               | (25)  | 90              | (13)  |                |       | 22               |  |      |   |      |  |      |
|                   |      | T6     | 241               | (35)  | 214             | (31)  | 69             | (10)  | 12               |  |      |   |      |  |      |
|                   |      | T832   | 290               | (42)  | 269             | (39)  |                |       | 12               |  |      |   |      |  |      |
| A96066            | 6066 | O      | 152               | (22)  | 83              | (12)  |                |       | 18               |  |      |   |      |  |      |
|                   |      | T4     | 359               | (52)  | 207             | (30)  |                |       | 18               |  |      |   |      |  |      |
|                   |      | T6     | 393               | (57)  | 359             | (52)  | 110            | (16)  | 12               |  |      |   |      |  |      |
| A96070            | 6070 | T6     | 379               | (55)  | 352             | (51)  | 97             | (14)  | 10               |  |      |   |      |  |      |
| A96101            | 6101 | T6     | 221               | (32)  | 193             | (28)  |                |       | 15               |  |      |   |      |  |      |
| A96262            | 6262 | T9     | 400               | (58)  | 379             | (55)  | 90             | (13)  | 10               |  |      |   |      |  |      |
| A96463            | 6463 | T1     | 152               | (22)  | 90              | (13)  | 69             | (10)  | 20               |  |      |   |      |  |      |
|                   |      | T6     | 241               | (35)  | 214             | (31)  | 69             | (10)  | 12               |  |      |   |      |  |      |
| A97001            | 7001 | O      | 255               | (37)  | 152             | (22)  |                |       | 14               |  |      |   |      |  |      |
|                   |      | T6     | 676               | (98)  | 627             | (91)  | 152            | (22)  | 9                |  |      |   |      |  |      |
|                   |      | T75    | 579               | (84)  | 496             | (72)  |                |       | 12               | 26   | (24) | 22  | (20) |  |      |
|                   |      | T73    |                   |       | 414             | (60)  |                |       | 12               | 33   | (30) |   |      |  |      |
| A97005            | 7005 | T53    | 393               | (57)  | 345             | (50)  |                |       | 15               |  |      |   |      |  |      |
|                   |      | T6351  |                   |       | 324             | (47)  |                |       |                  | 52   | (47) | 44  | (40) | 31   | (28) |
| A97039            | 7039 | T6151  | 455               | (66)  | 379             | (55)  |                |       | 13               | 53   | (48) | 44  | (40) | 33   | (30) |
|                   |      | T63    | 434               | (63)  | 365             | (53)  |                |       | 13               | 48   | (44) | 40  | (36) | 25   | (23) |
|                   |      | T64    | 434               | (63)  | 372             | (54)  |                |       |                  | 44   | (40) | 44  | (40) | 33   | (30) |
| A97049            | 7049 | T73    | 531               | (77)  | 476             | (69)  |                |       | 11               | 32   | (29) | 29  | (26) | 22   | (20) |
| A97050            | 7050 | T736   | 558               | (81)  | 503             | (73)  |                |       | 11               | 38   | (35) | 30  | (27) | 24   | (22) |
| A97075            | 7075 | T6     | 572               | (83)  | 503             | (73)  | 159            | (23)  | 11               | 29   | (26) | 25  | (23) | 20   | (18) |
|                   |      | T76    | 538               | (78)  | 469             | (68)  |                |       | 12               | 30   | (27) | 26  | (24) | 21   | (19) |
|                   |      | T73    | 503               | (73)  | 434             | (63)  |                |       | 13               | 33   | (30) | 27  | (25) | 22   | (20) |
| A97079            | 7079 | T651   | 538               | (78)  | 469             | (68)  | 159            | (23)  | 14               | 30   | (27) | 25  | (23) | 20   | (18) |
| A97175            | 7175 | T66    |                   |       |                 |       |                |       |                  | 32   | (29) | 27  | (25) | 25   | (23) |
|                   |      | T736   | 531               | (77)  | 483             | (70)  |                |       | 11               | 36   | (33) | 32  | (29) | 26   | (24) |
| A97178            | 7178 | T6     | 607               | (88)  | 538             | (78)  |                |       | 10               | 24   | (22) | 23  | (21) | 16   | (15) |
|                   |      | T76    | 572               | (83)  | 503             | (73)  |                |       | 11               | 30   | (27) | 24  | (22) | 19   | (17) |
| A97475            | 7475 | T651   | 558               | (81)  | 490             | (71)  |                |       | 12               | 44   | (40) | 38  | (35) | 30   | (27) |
|                   |      | T7651  | 531               | (77)  | 462             | (67)  |                |       | 12               | 47   | (43) | 42  | (38) | 32   | (29) |
|                   |      | T7351  |                   |       |                 |       |                |       |                  | 55   | (50) | 49  | (45) | 36   | (33) |



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TABLE 4-8. TYPICAL APPLICATIONS FOR WROUGHT ALUMINUM ALLOYS (Ref. 3)

| ALLOY  | DESIGNATION | APPLICATIONS OF ALLOYS  |
|--------|-------------|---|
| UNS    | AA<br>EC    | Electrical conductors   |
| A91060 | 1060        | Chemical equipment, railroad tank cars  |
| A91100 | 1100        | Sheet metal work, spun hollowware, fin stock  |
| A92011 | 2011        | Screw machine products  |
| A92014 | 2014        | Truck frames, aircraft structures   |
| A92017 | 2017        | Screw machine products, fittings  |
| A92020 | 2020        | Structural use at high temperatures   |
| A92021 | 2021        | High-strength weldments, cryogenics   |
| A92024 | 2024        | Aircraft structures, truck wheels, hard hats, screw machine products  |
| A92048 | 2048        | Aircraft structural parts   |
| A92025 | 2025        | Forgings, aircraft propellers   |
| A92117 | 2117        | Rivets  |
| A92124 | 2124        | As 2024   |
| A92214 | 2214        | As 2014   |
| A92218 | 2218        | Jet engine impellers and rings  |
| A92219 | 2219        | Structural uses at high temperatures to 316°C (601°F) high-strength weldments   |
| A92419 | 2419        | As 2219   |
| A92618 | 2618        | Aircraft engines, structural uses at elevated temperatures  |
| A93003 | 3003        | Pressure vessels, storage tanks, chemical equipment   |
| A93004 | 3004        | Sheet metal work, storage tanks   |
| A93105 | 3105        | Residential siding, mobile homes, sheet metal work  |
| A94032 | 4032        | Pistons   |
| A95005 | 5005        | Appliances, utensils, electrical conductor  |
| A95050 | 5050        | Builder's hardware, refrigerator trim, coiled tubes   |
| A95052 | 5052        | Sheet metal work, hydraulic tube, appliances  |
| A95056 | 5056        | Cable sheathing, rivets for magnesium, screen wire, zippers   |
| A95083 | 5083        | Marine structures, unfired welded pressure vessels, automobiles, aircraft cryogenics, armor, television towers, drilling rigs, transportation equipment, missile components |
| A95086 | 5086        |   |
| A95090 | 5090        | High-strength, corrosion-resistant sheet  |
| A95154 | 5154        | Welded structures, storage tanks, pressure vessels, saltwater service   |
| A95252 | 5252        | Automotive and appliance trim   |
| A95254 | 5254        | Hydrogen peroxide and other chemical storage vessels  |
| A95454 | 5454        | Welded structures, pressure vessels, marine service   |
| A95456 | 5456        | High-strength welded structures, storage tanks, pressure vessels, marine applications   |
| A96005 | 6005        | Heavy-duty structures requiring good corrosion resistance, truck and marine railroad cars, furniture, pipelines   |
| A96053 | 6053        | Pipe railing, furniture, architectural extrusions   |
| A96066 | 6066        | Forgings and extrusions for welded structures   |
| A96070 | 6070        | Heavy-duty welded structures, pipelines   |
| A96101 | 6101        | High-strength bus conductors  |
| A96201 | 6201        | High-strength electric conductor wire   |
| A96262 | 6262        | Screw machine products  |
| A96463 | 6463        | Extruded architectural and trim sections  |
| A97001 | 7001        | High-strength structures  |
| A97005 | 7005        | Weldable structures, mobile bridges, dump trucks  |
| A97039 | 7039        | Welded cryogenic and missile applications, armor  |
| A97049 | 7049        | Forgings for aircraft and other structures  |
| A97050 | 7050        | Aircraft structural parts   |
| A97075 | 7075        | Aircraft and other high-strength structures   |
| A97079 | 7079        | Structural parts for aircraft   |
| A97175 | 7175        | Forgings for aircraft and other structures  |
| A97178 | 7178        | Aircraft and other structures   |
| A97575 | 7475        | Sheet and plate for aircraft and other structures   |

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Mechanical properties of some aluminum-lithium alloys are shown in Table 4-9, whereas the nominal compositions are listed in Table 4-10. The conventional high-strength alloys 2024 and 7075 are shown for comparison. Alloy 2090 is considered a replacement for 7075-T6X. A T-8-type temper (T8 E41) is being used for 2090 sheet, plate, and extrusion products that are cold worked to improve strength and toughness. A stress-corrosion resistant, T6 E203 is being used for forgings.

Aluminum-lithium alloys exhibit brittle behavior. Studies suggest that the brittleness results from the formation of a liquid phase as discrete particles along the grain boundary (Ref. 5). The liquid phase is produced at room temperature and below by impurity elements in the alloy. Several elements—sodium, potassium, cesium, mercury, and thallium—form binary alloys with aluminum at these temperatures. In addition, low-melting ternary and quaternary alloys are also possible. The solution to this problem is to exclude impurity elements from the production of aluminum-lithium alloys.

#### 4-2-1.1 Types of Corrosion

Although aluminum is an active metal, as indicated in the electromotive force series of Table 2-2, it is resistant to corrosion in many environments. The corrosion resistance of aluminum results from the formation of a passive oxide

**TABLE 4-10. COMPOSITION OF SOME ALUMINUM-LITHIUM ALLOYS (Ref. 4)**

| ALLOY | NOMINAL COMPOSITION, wt% |     |     |     |     |     |     |
|-------|--------------------------|-----|-----|-----|-----|-----|-----|
|       | Cu                       | Mg  | Mn  | Zr  | Li  | Zn  | Cr  |
| 2090  | 2.8                      | —   | —   | 0.1 | 2.2 | —   | —   |
| 8091  | 2.0                      | 0.9 | —   | 0.1 | 2.6 | —   | —   |
| 2091  | 2.2                      | 1.5 | —   | 0.1 | 2.0 | —   | —   |
| 8090  | 1.3                      | 1.0 | —   | 0.1 | 2.5 | —   | —   |
| 2024  | 4.4                      | 1.5 | 0.6 | —   | —   | —   | —   |
| 7075  | 1.6                      | 2.5 | —   | —   | —   | 5.6 | 0.2 |

From *Light Metal Age*, "Advanced Aluminum Materials for Aerospace Applications", August 1986. These tables are the only portions of the article used.

film, which is 0.005- to 0.010- $\mu\text{m}$  ( $1.97 \times 10^{-4}$  to  $3.94 \times 10^{-4}$ -mil) thick in air. A thin protective film is also formed in water at ambient temperatures. As temperature increases, the film becomes thicker and more protective. However, the protective film does not form in water or steam above approximately 230°C (446°F).

The general corrosion resistance of wrought aluminum alloys is shown in Table 4-11, which also shows the resistance to stress-corrosion cracking.

**TABLE 4-9. MECHANICAL PROPERTIES OF ALUMINUM-LITHIUM ALLOYS (Ref. 4)**

| ALLOY      | TENSILE    | YIELD      | ELONGATION, | YOUNG'S                                  | DENSITY,                                 |
|------------|------------|------------|-------------|--|--|
|            | STRENGTH,  | STRENGTH,  |             | MODULUS,                                 | DENSITY,                                 |
|            | MPa (ksi)  | MPa (ksi)  | %           | MPa (ksi)                                | kg/m <sup>3</sup> (lbm/ft <sup>3</sup> ) |
| 7075-T6    | 537.8 (78) | 468.8 (68) | 7           | 71.7 $\times 10^3$ (10.4 $\times 10^3$ ) | 2810 (175.4)                             |
| 2090-T8E41 | 565.4 (82) | 517.1 (75) | 6           | 78.6 $\times 10^3$ (11.4 $\times 10^3$ ) | 2600 (162.3)                             |
| 8091-T651  | 530.9 (77) | 461.9 (67) | 6           | 80.0 $\times 10^3$ (11.6 $\times 10^3$ ) | 2550 (159.2)                             |
| 2024-T3    | 434.4 (63) | 289.6 (42) | 8           | 73.1 $\times 10^3$ (10.6 $\times 10^3$ ) | 2780 (173.5)                             |
| 2091-T6X   | 468.8 (68) | 372.3 (54) | 12          | 78.6 $\times 10^3$ (11.4 $\times 10^3$ ) | 2580 (161.1)                             |
| 8090-T651  | 482.6 (70) | 427.5 (62) | 6           | 79.3 $\times 10^3$ (11.5 $\times 10^3$ ) | 2540 (158.6)                             |

From *Light Metal Age*, "Advanced Aluminum Materials for Aerospace Applications", August 1986. These tables are the only portions of the article used.

**TABLE 4-11. GENERAL AND STRESS CORROSION RESISTANCE OF WROUGHT ALUMINUM ALLOYS (Ref. 3)**

| ALLOY DESIGNATION |      | TEMPER           | CORROSION RESISTANCE FIRST LETTER:*<br>GENERAL CORROSION,<br>SECOND LETTER:**<br>STRESS CORROSION |                    | Estimate of the highest sustained tension stress at which test specimens of different orientations to the grain structure would not fail in the 3.5% NaCl alternate immersion test in 84 days. |   |                            |                                       |  |                                  |
|-------------------|------|------------------|---|--------------------|--|---|----------------------------|---------------------------------------|--|----------------------------------|
| UNS               | AA   |                  | TEST DIRECTION  | PLATE<br>MPa (ksi) | ROLLED ROD + BAR<br>MPa (ksi)  | EXTRUDED SHAPES SECTION THICKNESS<br>6-25 mm (0.24-0.98 in.)<br>MPa (ksi) |                            | 30-75 mm (1.18-2.95 in.)<br>MPa (ksi) |  | FORGINGS<br>MPa (ksi)            |
| A96005            | 6005 | T51              | B   | A                  |  |   |                            |                                       |  |                                  |
| A96061            | 6061 | O<br>T4<br>T6    | B<br>B<br>B   | A<br>B<br>A        | L††<br>S   | >262 (>38)<br>>110 (>16)  |                            |                                       |  | >110 (>16)                       |
| A96063            | 6063 | T4<br>T6<br>T832 | A<br>A<br>A   | A<br>A<br>A        |  |   |                            |                                       |  |                                  |
| A96066            | 6066 | O<br>T4<br>T6    | C<br>C<br>C   | A<br>B<br>B        | S  |   |                            |                                       |  | >179 (>26)                       |
| A96070            | 6070 | T6               | B   | B                  |  |   |                            |                                       |  |                                  |
| A96101            | 6101 | T6               | A   | A                  |  |   |                            |                                       |  |                                  |
| A96262            | 6262 | T9               | B   | A                  |  |   |                            |                                       |  |                                  |
| A96463            | 6463 | T1<br>T6         | A<br>A  | A<br>A             |  |   |                            |                                       |  |                                  |
| A97001            | 7001 | T6<br>T75<br>T73 | C<br>C<br>C   | C<br>C<br>B        | L<br>S<br>S  | 345 (50)<br>172 (25)<br>310 (45)  |                            |                                       |  | 345 (50)<br>172 (25)<br>310 (45) |
| A97005            | 7005 | T53<br><br>T6351 | A<br><br>A  | C<br><br>C         | L<br>T<br>S<br>L<br>T<br>S   | 69 (10)†<br>≈200 (≈29)<br>≈200 (≈29)<br><138 (<20)                        | >331 (>48)†<br>>310 (>45)† | >331 (>48)†<br>241 (35)†<br>69 (10)†  |  |                                  |

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\*Ratings A through D are relative ratings in decreasing order of merit based on exposures to sodium chloride solution by intermittent spraying or immersion. Alloys with A and B ratings can be used in industrial and seacoast atmospheres without protection; other alloys should be protected.

\*\*Stress-corrosion cracking ratings are based on service experience and on laboratory tests of specimens exposed to the 3.5% sodium chloride alternate immersion test:

A = No known instance of failure in service or in laboratory tests

B = No known instance of failure in service; limited failures in laboratory tests of short transverse specimens

C = Service failures with sustained tension stress acting in short transverse direction relative to grain structure; limited failures in laboratory tests of long transverse specimens

D = Limited service failures with sustained longitudinal or long transverse stress.

†Specimens exposed in inland industrial atmosphere, which for these alloys provides more realistic values than alternate immersion in 3.5% NaCl

††L, S, and T are defined in par. 2-2.9.2.

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TABLE 4-11. (cont'd)

| ALLOY DESIGNATION |      | TEMPER       | CORROSION RESISTANCE<br>FIRST LETTER:* |            | Estimate of the highest sustained tension stress at which test specimens of different orientations to the grain structure would not fail in the 3.5% NaCl alternate immersion test in 84 days. |                    |                               |   |            |                                       |                       |
|-------------------|------|--------------|--|------------|--|--------------------|-------------------------------|---|------------|---------------------------------------|-----------------------|
| UNS               | AA   |              | GENERAL CORROSION,<br>SECOND LETTER:** |            | TEST DIRECTION   | PLATE<br>MPa (ksi) | ROLLED ROD + BAR<br>MPa (ksi) | EXTRUDED SHAPES SECTION THICKNESS<br>6-25 mm (0.24-0.98 in.)<br>MPa (ksi) |            | 30-75 mm (1.18-2.95 in.)<br>MPa (ksi) | FORGINGS<br>MPa (ksi) |
| A97039            | 7039 | T6151<br>T63 | C                                      | D          | S  | <34 (<5)           |                               |   |            |                                       |                       |
|                   |      |              | C                                      | D          | L  | >290 (>42)†        |                               |   |            |                                       |                       |
|                   |      | T64          | C                                      | D          | T  | 241 (35)           |                               |   |            |                                       |                       |
|                   |      |              |  | S          | 48 (7)†  |                    |                               |   |            |                                       |                       |
|                   |      |              |  | S          | <34 (<5)   |                    |                               |   |            | <69 (<10)                             |                       |
| A97049            | 7049 | T73          | C                                      | B          | S  |                    |                               |   |            | >172 (>25)                            |                       |
| A97050            | 7050 | T736         | C                                      | B          | S  | >310 (>45)         |                               |   |            | >172 (>25)                            |                       |
| A97075            | 7075 | T6           | C                                      | D          | L  | 345 (50)           | 345 (50)                      | 414 (60)  | 414 (60)   | 241 (35)                              |                       |
|                   |      |              |  |            | T  | 310 (45)           |                               | 345 (50)  | 221 (32)   | 172 (25)                              |                       |
|                   |      |              |  |            | S  | 48 (7)             | 103 (15)                      |   | 48 (7)     | 48 (7)                                |                       |
|                   |      | T76          | C                                      | C          | L  | >338 (>49)         |                               | >359 (>52)  |            |                                       |                       |
|                   |      |              |  |            | T  | >338 (>49)         |                               | >338 (>49)  |            |                                       |                       |
|                   |      |              |  |            | S  | 172 (25)           |                               | 172 (25)  |            |                                       |                       |
| T73               | C    | B            | L                                      | >345 (>50) | >345 (>50)   | >372 (>54)         | >365 (>53)                    | >345 (>50)  |            |                                       |                       |
|                   |      |              | T                                      | >331 (>48) | >331 (>48)   | >331 (>48)         | >331 (>48)                    | >331 (>48)  |            |                                       |                       |
|                   |      |              | S                                      | 276 (40)   | >296 (>43)   | >296 (>43)         | >296 (>43)                    | >296 (>43)  |            |                                       |                       |
| A97076            | 7076 | T61          |  | D          | S  |                    |                               |   |            | ≈48 (≈7)                              |                       |
| A97079            | 7079 | T651         | C                                      | D          | L  | >379 (>55)         |                               | >414 (>60)  | >414 (>60) | >345 (>50)                            |                       |
|                   |      |              |  |            | T  | 276 (40)           |                               | 345 (50)  | 103 (15)   | 207 (30)                              |                       |
|                   |      |              |  |            | S  | 48 (7)             |                               |   | 48 (7)     | <48 (<7)                              |                       |
| A97175            | 7175 | T66          | C                                      | D          | S  |                    |                               |   |            | 48 (7)                                |                       |
|                   |      | T736         | C                                      | B          | S  |                    |                               |   |            | >172 (>25)                            |                       |
| A97178            | 7178 | T6           | C                                      | D          | L  | 379 (55)           |                               | 448 (65)  | 448 (65)   |                                       |                       |
|                   |      |              |  |            | T  | 262 (38)           |                               | 310 (45)  | 172 (25)   |                                       |                       |
|                   |      |              |  |            | S  | 48 (7)             |                               |   | 48 (7)     |                                       |                       |
|                   |      | T76          | C                                      | B          | L  | >359 (>52)         |                               | >379 (>55)  |            |                                       |                       |
|                   |      |              |  |            | T  | >359 (>52)         |                               | >359 (>52)  |            |                                       |                       |
|                   |      |              |  |            | S  | 172 (25)           |                               | 172 (25)  |            |                                       |                       |

\*Ratings A through D are relative ratings in decreasing order of merit based on exposures to sodium chloride solution by intermittent spraying or immersion. Alloys with A and B ratings can be used in industrial and seacoast atmospheres without protection; other alloys should be protected.

\*\*Stress-corrosion cracking ratings are based on service experience and on laboratory tests of specimens exposed to the 3.5% sodium chloride alternate immersion test:

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B = No known instance of failure in service; limited failures in laboratory tests of short transverse specimens

C = Service failures with sustained tension stress acting in short transverse direction relative to grain structure; limited failures in laboratory tests of long transverse specimens

D = Limited service failures with sustained longitudinal or long transverse stress.

†Specimens exposed in inland industrial atmosphere, which for these alloys provides more realistic values than alternate immersion in 3.5% NaCl.

††L, S, and T are defined in par. 2-2.9.2.

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TABLE 4-11. (cont'd)

| ALLOY DESIGNATION |      | TEMPER               | CORROSION RESISTANCE |                                     | Estimate of the highest sustained tension stress at which test specimens of different orientations to the grain structure would not fail in the 3.5% NaCl alternate immersion test in 84 days. |            |                         |                                   |            |          |
|-------------------|------|----------------------|----------------------|-------------------------------------|--|------------|-------------------------|-----------------------------------|------------|----------|
| UNS               | AA   |                      | FIRST LETTER:*       | GENERAL CORROSION, SECOND LETTER:** | TEST DIRECTION   | PLATE      | ROLLED ROD + BAR        | EXTRUDED SHAPES SECTION THICKNESS |            | FORGINGS |
|                   |      |                      |                      |                                     |  |            | 6-25 mm (0.24-0.98 in.) | 30-75 mm (1.18-2.95 in.)          |            |          |
|                   |      |                      |                      |                                     |  | MPa (ksi)  | MPa (ksi)               | MPa (ksi)                         | MPa (ksi)  |          |
| A97475            | 7475 | T61<br>T761<br>T7351 | C                    | D                                   | L  | >345 (>50) |                         |                                   |            |          |
|                   |      |                      | C                    | C                                   | T  | >331 (>48) |                         |                                   |            |          |
|                   |      |                      |                      | B                                   | S  | >296 (>43) |                         |                                   |            |          |
|                   | EC   | O<br>H19             | A                    | A                                   |  |            |                         |                                   |            |          |
|                   |      |                      | A                    | A                                   |  |            |                         |                                   |            |          |
| A91060            | 1060 | O<br>H18             | A                    | A                                   |  |            |                         |                                   |            |          |
|                   |      |                      | A                    | A                                   |  |            |                         |                                   |            |          |
| A91100            | 1100 | O<br>H18             | A                    | A                                   |  |            |                         |                                   |            |          |
|                   |      |                      | A                    | A                                   |  |            |                         |                                   |            |          |
| A92011            | 2011 | T3<br>T8             | D                    | D                                   | L  |            | 172 (25)                |                                   |            |          |
|                   |      |                      |                      |                                     | T  |            | 69 (10)                 |                                   |            |          |
|                   |      |                      | D                    | B                                   | L  |            | >276 (>40)              |                                   |            |          |
|                   |      |                      |                      |                                     | T  |            | >207 (>30)              |                                   |            |          |
| A92014            | 2014 | T4,T3<br>T651        | D                    | D                                   | L  | 310 (45)   | 310 (45)                | 345 (50)                          | 310 (45)   |          |
|                   |      |                      | D                    | C                                   | T  | 207 (30)   |                         | 186 (27)                          | 152 (22)   |          |
|                   |      |                      |                      |                                     | S  | 41 (6)     | 103 (15)                | 48 (7)                            | 48 (7)     |          |
| A92017            | 2017 | T451                 | D                    | C                                   |  |            |                         |                                   |            |          |
| A92020            | 2020 | T651                 |                      | B                                   | L  | >393 (>57) |                         |                                   |            |          |
|                   |      |                      |                      |                                     | T  | >386 (>56) |                         |                                   |            |          |
|                   |      |                      |                      |                                     | S  | >234 (>34) |                         |                                   |            |          |
| A92021            | 2021 | T8                   |                      | B                                   | L  | >331 (>48) |                         | >331 (>48)                        | >317 (>46) |          |
|                   |      |                      |                      |                                     | T  | >317 (>46) |                         | >317 (>46)                        | >310 (>45) |          |
|                   |      |                      |                      |                                     | S  | 241 (35)   |                         | >310 (>45)                        | 241 (35)   |          |

\*Ratings A through D are relative ratings in decreasing order of merit based on exposures to sodium chloride solution by intermittent spraying or immersion. Alloys with A and B ratings can be used in industrial and seacoast atmospheres without protection; other alloys should be protected.

\*\*Stress-corrosion cracking ratings are based on service experience and on laboratory tests of specimens exposed to the 3.5% sodium chloride alternate immersion test:

A = No known instance of failure in service or in laboratory tests

B = No known instance of failure in service; limited failures in laboratory tests of short transverse specimens

C = Service failures with sustained tension stress acting in short transverse direction relative to grain structure; limited failures in laboratory tests of long transverse specimens

D = Limited service failures with sustained longitudinal or long transverse stress.

†Specimens exposed in inland industrial atmosphere, which for these alloys provides more realistic values than alternate immersion in 3.5% NaCl.

††L, S, and T are defined in par. 2-2.9.2.

(cont'd on next page)

TABLE 4-11. (cont'd)

| ALLOY DESIGNATION |      | TEMPER       | CORROSION RESISTANCE |                  | Estimate of the highest sustained tension stress at which test specimens of different orientations to the grain structure would not fail in the 3.5% NaCl alternate immersion test in 84 days. |            |                  |                                   |                                    |            |
|-------------------|------|--------------|----------------------|------------------|--|------------|------------------|-----------------------------------|------------------------------------|------------|
| UNS               | AA   |              | FIRST LETTER:*       | SECOND LETTER:** | TEST DIRECTION   | PLATE      | ROLLED ROD + BAR | EXTRUDED SHAPES SECTION THICKNESS |                                    | FORGINGS   |
|                   |      |              | STRESS CORROSION     |                  |  | MPa (ksi)  | MPa (ksi)        | 6-25 mm (0.24-0.98 in.) MPa (ksi) | 30-75 mm (1.18-2.95 in.) MPa (ksi) | MPa (ksi)  |
| A92024            | 2024 | T4,T351      | D                    | D                | L  | 241 (35)   | 207 (30)         | >345 (>50)                        | >345 (>50)                         |            |
|                   |      |              |                      |                  | T  | 138 (20)   |                  | 255 (37)                          | 124 (18)                           |            |
|                   |      | T6,T81, T851 | D                    | B                | S  | 41 (6)     | 69 (10)          |                                   | 48 (7)                             | 48 (7)     |
|                   |      |              |                      |                  | L  | >345 (>50) | >345 (>50)       | >414 (>60)                        | >414 (>60)                         | >296 (>43) |
|                   |      |              |                      |                  | T  | >345 (>50) |                  | 345 (50)                          | 345 (50)                           | 296 (43)   |
|                   |      |              |                      | S                | 186 (27)   | >296 (>43) |                  | >310 (>45)                        | 103 (15)                           |            |
| A92025            | 2025 | T6           | D                    | C                |  |            |                  |                                   |                                    |            |
| A92048            | 2048 | T851         |                      | B                | L  |            |                  |                                   |                                    |            |
|                   |      |              |                      |                  | T  |            |                  |                                   |                                    |            |
|                   |      |              |                      |                  | S  |            |                  |                                   |                                    |            |
| A92117            | 2117 | T4           | C                    | A                |  |            |                  |                                   |                                    |            |
| A92124            | 2124 | T3           |                      | D                |  |            |                  |                                   |                                    |            |
|                   |      | T6,T851      |                      | B                | L  | >345 (>50) |                  |                                   |                                    |            |
|                   |      |              |                      |                  | T  | >345 (>50) |                  |                                   |                                    |            |
|                   |      |              |                      |                  | S  | 207 (30)   |                  |                                   |                                    | ≈103 (≈15) |
| A92214            | 2214 |              |                      |                  |  |            |                  |                                   |                                    |            |
| A92218            | 2218 | T72          | D                    | C                |  |            |                  |                                   |                                    |            |
| A92219            | 2219 | T351         | D                    | D                | S  | <69 (<10)  |                  |                                   |                                    |            |
|                   |      | T37          | D                    | C                | L  | >234 (>34) |                  |                                   |                                    |            |
|                   |      | T62          | D                    | B                | S  | >221 (>32) |                  |                                   |                                    | >221 (>32) |
|                   |      | T8           | D                    | B                | L  | >276 (>40) |                  | >241 (>35)                        | >241 (>35)                         | >262 (>38) |
|                   |      |              |                      |                  | T  | >262 (>38) |                  | >241 (>35)                        | >241 (>35)                         | >262 (>38) |
|                   |      |              |                      |                  | S  | >262 (>38) |                  | >241 (>35)                        | >241 (>35)                         | >262 (>38) |
| A92419            | 2419 |              |                      |                  |  |            |                  |                                   |                                    |            |

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\*Ratings A through D are relative ratings in decreasing order of merit based on exposures to sodium chloride solution by intermittent spraying or immersion. Alloys with A and B ratings can be used in industrial and seacoast atmospheres without protection; other alloys should be protected.

\*\*Stress-corrosion cracking ratings are based on service experience and on laboratory tests of specimens exposed to the 3.5% sodium chloride alternate immersion test:

A = No known instance of failure in service or in laboratory tests

B = No known instance of failure in service; limited failures in laboratory tests of short transverse specimens

C = Service failures with sustained tension stress acting in short transverse direction relative to grain structure; limited failures in laboratory tests of long transverse specimens

D = Limited service failures with sustained longitudinal or long transverse stress.

†Specimens exposed in inland industrial atmosphere, which for these alloys provides more realistic values than alternate immersion in 3.5% NaCl.

††L, S, and T are defined in par. 2-2.9.2.

(cont'd on next page)

TABLE 4-11. (cont'd)

| ALLOY DESIGNATION |      | TEMPER                           | CORROSION RESISTANCE FIRST LETTER:* |                  | Estimate of the highest sustained tension stress at which test specimens of different orientations to the grain structure would not fail in the 3.5% NaCl alternate immersion test in 84 days. |                          |                  |                                   |                                    |            |
|-------------------|------|----------------------------------|-------------------------------------|------------------|--|--------------------------|------------------|-----------------------------------|------------------------------------|------------|
| UNS               | AA   |                                  | GENERAL CORROSION, SECOND LETTER:** |                  | TEST DIRECTION   | PLATE                    | ROLLED ROD + BAR | EXTRUDED SHAPES SECTION THICKNESS |                                    | FORGINGS   |
|                   |      |                                  |                                     |                  |  | MPa (ksi)                | MPa (ksi)        | 6-25 mm (0.24-0.98 in.) MPa (ksi) | 30-75 mm (1.18-2.95 in.) MPa (ksi) | MPa (ksi)  |
| A92618            | 2618 | T6                               | D                                   | C                | L<br>S   | >303 (>44)<br>>276 (>40) |                  |                                   |                                    | >221 (>32) |
| A93003            | 3003 | O<br>H18                         | A<br>A                              | A<br>A           | A  |                          |                  |                                   |                                    |            |
| A93004            | 3004 | O<br>H38                         | A<br>A                              | A<br>A           |  |                          |                  |                                   |                                    |            |
| A93105            | 3105 | O<br>H25                         | A<br>A                              | A<br>A           |  |                          |                  |                                   |                                    |            |
| A94032            | 4032 | T6                               | C                                   | B                |  |                          |                  |                                   |                                    |            |
| A95005            | 5005 | O<br>H38                         | A<br>A                              | A<br>A           |  |                          |                  |                                   |                                    |            |
| A95050            | 5050 | O<br>H38                         | A<br>A                              | A<br>A           |  |                          |                  |                                   |                                    |            |
| A95052            | 5052 | O<br>H38                         | A<br>A                              | A<br>A           |  |                          |                  |                                   |                                    |            |
| A95056            | 5056 | O<br>H18,H38<br>H192,H392        | A<br>A<br>B                         | C<br>D<br>D      |  |                          |                  |                                   |                                    |            |
| A95083            | 5083 | O<br>H321                        | A<br>A                              | B<br>C           | L<br>S   | >172 (>25)<br>>172 (>25) |                  |                                   |                                    |            |
| A95086            | 5086 | O<br>H32,H117<br>H34,H38<br>H111 | A<br>A<br>A<br>A                    | A<br>B<br>B<br>B |  |                          |                  |                                   |                                    |            |

\*Ratings A through D are relative ratings in decreasing order of merit based on exposures to sodium chloride solution by intermittent spraying or immersion. Alloys with A and B ratings can be used in industrial and seacoast atmospheres without protection; other alloys should be protected.

\*\*Stress-corrosion cracking ratings are based on service experience and on laboratory tests of specimens exposed to the 3.5% sodium chloride alternate immersion test:

A = No known instance of failure in service or in laboratory tests

B = No known instance of failure in service; limited failures in laboratory tests of short transverse specimens

C = Service failures with sustained tension stress acting in short transverse direction relative to grain structure; limited failures in laboratory tests of long transverse specimens

D = Limited service failures with sustained longitudinal or long transverse stress.

†Specimens exposed in inland industrial atmosphere, which for these alloys provides more realistic values than alternate immersion in 3.5% NaCl.

††L, S, and T are defined in par. 2-2.9.2.

(cont'd on next page)

TABLE 4-11. (cont'd)

| ALLOY DESIGNATION |       | TEMPER                    | CORROSION RESISTANCE |                                     | Estimate of the highest sustained tension stress at which test specimens of different orientations to the grain structure would not fail in the 3.5% NaCl alternate immersion test in 84 days. |                |           |                                   |                                    |           |
|-------------------|-------|---------------------------|----------------------|-------------------------------------|--|----------------|-----------|-----------------------------------|------------------------------------|-----------|
| UNS               | AA    |                           | FIRST LETTER:*       | GENERAL CORROSION, SECOND LETTER:** | STRESS CORROSION   | TEST DIRECTION | PLATE     | ROLLED ROD + BAR                  | EXTRUDED SHAPES SECTION THICKNESS  |           |
|                   |       |                           |                      |                                     |  | MPa (ksi)      | MPa (ksi) | 6-25 mm (0.24-0.98 in.) MPa (ksi) | 30-75 mm (1.18-2.95 in.) MPa (ksi) | MPa (ksi) |
|                   | X5090 |                           |                      |                                     |  |                |           |                                   |                                    |           |
| A95154            | 5154  | O<br>H38                  | A                    | B                                   |  |                |           |                                   |                                    |           |
| A95252            | 5252  | H25<br>H38,H28            | A                    | A                                   |  |                |           |                                   |                                    |           |
| A95254            | 5254  | O<br>H38                  | A                    | A<br>B                              |  |                |           |                                   |                                    |           |
| A95454            | 5454  | O<br>H34<br>H112          | A                    | A<br>A<br>B                         |  |                |           |                                   |                                    |           |
| A95456            | 5456  | O<br>H32†<br>H111<br>H116 | A                    | B<br>C<br>C<br>C                    |  |                |           |                                   |                                    |           |

\*Ratings A through D are relative ratings in decreasing order of merit based on exposures to sodium chloride solution by intermittent spraying or immersion. Alloys with A and B ratings can be used in industrial and seacoast atmospheres without protection; other alloys should be protected.

\*\*Stress-corrosion cracking ratings are based on service experience and on laboratory tests of specimens exposed to the 3.5% sodium chloride alternate immersion test:

A = No known instance of failure in service or in laboratory tests

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C = Service failures with sustained tension stress acting in short transverse direction relative to grain structure; limited failures in laboratory tests of long transverse specimens

D = Limited service failures with sustained longitudinal or long transverse stress.

†Specimens exposed in inland industrial atmosphere, which for these alloys provides more realistic values than alternate immersion in 3.5% NaCl.

††L, S, and T are defined in par. 2-2.9.2.



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## 4-2.1.1.1 Uniform Corrosion

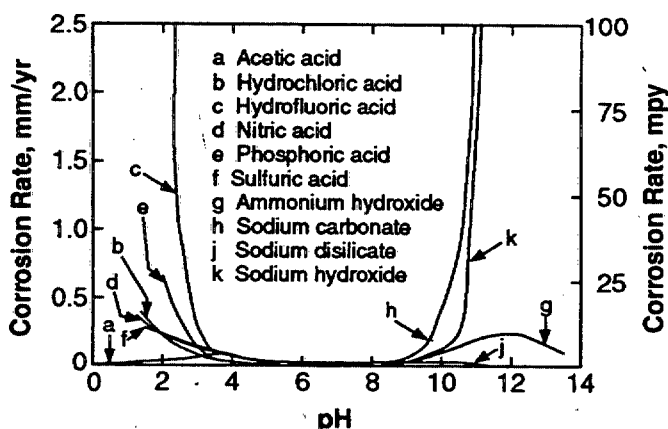
Aluminum is an amphoteric metal, i.e., it corrodes under both acid and alkaline conditions, as shown in Fig. 4-3. Exceptions shown on this figure are acetic acid and sodium disilicate. Other exceptions are ammonium hydroxide above about 30% concentration by weight, nitric acid above 80% concentration by weight, and sulfuric acid of 98 to 100% concentration by weight.

The resistance of aluminum alloys to general corrosion is impaired by the presence of about 0.25% copper as an alloying element. In moisture the copper forms ions that the aluminum reduces. During this process, aluminum is oxidized and metallic copper plates out on the alloy surface and establishes a galvanic cell.

Acid waters containing chlorides are especially corrosive to aluminum. Although sulfate-containing waters of low pH are also corrosive to aluminum, they are less corrosive than chloride-containing acid waters.

Aluminum and its alloys are resistant to attack by most organic chemicals, but some organic chemicals will react with aluminum if they are water free and at elevated temperatures, usually near their boiling points. Also some halogenated organic compounds will react with aluminum at elevated temperatures near their boiling points. Some halogenated organic refrigerants will react with aluminum if sufficient water is present to cause the hydrolysis necessary to form hydrochloric acid. The resistance of aluminum to organic chemicals is summarized in Table 4-12.

Many cases of corrosion in the presence of organic chemicals can be traced to the presence of heavy metal contaminants such as copper, lead, nickel, and mercury. Contaminants are more likely to be present in commercial-grade products than in laboratory reagent-grade chemicals. Also contaminants are more often found in used chemicals than in fresh batches.



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**Figure 4-3. Effect of pH on Corrosion of 1100-H14 Alloy by Various Chemical Solutions (Ref. 6)**

Aluminum used in military equipment is likely to encounter organic chemicals in degreasing and cleaning solutions, paint removers, coating preparations, fuels and lubricants, and working fluids such as coolants and hydraulic fluids.

## 4-2.1.1.2 Pitting Corrosion

Corrosion of aluminum in the pH range where aluminum is passive may be of the pitting type. When aluminum is exposed to weather environments—fresh- or saltwater or other neutral electrolytes—pits form at local defects in the passive oxide film.

The 1XXX, 3XXX, and 5XXX series of aluminum alloys have excellent resistance to corrosion in high-purity waters and are resistant to corrosion in many natural waters. Corrosion of these alloys in seawater is usually by pitting because aluminum pits in water containing halide ions. (Chloride is the most commonly encountered halide ion.) The rates of pitting in seawater are low (Refs. 7, 8, and 9). The older pits tend to become inactive. During the initial year of exposure, the pitting rates are from 3 to 6  $\mu\text{m}/\text{yr}$  (0.12 to 0.24 mil/yr (mpy)). Over a 10-yr period the average pitting rate is 0.8 to 1.5  $\mu\text{m}/\text{yr}$  (0.03 to 0.06 mpy). The 5XXX series of alloys has the highest resistance to seawater corrosion.

Waters containing traces of heavy metals, such as copper, lead, tin, nickel, or cobalt, can cause local corrosion of aluminum.

## 4-2.1.1.3 Atmospheric Corrosion

Aluminum alloys of the 1XXX, 3XXX, and 5XXX series have a high resistance to weathering in most atmospheres. The most common form of attack in corrosive atmospheric environments is pitting. Industrial contaminants such as sulfur dioxide, ammonia, cyanides, organic sulfur compounds, carbon particles, and particles containing absorbed acids tend to accelerate the attack. Airborne sea salts in temperate or tropical marine environments also contribute to the attack. After approximately two years of exposure, atmospheric attack on aluminum tapers off and continues at a much slower rate, as illustrated in Fig. 4-4.

Weathering of aluminum alloys also results in loss of strength. The loss of strength shows an initial rapid rise that tapers off after approximately two years. However, loss of strength does not decrease to as low a rate as does corrosion attack. This situation occurs because the older pits tend to become inactive while new ones develop; therefore, the cross-sectional area on which strength depends is decreased by the newer pitting sites and the maximum depth of attack is not increased.

The atmospheric corrosion resistance of the 3XXX series alloys is comparable to or better than the 1XXX series, and the 5XXX series alloys show resistance to atmospheric corrosion similar to that of the 1XXX and

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**TABLE 4-12. ORGANIC CHEMICALS IN WHICH ALUMINUM ALLOYS ARE RESISTANT TO CORROSION (Ref. 6)**

---

Organic acids, especially the low-molecular-weight fatty acids and anhydrides at temperatures near 49°C (120°F)  
 Acetic, propionic, and butyric acids at boiling temperatures if some water is present  
 Alcohols such as methyl, propyl, butyl, furfuryl, lanoyl, cetyl, glycerin, ethylene glycol, and phenyl-ethyl\*  
 Aldehydes such as acetaldehyde, benzaldehyde, butyraldehyde, furfuraldehyde, and propionaldehyde  
 Concentrated aliphatic and aromatic amines  
 Aqueous amine solution effectively inhibited by silicates  
 Esters such as amyl acetate, ethyl acetate, butyl acetate, cellulose acetate, vinyl acetate, methyl formate, and triacetin  
 Ethyl ether and some high boiling ethers such as ethylene glycol monoethyl ether and some other ethers\*  
 Ketones including acetone, methyl ethyl ketone, methyl propyl ketone, methyl cyclohexanone, acetophenone, and benzophenone  
 Phenols\*  
 Naval stores such as turpentine, rosin, copal, pentane, dipentene, and pinene  
 Halogenated hydrocarbons such as trichloroethylene and perchloroethylene. Others such as carbon tetrachloride will react with aluminum at elevated temperatures.  
 Aromatic compounds such as benzene, naphthalene, toluene, xylene, and styrene monomer  
 Mercaptans  
 Nitrated organic compounds such as nitrobenzene, nitroethylene, nitrocellulose, nitroglycerin, and nitroparaffins  
 Refrigerants such as common halogenated hydrocarbon refrigerants at moisture levels of 20 to 40 ppm or below; ammonia and sulfur dioxide refrigerants when dry  
 Essential oils  
 Some dyes; however, they must be considered individually.

---

\*Except when extremely dry and at elevated temperatures

3XXX series alloys on the basis of average penetration based upon weight loss. However, if the maximum pitting depth is used as the basis for comparison, 5XXX alloys are often more severely attacked than the 1XXX and 3XXX alloys.

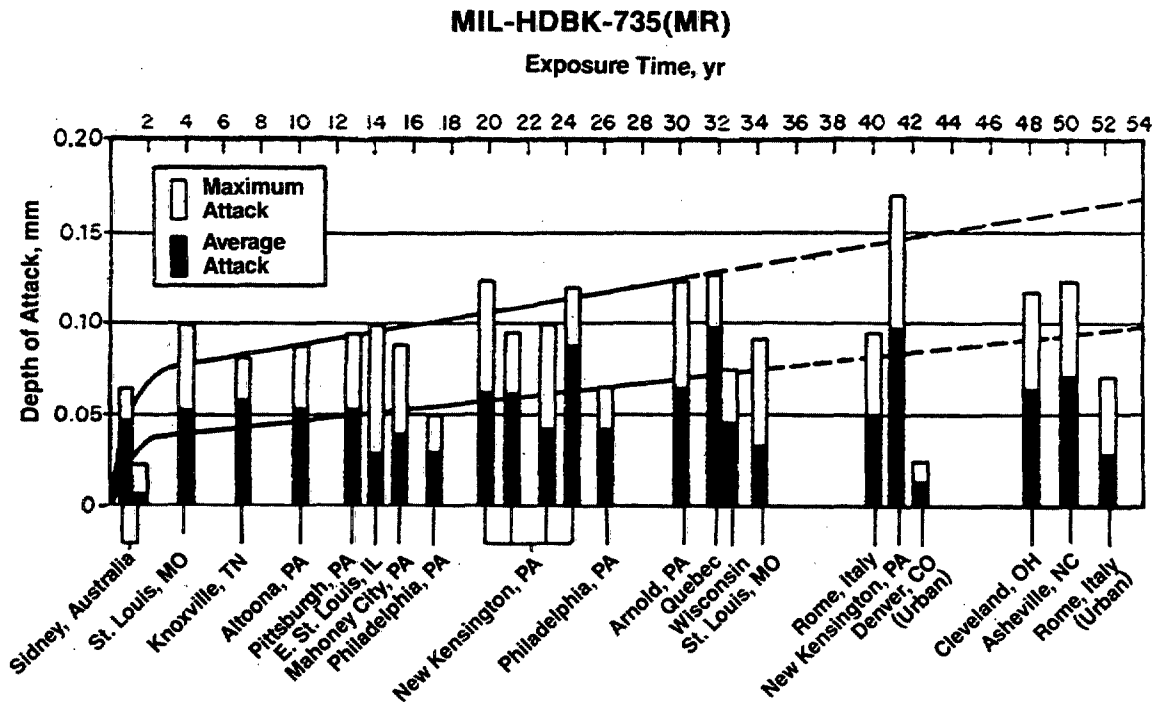
According to the general corrosion ratings of Table 4-11, the 6XXX series alloys and the noncopper-containing 7XXX series alloys perform adequately in weathering atmospheres. The weathering performance of these alloys, however, is below that of the 1XXX, 3XXX, and 5XXX series alloys.

In environments in which the noncopper-containing

aluminum alloys tend to pit, the copper-containing alloys are likely to experience intergranular attack or stress-corrosion cracking.

#### 4-2.1.1.4 Crevice Corrosion

Aluminum alloys are subject to crevice corrosion at the joints between faying surfaces, between the shank of a rivet or bolt and the hole walls, and in crevices resulting from incomplete weld penetration or braze coverage. Crevice corrosion occurs on aluminum in seawater but not in freshwater, and it can occur in marine weathering environments containing salt spray or mist.



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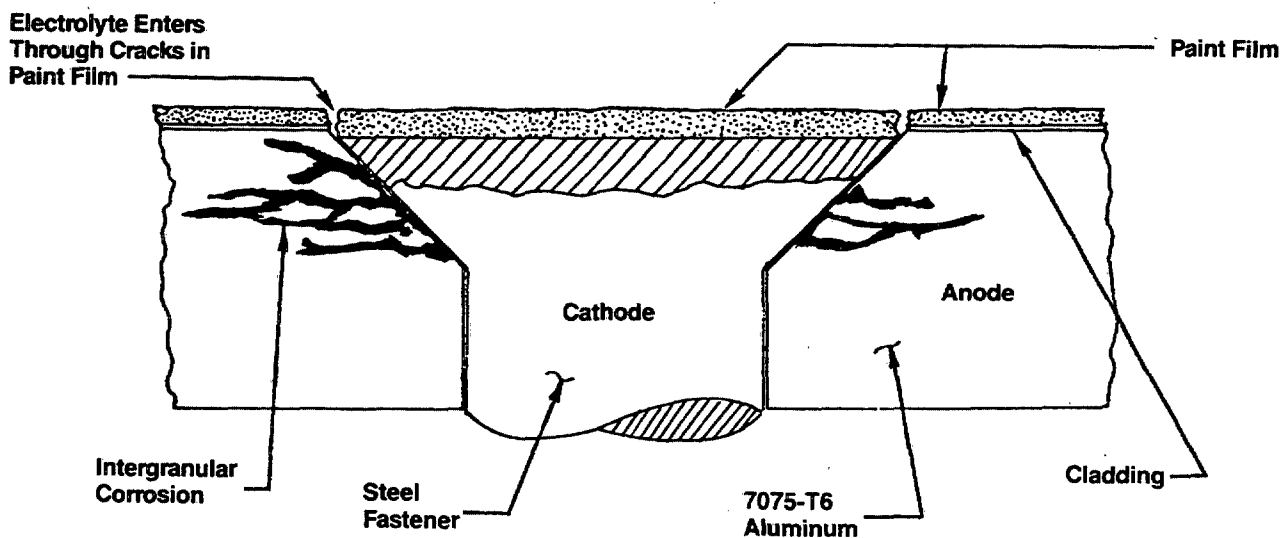
**Figure 4-4. Weathering Data for 1100, 3003, and 3004 Alloys in Industrial Atmosphere at New Kensington, PA, (Curves) and in Various Other Localities (Ref. 10)**

#### 4-2.1.1.5 Filiform Corrosion

Aluminum alloys are vulnerable to filiform corrosion under paint and other organic coatings. Although the coating integrity may degrade, aluminum alloys rarely undergo catastrophic failure as a result of filiform corrosion.

#### 4-2.1.1.6 Intergranular Corrosion

The copper-containing alloys of the 2XXX and 7XXX series undergo intergranular attack in aggressive environments. Fig. 4-5 illustrates the intergranular corrosion that occurs in 7075-T6 aluminum adjacent to a steel fastener. Those 6XXX series alloys in the T6 temper with silicon added in excess of the stoichiometric ratio equivalent to  $Mg_2Si$  are also susceptible to intergranular corrosion. The susceptible alloys include 6061-T6, 6063-T6, and 6351-T6.



**Figure 4-5. Intergranular Corrosion at 7075-T6 Aluminum Adjacent to Steel Fastener (Ref. 11)**

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### 4-2.1.1.7 Exfoliation

If the alloy has been highly deformed (as by rolling), it consists of an assembly of platelet-shaped grains. These grains are long in the direction of rolling, short in the transverse direction, and thin in the direction in which compressive stress was applied. Severe intergranular corrosion of an alloy in this condition results in the separation of thin flakes or sheets of the alloy. Separation occurs because the corrosion products occupy a greater volume than uncorroded material, which forces the grains apart. This form of intergranular attack is called exfoliation; exfoliation attack can occur in the unstressed condition. Alloys of the 2XXX, 5XXX, and 7XXX series are those most prone to exfoliation.

Exfoliation corrosion has occurred in alloy 2024 in the T3 and T4 conditions in missile systems. The exfoliation-resistant tempers T851 or T81 are recommended if exposure to marine atmospheres is expected. Exfoliation-resistant 7075-T73 or -T76 is preferred over the exfoliation-susceptible T6 temper.

Exfoliation corrosion has been experienced with alloys 5083, 5086, and 5456 in the H32 and H321 tempers under conditions related to the potential application of each as the primary structural material for watercraft, such as hydrofoils, surface effect ships, and fast patrol boats. Exfoliation-resistant tempers H116 and H117 were developed to solve this problem. The high-strength alloys in these exfoliation-resistant tempers have been tested for corrosion resistance in marine environments (Ref. 12) and for susceptibility to corrosion fatigue (Ref. 13).

Alloys 5083, 5086, and 5456 in the exfoliation-resistant tempers have good corrosion resistance. In general, the calculated corrosion rate for any exposure and for any condition (as-rolled and sensitized) is less than 25  $\mu\text{m}/\text{yr}$  (1 mpy). The corrosion rates decrease with time.

### 4-2.1.1.8 Stress-Corrosion Cracking

Aluminum alloys that contain appreciable amounts of soluble alloying elements of copper, magnesium, silicon, and zinc are subject to stress-corrosion cracking. Stress-corrosion cracking in aluminum is intergranular. Wrought alloys of the 2XXX, 5XXX, 6XXX, and 7XXX series contain soluble alloying elements in sufficient amounts to make them subject to stress-corrosion cracking.

Susceptibility to stress-corrosion cracking depends upon the metallurgical condition of the alloy, which is greatly influenced by the temper. Generally tempers that generate maximum strength in an alloy also produce the greatest susceptibility to stress-corrosion cracking. Susceptibility of aluminum alloys to stress-corrosion cracking is related to precipitation in the grain boundaries, which also influences the strength of an alloy. Usually these maximum-strength alloys are applied where there is significant sustained tensile stress.

Practically all in-service stress-corrosion cracking failures of aluminum alloy components involve the short transverse properties. The fractures would be designated S-L or S-T. A few in-service fractures are T-L or T-S. Longitudinal (L-T or L-S) stress-corrosion cracks actually occur very rarely. The grain structure orientations are described in par. 2-2.9.2.

According to the relative stress-corrosion ratings shown in Table 4-11, most of the 2XXX series alloys exhibit some degree of susceptibility in commercial tempers. Tempers have been developed for some alloys that reduce susceptibility to stress-corrosion cracking, e.g., the 2024 alloy. When the 2024 alloy is solution heat treated and cold worked (T3) or solution treated and naturally aged to a substantially stable condition (T4), it shows a high degree of susceptibility to intergranular attack. However, considerable improvement in corrosion resistance results from solution heat treating followed by artificial aging (T6). Improvement also results from cold-working and then artificial aging (T8). Another modification of T8, known as T851, involves stress relief by stretching. This modification gives the alloy high resistance to stress-corrosion cracking.

Tempers have been developed that increase the resistance to stress-corrosion cracking of the 7XXX series alloys. An example is alloy 7075-T73. Another special treatment involves rapid cooling of alloy 7075 through a critical temperature range of 399° to 288°C (750° to 550° F) in excess of 149 deg C (300 deg F) per second. This process produces immunity to stress-corrosion cracking, but it is not feasible with heavy sections. The T73 treatment is recommended for heavy sections.

Unfortunately, tempers that reduce susceptibility to stress-corrosion cracking also reduce the strength of the alloy. Therefore, selecting an alloy involves a tradeoff. For example, if highest strength is the primary consideration and a low level of susceptibility to stress-corrosion cracking can be tolerated, alloy 7178-T651 is the best choice. If, however, stress-corrosion cracking is the primary consideration and a lower yield strength is adequate, the stress-corrosion-immune alloy 7178-T76 would give adequate service.

Metallurgical treatments that improve resistance to stress-corrosion cracking also improve resistance to intergranular attack and exfoliation. Resistance to intergranular attack or exfoliation, however, is not a satisfactory criterion for predicting resistance to stress-corrosion cracking.

### 4-2.1.1.9 Corrosion Fatigue

Corrosion fatigue strength is expressed as the maximum stress endured by a metal without failure in a given number of stress cycles in a corrosive environment. This value is usually compared to a similar measure in air. Thus the corrosion fatigue characteristics of an alloy can

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be expressed as a fraction of the fatigue strength in air. Alloys can be compared with respect to their relative corrosion fatigue characteristics by comparing these fractions. Accordingly, the corrosion fatigue characteristics of the high-strength, less corrosion-resistant aluminum alloys (2XXX and 7XXX series) are not as good as those of the more corrosion-resistant alloys (5XXX and 6XXX series) in a corrosive medium. In other words, the corrosion fatigue strength of the 2XXX and 7XXX series alloys is a smaller fraction of the fatigue strength in air than is the corrosion fatigue strength of the 5XXX and 6XXX series alloys.

Corrosion fatigue fracture is predominantly intergranular. Directional grain structure has little influence on corrosion fatigue. Corrosion fatigue cracks can originate at sites of pitting or intergranular attack. It is difficult to distinguish between corrosion fatigue cracks that emanate from areas of intergranular attack and stress-corrosion cracks. As with intergranular attack and stress-corrosion cracking, the chloride ion is the major cause of corrosion fatigue failure.

Corrosion fatigue test results are shown in Fig. 4-6 for alloys 5083, 5086, and 5456 and in Fig. 4-7 for aluminum alloy weldments. The exfoliation-resistant H116 and

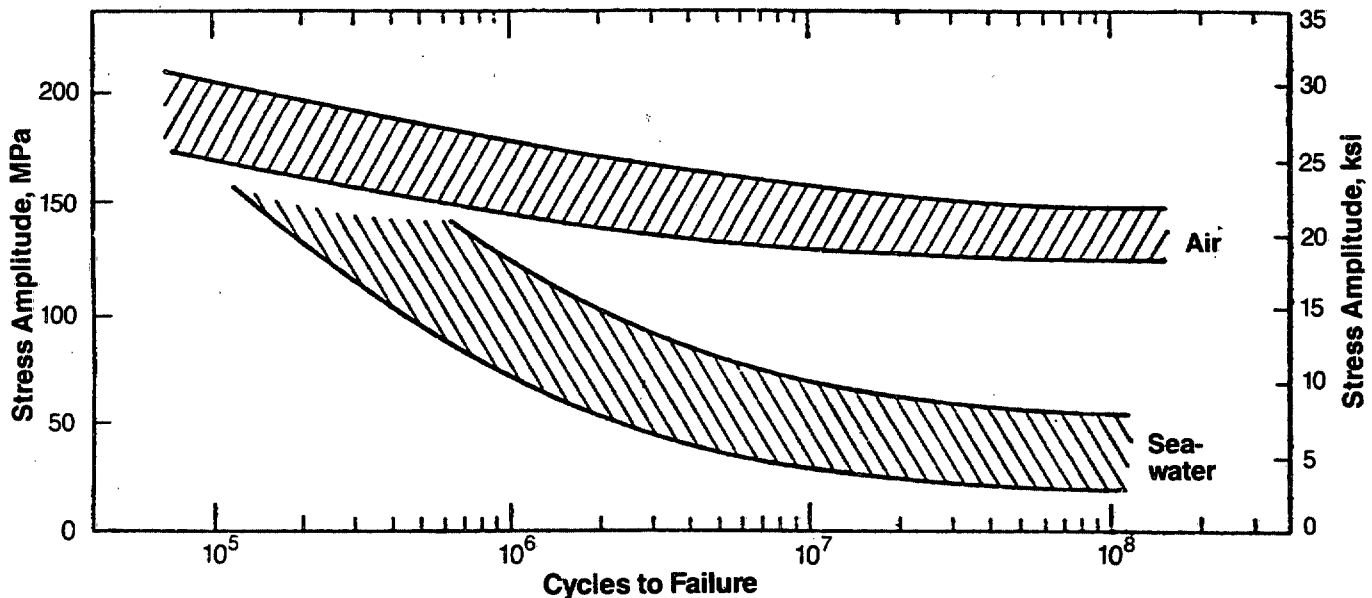


Figure 4-6. Scatter Bands for Fatigue Test Results of Marine Aluminum-Alloy-Base Metal Tempers (Ref. 11)

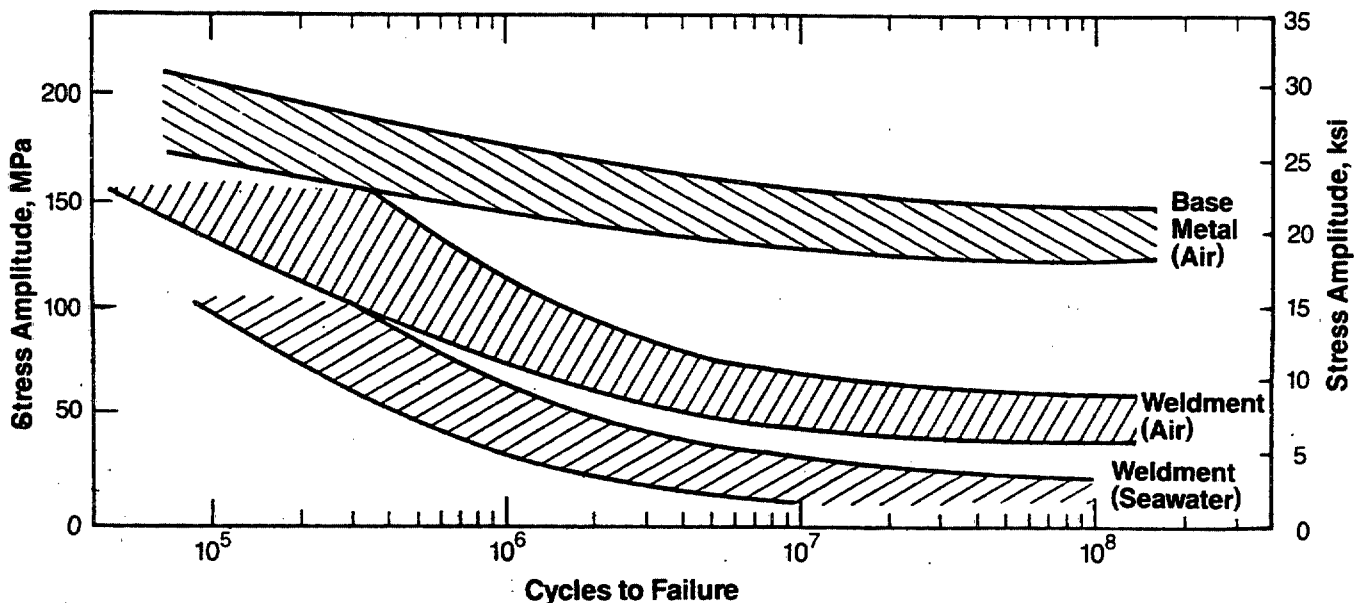


Figure 4-7. Scatter Bands for Fatigue Test Results of Marine Aluminum Weldments (Ref. 11)

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H117 tempers exhibit essentially the same corrosion fatigue characteristics as the H32 and H321 tempers. Despite differences in strength and composition among the alloys tested, different saltwater environments, different filler metals and joint designs, and specimen orientation, the fatigue behavior for any given set of testing conditions failed to indicate any distinction among the alloys.

As indicated in Fig. 4-6, the fatigue strength in air at  $10^8$  cycles for all alloys was about 138 MPa (20 ksi). It was severely reduced, however, in seawater to about 34 MPa (5 ksi) at  $10^8$  cycles.

As indicated in Fig. 4-7, the fatigue strength of weldments in air at  $10^8$  cycles was about 55 MPa (8 ksi), and all of the weldments failed in the weld material. In seawater the fatigue strength was reduced farther. The specimens could not sustain a stress of 28 MPa (4 ksi), the lowest available testing stress (Ref. 11).

**4-2.1.1.10 Galvanic Corrosion**

Aluminum and its alloys become the anode in galvanic cells with most metals. The rate of corrosion of aluminum coupled to a cathodic metal depends upon the degree of polarization of aluminum in the galvanic cell. In a couple with chromium or stainless steel in atmospheric or other

mild environments, the corrosion rate of aluminum is low. In a couple with copper, however, the corrosion rate of aluminum is high.

Table 4-13 indicates the compatibility of various aluminum alloys with dissimilar materials. Class I is considered to be compatible because the relative increase in the dissolution rate as a result of the couple is below a factor of 5. Class III is considered to be not compatible because the relative increase in the dissolution rate is greater than a factor of 15. Class II ranges from borderline compatibility to unacceptable because the relative increase in the dissolution rate is between a factor of 5 and 15. For example, 1100 aluminum is compatible only with cadmium, whereas 2024 aluminum is compatible with most of the metals. Galvanic problems for aluminum can result from fasteners. A compatible aluminum alloy is the safest, but often a higher strength steel fastener is used. Zinc, cadmium, chromium, and tin-coated fasteners may be used. Tin-zinc coatings are best for steel fasteners. Cadmium is preferred over zinc if the coating thicknesses are equal; however, sufficiently thick plated cadmium fasteners may not be available. Stainless steel fasteners may be used under most conditions. Brass or plated brass items should be avoided.

Table 4-14 shows a galvanic series of aluminum alloys

**TABLE 4-13. COMPATIBILITY OF ALUMINUM ALLOYS AND DISSIMILAR MATERIALS (Ref. 14)**

| CLASS                   | Al 1100  | Al 2024   | Al 2219   | Al 6061   | Al 7075   |
|-------------------------|--|---|---|---|---|
| I<br>(Compatible)       | Cd   | Cd, 7075, 1100, Sn, Haynes 188, 2219, Ti-6-4, 6061, Zn, Inco 718, PH13-8Mo, SS347, A286, SS304, Ni, SS301 | Cd, 2024, 6061, 1100, Haynes 188, 7075, Zn, PH13-8Mo, SS301, SS304, A286, Inco 718, Ti-6-4, SS347 | 7075, 2219, 2024                                      | 1100, 6061, 2024, Zn, 2219                            |
| II<br>(Marginal)        | 2024, 6061   | 4130, Cu, Ag  | Ni, Zn, 4130, Cu, Ag  | 1100, Cd, Sn, Inco 718, Zn, Haynes 188, Ti-6-4        | Cd, Haynes 188, Sn, Ti-6-4, Inco 718                  |
| III<br>(Not Compatible) | Sn, 7075, Haynes 188, Ti-6-4, Zn, Inco 718, A286, SS304, PH13-8Mo, SS301, 4130, Cu, Ag |   |   | SS304, SS301, A286, PH13-8Mo, SS347, 4130, Ni, Cu, Ag | SS304, SS347, PH13-8Mo, SS301, A286, Ni, 4130, Cu, Ag |

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TABLE 4-14. GALVANIC POTENTIALS OF METALS IN SEAWATER (Ref. 15)

| POTENTIAL RELATIVE TO<br>SATURATED CALOMEL<br>ELECTRODE AT 25°C (77°F), V |       |
|---|-------|
| Anodic End (less noble, reactive)   |       |
| Magnesium   | -1.80 |
| Magnesium alloys  | -1.60 |
| Zinc  | -1.10 |
| Zinc—hot dip, galvanized steel  | -1.05 |
| Aluminum—cast, other than silicon type                                    | -0.95 |
| Cadmium—plated and chromated  | -0.80 |
| Aluminum—wrought, other than copper type                                  | -0.75 |
| Aluminum—cast, silicon type   | -0.75 |
| Iron—wrought carbon or low-alloy steels<br>gray or malleable cast iron    | -0.70 |
| Aluminum—wrought, copper type   | -0.60 |
| Steel, stainless—13% chromium, active                                     | -0.55 |
| Lead—solid or plated, high-lead alloys                                    | -0.55 |
| Steel, stainless—18% chromium, 8% nickel                                  | -0.50 |
| Tin—plate, terneplate, tin-lead solders                                   | -0.50 |
| Chromium—plated   | -0.45 |
| Steel, stainless—13% chromium, passive                                    | -0.45 |
| Brass—yellow, naval, cartridge, muntz metal                               | -0.40 |
| Brass—red, gliding  | -0.35 |
| Copper—solid or plated  | -0.30 |
| Nickel—solid or plated, passive   | -0.30 |
| Monel   | -0.30 |
| Steel, stainless—18% chromium, 8% nickel,<br>passive                      | -0.20 |
| Silver, solder  | -0.20 |
| Steel, stainless—18% chromium, 12% nickel,<br>3% molybdenum, passive      | -0.20 |
| Titanium, commercial  | -0.15 |
| Hastelloy C   | -0.10 |
| Silver—solid or plated, high-silver alloys                                | 0.0   |
| Rhodium   | +0.20 |
| Graphite  | +0.25 |
| Gold—solid or plated, high-gold alloys                                    | +0.25 |
| Platinum—wrought, high-platinum alloys                                    | +0.25 |
| Cathodic End (more noble, unreactive)                                     |       |

and other metals that represents the electrochemical behavior of each in seawater and in most natural waters and atmospheres. There is a wide range in the galvanic potential of the various aluminum alloys, as indicated in Table 4-15. Some of the alloys show a significant effect of temper on the galvanic potential. Permissible couples are limited to a potential difference of 0.10 V on the galvanic series (Ref. 16).

Aluminum is often used in a clad condition, and the cladding alloy may be slightly anodic or cathodic to the

base alloy, depending on the application. The usual clad product consists of a core alloy and a more anodic cladding alloy metallurgically bonded to one or both sides of the core alloy. Because the core alloy is cathodic to the cladding, any corrosion penetrates only to the cladding-to-core interface. It then spreads laterally and thus prevents perforation of the core. Table 4-16 lists the compositions of various claddings used on aluminum alloys.

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TABLE 4-15. ELECTRODE POTENTIALS OF REPRESENTATIVE ALUMINUM ALLOYS\* (Adapted From Ref. 10)

| ALUMINUM ALLOY**                                     | POTENTIAL, V |
|--|--------------|
| 2219-T3, T4  | -0.64†       |
| 2024-T3, T4  | -0.69†       |
| 295.0-T4 (SC or PM)††                                | -0.70        |
| 295.0-T6 (SC or PM)                                  | -0.71        |
| 2014-T6, 355.0-T4 (SC or PM)                         | -0.78        |
| 355.0-T6 (SC or PM)                                  | -0.79        |
| 2219-T6, 6061-T4                                     | -0.80        |
| 2024-T6  | -0.81        |
| 2219-T8, 2024-T8, 356.0-T6 (SC or PM), 443.0-F (PM)  | -0.82        |
| 1100, 3003, 6061-T6, 6063-T6, 7075-T6†, 443.0-F (SC) | -0.83        |
| 1060, 1350, 3004, 7050-T73, 7075-T73†                | -0.84        |
| 5052, 5086   | -0.85        |
| 5454   | -0.86        |
| 5456, 5083   | -0.87        |
| 7072   | -0.96        |

\*Measured in an aqueous solution of 53 g of NaCl and 3 g of H<sub>2</sub>O<sub>2</sub>/liter at 25°C (77°F); 0.1 normal calomel reference electrode

\*\*The potential of an aluminum alloy is the same in all tempers wherever the temper is not designated.

†The potential varies ±0.01 to 0.02 V with quenching rate.

††SC = sand cast alloys.

PM = permanent mold cast alloys

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TABLE 4-16. COMPOSITION OF CLADDING USED FOR ALUMINUM-CLAD ALLOYS (Ref. 17)

| CLADDING ALLOY | COMPOSITION, WT % |           |      |      |         |           |           | ALLOYS CLADDED   |
|----------------|-------------------|-----------|------|------|---------|-----------|-----------|--|
|                | Si                | Fe        | Cu   | Mn   | Mg      | Cr        | Zn        |  |
| 1050           | 0.25              | 0.40      | 0.05 | 0.05 | 0.05    | —         | —         | 2024   |
| 1175           | 0.15              | (Si + Fe) | 0.10 | —    | —       | —         | —         | (Cladding for reflector sheet)                             |
| 1230           | 0.7               | (Si + Fe) | 0.10 | 0.05 | —       | —         | 0.10      | (Older cladding for 2017, 2074)                            |
| 6003           | 0.7               | —         | —    | —    | 1.2     | —         | —         | 2014   |
| 6053           | *                 | 0.35      | 0.10 | —    | 1.1-1.4 | —         | 0.15-0.35 | 2014   |
| 6253           | *                 | 0.50      | 0.10 | —    | 1.0-1.5 | 0.15-0.35 | 1.6-2.4   | 5056   |
| 7072           | *                 | 0.50      | 0.10 | —    | 0.10    | —         | 0.8-1.3   | 2219, 3003, 3004, 3005, 5050, 5155, 6061, 7075, 7079, 7178 |

\*Silicon content is 45% to 65% of magnesium content.

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**MIL-HDBK-735(MR)****4-2.1.1.11 Cavitation and Erosion Corrosion**

Aluminum depends upon a passive film to protect it from corrosion; therefore, any mechanical action that damages or removes the film enhances the corrosive action of the environment. Aluminum is vulnerable to corrosion under conditions in which the film is eroded away by liquid moving at high velocity, local flow turbulence, solids in suspension, and droplet impingement. It is also subject to the film-damaging mechanism of cavitation in a liquid medium.

**4-2.1.1.12 Fretting Corrosion**

If an aluminum article in contact with another metal article is subject to relative oscillatory or vibratory movement, fretting can occur. Fretting damage is more likely to occur between aluminum articles than between articles of aluminum and a dissimilar metal. Fretting corrosion occurs at bolted or riveted joints in vehicle structures. Fretting also occurs in coils of aluminum sheet or stacks of aluminum articles under shipping conditions. A fine, black oxide powder is produced by aluminum fretting.

**4-2.1.2 Interface Problems**

Removal of residual flux from all weld, braze, and solder joints is vital.

Some treated woods contain copper salts. Aluminum in contact with this type of treated wood can be severely damaged if the wood is wet, i.e., contains greater than 18% moisture. Also water that condenses on copper

surfaces can pick up enough copper to damage aluminum that it subsequently contacts.

Antifouling paints contain copper and sometimes mercury. These paints should not be used on aluminum surfaces nor should they be used where the copper and/or mercury released by these paints can subsequently contact aluminum surfaces.

Other commonly encountered metals that can damage aluminum are cobalt, lead, nickel, and tin. An example is aluminum piping that carries cooling water containing trace amounts of a heavy metal. The heavy metal displaces the aluminum and a galvanic cell is established.

Some adhesives, coatings, elastomers, and organic-based solids can undergo decomposition, reversion, reaction, and leaching that can result in liquids and vapors that damage aluminum alloys. For example, materials based on polyvinyl chloride can damage aluminum if they release hydrogen chloride upon aging. Table 4-17 presents the relative corrosivity of vapors that can emanate from various materials.

The chloride ion in human perspiration can damage unprotected aluminum alloys that are continually handled.

Corrosion of aluminum alloys can result from contact with wet materials that produce solutions of  $\text{pH} \geq 9$ , e.g., wet concrete. Although aluminum alloys can corrode in contact with wet concrete because of its high pH, they are not seriously corroded by long-term exposure to dry cement. Magnesia insulation is also corrosive to aluminum when wet but not when dry.

Aluminum and its alloys can be damaged by cutting

**TABLE 4-17. SOURCES OF CORROSIVE VAPOR (Ref. 11)**

| MATERIAL             | SEVERELY<br>CORROSIVE                              | SOMEWHAT<br>CORROSIVE              | NOT<br>CORROSIVE                  |
|----------------------|--|------------------------------------|-----------------------------------|
| Adhesive             | Ureaformaldehyde                                   | Phenolformaldehyde                 | Epoxy                             |
| Gasket               | Neoprene/asbestos resin/cork                       | Nitrile/asbestos<br>glue/cellulose | —                                 |
| Insulation<br>(Wire) | Vinyl<br>Polyvinyl chloride<br>Vinylidene fluoride | Teflon<br>Nylon<br>Polyimide       | Polyurethane<br>Polycarbonate     |
| Sealer               | Silicone (acetic acid evolving)                    | Epoxy<br>Polysulfide               | Silicone                          |
| Sleeving             | Vinyl<br>Polyvinyl chloride                        | Silicone                           | —                                 |
| Tubing               | Neoprene, shrinkable                               | —                                  | —                                 |
| Plastics             | Malamine<br>ABS<br>Phenolic                        | Polyester<br>Diallyl phthalate     | Silicone<br>Epoxy<br>Polyurethane |
| Vanish               | Vinyl  | Alkyd                              | —                                 |

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oils, which contain soaps that leave an alkaline residue during subsequent furnace treatment.

Dust particles that settle on aluminum surfaces can initiate corrosion because some dusts are highly alkaline, which is damaging to aluminum, and other dusts contain soluble chlorides. Also dusts can absorb sufficient atmospheric chlorides to create an electrolyte.

Materials containing carbon and graphite, including graphite-containing lubricants and common "lead" pencils, should never be used on aluminum surfaces; carbon is highly cathodic to aluminum.

"Purple plague" causes cracks and open circuits in electronic equipment. It is a brittle, intermetallic compound of gold and aluminum that forms in the presence of silicon. A special problem is bonding aluminum to gold-plated Kovar posts in silicon transistors and integrated circuits. Sometimes it is necessary to remove the gold plate from the post to prevent formation of purple plague.

#### 4-2.1.3 Methods for Prevention of Corrosion

##### 4-2.1.3.1 Selection of Materials

Where possible, alloy selection should consider compositions and tempers that have good resistance to corrosion and stress-corrosion cracking in the service environment.

Heat-treatable aluminum alloys are selected over non-heat-treatable alloys because of their higher strength. These alloys show a range of strengths, the highest of which are developed in the copper-containing alloys. The optimum levels of strength are developed by heat treat-

ments that may also generate high levels of susceptibility to stress-corrosion cracking, intergranular corrosion, and exfoliation. Heat treatments have been developed that reduce this susceptibility, but some strength is lost. If this lower strength is not adequate, some means of protection for the highly susceptible alloys may be necessary. Clad alloy is used widely to protect the high-strength, heat-treatable aluminum alloys.

Table 4-18 rates qualitative stress-corrosion cracking resistance for heat-treatable alloys having various shapes and tempers. The susceptibility of these alloys to corrosion and stress-corrosion cracking requires that all aluminum sheets used in external environments in Army aircraft be clad on both sides (Ref. 18). There are exceptions, however:

1. If the design requires surface metal removal by machining or chemical milling
2. If the design requires adhesive bonding
3. If the design uses alloys of the 5000 or 6000 series.

There are constraints on aluminum alloy selection for Army aircraft applications:

1. Mill product forms of aluminum alloys 2020, 7079, and 7178 in all temper conditions shall not be used for structural applications.
2. The use of 7XXX-T6 alloys shall be limited to thicknesses not to exceed 4.78 mm (0.188 in.).
3. The use of 2XXX series alloys in the T3 and T4 tempers shall require specific approval of the procuring activity.

The 5XXX series alloys develop the highest strength of

**TABLE 4-18. STRESS-CORROSION CRACKING RATINGS\* FOR HIGH-STRENGTH ALUMINUM ALLOY PRODUCTS (Ref. 18)**

| ALLOY AND TEMPER | ROLLED PLATE | ROD AND BAR | EXTRUDED SHAPES | FORGINGS     |
|------------------|--------------|-------------|-----------------|--------------|
| 2014-T6          | Poor         | Poor        | Poor            | Poor         |
| 2024-T3, T4      | Poor         | Poor        | Poor            | —            |
| 2024-T6          | —            | Good        | —               | Poor         |
| 2024-T8          | Good         | Excellent   | Good            | Intermediate |
| 2124-T851        | Good         | —           | —               | —            |
| 2219-T3, T37     | Poor         | —           | Poor            | —            |
| 2219-T6, T8      | Excellent    | Excellent   | Excellent       | Excellent    |
| 6061-T6          | Excellent    | Excellent   | Excellent       | Excellent    |
| 7049-T73         | Excellent    | —           | Good            | Good         |
| 7149-T73         | —            | —           | Good            | Good         |
| 7049-T6          | —            | —           | Intermediate    | —            |
| 7X75-T736        | —            | —           | —               | Good         |
| 7050-T736        | Good         | —           | Good            | Good         |
| 7050-T76         | Intermediate | —           | Intermediate    | —            |
| 7X75-T6          | Poor         | Poor        | Poor            | Poor         |
| 7X75-T73         | Excellent    | Excellent   | Excellent       | Excellent    |
| 7X75-T76         | Intermediate | —           | Intermediate    | —            |

\*Ratings are for the short transverse direction.

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the nonheat-treatable aluminum alloys and have the highest resistance to seawater corrosion. However, the fatigue strength of some of these alloys is severely reduced in seawater, as described in par. 4-2.1.1.9. Some 5XXX series alloys are susceptible to exfoliation in some tempers. However, exfoliation-resistant tempers have been developed, as described in par. 4-2.1.1.7. Those 5XXX alloys containing more than 3% magnesium may be susceptible to stress-corrosion cracking in strain-hardened tempers, particularly after exposure to temperatures above 150°C (302°F). The resistance of the 5XXX series alloys to pitting in weathering atmospheres is comparable to the 1XXX and 3XXX series alloys, but the 5XXX series alloys develop deeper pits. The 5XXX series alloys are used in watercraft applications requiring high strength, as indicated in Table 4-8.

Where dissimilar metals are to be joined, galvanically compatible alloys should be chosen. 5XXX and 6XXX series aluminum alloys are most compatible with magnesium. For bimetallic couples use metals or alloys in the same galvanic groups according to MIL-STD-889 (Ref. 16) or as close as possible. If this choice is not possible, use tapes or primers on faying surfaces to prevent metallic or electrical contact.

Aluminum should never be coupled to copper metals or alloys, nor should it be exposed to water containing traces of copper or other heavy metals. Mercury should never be allowed to contact aluminum. Aluminum can be anodic or cathodic to steel, depending on the composition of the electrolyte. Materials containing carbon and graphite should never be used on aluminum surfaces. Nongraphitic marking pencils covered by MIL-P-83953 (Ref. 19) shall be used rather than common "lead" pencils.

Fasteners used to join an aluminum alloy with a noncompatible alloy should be cathodic or galvanically neutral to both metals. As an alternative, the fastener should be electrically insulated from the cathodic alloy with an insulating sleeve or washer. Installation with wet primer and cap seal with a conformal coating may be required to prevent exfoliation corrosion at the exposed short transverse grain structure.

Fasteners that join aluminum to aluminum should be cathodic to the alloy being joined. Titanium fasteners should be aluminum coated. Cadmium-plated steel fasteners and trim can be used safely with aluminum provided that the plating is sufficiently thick. Zinc-plated or galvanized metal is satisfactory in neutral or acid media. Fasteners should be installed with wet primer.

**4-2.1.3.2 Surface Treatments**

An oxide film that naturally forms on aluminum provides adequate protection against corrosion in many environments. Regular cleaning with a mild abrasive and detergent maintains aluminum exposed to weathering. Neither steel wool nor copper alloy wire pads should be

used to scour aluminum because any residual steel particles trapped in the softer aluminum will cause unsightly rust spots and residual copper particles will cause pitting. Also a nonmetallic brush should be used.

Chemical conversion coatings can provide a limited degree of corrosion protection, and anodic coatings can provide a higher degree of protection. Military specifications for chemical conversion and anodic coatings and cleaning processes are referenced in par. 3-6.1.1 and par. 3-7.3.4.2, respectively. The processes used to generate these coatings on aluminum alloys are usually proprietary; the examples given in Tables 4-19, 4-20, and 4-21 are illustrative only. The military specifications for these coatings do not detail process parameters, but they do base requirements on coating performance or thickness.

Chemical conversion coatings are thin and provide much less protection than anodized coatings. The usual purpose of a chemical conversion coating is to provide a base for an organic coating. Most processes that generate a chemical conversion coating are based on mixtures of phosphate, phosphate-chromate, or chromate. The usual film thickness is 0.51  $\mu\text{m}$  (0.02 mil) or less. Examples of chemical conversion coating processes are given in Table 4-19.

Relatively thick and dense oxide films on aluminum alloys are formed by anodizing processes; however, anodizing alone cannot correct a material selection error. Processes based on either sulfuric acid or chromic acid are available. The sulfuric acid process is cheaper and more effective to use to coat alloys containing copper; therefore, it is more widely used. Chromic acid anodizing is used on aluminum alloys containing less than 5% copper or less than 7.5% total of all alloying constituents; therefore, it is not suitable for highly alloyed aluminum. Sulfuric acid anodizing is used for aluminum alloys with a nominal copper content in excess of 5% or nominal silicon content in excess of 7% and for alloys containing over 7.5% of total alloying elements. The two processes are compared in Table 4-20. A sulfuric acid process deposits a film of a given thickness in one-eighth the time required in a chromic acid process. Oxide films formed by anodizing processes are colorless and transparent and contain submicroscopic pores; however, a virtually nonporous, dense barrier layer is formed next to the metal. Type I anodic coatings are formed in a bath containing chromic acid, and the coating thickness ranges from 1.3 to 7.6  $\mu\text{m}$  (0.05 to 0.3 mil). Type II anodic coatings are formed in a bath containing sulfuric acid, and the coating thickness ranges from 2.5 to 25  $\mu\text{m}$  (0.1 to 1.0 mil) (Ref. 23). The anodic coatings produced by these processes are not suitable for wear and sliding applications.

Thick, abrasive-resistant coatings can be provided by hard-coat anodizing. Type III hard coatings are prepared by any anodizing process that proves effective. Hard coatings range in thickness from 13 to 114  $\mu\text{m}$  (0.5 to 4.5

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mil) (Ref. 23). The process characteristics of two well-known hard-coating processes, Martin and Alumilite, are presented in Table 4-21. Alloys that respond to these treatments are limited in their copper and silicon concentrations. For atmospheric corrosion protection in architectural applications, coatings 25 to 76  $\mu\text{m}$  (1 to 3

mil) thick are used (Ref. 20). A 7.6- $\mu\text{m}$  (0.3-mil) thick coating is used in aluminum automobile trim. Dense coatings are more difficult to form on aluminum alloys containing copper, but the Martin process is more effective on copper-containing alloys than the Alumilite process.

**TABLE 4-19. EXAMPLES OF CHEMICAL CONVERSION COATING PROCESSES FOR ALUMINUM (Ref. 20)**

| TYPES OF COATING      | SOLUTION COMPOSITION, wt %   | TREATING CONDITIONS            | COLOR         |
|-----------------------|--|--------------------------------|---------------|
| Alkaline oxide        | 3% $\text{Na}_2\text{CO}_3$  | Boiling                        | Gray          |
|                       | 1% $\text{Na}_2\text{CrO}_4$<br>0.5% $\text{NaAlO}_2$<br>0.25% Na salicylate           | 5 min<br>93°C (200°F)<br>5 min | Colorless     |
| Crystalline phosphate | 0.7% $\text{Zn}^{++}$  | 54° to 57°C<br>(130° to 135°F) | Colorless     |
|                       | 1.0% $\text{PO}_4^{3-}$<br>2.0% $\text{NO}_3$<br>1.0% $\text{BF}_4$                    | 2 to 5 min                     |               |
| Amorphous phosphate*  | 7% $\text{H}_3\text{PO}_4$   | 38° to 54°C<br>(100° to 130°F) | Green         |
|                       | 0.2% $\text{KHF}_2$<br>0.4% $\text{CrO}_3$   | 0.5 to 5 min                   |               |
| Amorphous chromate**  | 0.75% $\text{Na}_2\text{Cr}_2\text{O}_7$   | 21° to 32°C<br>(70° to 90°F)   | Yellow to tan |
|                       | 0.5% $\text{K}_3\text{Fe}(\text{CN})_6$<br>0.1% NaF<br>0.3% $\text{HNO}_3$<br>pH = 1.5 | 0.5 to 5 min                   |               |
| Boehmite              | Distilled or deionized water   | Boiling 15 min to 5 h          | Colorless     |

\*US Patent 2,438,877 (1948)

\*\*US Patent 2,796,370 (1957)

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**TABLE 4-20. A COMPARISON OF TYPICAL THICKNESSES AND WEIGHTS OF ANODIC COATINGS FORMED ON SOME WROUGHT ALUMINUM ALLOYS IN CONVENTIONAL SULFURIC- AND CHROMIC-ACID ELECTROLYTES (Ref. 21)**

| ALLOY AND TEMPER | SULFURIC ACID, 15 wt % AT 22°C (72°F)<br>FOR 15 min AT 129 A/m <sup>2</sup> (12 A/ft <sup>2</sup> ) |      |                    |                     | CHROMIC ACID, 10 wt % AT 35°C (95°F)<br>FOR 60 min AT 40 V |      |                    |                     |
|------------------|---|------|--------------------|---------------------|--|------|--------------------|---------------------|
|                  | COATING THICKNESS   |      | COATING MASS       |                     | COATING THICKNESS  |      | COATING MASS       |                     |
|                  | $\mu\text{m}$   | mil  | mg/mm <sup>2</sup> | mg/in. <sup>2</sup> | $\mu\text{m}$  | mil  | mg/mm <sup>2</sup> | mg/in. <sup>2</sup> |
| 7075-T6          | 5.6   | 0.22 | 0.0135             | 8.7                 | 2.8  | 0.11 | 0.0051             | 3.3                 |
| 6061-T6          | 6.1   | 0.24 | 0.0158             | 10.2                | 3.3  | 0.13 | 0.0093             | 6.0                 |
| 2024-T6          | 5.1   | 0.20 | 0.0102             | 6.6                 | 2.5  | 0.10 | 0.0047             | 3.0                 |
| 5052-0           | 6.1   | 0.24 | 0.0160             | 10.3                | 2.8  | 0.11 | 0.0088             | 5.7                 |
| 3003-0           | 6.4   | 0.25 | 0.0157             | 10.1                | 2.8  | 0.11 | 0.0088             | 5.7                 |
| 1100-0           | 5.8   | 0.23 | 0.0160             | 10.3                | 3.0  | 0.12 | 0.0088             | 5.7                 |

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TABLE 4-21. COMPARISON OF PROCESSES FOR HARD COAT ANODIZING (Ref. 22)

| VARIABLES             | ALUMILITE   | MARTIN  |
|-----------------------|---|---|
| Solution composition  | 12% Sulfuric acid, 1% Oxalic acid                                     | 15% Sulfuric acid saturated with carbon dioxide |
| Operating temperature | 9° to 11°C (48° to 52° F)   | -4° to 0°C (25° to 32° F)                       |
| Current density       | 387.5 A/m <sup>2</sup> (36 A/ft <sup>2</sup> ) (lower on thin sheets) | 269.1 A/m <sup>2</sup> (25 A/ft <sup>2</sup> )  |
| Voltage               | 10 to 60 dc (or higher for thicker coatings)                          | 10 to 75 dc                                     |
| Thickness versus time | 25.4 μm (1 mil)/20 min up to 102 μm (4 mil) coating thickness         | 25.4 μm (1 mil)/40 min                          |
| Alloy limitations     | Over 3% Cu or 7% Si or 7 to 9% combined                               | Over 5% Cu                                      |

Courtesy of the American Electroplaters and Surface Finishers Society, monthly Journal *Plating*, September 1962.

A loss of only 5.1 to 7.6 μm (0.2 to 0.3 mil) of anodized, protected aluminum after an exposure of 18 yr to an industrial atmosphere has been measured (Ref. 24). A coating of at least 18 μm (0.7 mil) is recommended for atmospheric exposure in which no maintenance is performed.

Shot peening is frequently used to increase stress corrosion resistance. The application of shot peening to generate compressive stresses on the surface of metals is described in par. 3-6.4. The application of shot peening to aluminum alloys used in Army air vehicles is described in ADS-13 (Ref. 18).

#### 4-2.1.3.3 Coatings

Many durable paint coatings are available to protect aluminum alloy surfaces. Almost any type of paint suitable for metals is suitable for aluminum alloys. Paint coatings are discussed in par. 3-7.3.1. Surface preparation is important for good paint adherence. Chemical conversion coatings of the chromate or phosphate type are recommended for use in conjunction with paint for aluminum surfaces. The most durable paint coating systems consist of a chemical conversion coat, a chromated primer coat, and a top coat. The organic finish for Army aircraft (Ref. 18) is aliphatic polyurethane as specified in MIL-C-46168 (Ref. 25), over epoxy polyamide primer which conforms to MIL-P-23377 (Ref. 26).

Various adhesives, sealants, encapsulants, and potting compounds may be used on aluminum surfaces, and these materials are discussed in par. 3-7.3.2. It is vital that all exposed edges of aluminum alloy sheets and plates be protected, e.g., all rivets should be installed wet with zinc chromate primer. All permanently installed fasteners in Army aircraft (Ref. 18) are installed wet with a corrosion-inhibiting sealant that conforms to MIL-S-81733 (Ref. 27), or an epoxy primer that conforms to MIL-P-23377 (Ref. 26).

Organic coatings and plastic films of various types may be factory-applied using high-speed coil-coating machines. Generally these coatings are more durable than those applied during fabrication. However, the exposed edges and the surface damage resulting from fabrication should be protected as part of the fabrication process.

The various rust-preventive compounds discussed in par. 3-7.3.3 are applicable to aluminum alloys.

The various aluminum alloys can be metallurgically bonded to one another. Therefore, alloys that are susceptible to attack in particular environments can be clad on one or both sides with a layer of commercially pure aluminum or one of the more corrosion-resistant alloys that is more active in the galvanic series than is the core alloy. This method of protection is normally used for the higher strength alloys. The benefits of the high-strength core combine with the corrosion resistance of the cladding. Cladding is further described in par. 4-2.1.1.10.

Aluminum can be electroplated with most common metals, but the usual plating process requires the application of a zinc immersion coating followed by a copper strike, over which a nickel and chromium plate or other similar, protective metal is applied.

Aluminum is strongly anodic to most of the metals used for electroplated coatings; therefore, it will experience local attack at any break in the cathodic coating. A pore-free, resistant coating is essential. The electroplating technology for aluminum is similar to that successfully employed for zinc-base die castings.

Aluminum alloys and other metallic coatings can be applied to aluminum alloys by thermal spray processes.

Alloys such as 1100, 3003, and 6061 aluminum can be enameled with lead-bearing glass frits that have a high thermal expansion coefficient and can be fired at low temperature.

Various metal oxides such as aluminum, zirconium, and boron can be applied to aluminum surfaces by

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thermal spray processes.

Inorganic coatings do not form a chemical bond with the substrate metal and therefore must match the thermal expansion coefficient of the substrate and have some inherent strength.

Corrosion-inhibiting dry film lubricants may be used to prevent corrosion of aluminum alloys in some applications. Dry film lubricants must not contain powdered carbon, graphite, or heavy metals. Dry film lubricants are discussed in par. 3-6.3.

Fretting corrosion is avoided during shipping of aluminum articles by packaging so that the separate pieces cannot move. Separating individual pieces with paper or plastic sheets is also helpful. Sheet aluminum in coils is sometimes oiled.

Packaging materials that can emit vapors, such as hydrogen chloride gas (which is from polyvinyl chloride plastics), or that can release copper or other heavy metal ions when wet should not be used with aluminum.

#### 4-2.1.3.4 Design Considerations

Potential moisture traps, e.g., such as sump areas in an aluminum assembly, should be minimized by design. Unavoidable traps should have adequate drain vents that minimize the entry of solid matter because solid matter can accumulate in the liquid traps and plug drain vents. Maintenance procedures should require periodic examination of sump areas and drain holes, accumulated solid matter should be cleaned out, and drain vents should be cleared.

Aluminum alloy joints should not form crevices. Butt-welded joints are preferable to lap joints, and welded lap joints should have a weld bead along the edge of each piece to seal the crevice that is formed. Crevices may also be filled with a sealant such as tapes, films, sealing compounds, and primers. Exposed edges of clad aluminum should be sealed.

Gas-shielded arc welding processes are preferred for aluminum alloys because they do not require a flux of any kind. Metal inert gas (MIG) and tungsten inert gas (TIG) are the processes employed. Properly made MIG or TIG welds show no loss of mechanical properties after 10 or more years in atmospheric environments. High-strength welds of 2XXX and 7XXX series alloys are more likely to cause problems than those of the other classes of aluminum alloys. The heat resulting from the welding process may result in microstructural changes in the heat-affected zone that are more susceptible to corrosion and stress-corrosion cracking. However, postweld heat treatment may reduce the corrosion susceptibility of the heat-affected zone.

Removing the weld bead increases susceptibility to attack.

Table 4-22 lists recommended filler alloys for MIG and TIG welding of aluminum alloys for corrosive environments. The left-most vertical column and the horizontal row across the top indicate the alloys to be joined. The intersection of a vertical column and a horizontal row indicates the appropriate filler alloys.

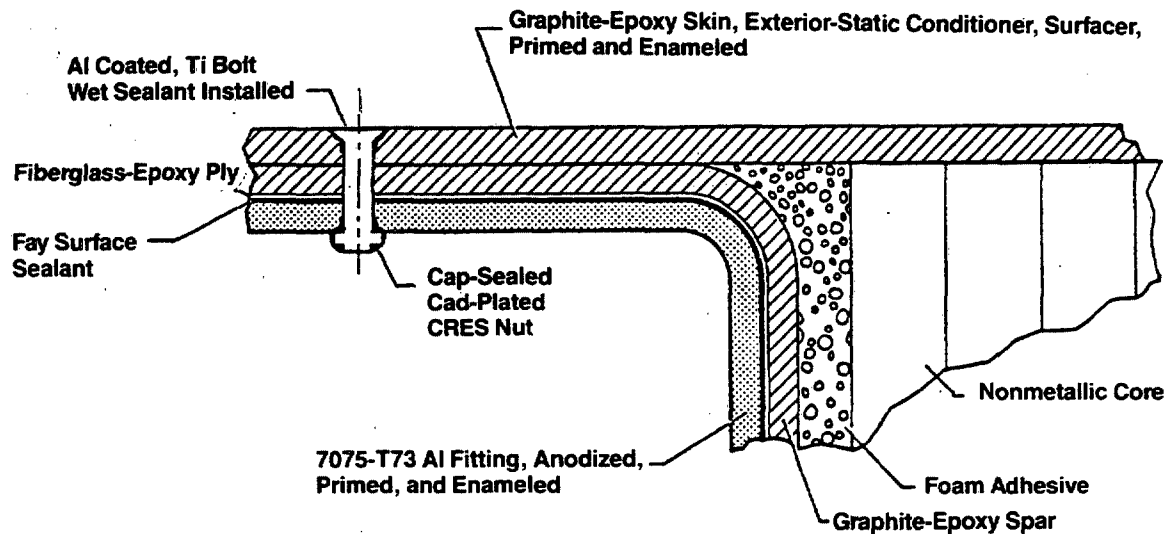
Extraordinary corrosion prevention measures are required when graphite-reinforced parts are directly coupled with aluminum components. Typical prevention details for the joining of 7075-T73 aluminum with graphite-reinforced epoxy composite are indicated in Fig. 4-8. The aluminum is anodized, primed, and enameled. The graphite-epoxy (gr/ep) composite is coated with one ply of fiberglass or Kevlar film cured on the composite surface that is faying on the aluminum. This film should extend 102 mm (4 in.) beyond the faying surface. The remainder of the graphite surface is covered with Tedlar film, a fiberglass, or Kevlar ply, or it is treated with a pinhole filler plus two coats of primer. The cut edges of the composite should be treated with either sealant or primer plus enamel. During assembly of the composite to the alloy, the faying surface is sealed. Then it is fastened with aluminum-coated titanium fasteners installed on the aluminum side with wet sealant and aluminum- or cadmium-plated, corrosion-resistant steel washers, nuts, or collars that are cap sealed.

#### 4-2.2 CAST ALUMINUM ALLOYS

The types of aluminum casting alloys correspond to the types of wrought alloys. There is a heat-treatable class and a nonheat-treatable class. The tempers of heat-treatable casting alloys are designated by a "T" following the alloy designation. Those of nonheat-treatable casting alloys are designated by an "F". A heat-treatable alloy that is given no thermal treatment following casting may be used in the "F" temper.

Die, permanent mold, and sand casting account for most of the production of cast aluminum products. The selection of a casting alloy involves consideration of casting characteristics as well as corrosion resistance and other characteristics.

Although there is a wide range of cast aluminum alloy compositions, most aluminum casting applications can be satisfied by three alloys: 356, 443, and 514 (Ref. 30). These alloys contain only impurity amounts of copper. The composition of these alloys is given in Table 4-23, and additional casting alloy compositions are given in Table 4-6.

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**Figure 4-8. Graphite to Aluminum Corrosion Prevention Details (Ref. 29)**

**TABLE 4-22. RECOMMENDED FILLER ALLOYS FOR MIG AND TIG WELDING OF WROUGHT ALUMINUM ALLOYS FOR CORROSIVE ENVIRONMENTS (Ref. 28)**

| ALLOYS TO BE JOINED | 1100<br>1150<br>1200<br>3003 | 6063<br>6351<br>6061    | 5052<br>5454          | 5083<br>5056          | 7039  |
|---------------------|------------------------------|-------------------------|-----------------------|-----------------------|-------|
| 7039                | 5356*                        | 5356*                   | 5356*                 | 5356*                 | 5356* |
| 5083                | 5554                         | 5183                    | 5554                  | 5554                  |       |
| 5056                | 5254<br>5183<br>5356*        | 5356*<br>5254**         | 5254<br>5183<br>5356* | 5254<br>5183<br>5356* |       |
| 5052                | 5554                         | 5554**                  | 5554***               |                       |       |
| 5454                | 5254<br>5183<br>5356*        | 5254**<br>5183<br>5356* | 5254<br>5183<br>5356* |                       |       |
| 6063                | 5254**                       | 5254**,†                |                       |                       |       |
| 6351                | 5356*                        | 5183                    |                       |                       |       |
| 6061                | 4043††                       | 5356*<br>4043††         |                       |                       |       |

MIG = metal inert gas

TIG = tungsten inert gas

\* In Canada, 5056 filler is used in place of 5356.

\*\* Except for highly restrained joints

\*\*\* Must be used for elevated-temperature service

† For pipe

†† For electrical joints

NOTE: The filler alloys recommended in this table have been selected on the basis of the performance of the welds in corrosive environments. They are listed in order of preference from a corrosion point of view. They do not necessarily provide the best weldability or the greatest joint strengths obtainable.

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TABLE 4-23. CAST ALUMINUM ALLOY COMPOSITIONS AND PROPERTIES (Ref. 30)

| CAST ALLOY DESIGNATION | COMPOSITION* |         |      |      |      |           |      | HEAT-TREATED CONDITION | TENSILE STRENGTH |       | ELONGATION IN 51 mm (2 in.),** % |
|------------------------|--------------|---------|------|------|------|-----------|------|------------------------|------------------|-------|----------------------------------|
|                        | Mn           | Si      | Zn   | Ti   | Cu   | Mg        | Fe   |                        | MPa**            | ksi** |                                  |
| A356                   | 0.20         | 6.5/7.5 | 0.10 | 0.20 | 0.20 | 0.20-0.40 | 0.20 | T6†                    | 255              | 37    | 5.0                              |
| B443                   | 0.35         | 4.5/6.0 | 0.35 | 0.25 | 0.15 | 0.05      | 0.8  | F††                    | 117              | 17    | 3.0                              |
| 514                    | 0.35         | 0.35    | 0.15 | 0.25 | 0.15 | 3.5-4.5   | 0.50 | F††                    | 152              | 22    | 6.0                              |

\*Maximum unless otherwise noted

\*\*Minimum unless otherwise noted

†T6, solution heat treated, artificially aged

††F, sand cast, no heat treatment

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## 4-2.2.1 Types of Corrosion

## 4-2.2.1.1 Uniform and Pitting Corrosion

The alloying element that is most conducive to general corrosion is copper. The corrosion of casting alloys is generally greater with a given copper content than that of a wrought alloy; otherwise, the general corrosion of cast alloys is comparable to wrought alloys.

## 4-2.2.1.2 Stress-Corrosion Cracking

Stress-corrosion cracking of casting alloys in service has occurred only with the aluminum-magnesium and aluminum-zinc-magnesium types that have large amounts of soluble alloying elements in order to produce the highest strength. The susceptibilities of several cast alloys to stress-corrosion cracking are given in Table 4-24.

TABLE 4-24. SUSCEPTIBILITY OF CAST ALUMINUM ALLOYS TO STRESS-CORROSION CRACKING (Ref. 31)

| HIGH RESISTANCE TO STRESS-CORROSION CRACKING |           |         |
|--|-----------|---------|
| Alloy  | Condition |         |
| 355.0  | C355.0    | T6      |
| 356.0  | A356.0    | All     |
| 357.0  |           | All     |
| B358.0                                       |           | All     |
| 359.0  |           | All     |
| 380.0  | A380.0    | As cast |
| 514.0  |           | As cast |
| 518.0  |           | As cast |
| 535.0  |           | As cast |
| A712.0                                       | C712.0    | As cast |
| LOW RESISTANCE TO STRESS-CORROSION CRACKING  |           |         |
| Alloy  | Condition |         |
| 295.0  |           | T6      |
| B295.0                                       |           | T6      |
| 520.0  |           | T4      |
| 707.0  |           | T6      |
| D712.0                                       |           | As cast |

## 4-2.2.2 Interface Problems

Cast aluminum alloys are more likely to be drilled and tapped for screw threads and bolt holes than wrought alloys. Dissimilar metal bolts are likely to cause galvanic corrosion and seizing. A nongraphite antiseizing compound or 18-8 stainless steel wire thread inserts may be used. Wire thread inserts provide higher loading strengths than standard tapped threads in the same material, and they should be dipped in zinc chromate primer before being placed in the tapped hole. See Tables 4-14 and 4-15 for the galvanic potentials of cast aluminum.

## 4-2.2.3 Methods for Prevention of Corrosion

The casting process usually results in cast aluminum products having relatively thick cross sections, which can tolerate a greater amount of corrosion than can the typical product fabricated from wrought aluminum sheets.

The methods for prevention of corrosion that are applicable to wrought aluminum are also applicable to cast aluminum alloys and are described in par. 4-2.1.3.

## 4-2.3 POWDER METALLURGY ALLOYS

## 4-2.3.1 Types of Alloys

Powder metallurgy products are formed by compacting metal powder under compressive forces and heating in a reducing atmosphere, such as hydrogen gas. The heating improves the bonding between particles and the reducing gas removes oxides and other impurities. However, the oxide film that forms on the surface of aluminum particles is not reducible by hydrogen or other gases at temperatures below the melting point of aluminum. Therefore, articles formed from aluminum powders contain aluminum oxide. Mechanical properties can be improved by hot working to break up the oxide film and disperse it in the aluminum matrix.

Aluminum-base compositions and powder metallurgy products that cannot be made by conventional ingot casting can be made from prealloyed powders. Aluminum-base alloys can contain iron, magnesium, chromium, molybdenum, tungsten, titanium, zirconium, beryllium, boron, tin, and/or lead. These alloys exhibit high strength



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at room and elevated temperatures, good resistance to attack by water at high temperature, high modulus of elasticity, and good bearing characteristics.

Various composite products with useful properties can be made by mixing powders of different alloys. The properties and applications of some powder metal aluminum alloys are given in Table 4-25.

**4-2.3.2 Types of Corrosion**

The general corrosion resistance of aluminum-aluminum oxide alloys is comparable to that of 6061-T6 alloy. The corrosion resistance of these alloys is better than 7075-T6 and 2024-T6 alloys, but it is not as good as the resistance

of 1100 or 3003 alloy. The powder metallurgy alloys are resistant to stress-corrosion cracking even in the transverse orientation.

Powder metallurgy products can be made that have mechanical properties and resistance to stress-corrosion cracking that surpass those of conventional aluminum alloy products.

**4-2.3.3 Interface Problems**

The powder metallurgy alloys are subject to the same interface problems as are the wrought and cast aluminum alloys. These are described in pars. 4-2.1.2 and 4-2.2.2.

**TABLE 4-25. PROPERTIES AND APPLICATIONS OF ALUMINUM POWDER METAL PRODUCTS**

| MATERIAL AND SPECIFICATION DESIGNATION   | TREATMENT       | DENSITY, kg/m <sup>3</sup> | TENSILE STRENGTH, |      | YIELD STRENGTH, |      | HARDNESS | ELONGATION, % | APPLICATION   |
|--|-----------------|----------------------------|-------------------|------|-----------------|------|----------|---------------|---|
|  |                 |                            | MPa               | ksi  | MPa             | ksi  |          |               |   |
| Aluminum alloys<br>601AB (Alcoa): 0.25<br>Cu, 0.6 Si, 1.0 Mg,<br>1.5 lubricant, bal<br>1202(e) | Sintered (T1)   | 2550                       | 124               | 18   | 58.6            | 8.5  | 65-70 HB | 8.0           | Similar to wrought<br>6061: strength, ductility, corrosion<br>resistance  |
|  | Heat treated(f) | 2550                       | 248               | 36   | 241             | 35   | 80-85 Re | 2.0           |   |
| 201AB (Alcoa): 4.4<br>Cu, 0.8 Si, 0.5 Mg,<br>1.5 lubricant, bal<br>1202(e)                     | Sintered (T1)   | 2640                       | 208.9             | 30.3 | 180.6           | 26.2 | 70-75 Re | 3.0           | Similar to wrought<br>2014 but without<br>manganese. Good<br>strength properties  |
|  | Heat treated(f) | 2640                       | 331.6             | 481  | 327.5           | 47.5 | 70-75 Re | 2.0           |   |
| 202AB (Alcoa): 4.0<br>Cu, 1.5 lubricant, bal<br>1202(e)  | Sintered (T1)   | 2490                       | 160.0             | 23.2 | 75.2            | 10.9 | 55-60 HB | 10.0          | Good ductility.<br>Suitable for cold-<br>formed parts   |
|  | Heat treated(g) | 2490                       | 228               | 33   | 146.9           | 21.3 | 45-50 Re | 7.3           |   |
| 602AB (Alcoa): 0.4<br>Si, 0.6 Mg, 1.5<br>lubricant, bal 1202(e)                                | Sintered (T1)   | 2550                       | 131               | 19   | 62              | 9    | 55-60 HB | 9.0           | Good electrical<br>conductivity (from<br>42.0 to 48.5% IACS,<br>depending on treat-<br>ment): ductility, and<br>finishability |
|  | Heat treated(f) | 2550                       | 186               | 27   | 172             | 25   | 65-70 Re | 3.0           |   |
| 601AC (Alcoa): 0.25<br>Cu, 0.6 Si, 1.0 Mg,<br>bal 1202(e)                                      | Sintered (T1)   | 2550                       | 133.8             | 19.4 | 53.1            | 7.7  | —        | 10.7          | Same as 601AB,<br>without lubricant; for<br>isostatic compacting  |
|  | Heat treated(f) | 2550                       | 269               | 39   | 261.3           | 37.9 | —        | 2.0           |   |
| 201AC (Alcoa): 4.4<br>Cu, 0.8 Si, 0.5 Mg,<br>bal 1202(e)                                       | Sintered (T1)   | 2640                       | 204.8             | 29.7 | 146.9           | 21.3 | —        | 4.0           | Same as 201AB,<br>without lubricant; for<br>isostatic compacting  |
|  | Heat treated(f) | 2640                       | 382.0             | 55.4 | 368.9           | 53.5 | —        | 2.0           |   |
| 22 (Alcan)(h): 2.0<br>Cu, 1.0 Mg, 0.3 Si,<br>bal Al  | Sintered        | 2530                       | 165               | 24   | 110             | 16   | 83 HB    | 6.0           | Has good mechanical<br>properties in sintered<br>or heat-treated forms  |
|  | Heat treated(i) | 2530                       | 262               | 38   | 200             | 29   | 74 Re    | 3.0           |   |

(e) 1202 composition: 99.4 Al, 0.3 Al<sub>2</sub>O<sub>3</sub>, 0.15 Fe, 0.07 Si, balance other metallics. (f) Solutioned at 521°C (970°F), 504°C (940°F) for Grade 201AB and 201AC for 30 min, quenched in cold water, and aged at 160°C (320°F) for 18 h to the T6 condition. (g) Solutioned at 540°C (1000°F) for 30 min, quenched in cold water, and aged at 149°C (300°F) for 20 h to the T6 condition. (h) Grade number includes suffix: FF = premix with 1.5% lubricant; NL = premix without lubricant. (i) Solutioned at 521°C (970°F) for 30 min, quenched in water, and aged at 149°C (300°F) for 18 h. (j) Solutioned at 499°C (930°F) for 60 min, quenched in water, and aged at 149°C (300°F) for 18 h. (k) Solutioned at 477°C (890°F) for 60 min, quenched in water, and aged at 127°C (260°F) for 18 h. (m) Breaking strength in newton (N) and pound (lb).

(cont'd on next page)

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TABLE 4-25. (cont'd)

| MATERIAL AND SPECIFICATION DESIGNATION                         | TREATMENT           | DENSITY, kg/m <sup>3</sup> | TENSILE STRENGTH, |        | YIELD STRENGTH, |     | HARDNESS | ELONGATION, % | APPLICATION  |
|--|---------------------|----------------------------|-------------------|--------|-----------------|-----|----------|---------------|--|
|  |                     |                            | MPa               | ksi    | MPa             | ksi |          |               |  |
| 24 (Alcan)(h)(2014):<br>4.4 Cu, 0.5 Mg, 0.9 Si, 0.4 Mn, bal Al | Sintered            | 2540                       | 165               | 24     | 97              | 14  | 80 HB    | 5.0           | Properties resemble those of its wrought counterpart, 2014. Good mechanical properties                               |
|  | Heat treated(j)     | 2540                       | 241               | 35     | 193             | 28  | 72 Re    | 3.0           |  |
| 67 (Alcan)(h): 0.5 Cu, bal Al                                  | Sintered (T1)       | 2520                       | 103               | 15     | 55              | 8   | 60 HB    | 12.0          | High electrical conductivity (48% IACS) and ductility. Similar to wrought 1100                                       |
| 68 (Alcan)(h): 0.6 Mg, 0.4 Si, bal Al                          | Sintered (T1)       | 2520                       | 117               | 17     | 62              | 9   | 64 HB    | 9.0           | Good surface finish: high ductility and conductivity (42% IACS). Similar to wrought 6101                             |
| 69 (Alcan)(h)(6061):<br>0.25 Cu, 1.0 Mg, 0.6 Si, 0.10 Cr       | Sintered            | 2500                       | 127.6             | 18.5   | 69              | 10  | 66 HB    | 10.0          | Properties are similar to those of 6061. Good strength, corrosion resistance, ductility, and conductivity (40% IACS) |
|  | Heat treated(i)     | 2500                       | 207               | 30     | 193             | 28  | 71 Re    | 2.0           |  |
| 76 (Alcan)(h)(7075):<br>1.6 Cu, 2.5 Mg, 0.20 Cr, 5.6 Zn        | Sintered            | 2510                       | 207               | 30     | 152             | 22  | 90 HB    | 3.0           | Properties are similar to those of 7075. High strength and hardness  |
|  | Heat treated(k)     | 2510                       | 310               | 45     | 276             | 40  | 80 Re    | 2.0           |  |
| 91 (Alcan)(h): 26.3 tribaloy                                   | Sintered (T1)       | 3050                       | 93.8              | 13.6   | —               | —   | —        | 2.0           | Excellent wear resistance  |
|  | Heat treated        | 3050                       | 106.2             | 15.4   | —               | —   | —        | 1.0           |  |
| 4040 (Alcan): 1.0 Cu, 1.0 Si, bal Al—150 + 325 mesh            | Loose sintered (T1) | 1400                       | 445 (m)           | 100(m) | —               | —   | —        | —             | High-porosity parts for controlling contamination, pressure, sound, catalytic reactions, etc.                        |
| 4090 (Alcan): 1.0 Cu, 1.0 Si, bal Al—60 + 150 mesh             | Loose sintered (T1) | 1350                       | 445 (m)           | 100(m) | —               | —   | —        | —             |  |
| 4160 (Alcan): 1.0 Cu, 1.0 Si, bal Al—30 + 60 mesh              | Loose sintered (T1) | 1300                       | 445 (m)           | 100(m) | —               | —   | —        | —             |  |

(e) 1202 composition: 99.4 Al, 0.3 Al<sub>2</sub>O<sub>3</sub>, 0.15 Fe, 0.07 Si, balance other metallics. (f) Solutioned at 521°C (970°F), 504°C (940°F) for Grade 201AB and 201AC for 30 min, quenched in cold water, and aged at 160°C (320°F) for 18 h to the T6 condition. (g) Solutioned at 540°C (1000°F) for 30 min, quenched in cold water, and aged at 149°C (300°F) for 20 h to the T6 condition. (h) Grade number includes suffix: FF = premix with 1.5% lubricant; NL = premix without lubricant. (i) Solutioned at 521°C (970°F) for 30 min, quenched in water, and aged at 149°C (300°F) for 18 h. (j) Solutioned at 499°C (930°F) for 60 min, quenched in water, and aged at 149°C (300°F) for 18 h. (k) Solutioned at 477°C (890°F) for 60 min, quenched in water, and aged at 127°C (260°F) for 18 h. (m) Breaking strength in newton (N) and pound (lb).

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### 4-2.3.4 Methods for Prevention of Corrosion

The methods for prevention of corrosion that are applicable to wrought aluminum are also applicable to powder metallurgy products and are described in par. 4-2.1.3.

## 4-2.4 EXAMPLES OF CORROSION

### 4-2.4.1 Stress-Corrosion Cracking

Over a period of years an individual antitank weapon—an antitank rocket—has experienced a number of malfunctions traceable to failures of either the rocket motor closure or the rocket motor itself (Ref. 32). Both of these components are made of alloy 7001-T6. Analysis of the rocket motor during launch indicates a maximum effective stress of 572 MPa (83 ksi) occurring in the throat area of the rocket nozzle. Of the commercially available aluminum alloys, only 7001-T6 has a yield strength high enough to withstand this level of stress. However, examination of test specimens from the initial failures revealed that 7001-T6 has a low fracture toughness and extremely poor flaw tolerance. A fix was adopted, and the 7001-T6 alloy retained. The fix was to reduce the stress in the closure and strengthen the warhead/closure joint with a fiberglass overwrap.

A new round of failures occurred a few years later. These failures were confined to rocket motors produced by a single manufacturer, and examination showed the primary origins to be stress-corrosion cracks on the order of 1.02 mm (0.040 in.) in depth. Later demonstration indicated that the condition leading to the formation of these stress-corrosion cracks was most likely introduced by one of the proof tests used as a quality assurance measure during motor production. The proof test resulted in a flaw that became the initiating site for a stress-corrosion crack. Fracture toughness measurements made on specimens from the failures indicated a critical flaw depth of 0.30 mm (0.012 in.), a much smaller depth than the observed stress-corrosion cracks.

The remaining stockpile was salvaged by overwrapping the rocket motor with fiberglass. More failures occurred, however, that resembled, in most aspects, the previous motor failures. Perhaps the anodized coating at the base of the fin slots was damaged when the fins were removed for the fiberglass wrapping operation. This occurrence would have contributed to the later corrosion problem.

Of the three manufacturers involved in rocket production over the years, one has had a far worse malfunction rate than the others. The various metallurgical and process parameters used by the three manufacturers were examined carefully, but it is not possible to draw conclusions concerning the importance of these parameters in stress-corrosion cracking of 7001-T6. What does appear evident is that subtle differences in processing result in subtle differences in the character of the metal in the final product. More significantly, it is beyond the

ability of existing material and product specifications to control these characteristics. Therefore, materials selected for critical application must be tolerant of the inevitable processing variability and production defects that contemporary quality control measures are unable to discriminate.

### 4-2.4.2 Exfoliation

After a rifle had been in service for 3 yr in a hot and humid climate (Southeast Asia), exfoliation corrosion was detected on parts of the lower receiver (Ref. 33). The part affected had been protected with an anodic coating, but the affected areas were those frequently in contact with the hands of the soldiers and thus were exposed to the chloride ion in perspiration. The original specification required a minimum yield strength for the aluminum forging of 448 MPa (65 ksi). The manufacturers supplied alloy 7075 in the T6 temper, which did have adequate strength.

An investigation was conducted on alternative tempers of alloy 7075 that might have adequate strength and greater exfoliation resistance than the T6 temper. Newer alloys with adequate strength and greater resistance to exfoliation were also investigated.

Some conclusions of the investigation are

1. Alloy 7075 die forgings can be thermally treated to produce an exfoliation-resistant material with a minimum yield strength of 448 MPa (65 ksi).

2. In the T6 temper, 7075 forgings exhibiting a randomized grain structure, as found in those produced from rolled bar stock, are more resistant to exfoliation corrosion.

3. Other 7XXX series alloys, such as X7050 and premium grade 7175, can be thermally treated to produce a variety of exfoliation-resistant forgings with much higher strength than 7075.

4. Temperature and length of aging are very important factors to control to insure that the optimum combination of strength and exfoliation corrosion resistance is obtained.

### 4-2.4.3 Biological Corrosion

The aluminum diesel fuel tank of a combat tank experienced internal corrosion (Ref. 34). The corrodent was the metabolic product of microorganisms that are the result of diesel fuel contamination. This contamination has several sources:

1. Contamination of fuel in bulk storage
2. Water condensation inside the fuel cell
3. Solids introduced into the fuel cell by dirty fuel transfer hoses.

Pitting corrosion eventually penetrates the fuel tank sump; thus replacement is required. The problem was solved by adding an icing inhibitor to the fuel in the fuel tank, which dissolves the aqueous phase and acts as a

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biocide (Ref. 35). Biocides also are available to be added to the fuel in bulk storage.

**4-3 BERYLLIUM**

Beryllium has a density of 1849.17 kg/m<sup>3</sup> (115.44 lbm/ft<sup>3</sup>) and a melting point of 1285°C (2345°F). The metal has excellent electrical and thermal conductivities, and high heat capacity. It can absorb more heat energy for an equivalent increase in temperature than the same weight or the same volume of any other metal. Beryllium has an extremely high modulus of elasticity; therefore, it is a very stiff metal. The metal, however, is very brittle and in this respect acts more like a ceramic than a metal. Beryllium and its compounds are very toxic. Although beryllium is a costly metal, its characteristics make it a special metal for special applications, such as heat-absorbing nose cones, heat shields, skin panels, and structural members of spacecraft and missiles. It has also been used as a heat sink for aircraft air-cooled wheel brakes, it is an ideal heat-radiating material for dissipating heat from spacecraft electricity-generating systems, and it has been used as an antenna material in data-gathering satellites.

The stiffness, light weight, and dimensional stability of beryllium over prolonged periods have led to its use in inertial guidance devices and other control systems using gyroscopes, gimbals, torque tubes, and high-speed rotating elements.

Commercial grade beryllium is made by two processes. A pebble material is produced by reduction of beryllium fluoride with magnesium. The concentration of impurities in this product is reduced by melting it in a vacuum to produce refined ingots. A flake material is produced by fused salt electrolysis of beryllium chloride. Several commercial grades and forms of beryllium are available. They range from a vacuum-distilled or electrorefined material of high purity to a product that contains about 92% beryllium and 4.5% beryllium oxide. The oxide-containing material possesses high rigidity and resistance to flow under heat and pressure.

Vacuum hot-pressing of powder is used extensively in forming beryllium shapes. Because of the random grain orientation left by vacuum hot-pressing, the mechanical properties of hot-pressed beryllium are isotropic. Beryllium crystals, however, are extremely anisotropic in mechanical behavior. Therefore, processes that improve ductility in the direction of working also reduce ductility in the transverse direction.

**4-3.1 TYPES OF CORROSION**

Beryllium is an active metal, as indicated by its position below magnesium but above aluminum in the electromotive force series of Table 2-2. At ambient conditions in air a thin, adherent film forms on the surface of beryllium that is protective provided it has no breaks.

Differences in the measured values of corrosion can be significant because of the variability in composition, metallurgical condition, and surface states of beryllium specimens.

**4-3.1.1 Uniform Corrosion**

Beryllium is an amphoteric metal. It is readily attacked by hydrochloric, hydrofluoric, or sulfuric acids at room temperature. Dilute nitric acid slowly attacks beryllium, but concentrated nitric acid has little effect. At higher temperatures, however, the reaction with nitric acid becomes violent. Phosphoric and oxalic acids attack beryllium. Acetic, citric, and tartaric acids attack beryllium, but the reaction stops after a time because a protective film forms. Beryllium reacts slowly with dilute alkaline solutions; however, the rate of attack increases at higher concentrations. A hot, concentrated alkali reacts vigorously with beryllium, and nitrate and chromate ions passivate beryllium.

**4-3.1.2 High-Temperature Oxidation**

In dry gases oxidation is no problem up to 649°C (1200°F). In the temperature range from 749° to 899°C (1380° to 1650°F), the oxide film is initially protective and the oxidation rate is parabolic. After a time, however, the oxidation rate becomes linear. The duration of the protective period depends upon the microstructure and chemical purity of the beryllium and upon the oxygen pressure as well as temperature. Above 899°C (1650°F) the oxide film offers little protection, and burning starts at 1204°C (2200°F). In gases containing water the transition from parabolic to linear oxidation occurs earlier. In oxygen the transition occurs at a lower temperature.

Beryllium reacts slowly with nitrogen at 499°C (930°F) and forms a nitride. Up to about 900°C (1652°F) the reaction is parabolic with time. The rate of nitridation is less than the rate of oxidation at a given temperature.

Beryllium does not react with hydrogen at temperatures up to 1100°C (2012°F). It is attacked by steam at high temperatures and by carbon monoxide, the halogens, nitric oxide, hydrogen cyanide, and hydrogen sulfide.

**4-3.1.3 Pitting**

Beryllium may pit in storage conditions. Although the pitting would not be detectable if translated into uniform attack, even slight pitting can damage high-precision instrument components made of beryllium.

The average corrosion rate of beryllium in demineralized water expressed as penetration is about 25 μm/yr (1 mpy). However, this corrosion is experienced as deep pitting. Chlorides, fluorides, sulfates, and cupric and ferrous ions increase pitting corrosion attack. For example, the corrosion rate in natural seawater is 434 μm/yr (17.1 mpy) at 15°C (59°F) and 658 μm/yr (25.9

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mpy) at 35°C (95°F). The maximum pit depth after 18 days was 20  $\mu\text{m}$  (0.8 mil) in distilled water and 117  $\mu\text{m}$  (4.6 mil) in seawater. At 35°C (95°F) the maximum pit depth in natural seawater was 381  $\mu\text{m}$  (15 mil) with 75% of the surface covered (Ref. 36). Fluorinated oils that are used in gyroscopes can also corrode beryllium.

**4-3.1.4 Stress-Corrosion Cracking**

Beryllium is subject to stress-corrosion cracking in the presence of chloride ions. Both anodized and pickled beryllium fail prematurely at applied stresses well below the yield strength when exposed to natural seawater at 15°C (59°F) (Ref. 36).

**4-3.1.5 Liquid Metal Corrosion**

Beryllium has good resistance to most liquid metals, as illustrated in Table 4-26.

**4-3.1.6 Galvanic Corrosion**

Tests of beryllium coupled with stainless steel and with aluminum have been conducted in demineralized water at 85°C (185°F) (Ref. 40). Under static conditions the aluminum and stainless steel were attacked, but under dynamic conditions beryllium was attacked. In experiments that exposed beryllium-stainless steel couples to water at 250° and 254°C (482° and 490°F) for 1440 h, there was little attack of the beryllium member. However, beryllium underwent catastrophic corrosion when oxygen was added to the water (Ref. 41). Beryllium coupled with platinum and with zirconium showed no evidence of galvanic corrosion in demineralized water at 343°C (650°F) (Ref. 42).

**4-3.2 METHODS FOR PREVENTION OF CORROSION**

Anodized beryllium has good corrosion resistance in natural seawater compared to pickled beryllium. Electroless nickel plate coatings have been applied to beryllium with good results. Conversion coatings on beryllium, especially those based on chromates, protect in humid environments, in chloride-containing atmospheres, and in dry, oxidizing gases at 927°C (1700°F). Coatings of low-fired porcelain enamel also give excellent results (Ref. 43).

Additions of either sodium dichromate or sodium nitrate to aqueous test solutions inhibit the pitting attack in natural seawater.

**4-4 CARBON**

Carbon exists in a variety of structural forms ranging from nearly perfect single crystals of graphite and diamond to almost noncrystalline materials. Carbon is produced industrially by the pyrolysis of organic carbon at temperatures up to about 700°C (1292°F). When some of these materials are heated at temperatures up to about 3000°C (5432°F) in vacuum or in an inert atmosphere, a transition to the graphite structure and a change in properties occur. This transition is referred to as "graphitization", and the product is a "polycrystalline graphite". Not all carbons undergo this transition. Those that do are termed "graphitizing carbons", and those that do not are termed "nongraphitizing carbons". Examples of graphitizing carbon are pitch and petroleum cokes and the carbon derived from the pyrolysis of polyvinyl chloride. Examples of nongraphitizing carbons are those derived from polyvinylidene chloride, from cellulose, and from sucrose.

**TABLE 4-26. RESISTANCE OF BERYLLIUM TO CORROSION IN LIQUID METALS  
(Refs. 37, 38, and 39)**

| LIQUID METAL     | TEMPERATURE, °C (°F) |              |              |   |
|------------------|----------------------|--------------|--------------|---|
|                  | 360° (572°)          | 600° (1112°) | 800° (1472°) | 1000° (1832°)   |
| Bismuth          | Good                 | Good         | Good         | 1500-2500 mdd<br>(0.03-0.05 lbm/(ft <sup>2</sup> ·day)) |
| Bismuth lead     | Good                 | Good         | Limited      | Limited   |
| Bismuth lead tin | Good                 | Good         | —            | —   |
| Gallium          | Good                 | Good         | Poor         | Poor  |
| Lead             | Good                 | Good         | Limited      | Limited   |
| Lithium          | Good                 | Good         | Poor         | Poor  |
| Magnesium        | Good                 | Good         | —            | —   |
| Mercury          | Good                 | Good         | Good         | —   |
| Potassium        | Good                 | Limited      | Limited      | —   |
| Sodium           | Good                 | Good         | Limited      | —   |
| Sodium potassium | Good                 | Good         | Limited      | —   |
| Tin              | Good                 | —            | —            | —   |
| Tin lead         | Good                 | Good         | —            | —   |

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Carbon and graphite components are widely used in bearings, seals, and other load-bearing applications in which sliding motion occurs. Because of their ability to conduct electricity, carbon components are used where current is transferred between two bodies in relative motion. Carbon brushes in electric motors are an example.

The properties that follow are exhibited by most carbons:

1. Mechanical
  - a. Self-lubricating
  - b. Nonwelding
  - c. Low rates of wear
  - d. Nonabrasive to metal counterface
  - e. Chemical inertness
  - f. High thermal conductivity
  - g. Temperature stability
2. Electrical
  - a. High electrical conductivity for a nonmetal
  - b. High potential drop in sliding contact
  - c. Good resistance to erosion by arcing.

Pyrolytic carbon and chemical-vapor-deposited carbon refer to carbon material that is deposited at approximately 1100°C (2012°F) on a substrate by the thermal decomposition of a carbon-bearing vapor. Pyrolytic graphite refers to carbon material deposited from a hydrocarbon gas over a temperature range of 1750° to 2250°C (3182° to 4082°F). A low-molecular-weight gas, such as methane, is normally used.

When organic polymers are pyrolyzed to carbon, a "hard", low-density (1400.01 kg/m<sup>3</sup> (87.4 lbf/ft<sup>3</sup>)) carbon is formed. The polymer is often a particular structural shape. Heating to 1600°C (2912°F) produces an impermeable carbon. For example, phenol-formaldehyde resins are used to produce a material known as vitreous carbon.

Shapes consisting of compacted cellulose fibers are carbonized at 799°C (1471°F) and treated at about 1500°C (2732°F) to produce an impermeable product having a density of 1499.33 kg/m<sup>3</sup> (93.6 lbf/ft<sup>3</sup>).

Carbon/graphite fibers are produced by carbonizing materials, such as yarns or filaments of viscose rayon and polyacrylonitrile, and pitch. These fibers are heterogeneous materials that reflect the precursors used in preparation as well as the heat-treatment process employed in their production.

Carbon/graphite fibers are being used increasingly in composite structures. The matrix may be metal or nonmetal or even carbon. Carbon/graphite fibers have desirable stiffness properties (high elastic modulus).

Composites of carbon/graphite fibers and carbon matrices are used in high-temperature applications such as aircraft brakes and rocket nozzles.

### 4-4.1 TYPES OF CORROSION

Commercial graphites are constrained in applications for specific environments by the chemical reactions that follow:

1. Gaseous oxidation
2. Interstitial formation
3. Oxidation in solution
4. Carbide formation.

Therefore, the discussion of carbon corrosion considers these classes of reactions rather than the usual corrosion categories that characterize metals and alloys.

#### 4-4.1.1 Gaseous Oxidation

The oxidation rate of pure graphite is very low. Graphites that have a large surface area available for oxygen sorption and a higher impurity rate have a correspondingly higher oxidation rate. Walker *et al.* (Ref. 44) showed that at 800°C (1472°F) and a pressure of  $1.01 \times 10^4$  Pa (0.1013 bar or 0.1 atm), the relative rates of reactions with O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and H<sub>2</sub> are  $1 \times 10^5$ , 1, 3, and  $3 \times 10^{-3}$ , respectively. Bonnetain and Hoynant (Ref. 45) have shown that with O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O the oxidation rates at 1000°C (1832°F) and a pressure of  $1.01 \times 10^5$  Pa (1.013 bar or 1 atm) are  $54 \times 10^4$ , 21, and 98 mg carbon/m<sup>2</sup>-h ( $1.1 \times 10^{-1}$ ,  $4.3 \times 10^{-6}$ , and  $2.0 \times 10^{-5}$  lb carbon/ft<sup>2</sup>-h), respectively.

#### 4-4.1.2 Interstitial Formation

The graphitic structure consists of molecular layers that have weak binding forces between them. This characteristic makes graphite very susceptible to the formation of interlamellar compounds that increase the dimension between the molecular layers. This reaction, termed "intercalation", occurs spontaneously whenever certain elements, such as metal halides, sulfides, and some oxides, either come directly into contact with graphite or are heated to a vapor in the presence of graphite. Other examples of materials that cause intercalation are potassium from a sodium potassium liquid metal solution and bromine in a solution of carbon tetrachloride. The tube shown in Fig. 4-9 was used to bubble chlorine gas into molten aluminum; the corrodent was aluminum chloride. Heat-treating graphite-bromine intercalation compounds results in explosive exfoliation.

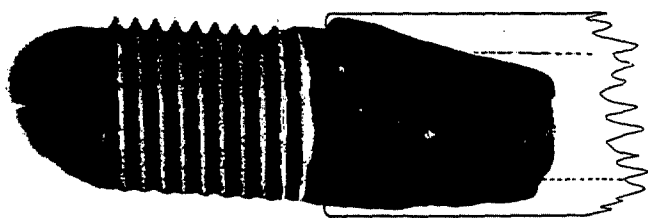
#### 4-4.1.3 Oxidation in Solution

Graphite undergoes two types of oxidation in solution:

1. Almost spontaneous oxidation by strong oxidizing agents
2. Anodic oxidation.

An example of spontaneous oxidation is the interlamellar compound of graphite and oxygen formed by the oxidation of graphite with potassium perchlorate in a mixture of concentrated nitric and sulfuric acids. Graphite

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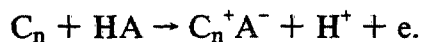


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**Figure 4-9. Corrosion of Graphite by Aluminum Chloride; Test Sample Screwed to End of Normal Tube Inlet; Original Shape is Indicated (Ref. 46)**

is oxidized by certain strong acids to form salts. Examples of acids in which this occurs are nitric, phosphoric, arsenic, selenic, perchloric, and sulfuric. Sulfuric acid also reacts to produce carbon bisulfite.

Anodic oxidation of graphite occurs by the formation of interlamellar compounds of oxyacids according to the reaction



Acids that have been intercalated during anodic oxidation are  $H_2SO_4$ ,  $ClSO_3H$ ,  $FSO_3H$ ,  $H_2SeO_4$ ,  $HNO_3$ ,  $BF_3(CH_3COOH)_2$ ,  $CF_3COOH$ ,  $H_3PO_4$ , and  $H_3AsO_4$  (Ref. 47). The net result is the swelling and disruption of graphite.

#### 4-4.1.4 Carbide Formation

Graphite reacts with a wide range of metals and metal oxides and yields carbides. The temperatures at which significant reaction takes place are normally in excess of  $500^\circ C$  ( $932^\circ F$ ) and frequently greater than  $1000^\circ C$  ( $1832^\circ F$ ).

#### 4-4.1.5 Galvanic Effects

Graphite behaves electrochemically like a noble metal, such as gold or platinum, and exhibits a noble potential in

most electrolytes; therefore, it is cathodic to most metals upon galvanic coupling. Graphite fibers in a nonmetallic matrix, e.g., epoxy, are insulated electrically from the metal to which the matrix is attached if the attachment does not expose the graphite fibers. Adhesively bonded graphite-epoxy composites do not exhibit galvanic corrosion, whereas mechanically fastened (bolted) assemblies do.

Galvanic corrosion rates for some alloys coupled to graphite-epoxy composites have been studied in neutral ( $pH = 7$ ) 3.5% by weight NaCl solutions (Ref. 48). Twenty-three alloys coupled to graphite-epoxy composites were examined, and the results were grouped into the following three classes:

1. Acceptable—less than  $5 \mu A/cm^2$  ( $32.3 \mu A/in.^2$ ) (stainless steel and titanium alloys)
2. Borderline—5 to  $15 \mu A/cm^2$  ( $32.3$  to  $96.8 \mu A/in.^2$ ) (aluminum alloys and some steels)
3. Unacceptable—over  $15 \mu A/cm^2$  ( $96.8 \mu A/in.^2$ ) (steels: AF1410, 300 M, and 4340; and aluminum alloys: 2024-T651).

A similar series of measurements was conducted with a graphite-epoxy composite coupled to several metals (Ref. 49). Table 4-27 shows the open-circuit potential of the materials as measured against a reference electrode. A potential difference of approximately 1 V exists between the composite and aluminum alloys. The potential difference between the composite and the titanium alloys was about 0.3 V for an as-received unpolished surface but was about 0.5 V for a freshly polished surface.

Actual zero impedance galvanic corrosion currents between the graphite-epoxy composite and the alloys are presented in Table 4-28. The chromate conversion coating on the cadmium-plated specimen reduces the corrosion current by 40% of that for cadmium. Nevertheless, the couple is only slightly less reactive than couples with aluminum, and this fact is a clear indication of a galvanic corrosion problem for graphite-epoxy composites coupled to structural aluminum alloys and cadmium-plated, high-strength fasteners.

**TABLE 4-27. OPEN CIRCUIT POTENTIAL MEASUREMENTS VS SATURATED CALOMEL ELECTRODE (Ref. 49)**

| MATERIAL   | POTENTIAL, mV |
|--|---------------|
| Graphite-epoxy composite (NARMCO 5206-II)          | +170          |
| Aluminum 5052-H38                                  | -760          |
| Aluminum 7075-T6                                   | -770          |
| Aluminum 7075-T651                                 | -780          |
| Cadmium  | -805          |
| Cadmium-plated steel (chromate conversion coating) | -735          |
| Titanium 6Al-4V (as received)                      | -140          |
| Titanium 6Al-4V (freshly polished surface)         | -375          |
| Titanium 6Al-4V (above specimen 24 h later)        | -260          |

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TABLE 4-28. ZERO IMPEDANCE GALVANIC CURRENT MEASUREMENTS BETWEEN GRAPHITE-EPOXY COMPOSITE MATERIAL AND DESIGNATED ALLOYS (Ref. 49)

|   | GALVANIC CURRENT          |                              | CORROSION RATE*                      |                                      |
|---|---------------------------|------------------------------|--------------------------------------|--------------------------------------|
|   | $\mu\text{A}/\text{cm}^2$ | $\mu\text{A}/\text{in.}^2$ * | $\text{mg}/(\text{dm}^2\text{-day})$ | $\text{lb}/(\text{ft}^2\text{-day})$ |
| Composite aluminum 5052-H38                           | 12.7                      | 81.9                         | 10.3                                 | $0.21 \times 10^{-3}$                |
| Composite aluminum 7075-T6                            | 12.5                      | 80.6                         | 10.1                                 | $0.21 \times 10^{-3}$                |
| Composite aluminum 7075-T651                          | 14.4                      | 92.9                         | 11.7                                 | $0.24 \times 10^{-3}$                |
| Composite cadmium                                     | 15.5                      | 100.0                        | 78.1                                 | $1.60 \times 10^{-3}$                |
| Composite cadmium plate + chromate conversion coating | 9.6                       | 61.9                         | 7.8                                  | $0.16 \times 10^{-3}$                |
| Composite titanium 6A1-4V (as received)               | 0.002                     | 0.013                        | 0.003                                | $6.1 \times 10^{-8}$                 |
| Composite titanium 6A1-4V (freshly polished surface)  | 0.19                      | 1.23                         | 0.27                                 | $5.5 \times 10^{-6}$                 |

\*Corrosion rate is calculated from the measured zero impedance currents.

Coupling graphite-epoxy composite to 7075-T651 aluminum has no effect on the stress-corrosion cracking rate of the alloy.

#### 4-4.2 INTERFACE PROBLEMS

An important interface problem is the wear of carbon brushes in motors and generators.

In the period immediately after new surfaces have been brought into contact, the surfaces wear so as to conform with each other. Once this "bedding" process is complete, wear normally continues at a constant rate (Ref. 50). Wear per unit distance is roughly independent of speed over a range of speeds of 200 to 40,000 mm/s (7.9 to 1575 in./s). The wear rate is proportional to the applied pressure over a pressure range of  $2 \times 10^4$  to  $2 \times 10^6$  Pa (0.2 to 20 atm). For a fixed graphite content, the harder the carbon, the lower the wear rate. Mineral ash in the carbon can cause rapid wear of both carbon and metal. Normally, however, high graphite content reduces wear. Typical values of wear coefficients are  $10^{-12}$  cm<sup>3</sup>/N·cm ( $6.9 \times 10^{-12}$  in.<sup>3</sup>/lb·in.). For example, the thickness of the carbon layer removed is  $10^{-10}$  times the distance traveled under a pressure of 96,527 Pa (14 psi).

In electrical applications much of the wear is associated with the passage of current (Ref. 50). At high current densities, wear rates decrease with increasing pressure; increasing pressure improves the electrical contact. At low current densities, however, the wear is essentially mechanical, and in this case the wear rate increases with pressure. Also the sparking caused by the commutation process results in a higher wear rate for a commutator brush than for a slip ring.

Low metal wear is associated with the formation of a good patina, or surface film, on the commutator brush or slip ring. In corrosive atmospheres, e.g., HCl, the film on the copper can disintegrate and leave the bare metal. Rapid wear of the brushes and commutator may then occur (Ref. 50). Other gases, such as hydrogen sulfide

(H<sub>2</sub>S), produce a very thick film on the copper. In atmospheres of very low absolute humidity—below  $4 \times 10^2$  Pa (3 torrs) water vapor pressure—catastrophic wear of the graphite occurs that can be a million times higher than normal (Refs. 51 and 52). These conditions can occur in high-altitude aircraft, in polar regions, and in areas in which the atmosphere is controlled at a low humidity.

#### 4-4.3 METHODS FOR PREVENTION OF CORROSION

Graphite is normally impregnated with a resin to make it impervious to various agents. Table 4-29 lists typical resins used in chemical applications. Table 4-29 also lists a few reagents and conditions in which graphite-resin systems survived for at least 3 months with a final weight loss of less than 1%. In some applications, such as exposure to a strong acid, a pyrolytic carbon coating provides better protection than the more traditional impregnants (Ref. 46).

The rate of gaseous oxidation of graphites can be reduced by the addition of certain borates and phosphates (Refs. 53 and 54). An alternative is to coat the graphite with a refractory coating. Silicon carbide coatings have been produced by depositing silicon onto a hot graphite substrate by thermal cracking of trichlorosilane (Ref. 55). This deposition is followed by heat treatment at 2000°C (3632°F) to form a chemically bonded layer of silicon carbide. A refractory metal, e.g., zirconium, can be thermosprayed onto the surface and heat-treated to form the carbide (Ref. 46).

Low-humidity wear of graphite can be prevented by additions, such as molybdenum disulfide, Teflon®, heavy-metal halides, waxes, and varnishes, in the brush (Ref. 50). Environments of pure oxygen or carbon dioxide inhibit this form of wear. Caution should be exercised with additions containing metals.

Care must be used when joining composites containing graphite to metals. Fig. 4-8 illustrates an approach for



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**TABLE 4-29. GENERAL CLASSIFICATION OF RESINS COMMONLY USED FOR IMPREGNATING CARBON AND GRAPHITE FOR CHEMICAL APPLICATIONS (Ref. 46)**

| DESCRIPTION                   | OPERATING RANGE                 |  | STABLE  | UNSTABLE         |
|-------------------------------|---------------------------------|--|---|------------------|
|                               | °C (°F)                         |  |   |                  |
| Phenolic derivatives          | 0 to 280<br>(32 to 536)         |  | Acids<br>Organic solvents<br>Alkalis up to 20%              |                  |
| Modified phenolic derivatives | 0 to 240<br>(32 to 464)         |  | Acids<br>Alkalis up to 40%                                  | Organic solvents |
| Furane derivatives            | 0 to 170<br>(32 to 338)         |  | Alkalis up to 90%<br>Organic solvents<br>Nonoxidizing acids | Oxidizing acids  |
| Linseed oil                   | 0 to 80<br>(32 to 176)          |  | Caustic/chlorine processes. Halogen and cyanide reactions   |                  |
| Paraffin waxes                | 0 (32) — softening point of wax |  | Alternative to linseed oil                                  |                  |

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joining graphite-epoxy composites with aluminum that avoids creating a galvanic couple.

#### 4-4.4 EXAMPLES OF CORROSION PROBLEMS

Graphite has good lubricating qualities; therefore, it is often incorporated into lubricating oils, greases, and dry lubricants and is also used in powder form as a lubricant. The potential for galvanic corrosion is so great, however, that lubricating products containing graphite should be used with great care.

Pencils containing graphite "leads" should never be used on metals, especially aluminum. Pencil markings have been known to penetrate an aircraft skin completely in a short period of time.

#### 4-5 COBALT AND COBALT ALLOYS

Elemental cobalt has a density of 8890.2 kg/m<sup>3</sup> (555 lbf/ft<sup>3</sup>). Its melting point is 1495°C (2723°F), and its boiling point is 2870°C (5198°F). Pure cobalt has found little use; however, alloys of cobalt have found widespread application.

Cobalt is usually alloyed with one or more of the following elements: iron, nickel, chromium, aluminum, silicon, manganese, tungsten, molybdenum, titanium, carbon, and small amounts of other elements.

There is no common alloy designation system. The cobalt alloys are known by the proprietary designations given by their producers.

Applications of cobalt alloys take advantage of one or more of the following properties:

1. Excellent wear resistance
2. Good mechanical properties at high temperature

3. Good oxidation and corrosion resistance.

For example, cobalt alloys are used as hard facings on machinery parts subject to wear, in the hot sections of gas turbine engines, and in exhaust valves of internal combustion engines.

#### 4-5.1 TYPES OF CORROSION

##### 4-5.1.1 General Corrosion (Uniform and Pitting Corrosion)

Pure cobalt has an extremely low corrosion rate in a marine atmosphere. After 3 yr at a site 244 m (800 ft) from the water, the corrosion rate was 5 μm/yr (0.2 mpy). At a site 24 m (78 ft) from the water, the corrosion rate was 3 μm/yr (0.1 mpy).

Wear-resistant cobalt alloys are not attacked in a marine air atmosphere. For example, a wear-resistant alloy (67 Co—30 Cr—2 W) lost none of its surface reflectivity after 18 months in the marine atmosphere at Kure Beach, NC (Ref. 56). However, after 2 yr immersed in seawater, the average corrosion rate of cobalt specimens was 18 μm/yr (0.7 mpy).

The wear-resistant cobalt alloys undergo little attack in acid mine water, seawater, or boiler water at ordinary temperatures. After 2 yr in the sea, wear-resistant cobalt alloys have an average corrosion rate of 3 μm/yr (0.1 mpy) and a maximum pitting penetration of 0.180 mm (7.09 mil) (Ref. 57).

The corrosion of three cobalt-base alloys in various chemical corrosives is shown in Table 4-30. Two of the alloys contain 30% chromium, whereas Haynes Alloy 25 contains 20% chromium. Alloying with chromium reduces attack in aggressive chemical environments. Haynes Alloy 25 also contains 10% nickel, whereas the other

TABLE 4-30. CORROSION OF COBALT-BASE ALLOYS IN VARIOUS CORROSIVES (Ref. 58)

| CORROSIVE         | CONCENTRATION, TEMPERATURE,<br>wt % °C (°F) |          | CORROSION RATE, mm/yr (mil/yr) |                  |                 |                  |                     |
|-------------------|---|----------|--------------------------------|------------------|-----------------|------------------|---------------------|
|                   |   |          | 44Co—31Cr—13 W                 |                  | 53Co—30Cr—4.5 W |                  | HAYNES<br>ALLOY 25* |
|                   |   |          | AS-CAST                        | HEAT-<br>TREATED | AS-CAST         | HEAT-<br>TREATED |                     |
| Acetic acid       | 10  | Boiling  | 0.05 (2)                       | 0.10 (4)         | <0.01 (0.3)     | <0.01 (0.3)      | <0.01 (0.1)         |
|                   | 99  | Boiling  | <0.01 (0.3)                    | <0.01 (0.3)      | <0.01 (0.3)     | 0.01 (0.4)       | Nil                 |
| Chlorine (wet)    | 100   | Room     | 5 (194)                        | 6.4 (251)        | 8.9 (350)       | 11.6 (455)       | <0.03 (1)           |
| Chromic acid      | 2   | 66 (150) | Nil                            | Nil              | Nil             | Nil              | Nil                 |
|                   | 10  | 66 (150) | 0.03 (1)                       | 0.64 (25)        | 0.71 (28)       | 0.58 (23)        | 0.13 (5)            |
| Cupric chloride   | 10  | Room     | <0.01 (0.5)                    | 0.05 (2)         | 0.01 (0.5)      | 0.05 (2)         | <0.01 (0.2)         |
| Ferric chloride   | 2   | Room     | 0.08 (3)                       | 0.25 (10)        | <0.01 (0.2)     | <0.01 (0.2)      | Nil                 |
| Formic acid       | 89  | 66 (150) | <0.01 (0.1)                    | Nil              | <0.01 (0.1)     | Nil              | <0.01 (0.1)         |
| Hydrochloric acid | 5   | Room     | 0.66 (26)                      | 0.41 (16)        | 1.3 (52)        | 0.23 (9)         | 0.61 (24)           |
| Hydrofluoric acid | 5   | Room     | 1.5 (59)                       | 1.4 (55)         | 1.3 (52)        | 0.81 (32)        | 0.13 (5)            |
| Nitric acid       | 10  | Boiling  | 0.15 (6)                       | 0.15 (6)         | 0.02 (0.8)      | 0.03 (1)         | <0.02 (0.5)         |
|                   | 40  | 66 (150) | 0.81 (32)                      | 0.05 (2)         | <0.01 (0.02)    | <0.01 (0.3)      | <0.02 (0.5)         |
| Phosphoric acid   | 50  | Boiling  | 1.7 (68)                       | 0.56 (22)        | 0.30 (12)       | 0.64 (25)        | 0.10 (4)            |
|                   | 85  | 66 (150) | Nil                            | 0.15 (6)         | Nil             | Nil              | <0.01 (0.1)         |
| Sodium hydroxide  | 50  | 66 (150) | <0.01 (0.3)                    | 0.15 (6)         | <0.01 (0.3)     | 0.01 (0.4)       | Nil                 |
| Sulfuric acid     | 77  | Room     | Nil                            | —                | Nil             | —                | Nil                 |
|                   | 96  | Room     | Nil                            | <0.01 (0.3)      | Nil             | Nil              | Nil                 |
|                   | 25  | 66 (150) | >25.4 (>1000)                  | >25.4 (>1000)    | 0.03 (1)        | Nil              | 0.28 (11)           |

\*9-11 Ni, 19-21 Cr, 14-16 W, 3.00 Fe max, 0.05-0.15 C, 1.00 Si max, 1.00-2.00 Mn, 0.030 P max, 0.030 S max, Balance Co

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alloys contain no nickel. In general, Haynes Alloy 25 has as good or better corrosion resistance than the other alloys to which it is compared in Table 4-28.

The chemical composition and mechanical properties of two cobalt-containing, high-strength bolting alloys are listed in Table 4-31. Each of these alloys exhibits a noble seawater galvanic potential near that of titanium. Based on standard laboratory tests, they are resistant to, but not necessarily immune to, crevice corrosion, stress corrosion, and hydrogen embrittlement (Ref. 59). The corrosion resistance of these alloys in chemical solutions is similar to that of Hastelloy C.

### 4-5.1.2 High-Temperature Corrosion

#### 4-5.1.2.1 Oxidation

Pure cobalt oxidizes rapidly at high temperatures (Ref. 57) and follows a parabolic relationship with time. Tests in air showed a weight gain of 240 mdd ( $4.92 \times 10^{-3}$  lb/ft<sup>2</sup>·day) at 696°C (1285°F) and 86,400 mdd (1.77 lb/ft<sup>2</sup>·day) at 1246°C (2275°F).

Chromium is the most effective alloying addition used to increase the oxidation resistance of cobalt. The scaling rate of cobalt-chromium alloys increases with increasing chromium content below about 25% chromium; the scaling rate decreases at chromium concentrations greater than 25%. Although 25% chromium is sufficient for

temperatures up to 999°C (1830°F), 30% chromium is needed for good resistance at temperatures as high as 1199°C (2190°F). Chromium additions greater than 30% decrease the scaling rate farther.

Cobalt-aluminum alloys have improved oxidation resistance but reduced mechanical properties (Ref. 60).

Cobalt-molybdenum alloys are a little better than cobalt alone up to 999°C (1830°F). Between 999°C (1830°F) and 1099°C (2010°F) the oxidation rate is less for the alloy, but above 1099°C (2010°F) the alloy oxidizes rapidly (Ref. 60).

The oxidation rate of cobalt decreases in proportion to added nickel content up to 40% nickel. The effect of 40% nickel on the oxidation of cobalt is indicated in Table 4-32, in which the corrosion of cobalt is compared with a 60Co—40Ni alloy.

To resist oxidation at elevated temperature, a material must meet the following conditions:

1. Diffusion through the oxide scale must be held to the lowest possible rate. This control can often be achieved by adding aluminum to the alloy.

2. The oxide scale must resist spalling. Spalling may occur because of the forces generated in the scale as it forms, as a result of erosion caused by flowing gas, or as a result of thermal cycling. Attempts to reduce spalling and improve scale adhesion often rely on the addition of a rare earth element.

**TABLE 4-31. PROPERTIES OF MULTIPHASE BOLTING ALLOYS (Ref. 59)**

| ALLOY | NOMINAL CHEMICAL COMPOSITION |    |    |    |    |    |     |     |
|-------|------------------------------|----|----|----|----|----|-----|-----|
|       | Co                           | Ni | Cr | Mo | Fe | Ti | Cb  | Al  |
| MP35N | 35                           | 35 | 20 | 10 | —  | —  | —   | —   |
| MP159 | 35                           | 26 | 19 | 7  | 8  | 3  | 0.6 | 0.2 |

| ALLOY | STRESS, MPa (ksi) |            |            | ELON-<br>GATION,<br>% | REDUC-<br>TION OF<br>AREA, % |
|-------|-------------------|------------|------------|-----------------------|------------------------------|
|       | UTS               | YIELD      | SHEAR      |                       |                              |
| MP35N | 1972 (286)        | 1758 (255) | 1000 (145) | 11                    | 39                           |
| MP159 | 1931 (280)        | 1896 (275) | 965 (140)  | 8                     | 35                           |

**TABLE 4-32. OXIDATION RESISTANCE OF COBALT AND A 60Co—40Ni ALLOY (Ref. 60)**

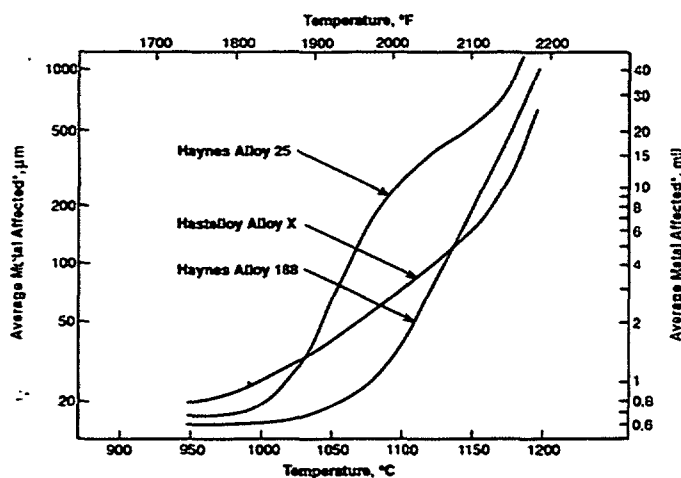
| TEMPERATURE, °C (°F) | WEIGHT GAIN*, mdd (lb/ft <sup>2</sup> ·day) |                                |
|----------------------|---|--------------------------------|
|                      | COBALT                                      | 60Co—40Ni ALLOY                |
| 799 (1470)           | 2000 ( $4.1 \times 10^{-2}$ )               | 80 ( $1.6 \times 10^{-3}$ )    |
| 899 (1650)           | 4200 ( $8.6 \times 10^{-2}$ )               | 960 ( $19.7 \times 10^{-3}$ )  |
| 999 (1830)           | 4500 ( $9.2 \times 10^{-2}$ )               | 2140 ( $43.8 \times 10^{-3}$ ) |
| 1099 (2010)          | 14,800 ( $30.3 \times 10^{-2}$ )            | 4580 ( $93.8 \times 10^{-3}$ ) |

\*In 24 h (specimens 3 to 5 cm<sup>2</sup> (0.47 to 0.78 in.<sup>2</sup>))

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The oxidation resistance in air of Haynes Alloy No. 188 is compared with Haynes Alloy No. 25 in Fig. 4-10. Haynes Alloy No. 188 contains nickel and the rare earth metal lanthanum, which was developed specifically to form a tenacious, protective film of chromia.



\*Metal loss plus average depth of internal penetration, both measured by metallographic evaluation

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**Figure 4-10. Oxidation Resistance in Dry Flowing Air, 1008-h Test, Cycled to Room Temperature Once a Week (Ref. 61)**

Results of two oxidation tests on several wear-resistant, high-temperature cobalt alloys are shown in Table 4-33. Four commercial cobalt alloys and two experimental

alloys are included. The test specimens were exposed to two sets of oxidation conditions. A dynamic oxidation test exposed the specimens to air heated to 927°C (1700°F) for 100 h. A thermal shock occurred every 30 min, which consisted of quenching to 260°C (500°F) with an air blast for 2 min and then reinsertion in the furnace. Weight losses in this test have two causes: scale spallation as a result of thermal stress and loss of volatile species.

In the second test the specimens were exposed to simulated combustion gases at 927°C (1700°F) for 1004 h, but they were cooled to room temperature every 24 h. The simulated combustion gas composition is shown in Table 4-34. Weight losses in this test were a direct result of scale spallation for the 24-h thermal cycle. The results given in Table 4-33 as metal losses show very significant differences between the dynamic oxidation test and the simulated combustion gas test. These differences illustrate

**TABLE 4-34. OXIDATION GAS COMPOSITION (Ref. 62)**

| COMPONENT       | VOLUME, % |
|-----------------|-----------|
| CO <sub>2</sub> | 15.0      |
| N <sub>2</sub>  | 82.0      |
| O <sub>2</sub>  | 3.0       |
| SO <sub>2</sub> | 0.026     |

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**TABLE 4-33. SUMMARY OF OXIDATION DATA (Ref. 62)**

| ALLOY                 | DYNAMIC OXIDATION, 1000 h, 927°C (1700°F) |  |   |  | SIMULATED COMBUSTOR, 1004 h, 927°C (1700°F) |                                  |   |  |
|-----------------------|---|--|---|--|---|----------------------------------|---|--|
|                       | METAL LOSS PER SURFACE, µm (mil)          | CONTINUOUS PENETRATION PER SURFACE, µm (mil) | MAXIMUM PENETRATION PER SURFACE, µm (mil) | TOTAL METAL AFFECTED PER SURFACE, µm (mil) | TOTAL METAL AFFECTED PER SURFACE, µm (mil)  | METAL LOSS PER SURFACE, µm (mil) | MAXIMUM PENETRATION PER SURFACE, µm (mil) |  |
| Stellite Alloy No. 12 | 28 (1.1)                                  | 104 (4.1)                                    | 131 (5.2)                                 | 157 (6.2)                                  | 84 (3.3)                                    | 1 (0.04)                         | 84 (3.3)                                  |  |
| Haynes Alloy No. 188  | 51 (2.0)                                  | 28 (1.1)                                     | 142 (5.6)                                 | 193 (7.6)                                  | 36 (1.4)                                    | 2 (0.08)                         | 33 (1.3)                                  |  |
| Stellite Alloy No. 1  | 10 (0.4)                                  | 109 (4.3)                                    | 145 (5.7)                                 | 155 (6.1)                                  | 23 (0.9)                                    | 1 (0.04)                         | 23 (0.9)                                  |  |
| Stellite Alloy No. 6B | 66 (2.6)                                  | 43 (1.7)                                     | 150 (5.9)                                 | 216 (8.5)                                  | 71 (2.8)                                    | 0                                | 71 (2.8)                                  |  |
| Haynes Alloy EB 1675  | 48 (1.9)                                  | 127 (5.0)                                    | 206 (8.1)                                 | 254 (10.0)                                 | 81 (3.2)                                    | 0                                | 81* (3.2)                                 |  |
| Haynes Alloy EB 1775  | 160 (6.3)                                 | 48 (1.9)                                     | 254 (10.0)                                | 414 (16.3)                                 | 51 (2.0)                                    | 2 (0.08)                         | 48 (1.9)                                  |  |

\*Internal oxidation

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the changes that can result from factors that disrupt the protective oxide scales.

The compositions of the alloys tested are shown in Table 4-35. Two experimental alloys contain rare earth additions as does Haynes Alloy No. 188. One of the experimental alloys, EB1775, is a lanthanum-containing modification of Haynes Alloy No. 6B. A cobalt-base alumina-scale-forming alloy (Haynes Experimental Alloy No. 1675) was also included in the test. This alloy contains what are considered to be optimal chromium and aluminum levels that are consistent with good fabricability, strength, and oxidation resistance. The rare earth metal, yttrium, is added to reduce oxide scale spallation.

The four commercial cobalt alloys represent a broad

range of carbon (0.1 to 2.5% by wt), chromium (20 to 30% by wt), and tungsten (4 to 15% by wt) content. Many cobalt-base alloys in commercial use are within these composition ranges.

The results of the two tests are summarized as follows:

1. The aluminum-rich experimental alloy did not form the desired continuous, protective alumina scale in either atmosphere. The alumina content (4.17%) was marginally low.

2. The lanthanum-modified experimental alloy did not prove effective in the dynamic oxidation test.

3. Behavior of the specimens exposed to the combustion-gas atmosphere was similar to that of specimens exposed to the air atmosphere. However, the effects on

TABLE 4-35. ALLOY COMPOSITIONS (Refs. 62 and 165)

| ALLOY   | Fe              | Co            | Ni    | Cr              | Al   | Si     | Mn   | W             | Mo             | Cu   | P      | S      | C    | OTHER           |                      |
|---|-----------------|---------------|-------|-----------------|------|--------|------|---------------|----------------|------|--------|--------|------|-----------------|----------------------|
| <i>State of the Art and Science Alloys</i>                    |                 |               |       |                 |      |        |      |               |                |      |        |        |      |                 |                      |
| Haynes Stellite<br>Alloy No. 1 (Heat<br>No. 5082)             | 0.65            | Bal.†         | 0.98  | 32.0            | —    | 1.10   | 0.16 | 12.0          | 0.18           | 0.02 | —      | 0.017  | 2.33 | 0.08B           |                      |
| Haynes Stellite<br>Alloy No. 6B<br>(Heat No. 1810-5-<br>1086) | 2.52            | Bal.†         | 2.78  | 30.70           | —    | 0.49   | 1.44 | 4.13          | 1.40           | —    | 0.008  | <0.005 | 1.06 | —               |                      |
| Haynes Stellite<br>Alloy No. 12<br>(Heat No. 142)             | 1.90            | Bal.†         | 1.03  | 30.07           | —    | 1.31   | 0.28 | 8.70          | 0.19           | 0.05 | —      | —      | 1.43 | —               |                      |
| Haynes Alloy No.<br>188 (Heat No.<br>1880-4-1689)             | 1.48            | Bal.†         | 22.32 | 22.39           | —    | 0.42   | 0.69 | 14.17         | —              | —    | 0.010  | 0.006  | 0.10 | 0.035L*         |                      |
| <i>Experimental Alloys</i>                                    |                 |               |       |                 |      |        |      |               |                |      |        |        |      |                 |                      |
| Haynes<br>Experimental<br>Alloy EB 1675-5-<br>0571            | 0.15            | Bal.†         | 19.59 | 15.27           | 4.17 | 0.27   | 0.50 | 7.50          | —              | —    | <0.001 | 0.003  | 0.22 | 0.03Y<br>0.55T* |                      |
| Haynes<br>Experimental<br>Alloy EB 1775-5-<br>0197            | 2.96            | Bal.†         | 2.61  | 31.03           | 0.13 | 0.46   | 1.08 | 3.75          | 0.18           | —    | <0.005 | 0.006  | 0.84 | 0.03L*          |                      |
| Hastelloy<br>Alloy X  | 17.00-<br>20.00 | 0.50-<br>2.50 |       | 20.50-<br>23.00 |      |        |      | 0.20-<br>1.00 | 8.00-<br>10.00 |      |        |        |      | 0.50-<br>0.15   | 0.008B**<br>0.15Ti** |
| Haynes Alloy 25   | 3.0**           | 51.0          | 10.0  | 20.0            |      | 0.40** | 1.5  | 15            |                |      |        |        |      | 0.1             |                      |

\* Nominal composition

\*\* Maximum

† Bal. = Balance

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the metals were not as extensive.

4. Sulfidation was not a problem in the combustion-gas atmosphere.

#### 4-5.1.2.2 Hot Corrosion

Alloy components in the turbine section (blades and vanes) of both marine and aircraft gas turbine engines often undergo unusually severe corrosion. This type of attack, known as hot corrosion, is caused by deposits of molten salt or ash. The design requirements for the alloys used in these components have emphasized high-temperature creep-rupture strength, fatigue life, and castability. The nickel- and cobalt-base alloys selected, therefore, have optimized mechanical and physical properties to match the mechanical and thermal loadings of particular applications. The result has been increased use of superalloys with lower oxidation and hot corrosion resistance. Alloy compositions have tended toward aluminum (4% to 5%) and chromium (8% to 12%) contents that are marginal for satisfactory oxidation and hot corrosion resistance. In addition, the alloys have relatively high refractory metal content, such as tungsten and molybdenum, which reduce their hot corrosion resistance.

The nickel-base superalloys are stronger than the cobalt-base alloys. Therefore, cobalt-base alloys are rarely used in rotating components, such as turbine blades. Because a relatively high density is not a great problem for stationary components, tungsten can be used in cobalt alloys as a solid solution strengthener in amounts up to 10% by weight. Also the carbon content may be as high as 1% by weight, and minor amounts of carbide formers are added to modify the carbide structure and enhance strengthening through carbide dispersion.

Conventional cobalt-base superalloys do not contain aluminum and therefore rely on chromia scale formation

for corrosion resistance. Nickel alloys, however, usually form an alumina scale for corrosion resistance.

An alumina scale thickens at a slower rate than a chromia scale. Alumina scale is more susceptible to spalling during thermal cycling or other mechanical disturbances but is less susceptible to vaporization loss in high-velocity, high-temperature gases. Chromia scales are more resistant to sulfate deposits unless considerable sodium chloride deposits are also involved (Ref. 63).

#### 4-5.1.2.3 Liquid Metal Corrosion

Cobalt has a weight loss of 2.4% after 50 h in molten zinc at 446°C (835°F) (Ref. 64) but experiences little attack in liquid sodium or sodium-potassium mixture up to 899°C (1650°F) (Ref. 65).

#### 4-5.1.2.4 Molten Salt Corrosion

In molten sodium hydroxide, cobalt has a corrosion rate of about 1.9 mm/yr (73 mpy) after 24 h at 538°C (1000°F) (Ref. 66).

#### 4-5.1.3 Erosion-Corrosion

The alloys described in Table 4-35 were exposed to impingement by 15- $\mu\text{m}$  (0.59-mil) alumina particles at two different velocities in the 927°C (1700°F) oxidizing flue gas environment described in Table 4-33. The results of this exposure are shown in Tables 4-36 and 4-37. At a particle velocity of 19 m/s (63 ft/s), the oxidation behavior was not significantly affected except for alloy 12, but at 52 m/s (170 ft/s) velocity, all alloys showed linear weight loss from the start of the exposure. The erosion-corrosion rates of the different alloys were not significantly different at this higher velocity. However, the erosion-corrosion rates of the alloys containing cobalt were higher than those of some nickel alloys that had been exposed to the same conditions.

**TABLE 4-36. COMPARISON OF METAL LOSS BY CORROSION AND CORROSION-EROSION AT 19 m/s (63 ft/s), 927° C (1700° F)**

| ALLOY | AVERAGE METAL LOSS, $\mu\text{m}$ (mil)                        |             |   |                      |
|-------|--|-------------|---|----------------------|
|       | CORROSION-EROSION, 19 m/s<br>(63 ft/s)<br>(FROM WEIGHT CHANGE) |             | CORROSION ALONE AT<br>EQUIVALENT TIME<br>(FROM WEIGHT CHANGE) |                      |
|       | ANGLE OF EXPOSURE, deg   |             | SIMULATED<br>COMBUSTOR  | DYNAMIC<br>OXIDATION |
|       | 30   | 90          |   |                      |
| 1     | 0.6 (0.024)  | 1.2 (0.047) | 0.8 (0.031)   | 1.4 (0.055)          |
| 12    | 2.6 (0.102)  | 30 (1.18)   | 0.7 (0.028)   | 0.5 (0.020)          |
| 6B    | 0.9 (0.035)  | 0.8 (0.031) | 1.3 (0.051)   | 0.3 (0.012)          |
| 1775  | 2.0 (0.079)  | 1.1 (0.043) | 0.8 (0.031)   | 0.5 (0.020)          |
| 188   | 0.8 (0.031)  | 0.8 (0.031) | 1.3 (0.051)   | 0.1 (0.004)          |
| 1675  | 1.1 (0.043)  | —           | 0.4 (0.016)   | 1.4 (0.055)          |

NOTE: Specimens exposed at a nominal angle of 90 deg experience twice the number of impacts/unit time compared to specimens exposed at nominally 30 deg.

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TABLE 4-37. COMPARISON OF METAL LOSS BY CORROSION-EROSION AND BY CORROSION ALONE AT 52 m/s (170 ft/s), 927° C (1700° F)

| ALLOY | AVERAGE METAL LOSS, $\mu\text{m}$ (mil)                         |              |   |                      |
|-------|---|--------------|---|----------------------|
|       | CORROSION-EROSION, 52 m/s<br>(170 ft/s)<br>(FROM WEIGHT CHANGE) |              | CORROSION ALONE AT<br>EQUIVALENT TIME<br>(FROM WEIGHT CHANGE) |                      |
|       | ANGLE OF EXPOSURE, deg  |              | SIMULATED<br>COMBUSTOR  | DYNAMIC<br>OXIDATION |
| 30    | 90  |              |   |                      |
| 1     | 21.1 (0.830)  | — —          | 0.3 (0.012)   | 0.3 (0.012)          |
| 12    | 22.4 (0.882)  | 57.5 (2.264) | 0.7 (0.028)   | 0.5 (0.020)          |
| 6B    | 22.2 (0.874)  | — —          | 1.1 (0.043)   | 0.4 (0.016)          |
| 1775  | 23.5 (0.925)  | 57.1 (2.248) | 0.3 (0.012)   | 0.4 (0.016)          |
| 188   | 27.9 (1.098)  | 57.3 (2.256) | 0.7 (0.028)   | 0.1 (0.004)          |
| 1675  | 33.6 (1.323)  | — —          | 0.1 (0.004)   | 0.9 (0.035)          |

NOTE: Specimens exposed at a nominal angle of 90 deg experience twice the number of impacts/unit time compared to specimens exposed at nominally 30 deg.

#### 4-5.2 METHODS FOR PREVENTION OF CORROSION

High-temperature coatings have been developed as a means of restoring oxidation and hot corrosion resistance to gas turbine blades and vanes. The coatings are of two types: (1) diffusion aluminide coatings that consist of a cobalt-aluminum intermetallic phase and are formed by slurry-fusion or pack cementation processes and (2) overlay coatings that provide significant improvements in oxidation and hot corrosion compared to diffusion aluminide.

The objective of both types is formation of a protective aluminum coating under service conditions.

The overlay coatings are of the type CoCrAlY. These coatings minimize the influence of the base alloy on the composition of the coatings, coatings that result in excellent oxidation and hot corrosion resistance can be applied. Chromium levels may be high (18 to 25%) at moderate aluminum concentrations (10 to 15%). Refractory elements are excluded, and rare earth elements (yttrium) are added to improve alumina scale adhesion. Electron beam, physical vapor deposition is commonly used to form the overlay coating on the substrate. Placing a platinum layer on CoCrAlY overlay coatings is effective in improving the oxidation resistance and in inhibiting the hot corrosion attack of coatings caused by sulfate-chloride salt deposition (Ref. 67).

A low-temperature form of hot corrosion attack has occurred on marine gas turbines operating at low or intermediate power levels (Ref. 68). These gas turbines have CoCrAlY-coated turbine blades. High-temperature (927° C (1700° F)) hot corrosion attack is characterized by depletion of aluminum from the coating to form aluminum oxide. This causes a layer depleted of aluminum-rich beta phase to form beneath the oxide/coating interface.

As the attack progresses, a network of aluminum oxide and depleted coating forms. The cobalt and chromium in the remaining portions of the depleted coating are oxidized at the surface. This oxidation completes the degradation of the coating. Sulfides do not appear in the depletion zone until the aluminum-rich phase is completely consumed.

With low-temperature (704° C (1300° F)) hot corrosion, little, if any, depletion of aluminum occurs. Instead there is almost uniform conversion to oxide scales of all the coating constituents at about the same rate. There is some chromium depletion beneath the scale/coating interface. The scale in contact with the coating is high in aluminum and chromium and low in cobalt. Frequently, a loosely adherent outer scale rich in cobalt is formed over the inner scale. Sulfur is found in the scale, particularly at the scale/coating interface.

#### 4-5.3 EXAMPLES OF CORROSION PROBLEMS

The cobalt-base alloy, Stellite 21, is an excellent liner for gun barrels in most respects. For example, it has excellent erosion resistance, optimal hot hardness and ductility, and good fabrication characteristics. Its melting point of 1280° C (2336° F), however, is not adequate for high-temperature propellants. The alloy fails by surface melting. In spite of this, liners of Stellite 21 are used in M60 machine-gun barrels (Ref. 69).

Because of their high resistance to corrosion in human tissue and body fluids and their high strength, cobalt alloys are used in orthopedic implant devices (Ref. 70). Cast Vitallium, which contains 27% by weight chromium, 65% by weight cobalt, 5% by weight iron, and small amounts of other elements, is a commonly used implant material.

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## 4-6 COLUMBIUM AND COLUMBIUM ALLOYS

Columbium (also called niobium) has moderate density, a high melting point, and considerable strength at elevated temperatures. Some properties of columbium are listed in Table 4-38. A typical columbium ingot is 99.8% pure.

Columbium is extremely ductile and easy to fabricate at room temperature, and it is compatible with conventional metalworking practices, but heating in air or any of the common gases embrittles the metal.

Use of columbium and its alloys is based upon their mechanical properties at high temperatures and corrosion resistance that is generally superior in many environments. Columbium is an expensive metal.

**TABLE 4-38. PROPERTIES OF COLUMBIUM (Ref. 71)**

|                              |  |
|------------------------------|--|
| Density at 20° (68° F)       | 8570 kg/m <sup>3</sup> (535 lb/ft <sup>3</sup> ) |
| Melting point                | 2468°C (4474° F)                                 |
| Boiling point                | 5127°C (9261° F)                                 |
| Tensile strength, MPa (ksi): |  |
| Room temperature             | 172 to 483 (25 to 70)                            |
| 500° C (932° F)              | 172 (25)   |
| 1000° C (1832° F)            | 55 to 117 (8 to 17)                              |

## 4-6.1 ALLOYS OF COLUMBIUM

Columbium can be alloyed with a wide range of elements. The nominal composition of two columbium alloys is given in Table 4-39. These two alloys are candidate materials for gas turbine applications because of their good mechanical properties at high temperatures.

## 4-6.2 TYPES OF CORROSION

## 4-6.2.1 General Corrosion

## 4-6.2.1.1 Uniform and Pitting Corrosion

Although columbium is an active metal in the electromotive force series, it is second only to tantalum in its general corrosion resistance, which results from the formation of a protective oxide film. The general corrosion resistance of columbium to various environments and chemical reagents is summarized in Table 4-40.

Columbium acquires only a slight tarnish after a 15-yr exposure to an industrial atmosphere.

**TABLE 4-39. COMPOSITION OF TWO COLUMBIUM ALLOYS**

| ELEMENT    | COMPOSITION, wt % |          |
|------------|-------------------|----------|
|            | NOMINAL           | ANALYSIS |
|            | <i>SU-31</i>      |          |
| Tungsten   | 17.0 - 18.0       | 18.50    |
| Hafnium    | 3.5               | 3.60     |
| Carbon     | 0.12              | 0.145    |
| Oxygen     | —                 | 85 ppm   |
| Nitrogen   | —                 | 25 ppm   |
| Columbium  | Balance           | Balance  |
|            | <i>FS-85</i>      |          |
| Tantalum   | 27.0              | 27.60    |
| Tungsten   | 11.0              | 10.60    |
| Zirconium  | 1.0               | 0.94     |
| Hafnium    | —                 | 100 ppm  |
| Molybdenum | —                 | 100 ppm  |
| Titanium   | —                 | 50 ppm   |
| Iron       | —                 | 50 ppm   |
| Silicon    | —                 | 50 ppm   |
| Carbon     | —                 | 40 ppm   |
| Oxygen     | —                 | 39 ppm   |
| Nitrogen   | —                 | 29 ppm   |
| Hydrogen   | —                 | 5 ppm    |
| Columbium  | Balance           | Balance  |



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TABLE 4-40. CORROSION RESISTANCE OF COLUMBIUM AT VARIOUS TEMPERATURES (Ref. 71)

| REAGENT  | TEMPERATURE    |                 |                  | REAGENT                    | TEMPERATURE    |                 |                  |
|--|----------------|-----------------|------------------|----------------------------|----------------|-----------------|------------------|
|  | 20°C<br>(68°F) | 60°C<br>(140°F) | 100°C<br>(212°F) |                            | 20°C<br>(68°F) | 60°C<br>(140°F) | 100°C<br>(212°F) |
| Acetaldehyde                                       | S              | S               | S                | Fluorine                   | NR             | NR              | NR               |
| Acetic acid (10%)                                  | S              | S               | S                | Formaldehyde               | S              | S               | S                |
| Acetic acid (glac and anh)*                        | S              | S               | S                | Formic acid                | S              | S               | S                |
| Acetone  | S              | S               | S                |                            |                |                 |                  |
| Acetylene  | S              | S               | S                | Glycerine                  | S              | S               | S                |
| Acid fumes (except H <sub>2</sub> F <sub>2</sub> ) | S              | NR              | NR               | Glycols                    | S              | S               | S                |
| Air  | S              | S               | S                |                            |                |                 |                  |
| Alcohols (most)                                    | S              | S               | S                | Hexamine                   | S              | S               | S                |
| Aliphatic esters                                   | S              | S               | S                | Hydrobromic acid (50%)     | DU             | DU              | DU               |
| Aliphatic halogens                                 | S              | S               | S                | Hydrochloric acid (10%)    | S              | NR              | NR               |
| compounds-chloroform                               |                |                 |                  | Hydrochloric acid (conc.)  | S              | NR              | NR               |
| Alum   | S              | S               | S                | Hydrocyanic acid           | DU             | DU              | DU               |
| Aluminum chloride                                  | S              | S               | S                | Hydrofluoric acid          | NR             | NR              | NR               |
| Ammonia anhydrous                                  | S              | S               | S                | Hydrogen peroxide (30%)    | DU             | DU              | DU               |
| Ammonium chloride                                  | S              | S               | S                | Hydrogen peroxide (30-90%) | DU             | DU              | DU               |
| Amyl acetate and chloride                          | S              | S               | S                | Hydrogen sulphide          | S              | S               | S                |
| Aniline and compounds                              | S              | S               | S                |                            |                |                 |                  |
| Aqua regia   | S              | NR              | NR               | Ketones                    | S              | S               | S                |
| Aromatic solvents                                  | S              | S               | S                |                            |                |                 |                  |
|  |                |                 |                  | Lactic acid (100%)         | S              | S               | S                |
| Benzoic acid                                       | S              | S               | S                |                            |                |                 |                  |
| Boric acid   | S              | S               | S                | Maleic acid                | S              | S               | S                |
| Brines, saturated                                  | S              | S               | S                | Mercuric chloride          | S              | S               | S                |
| Bromine, moist                                     | S              | S               | S                | Mercury                    | S              | S               | S                |
|  |                |                 |                  |                            |                |                 |                  |
| Calcium chloride                                   | S              | S               | S                | Naphtha                    | S              | S               | S                |
| Carbon disulphide                                  | S              | S               | S                | Naphthalene                | S              | S               | S                |
| Carbonic acid                                      | S              | S               | S                | Nickel salts               | S              | S               | S                |
| Chlorine, dry                                      | S              | S               | S                | Nitric acid (<25%)         | S              | S               | S                |
| Chlorine, wet                                      | S              | S               | S                | Nitric acid (50%)          | S              | S               | S                |
| Chlorides of Na, K, Mg                             | S              | S               | S                | Nitric acid (95%)          | S              | S               | S                |
| Chromic acid (80%)                                 | S              | S               | DU               | Nitrogen                   | S              | S               | S                |
| Citric acid  | S              | S               | S                |                            |                |                 |                  |
| Copper salts (most)                                | S              | S               | S                | Oils, essential            | S              | S               | S                |
| Cresylic acids (50%)                               | DU             | DU              | DU               | Oils, mineral              | S              | S               | S                |
| Cyclohexane  | S              | S               | S                | Oils, vegetable and animal | S              | S               | S                |
|  |                |                 |                  | Oxalic acid                | NR             | NR              | NR               |
| Detergent, synthetic                               | S              | S               | S                | Oxygen                     | S              | S               | S                |
|  |                |                 |                  | Ozone                      | DU             | DU              | DU               |
| Emulsifiers  | S              | S               | S                |                            |                |                 |                  |
| Ether  | S              | S               | S                | Perchloric acid            | S              | S               | S                |
|  |                |                 |                  | Phenol                     | S              | S               | S                |
| Fatty acids (C<C <sub>6</sub> )                    | S              | S               | S                | Phosphoric acid (25%)      | S              | S               | NR               |
| Ferric chloride                                    | S              | S               | S                | Phosphoric acid (50%)      | S              | S               | NR               |
| Ferric sulphate                                    | S              | S               | S                | Phosphoric acid (95%)      | S              | S               | NR               |

\*Glacial and anhydrous

(cont'd on next page)

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TABLE 4-40. (cont'd)

| REAGENT                    | TEMPERATURE    |                 |                  | REAGENT              | TEMPERATURE    |                 |                  |
|----------------------------|----------------|-----------------|------------------|----------------------|----------------|-----------------|------------------|
|                            | 20°C<br>(68°F) | 60°C<br>(140°F) | 100°C<br>(212°F) |                      | 20°C<br>(68°F) | 60°C<br>(140°F) | 100°C<br>(212°F) |
| Phosphorous chlorides      | DU             | DU              | DU               | Sulphur dioxide, wet | S              | S               | S                |
| Pyridine and compounds     | S              | S               | S                | Sulphur trioxide     | NR             | NR              | NR               |
|                            |                |                 |                  | Sulphuric acid (20%) | S              | S               | S                |
| Seawater                   | S              | S               | S                | Sulphuric acid (50%) | S              | NR              | NR               |
| Silicic acid               | S              | S               | S                | Sulphuric acid (70%) | S              | NR              | NR               |
| Silver nitrate             | S              | S               | S                | Sulphuric acid (95%) | S              | NR              | NR               |
| Sodium carbonate           | NR             | NR              | NR               | Tallow               | S              | S               | S                |
| Sodium hypochlorite        | NR             | NR              | NR               | Tannic acid (10%)    | S              | S               | S                |
| Sodium silicate            | NR             | NR              | NR               | Tartaric acid        | S              | S               | S                |
| Sodium sulphide            | S              | S               | S                | Trichloroethylene    | S              | S               | S                |
| Starch                     | S              | S               | S                |                      |                |                 |                  |
| Sugar and syrups           | S              | S               | S                | Vinegar              | S              | S               | S                |
| Sulphates of Na, K, Mg, Ca | S              | S               | S                |                      |                |                 |                  |
| Sulphites                  | S              | S               | S                | Yeast                | S              | S               | S                |
| Sulphonic acids            | S              | S               | S                |                      |                |                 |                  |
| Sulphur                    | S              | S               | S                | Zinc chloride        | S              | S               | S                |
| Sulphur dioxide, dry       | S              | S               | S                |                      |                |                 |                  |

S = Satisfactory

NR = Not recommended

DU = Data unavailable

NOTE: This information is intended only as a general guide. Because of diversity in processing methods and operating conditions, no guarantee concerning the use of columbium is to be implied. To ascertain more positively the value of the metal, it is suggested that samples be tested under actual operating conditions in the required media.

## 4-6.2.1.2 Caustic Embrittlement

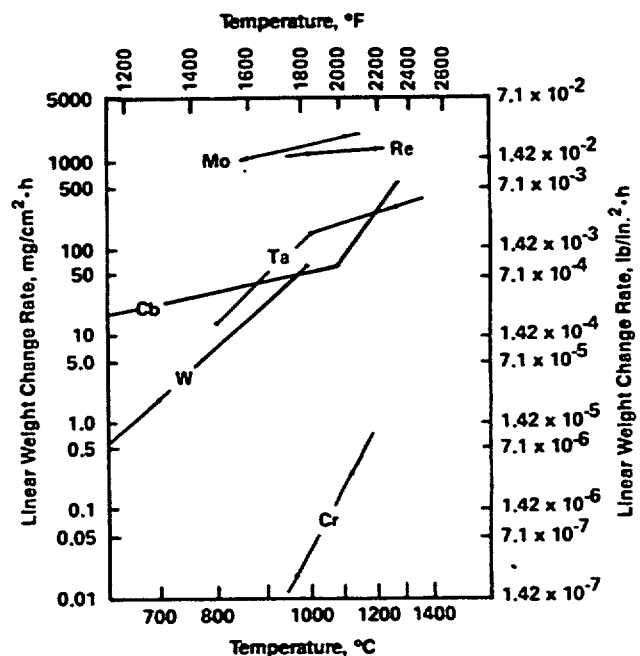
Columbium is not recommended for applications in alkaline solutions because it is embrittled by boiling solutions of low concentrations of sodium hydroxide and potassium hydroxide.

## 4-6.2.2 High-Temperature Corrosion

## 4-6.2.2.1 Oxidation

Pure columbium is not suited for service in air at elevated temperatures because it oxidizes readily. Also studies of the high-temperature oxidation of columbium have shown it to be complex. The initial oxidation rate is parabolic and is followed by a transition to an approximately linear relationship with time. The breakaway is associated with the formation of columbium oxide  $Cb_2O_3$ , which is porous and offers little resistance to further oxidation. The data in Fig. 4-11 indicate that the basic reaction kinetics of columbium change at approximately 1093°C (2000°F). Table 4-41 lists the corrosion rate in air of columbium and other metals and alloys at 1204°C (2200°F) relative to Type 310 stainless steel.

Improvements in the oxidation rate in air of columbium at high temperatures can be made by alloying it with various metals. Additions of up to 10% of tungsten, iron, titanium, vanadium, chromium, or molybdenum can



NOTE: Data for Cr, W, Cb, and Ta are weight gains, and data for Mo and Re are weight losses.

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Figure 4-11. Oxidation of Refractory Metals (Ref. 72)

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**TABLE 4-41. AIR-CORROSION AT 1204° C (2200° F) (Ref. 72)**

| METAL                     | RELATIVE CORROSION RATES* |
|---------------------------|---------------------------|
| Silicon                   | small                     |
| 81Ni—12.5Cr—6.5Al         | 0.4                       |
| 310 Stainless (25Cr—20Ni) | 1.0                       |
| 67Cr—33Ni                 | 1.9                       |
| Chromium                  | 5.0                       |
| Titanium                  | 29.6                      |
| Zirconium                 | 59                        |
| 93Cb—7Mo                  | 89                        |
| Tungsten                  | 114                       |
| Columbium                 | 696                       |
| Tantalum                  | 1140                      |
| Molybdenum                | 1600                      |

\*Refer to Type 310 stainless steel

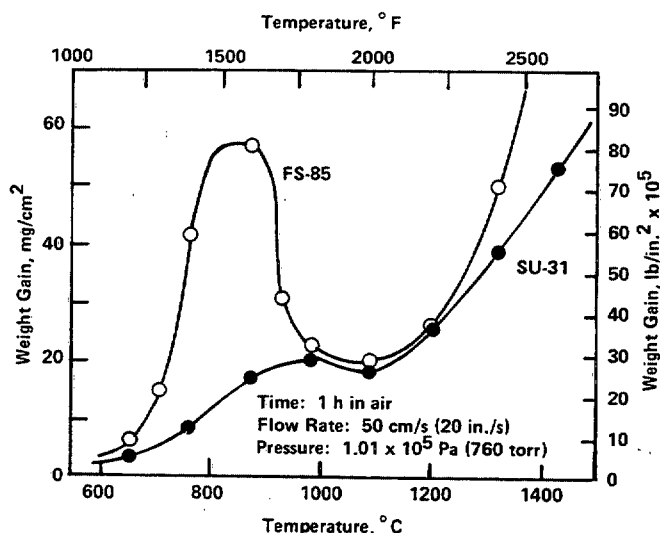
Reprinted with permission. From *Metallurgical Society Conferences, Volume II, Refractory Metals and Alloys*, "Oxidation Behavior of Refractory Metals and Alloys" by J. W. Semmel, Jr., p. 161, The Metallurgical Society, 1961.

decrease the corrosion rate in air of columbium. However, larger amounts can reverse the trend and result in greater corrosion than if the columbium were unalloyed (Ref. 72). The results of tests of the corrosion rate in air of columbium alloyed with varying amounts of chromium are given in Table 4-42. The addition of any amount of rhenium or zirconium up to 20% will result in higher corrosion rates in air than if the columbium were unalloyed (Ref. 72).

Columbium alloys are promising candidates for use in gas turbine engines because of their favorable strength-to-weight ratio at high temperatures. The nominal composition and chemical analysis of two candidate alloys are given in Table 4-39, but neither of these columbium alloys can be used for gas turbine applications above 1093°C (2000°F) without protective coatings. Oxidation test results are shown in Fig. 4-12. The SU31, columbium-

**TABLE 4-42. AIR CORROSION OF COLUMBIUM AND COLUMBIUM CHROMIUM ALLOYS AT 1000° C (1832° F) FOR 5 h (Ref. 72)**

| MATERIAL                  | WEIGHT GAIN, mg/cm <sup>2</sup> (lb/in. <sup>2</sup> ) |
|---------------------------|--|
| Pure columbium            | 138 (1.96 × 10 <sup>-3</sup> )                         |
| Columbium + 3.5% chromium | 80 (1.14 × 10 <sup>-3</sup> )                          |
| Columbium + 12% chromium  | 34 (0.48 × 10 <sup>-3</sup> )                          |
| Columbium + 22% chromium  | 138 (1.96 × 10 <sup>-3</sup> )                         |
| Columbium + 24% chromium  | 650 (9.23 × 10 <sup>-3</sup> )                         |

**Figure 4-12. Comparison of SU-31 and FS-85 Oxidation After 1 h at Temperatures Between 649° and 1482° C (1200° and 2700° F) (Ref. 73)**

tungsten-hafnium, alloy is marginally more resistant than the FS-85, columbium-tantalum-zirconium, alloy.

**4-6.2.2.2 Liquid Metals**

Experimental measurements of columbium corrosion in several liquid metals is given in Table 4-43.

**4-6.2.2.3 Other High-Temperature Media**

The molten alkalis are corrosive to columbium. Sodium hydroxide causes severe attack at 538°C (1000°F), potassium hydroxide dissolves columbium readily at 360°C (680°F) (Refs. 66 and 76), and refractory oxides have little effect on columbium up to 1599°C (2910°F) (Ref. 77).

**4-6.3 METHODS FOR PREVENTION OF CORROSION**

Efforts have been directed toward developing coatings for columbium that can provide protection against corrosion in air at high temperatures. Coatings that give protection to columbium at very high temperatures, i.e., 1371°C (2500°F), include (Ref. 78)

1. Layers of molybdenum disilicide
2. Metallic chromium or nickel-chromium subsequently sprayed with aluminum oxide
3. Metallic aluminum plus chromium plus silicon
4. Titanium and its compounds, such as oxides, nitrides, carbides, and silicides, and various combinations of these.

A 90% tantalum, 10% tungsten alloy was protected against static oxidation for a minimum period of 200 h at temperatures between 927° and 1482°C (1700° and

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TABLE 4-43. CORROSION OF COLUMBIUM IN LIQUID METALS (Refs. 37, 72, 74, and 75)

| LIQUID METAL             | TEMPERATURE AT WHICH<br>RESISTANCE EXHIBITED |      | CORROSION<br>TEMPERATURE | CORROSION<br>CHARACTERISTIC |
|--------------------------|--|------|--------------------------|-----------------------------|
|                          | °C   | °F   |                          |                             |
| Bismuth                  | 300  | 570  |                          |                             |
| Bismuth-lead<br>eutectic |  |      | 1090°C (2000°F)          | 635 cm/yr (250,000 mpy)     |
| Gallium                  | 450  | 840  | 600°C (1110°F)           | Rapid corrosion             |
| Lead                     | 1000   | 1830 |                          |                             |
| Lithium                  | 900  | 1650 |                          |                             |
| Mercury                  | 150  | 300  | <300°C (570°F)           | Slight corrosion            |
|                          |  |      | >350°C (660°F)           | Severe corrosion            |
| Sodium                   | 900  | 1650 |                          |                             |
| Zinc                     |  |      | 445°C (835°F)            | Rapid corrosion             |

2700°F) by a complex disilicide coating (Ref. 79). Therefore, the columbium alloys whose compositions are given in Table 4-37 were coated with the same modified disilicide coating by the procedure described in Table 4-44. This coating protected both alloys for 1000 h at 1371°C (2500°F) under static oxidizing conditions (Ref. 80).

TABLE 4-44. APPLICATION PROCEDURE FOR SOLAR DUPLEX COATING NS-4/Si (Ref. 73)

1. Barrel finish
2. Vapor degrease
3. Sandblast
4. Pickle (acid etch-rinse)
5. Spray with NS-4 coating (50W, 20Mo, 15V, 15Ti)
6. Dry
7. Sinter at 1527°C ± 17 deg C (2780 ± 30 deg F) at  $1.33 \times 10^{-3}$  Pa ( $10^{-3}$  torr) for 15 h
  - a. Weight gain 55 to 65 mg/cm<sup>2</sup> ( $0.78 \times 10^{-3}$  to  $0.92 \times 10^{-3}$  lb/in.<sup>2</sup>) (NS-4)
  - b. Thickness increase 114.3 to 127.0 μm (4.5 to 5.0 mils)/surface (NS-4)
8. Silicide at 1177°C (2150°F) at  $1.07 \times 10^5$  Pa (800 torr) argon for 16 h or equivalent
  - a. Weight gain 34 to 40 mg/cm<sup>2</sup> ( $0.48 \times 10^{-3}$  to  $0.57 \times 10^{-3}$  lb/in.<sup>2</sup>) (silicide)
  - b. Thickness increase 71.1 to 83.8 μm (2.8 to 3.3 mils)/surface
9. No postclean
10. Postoxidation at 1316°C (2400°F) for 1h

NOTE: Total thickness increase was 177.8 to 215.9 μm (7.0 to 8.5 mils)/surface.

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## 4-6.4 EXAMPLES OF CORROSION PROBLEMS

In addition to potential application in gas turbine engines when it is protected by a coating, columbium and its alloys have potential application as liners for gun tubes.

Fig. 4-13 shows idealized stress-strain curves of some refractory metals and gun steel. Refractory metals that have an elastic modulus, i.e., stiffness, higher than gun steel, such as tungsten, molybdenum, and chromium, usually fail by cracking when applied as liners or coatings in steel gun tubes. Those metals with an elastic modulus lower than steel, such as tantalum and columbium, effectively transfer the liner loads to the steel jacket when they are used as gun tube liners. Columbium, however, tends to undergo swagging, or metal flow, on the lands of the gun bore (Ref. 69).

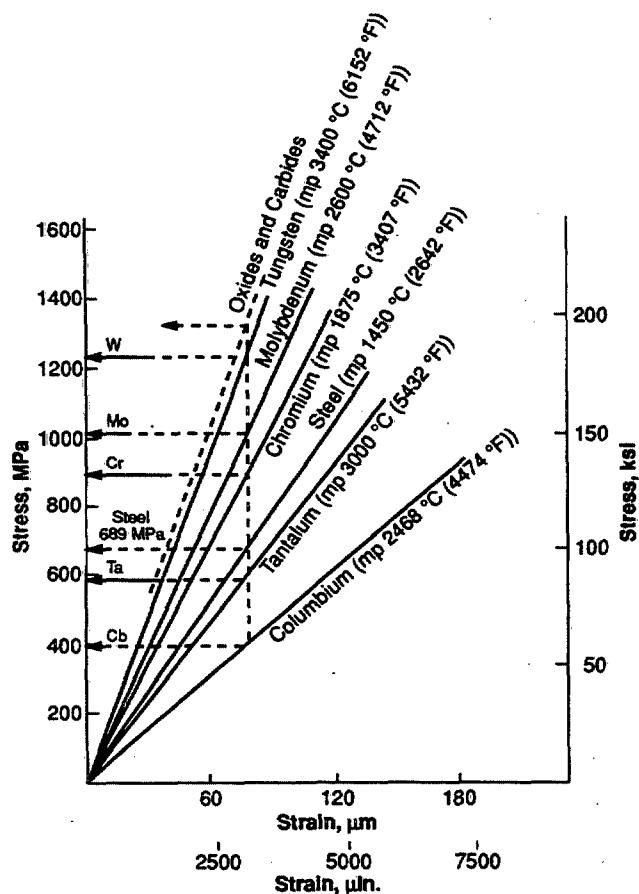
## 4-7 COPPER AND COPPER ALLOYS

Elemental copper has a density of 8954.32 kg/m<sup>3</sup> (559 lbm/ft<sup>3</sup>) and a melting point of 1083°C (1981°F). It has excellent electrical and thermal conductivities and is malleable and readily formed and machined; however, it exhibits relatively poor mechanical properties. Therefore, it must be cold worked or alloyed to improve its strength. Copper also possesses good corrosion resistance. It is below the noble metals and nickel in the galvanic series but above stainless steel.

## 4-7.1 TYPES OF ALLOYS

Important classes of copper alloys contain zinc (brass), tin (tin or phosphor bronze), aluminum (aluminum bronzes), and nickel (cupronickels). In the Unified Numbering System (UNS) for copper and its alloys, the numbers C10000 through C79999 designate wrought alloys. Cast copper and copper alloys are numbered from C80000 through C99999. However, usually a copper-base

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**Figure 4-13. Idealized Stress-Strain Curves of Refractory Metals and Gun Steel (Ref. 69)**

alloy is designated only by the first three digits. Many alloys are associated with popular names, e.g., red brass or admiralty metal. Table 4-45 gives the composition and mechanical properties of several copper alloys.

#### 4-7.1.1 Copper and High-Copper Alloys

Commercially pure copper contains a minimum of 99.3% copper. It is used primarily in electrical and electronic applications, in metallic motor vehicle radiators, in tubing for hydraulic and fuel lines, and in tubing and pipe for potable water systems. Copper is also used in downspouts, flashing, gutters, roofing, screening, and exterior cladding in architectural applications. High-copper alloys contain a minimum of 96% copper if in the wrought form and 94% copper if in the cast form. The high-copper alloys have better mechanical properties than the commercially pure copper and about the same corrosion resistance. For example, copper-beryllium alloys are high-strength, age-hardenable alloys. They contain about 2% beryllium and 0.25% cobalt or nickel. Their corrosion resistance is slightly better than that of pure copper in most environments. The high-copper alloys are used principally in electrical and electronic

applications, whereas the copper-beryllium alloys are used as springs, diaphragms, bearing parts, and valves.

#### 4-7.1.2 Copper-Zinc Alloys

Zinc is the principal alloying element in brass. Much brass goes into plumbing hardware, such as valves, fittings, and piping. Many seagoing vessels use brass in steam condensers. Alloy C4430 is commonly used in the tubing, and alloy C46400 is commonly used in the tube sheets.

#### 4-7.1.3 Copper-Tin Alloys

Tin is the principal alloying element in tin bronzes. Tin bronzes, also called phosphor bronzes because less than 0.5% phosphorus is present, are used as valve bodies, valve trim, pump housings, and pump impellers.

#### 4-7.1.4 Copper-Aluminum Alloys

The aluminum bronzes, which consist principally of copper and aluminum, are available in both wrought and cast forms. The aluminum bronzes have good combinations of strength, corrosion resistance, and wear resistance. Their composition ranges from a simple alloy of copper and aluminum to complex alloys with the addition of iron, nickel, silicon, manganese, and other elements.

#### 4-7.1.5 Copper-Nickel Alloys

Copper-nickel alloys containing from 10% to 30% nickel and a small amount of iron and manganese have good mechanical properties at moderately high temperatures. The corrosion resistance of cupronickels is influenced by their iron content; therefore, 0.5% iron is added to copper-30% nickel, and 1.5% is added to copper-10% nickel. The copper-nickel alloys are single-phase alloys.

The greatest application of cupronickels is in saltwater service. They are also used in brackish water and freshwater. They are used as pipe, fittings, condenser tubes and plates, and pump castings.

TABLE 4-45. COPPER ALLOYS (Ref. 2)

| ALLOY                                     | CDA† | UNS    | COMPOSITION %* |       |          |          |          |                                    | MECHANICAL PROPERTIES**     |                               |                                      |
|---|------|--------|----------------|-------|----------|----------|----------|------------------------------------|-----------------------------|-------------------------------|--------------------------------------|
|   |      |        | Cu             | Zn    | Sn       | Al       | Ni       | OTHER                              | YIELD STRENGTH<br>MPa (ksi) | TENSILE STRENGTH<br>MPa (ksi) | ELONGATION<br>IN 51 mm<br>(2 in.), % |
| Wrought<br>Copper<br>Commercial<br>bronze | 110  | C11000 | 99.90          | —     | —        | —        | —        | —                                  | 69 (10)                     | 221 (32)                      | 55                                   |
| Red brass                                 | 220  | C22000 | 89-91          | rem†† | —        | —        | —        | —                                  | 69 (10)                     | 255 (37)                      | 50                                   |
| Cartridge brass                           | 230  | C23000 | 84-88          | rem   | —        | —        | —        | —                                  | 69 (10)                     | 276 (40)                      | 55                                   |
| Yellow brass                              | 260  | C26000 | 68.5-71.5      | rem   | —        | —        | —        | —                                  | 76 (11)                     | 303 (44)                      | 66                                   |
| Muntz metal                               | 270  | C27000 | 63.0-68.5      | rem   | —        | —        | —        | —                                  | 97 (14)                     | 317 (46)                      | 65                                   |
| Admiralty brass                           | 280  | C28000 | 59-63          | rem   | —        | —        | —        | —                                  | 145 (21)                    | 372 (54)                      | 52                                   |
| Admiralty brass                           | 443  | C44300 | 70-73          | rem   | 0.9-1.2  | —        | —        | 0.02-0.1 As                        | 124 (18)                    | 331 (48)                      | 65                                   |
| Admiralty brass                           | 444  | C44400 | 70-73          | rem   | 0.9-1.2  | —        | —        | 0.02-0.1 Sb                        | 124 (18)                    | 331 (48)                      | 65                                   |
| Admiralty brass                           | 445  | C44500 | 70-73          | rem   | 0.9-1.2  | —        | —        | 0.02-0.1 P                         | 124 (18)                    | 331 (48)                      | 65                                   |
| Naval brass                               | 464  | C46400 | 59-62          | rem   | 0.5-1.0  | —        | —        | —                                  | 172 (25)                    | 400 (58)                      | 50                                   |
| Phosphor bronze                           | 510  | C51000 | rem            | 0.3   | 4.2-5.8  | —        | —        | 0.03-0.35 P                        | 131 (19)                    | 324 (47)                      | 64                                   |
| Phosphor bronze                           | 524  | C52400 | rem            | 0.2   | 9.0-11.0 | —        | —        | 0.03-0.35 P                        | 193 (28)                    | 455 (66)                      | 70                                   |
| Aluminum<br>bronze                        | 613  | C61300 | 88.5-93.8      | —     | 0.2-0.5  | 6.0-8.0  | 0.5      | 3.5 Fe                             | 207 (30)                    | 483 (70)                      | 42                                   |
| Aluminum<br>bronze D                      | 614  | C61400 | 88.0-92.5      | 0.2   | —        | 6.0-8.0  | —        | 1.5-3.5 Fe<br>1.0 Mn               | 228 (33)                    | 524 (76)                      | 45                                   |
| Nickel aluminum<br>bronze                 | 630  | C63000 | 78-85          | 0.3   | 0.2      | 9.0-11.0 | 4.0-5.5  | 2.0-4.0 Fe<br>1.5 Mn<br>0.25 Si    | 248 (36)                    | 621 (90)                      | 10                                   |
| High-silicon<br>bronze                    | 655  | C65500 | 94.8           | 1.5   | —        | —        | 0.6      | 0.8 Fe<br>0.5-1.3 Mn<br>2.8-3.8 Si | 145 (21)                    | 386 (56)                      | 63                                   |
| Manganese<br>bronze                       | 675  | C67500 | 57-60          | rem   | 0.5-1.5  | 0.25     | —        | 0.05-0.5 Mn<br>0.8-2.0 Fe          | 207 (30)                    | 448 (65)                      | 33                                   |
| Inh. aluminum<br>bronze                   | 687  | C68700 | 76-79          | rem   | —        | 1.8-2.5  | —        | 0.02-0.1 As                        | 186 (27)                    | 414 (60)                      | 55                                   |
| 90/10 Copper<br>nickel                    | 706  | C70600 | 86.5           | 1.0   | —        | —        | 9.0-11.0 | 1.0-1.8 Fe<br>1.0 Mn               | 110 (16)                    | 303 (44)                      | 42                                   |

\*Single values are maximum values except for Cu, which is minimum.

\*\*Typical room temperature properties of annealed or as-cast material.

†CDA = Copper Development Association

††rem = remainder

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(cont'd on next page)

TABLE 4-45. (cont'd)

| ALLOY               | CDA† | UNS    | COMPOSITION %* |         |          |         |           |                                     | MECHANICAL PROPERTIES**     |                               |                                      |
|---------------------|------|--------|----------------|---------|----------|---------|-----------|-------------------------------------|-----------------------------|-------------------------------|--------------------------------------|
|                     |      |        | Cu             | Zn      | Sn       | Al      | Ni        | OTHER                               | YIELD STRENGTH<br>MPa (ksi) | TENSILE STRENGTH<br>MPa (ksi) | ELONGATION<br>IN 51 mm<br>(2 in.), % |
| 70/30 Copper nickel | 715  | C71500 | rem            | 1.0     | —        | —       | 29.0-33.0 | 0.4-1.0 Fe<br>1.0 Mn                | 138 (20)                    | 372 (54)                      | 45                                   |
| 65-18 Nickel silver | 752  | C75200 | 63.0-68.5      | rem     | —        | —       | 16.5-19.5 | 0.25 Fe<br>0.5 Mn                   | 172 (25)                    | 386 (56)                      | 45                                   |
| <b>Cast</b>         |      |        |                |         |          |         |           |                                     |                             |                               |                                      |
| Ounce metal         | 836  | C83600 | 84-86          | 4.0-6.0 | 4-6      | 0.005   | 1.0       | 4-6 Pb                              | 117 (17)                    | 255 (37)                      | 30                                   |
| Manganese bronze    | 865  | C86500 | 55-65          | 36-42   | 1.0      | 0.5-1.5 | 1.0       | 0.4-2.0 Fe<br>0.1-1.5 Mn            | 193 (28)                    | 490 (71)                      | 30                                   |
| G bronze            | 905  | C90500 | 86-89          | 1.0-3.0 | 9.0-11.0 | 0.005   | 1.0       | —                                   | 152 (22)                    | 310 (45)                      | 25                                   |
| M bronze            | 922  | C92200 | 86-90          | 3.0-5.0 | 5.5-6.5  | 0.005   | 1.0       | 1.0-2.0 Pb                          | 138 (20)                    | 276 (40)                      | 30                                   |
| Ni-Al-Mn bronze     | 957  | C95700 | 71             | —       | —        | 7.0-8.5 | 1.5-3.0   | 2.0-4.0 Fe<br>11-14 Mn              | 310 (45)                    | 655 (95)                      | 26                                   |
| Ni-Al bronze        | 958  | C95800 | 79             | —       | —        | 8.5-9.5 | 4.0-5.0   | 3.5-4.5 Fe<br>0.8-1.5 Mn            | 262 (38)                    | 655 (95)                      | 25                                   |
| Copper nickel       | 964  | C96400 | 65-69          | —       | —        | —       | 28-32     | 0.5-1.5 Cb<br>0.25-1.5 Fe<br>1.5 Mn | 255 (37)                    | 469 (68)                      | 28                                   |

\*Single values are maximum values except for Cu, which is minimum.

\*\*Typical room temperature properties of annealed or as-cast material.

†CDA = Copper Development Association

††rem = remainder

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## 4-7.2 TYPES OF CORROSION OF COPPER AND HIGH-COPPER ALLOYS

## 4-7.2.1 Uniform Corrosion

## 4-7.2.1.1 Weathering Corrosion

Copper exhibits good resistance to corrosion in urban, marine, and industrial atmospheres. The major factors that control the initial rate of attack on copper are moisture, temperature, and the level of pollution.

Table 4-46 shows the relative intensity of these factors at various locations along with the resultant relative corrosivity of these sites based upon copper (Ref. 81). Soon after exposure of copper to the atmosphere, the bright copper surface takes on a dull tan tarnish. After a few years this tarnish gradually changes to dark brown or black. At a later stage the corrosion products of copper turn green. The corrosion rate of several types of copper in a 20-yr test averaged  $1 \mu\text{m/yr}$  (0.05 mpy) in an industrial atmosphere,  $0.8 \mu\text{m/yr}$  (0.03 mpy) in a marine atmosphere, and  $0.5 \mu\text{m/yr}$  (0.02 mpy) in a rural atmosphere (Ref. 82).

## 4-7.2.1.2 Corrosion in Natural Waters

Copper has good resistance to corrosion by all types of freshwater; corrosion rates are from  $5$  to  $25 \mu\text{m/yr}$  (0.2 to 1 mpy). Corrosion rates for water saturated with air and carbon dioxide are an order of magnitude greater than those for municipal or distilled water. Copper also has good resistance to corrosion in seawater. Because of its outstanding resistance to fouling by marine organisms, it is widely used for sheathing on surfaces exposed to seawater. Copper is sometimes used in seawater piping, but it is subject to corrosion-erosion where the flow velocity is greater than  $0.9$  to  $1.2 \text{ m/s}$  (3 to 4 ft/s). These velocities are often attained at changes in pipe cross section or flow direction.

## 4-7.2.1.3 Corrosion in Neutral Solutions

Copper has good resistance to many salt solutions, such as the sulfates and nitrates of sodium and potassium. Typical corrosion rates are  $5 \mu\text{m/yr}$  (0.2 mpy). It also has reasonably good resistance to the nonoxidizing chlorides of sodium and calcium. Corrosion rates may range from  $15$  to  $279 \mu\text{m/yr}$  (0.6 to 11 mpy). Copper does, however, have poor resistance to oxidizing substances, such as ferric and cupric salts, and to ammonium salts. Cyanides are also very corrosive to copper.

## 4-7.2.1.4 Corrosion in Acid Solutions

The action of acids on copper can be generalized as follows (Ref. 57):

1. Acid solutions in concentrations up to 0.01% are only slightly corrosive to copper. The rates are usually below  $254 \mu\text{m/yr}$  (10 mpy), and aeration is relatively unimportant.

2. Nonoxidizing acids free from air corrode copper at rates less than  $5 \mu\text{m/yr}$  (0.2 mpy).

3. Solutions of nonoxidizing acids (hydrochloric acid excepted) containing small amounts of oxygen, such as might be absorbed from air in contact with the solution surface, are weakly corrosive, independent of the concentration. Rates may be up to  $254 \mu\text{m/yr}$  (10 mpy).

4. Air-saturated solutions of nonoxidizing acids may be very corrosive, i.e., from  $203$  to  $1270 \mu\text{m/yr}$  (8 to 50 mpy).

5. Oxidizing acids, except in dilute solutions, corrode copper rapidly at rates greater than  $2032 \mu\text{m/yr}$  (80 mpy), independent of aeration. Nonoxidizing acids containing oxidizing materials behave similarly.

6. Increasing the temperature of an acid solution usually increases its corrosivity. However, at high temperatures solubility of oxygen is so low that the corrosion rate decreases.

**TABLE 4-46. THE RELATIONSHIP BETWEEN THE CORROSIVITY OF COPPER DURING ATMOSPHERIC EXPOSURE AND THREE ATMOSPHERIC FACTORS (Ref. 81)**

| SITE                                 | CORROSIVITY | ATMOSPHERIC FACTORS |                               |             |
|--------------------------------------|-------------|---------------------|-------------------------------|-------------|
|                                      |             | DURATION OF WETNESS | SO <sub>2</sub> CONCENTRATION | TEMPERATURE |
| Kure Beach, NC (244-m (800-ft) site) | 1           | 1                   | 5                             | 1           |
| Trail, BC                            | 2           | 3                   | 3                             | 5           |
| South Bend, PA                       | 3           | 2                   | 4                             | 3           |
| Cleveland, OH                        | 4           | 4                   | 2                             | 2           |
| Ottawa, Ontario                      | 5           | 5                   | 1                             | 4           |

NOTE: In the ratings, a value of 1 denotes the highest corrosivity, the longest time of wetness, the highest SO<sub>2</sub> concentration, and the highest temperature.

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**MIL-HDBK-735(MR)****4-7.2.1.5 Corrosion in Alkaline Solutions**

The corrosion of copper in caustic solutions is significant, but not intolerable, if the application of copper is for purposes other than corrosion resistance. For example, 30% to 50% concentrated caustic soda at 82°C (179°F) corrodes copper at a rate of 51  $\mu\text{m}/\text{yr}$  (2 mpy).

Moist ammonia and ammonium hydroxide solutions corrode copper rapidly in the presence of oxygen. This corrosion occurs because copper forms a complex ammonium ion. Substituted ammonia compounds, such as amines, are also corrosive to copper.

**4-7.2.1.6 Corrosion in Organic Chemicals**

Chlorinated hydrocarbons can be corrosive to copper under conditions in which hydrolysis results in the formation of hydrochloric acid. The presence of water facilitates hydrolysis.

**4-7.2.2 Pitting and Crevice Corrosion**

Although the failure of domestic copper plumbing systems is rare, pitting failure occurs in cold-water lines that conduct aggressive well waters. Aggressive well waters are those contaminated with corrosive compounds. Hot-water pitting is rare and is usually associated with a soft water.

Copper is susceptible to crevice corrosion attack.

**4-7.2.3 Stress-Corrosion Cracking**

Oxygen-free, high-conductivity copper and electrolytically refined copper are not susceptible to stress-corrosion cracking. Phosphorous-deoxidized copper containing as little as 0.004% phosphorus is susceptible to stress-corrosion cracking; however, the susceptibility is low compared to some copper alloys. Mercury can cause stressed copper to crack.

**4-7.2.4 High-Temperature Corrosion**

Copper is not considered a high-temperature material. Its strength in and resistance to hot atmospheres are low compared with alternative materials, such as iron, steel, and stainless steel.

Copper is not a satisfactory metal for handling molten metals, such as tin, zinc, bismuth, antimony, and lead.

Fused caustic soda at 316° to 593°C (600° to 1100°F) is corrosive to copper.

**4-7.2.5 Galvanic Corrosion**

The relative galvanic effect of copper on other metals in the atmosphere is shown in Table 4-47. The table is based on 7 yr of exposure to industrial, marine, and rural atmospheres. In particular, couples of copper and aluminum or copper and steel can lead to severe galvanic corrosion.

**TABLE 4-47. RELATIVE GALVANIC EFFECT OF COPPER ON OTHER METALS IN ATMOSPHERIC EXPOSURE (Ref. 83)**

| OTHER METAL | TYPE OF ATMOSPHERE |          |        |
|-------------|--------------------|----------|--------|
|             | INDUSTRIAL         | MARINE   | RURAL  |
| Aluminum    | Severe             | Severe   | Slight |
| Iron        | Moderate           | Severe   | Slight |
| Lead        | None               | Slight   | Slight |
| Nickel      | Slight             | Slight*  | None   |
| Tin         | Moderate           | Moderate | Slight |
| Zinc        | Moderate           | Moderate | Slight |

\*Nickel is cathodic to copper in this environment.

The degree of risk in coupling copper to other metals in water, salt solutions, or acids depends upon the effectiveness of the solution as an electrolyte.

**4-7.3 TYPES OF CORROSION OF COPPER ALLOYS****4-7.3.1 Dealloying****4-7.3.1.1 Copper-Zinc Alloys**

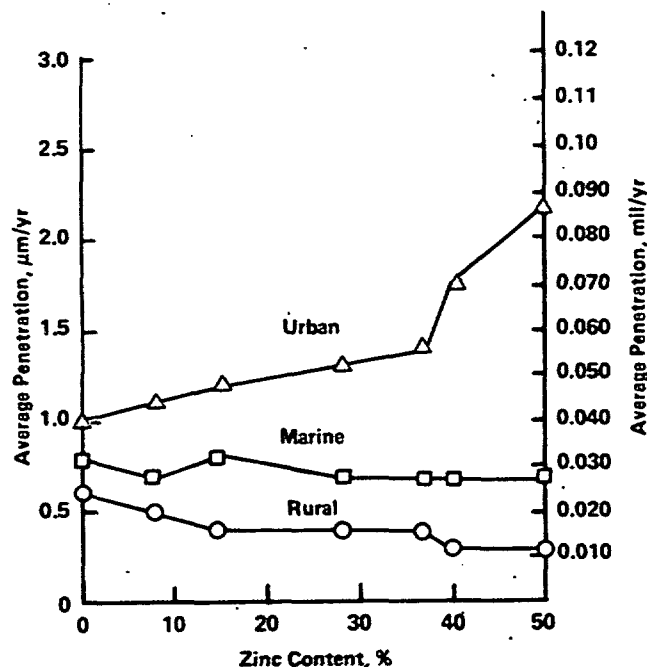
Brasses that contain at least 85% copper are practically immune to dezincification, whereas brasses that contain 15% zinc or more are vulnerable. Increasing the amounts of zinc increases susceptibility. Iron and manganese in brass accelerate dezincification, which can occur in localized areas or uniformly over the surface of the metal.

The environmental factors that follow increase susceptibility:

1. High temperatures
2. Low degree of aeration
3. Stagnant flow conditions, especially in acidic media
4. Porous inorganic scale formation on the metal surface
5. Acids, both organic and inorganic
6. Dilute and concentrated alkalies
7. Neutral solutions of chlorides and sulfates
8. Oxidizing agents, such as hydrogen peroxide.

Corrosion of brasses in the atmosphere is principally dezincification. Fig. 4-14 shows the penetration based upon weight loss for urban, marine, and industrial atmospheres. Increased zinc content increased corrosion in the urban atmosphere. In rural and marine atmospheres the penetration was independent of zinc content. The depth of penetration based upon metallographic examination is much higher than that based upon weight loss. Dezincification occurs slowly in atmospheric exposure and is a problem only if brass is exposed in thin sections.

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**Figure 4-14. Average Penetration in Cu-Zn Alloys in Relation to Zinc Content During 7-yr Exposure (Ref. 269)**

Brasses that contain about 1% tin, such as admiralty brass, naval brass, and manganese bronzes, have good resistance to dezincification. Arsenic, antimony, or phosphorus is added to admiralty brass to inhibit dezincification; the amount added ranges from 0.02 to 0.1%. The relative susceptibility to dezincification of some copper alloys in a 3.4% salt solution is indicated in Table 4-48.

#### 4-7.3.1.2 Copper-Tin Alloys

Copper-tin alloys have good resistance to dealloying.

#### 4-7.3.1.3 Copper-Aluminum Alloys

Dealloying is rare in a single-phase alloy. If the aluminum content of the alloy is above 9% and the cooling rate through the temperature range 899° to 399° C (1650° to 750° F) is slow, a second phase forms a continuous network. This second phase is susceptible to dealuminification, but proper heat treatment can make these duplex alloys more resistant to dealloying.

Dealloying is reduced by the addition of at least 4% nickel. This alloy is referred to as nickel-aluminum bronze. In the cast condition, however, nickel-aluminum bronze often contains nonequilibrium microconstituents that are susceptible to dealloying attack. The use of a temper-anneal heat treatment in the range of 649° to 704° C (1200° to 1300° F) reduces the susceptibility of these alloys to dealloying attack (Ref. 85), but the response of castings to heat treatment is not uniform.

**TABLE 4-48. RELATIVE DEZINCIFICATION SUSCEPTIBILITY OF COPPER ALLOYS IN 3.4% NaCl AT 40° C (104° F) (Ref. 84)**

| ALLOY CDA NO. | ZINC, wt % | RELATIVE RESISTANCE TO DEZINCIFICATION* |
|---------------|------------|---|
| 230           | 15         | 4                                       |
| 260           | 30         | 10                                      |
| 422           | 12         | 4                                       |
| 688           | 22.7       | 3                                       |
| 766           | 31         | 8                                       |
| 770           | 27         | 9                                       |
| 194           | 0.12       | 0                                       |
| 638           | 0          | 0                                       |
| 110           | 0          | 0                                       |

\*Based on a scale of 0 to 10 on which 0 is complete immunity and 10 is highly susceptible. Rankings are based on laboratory data generated in a 3.4% NaCl solution. These rankings may be altered if different environments are used.

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Heat treatment is highly effective on smaller castings with fine and uniformly distributed microconstituents, whereas large castings having coarser and more segregated microconstituents are less responsive.

Dealloying in nickel-aluminum bronze castings containing a minimum of 4% nickel appears limited to a depth of approximately 6 mm (0.25 in.).

#### 4-7.3.1.4 Copper-Nickel Alloys

Cupronickels are highly resistant to dealloying attack. However, dealloying of a 30% nickel alloy has been reported in boiler feedwater preheaters and at hot spots in condenser tubing. The presence of nickel does not inhibit dezincification in a copper-zinc-nickel alloy, as shown in Table 4-48. Alloy 766 (31% Zn, 12% Ni) and alloy 770 (27% Zn, 18% Ni) are highly susceptible to dezincification.

#### 4-7.3.2 Uniform Corrosion

##### 4-7.3.2.1 Weathering Corrosion

The average penetration rate for various copper-base alloys varies little on long-term exposures. It is 1 to 2 μm/yr (0.04 to 0.08 mpy) in urban atmospheres, up to 2.5 μm/yr (0.1 mpy) in industrial atmospheres, about 1 μm/yr (0.04 mpy) in marine atmospheres, and about 0.5 μm/yr (0.02 mpy) in rural atmospheres (Ref. 86). In tropical atmospheres the corrosion rate may be slightly higher in regions of high humidity and high salt content. However, as mentioned in par. 4-7.3.1.1, brasses undergo dezincification in weathering environments. The dezincification rate decreases in the order of urban, marine, and rural atmospheres.

**MIL-HDBK-735(MR)****4-7.3.2.2 Corrosion in Natural Waters**

Copper alloys are widely used for systems that handle freshwater. Certain of the alloys have become associated with particular components, such as heat exchangers, and with particular types of freshwaters, such as river water containing acid mine drainage.

Copper alloys are widely employed in systems exposed to seawater. Table 4-49 shows the typical applications of the various copper alloys in marine components. The corrosion rates of copper alloys in seawater vary; they depend on many factors including the composition, i.e., concentration, of the seawater, the temperature, the velocity past the metal surface, and the degree and kind of pollution. The good resistance of copper alloys to cor-

rosion by seawater depends partly upon the inherent cathodic nobility of the metal, but it also depends on the ability to form protective films. High-velocity and turbulent flow conditions can remove these films and permit local and rapid corrosion. The corrosion rates of some copper alloys immersed in quiet seawater are indicated in Fig. 4-15.

The effect of seawater velocity within the range experienced in piping is shown in Fig. 4-16, whereas the effect of seawater velocity within the range experienced in pumps and hydrofoils is indicated in Fig. 4-17. The good resistance of the copper alloys in general and the excellent resistance of cupronickels are evident.

**TABLE 4-49. USE OF COPPER-BASE ALLOYS IN SEAWATER (Adapted From Ref. 87)**

| ALLOY  | USE   |
|--|---|
| Red brass (85 Cu, 15 Zn: copper alloy 230)   | Limited use as piping   |
| Cast manganese bronze (58 Cu, 39 Zn, 1 Fe, 1 Al, 0.25 Mn)  | Principal use: propellers   |
| Cast nickel-aluminum bronze (78 Cu, 10 Al, 4 Ni, 4 Fe, 3.5 Mn, 0.5 other)                            | Principal use: propellers<br>Advantages: higher strength, greater durability and erosion resistance compared to manganese bronze  |
| Cast nickel-aluminum-manganese bronze (74 Cu, 12.5 Mn, 8 Al, 3 Fe, 2 Ni, 0.5 other)                  |   |
| Cast G bronze (88 Cu, 10 Sn, 2 Zn)   | Principal uses: pump and valve bodies and impellers   |
| Cast M bronze (88 Cu, 6 Sn, 4.5 Zn, 1.5 Pb)  |   |
| Cast red brass (85 Cu, 5 Zn, 5 Sn, 5 Pb) (ounce metal)   | Limited use as pipe fittings  |
| Inhibited admiralty (70 Cu, 29 Zn, 1 Sn with 0.1 As or 0.1 Sb or 0.1 P: copper alloys 443, 444, 445) | Marine condenser tube alloy developed by the British Admiralty about the turn of the century. Largely displaced by aluminum brass and/or copper-nickel to secure better resistance to velocity effects  |
| Inhibited aluminum brass (77 Cu, 21 Zn, 1 Sn, 0.1 As: copper alloy 687)                              | Widely used marine and condenser tube alloy developed by the Yorkshire Copper Company (now Yorkshire Imperial Metals) about 1928 for better resistance to velocity effects. Displaced by 70/30 copper-nickel and 90/10 copper-nickel alloys in naval service starting about 1935 to secure greater dependability. Still widely used in coastal power plants and merchant vessels and has an advantage in first cost over copper-nickel. |
| Naval brass (60 Cu, 39 Zn, 1 Sn: copper alloy 464)   | Principal use: tube sheets  |
| Inhibited naval brass (same except 0.1 As, 0.15 Sb, or 0.1 P: copper alloys 465, 466, 467)           |   |
| Muntz metal (60 Cu, 40 Zn: copper alloy 280)   |   |

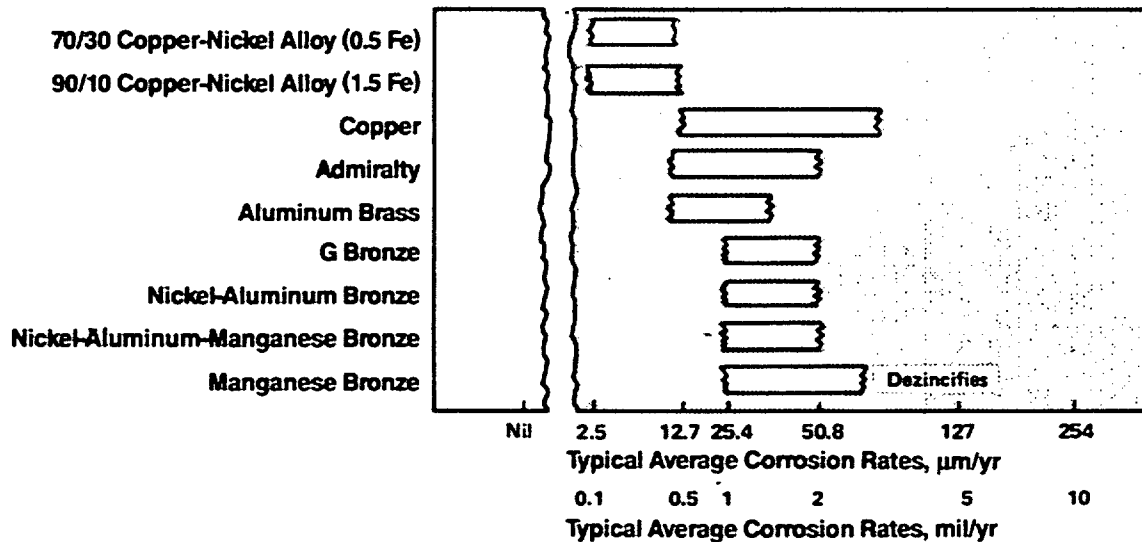
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TABLE 4-49. (cont'd)

| ALLOY  | USE  |
|--|--|
| 90/10 copper-nickel (1.5 Fe: copper alloy 706)<br>70/30 copper-nickel (0.5 Fe: copper alloy 715) | <p>Condenser tube alloys that have proven their durability and have become standard in both British and American naval vessels. They are also widely used in merchant ships and coastal power plants where the premium in first cost is justified by long-term savings.</p> <p>The 70/30 copper-nickel 0.5 Fe alloy is commonly used for the most severe services: highest temperatures, greatest velocities, and where reliability and dependability are paramount. A recent development is the high (5% Fe) version, which shows promise of improved resistance to refinery sulfide corrosion and to hydrofoil velocities.</p> <p>The unique combination of resistance to pitting, resistance to general corrosion, resistance to fouling, excellent fabricability, and the reasonable cost of the 90/10 copper-nickel 1.5 Fe alloy has led to substantial recent increases in the usage of this alloy, particularly where welded fabrication is advantageous, such as for piping and water boxes.</p> |
| Nickel-silver 18% (65 Cu, 17 Zn, 18 Ni)  | A copper-nickel alloy with zinc, which gives the alloy excellent deep drawing characteristic. Limited use in saltwater fishing reels and zippers   |

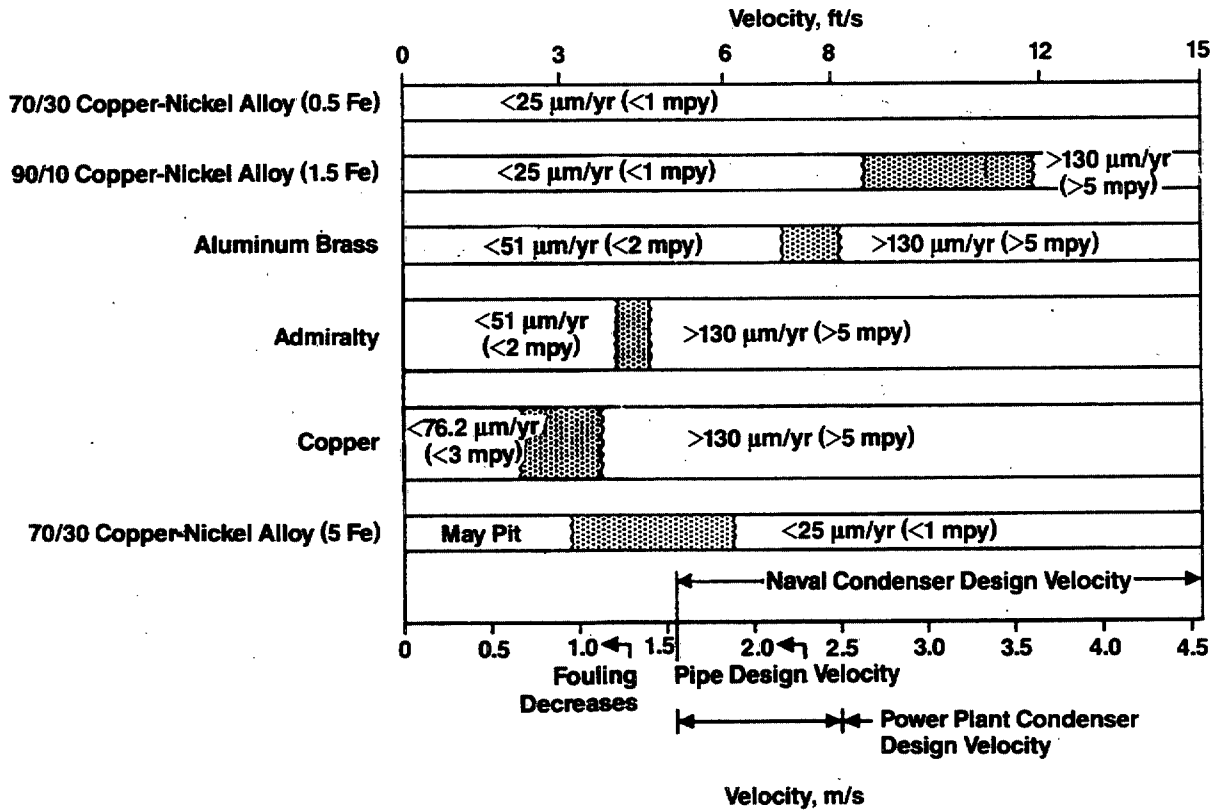
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Figure 4-15. General Wasting (Immersed in Quiet Seawater Less Than 0.61 m/s (2 ft/s) (Adapted from Ref. 87)

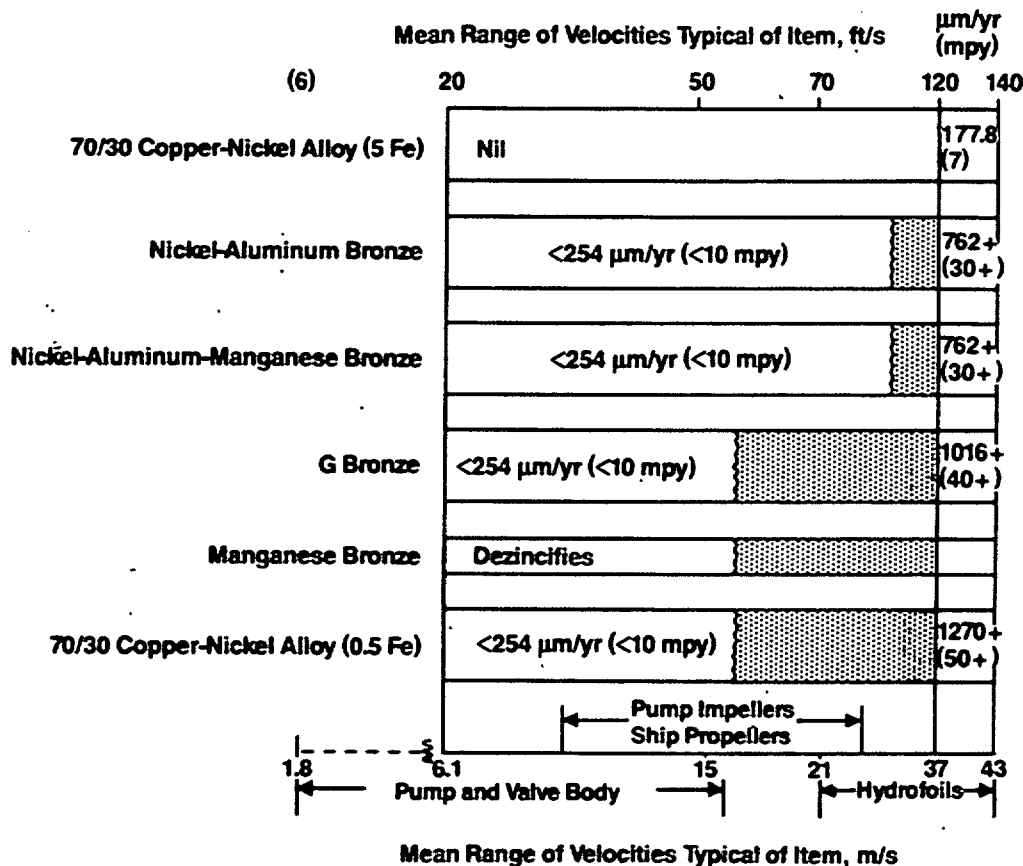
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**Figure 4-16. Seawater Velocity (Pipe and Tube Ranges) (Adapted from Ref. 87)**

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Figure 4-17. Seawater Velocity (Pump to Hydrofoil Ranges) (Adapted from Ref. 87)

#### 4-7.3.2.3 Corrosion in Salt Solutions

Copper alloys are widely used in handling salt solutions, such as nitrates, sulfates, and chlorides of sodium, potassium, magnesium, and calcium. The corrosion rates, which are about  $5 \mu\text{m}/\text{yr}$  (0.2 mpy) under quiet conditions, are somewhat higher in agitated aerated exposure. Also chlorides are usually more corrosive than other salts.

Ammonium salts are corrosive to copper alloys and are especially so when the solutions are aerated. Cupronickel is the most resistant of the copper alloys.

The alkaline salts, such as carbonates, silicates, and phosphates, have little corrosive effect on the high-copper alloys. The chromates have no corrosive effect on copper alloys in neutral or alkaline solutions. Acid solutions of the chromates, however, are very corrosive.

Hypochlorites are corrosive to copper alloys. Pitting corrosion with an effective corrosion rate of more than  $508 \mu\text{m}/\text{yr}$  (20 mpy) can be expected. Cyanide solutions are also corrosive.

Solutions of acid salts, such as aluminum chloride, act like dilute solutions of the corresponding acid and are mildly to moderately corrosive in quiet solutions. Ferric,

stannic, and cupric salt solutions are not only acid but also are oxidative; therefore, they are corrosive. Metallic mercury and silver deposit from solutions of their salts on copper alloys.

#### 4-7.3.2.4 Corrosion in Acid Solutions

Copper alloys containing more than about 15% zinc are not suitable for handling acids because of dealloying attack. Aluminum bronzes containing more than 8% aluminum are also subject to dealloying attack in acids. The attack by air-free acids is relatively slow, whereas aerated solutions are more corrosive. Attack is intensified when the acid solution is moving at a significant velocity relative to the copper alloy.

Copper alloys are not suitable for nitric acid in concentrations much greater than 0.1%.

Hydrochloric acid is the most corrosive to copper alloys of the nonoxidizing acids. At room temperature the corrosion rate may vary from 102 to  $813 \mu\text{m}/\text{yr}$  (4 to 32 mpy) for the more corrosion-resistant alloys. The corrosion rate can be as great as  $6502 \mu\text{m}/\text{yr}$  (256 mpy) for concentrated acid at higher temperatures.

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Many copper alloys have useful resistance to certain concentrations of hydrofluoric acid. Red brass, silicon bronze, aluminum bronze, phosphor bronze, commercial bronze, and admiralty brass resist all concentrations below 70% and at temperatures up to the boiling point. High velocity, aeration, and the presence of oxidizing agents considerably increase the corrosion rates of these alloys. The copper-nickel alloys, particularly 70 Cu:30 Ni alloy, are the most resistant copper alloys. It will resist all concentrations of the acid, including hot concentrated acid, provided no air is present.

Copper alloys are fairly resistant to sulfuric acid solutions. Corrosion rates vary from 20 to 406  $\mu\text{m}/\text{yr}$  (0.8 to 16 mpy) at room temperatures. Corrosion rates at 100°C (212°F) may be as high as 4064  $\mu\text{m}/\text{yr}$  (160 mpy). Generally copper alloys are suitable for service at all concentrations at room temperatures, i.e., up to 80% acid at 60°C (140°F), up to 70% at 80°C (176°F), and up to 50% acid at 100°C (212°F). These values assume quiet immersion conditions. Aeration and agitation greatly increase the corrosion rates.

Un-aerated phosphoric acid solutions at room temperature corrode copper alloys at rates of about 406  $\mu\text{m}/\text{yr}$  (16 mpy). Higher temperatures and aeration increase the corrosion rate to about 1651  $\mu\text{m}/\text{yr}$  (65 mpy). Crude phosphoric acid containing oxidizing agents such as ferric salts is highly corrosive.

Copper alloys are suitable for handling acetic and other organic acids. Aeration should be kept low. Corrosion

rates range from 51 to 508  $\mu\text{m}/\text{yr}$  (2 to 20 mpy) for quiet, room-temperature immersion but increase up to 203 to 2540  $\mu\text{m}/\text{yr}$  (8 to 100 mpy) for aerated, agitated solutions at elevated temperatures.

#### 4-7.3.2.5 Corrosion in Alkaline Solutions

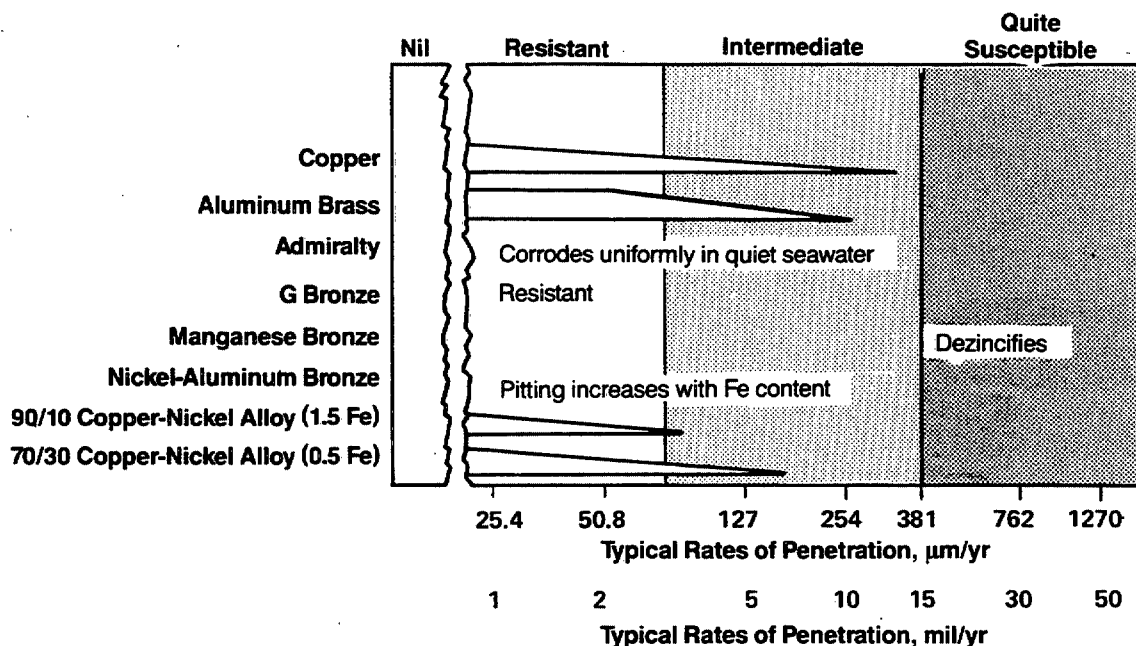
Copper alloys are useful for contact with sodium hydroxide and potassium hydroxide solutions. Corrosion rates vary from 5 to 51  $\mu\text{m}/\text{yr}$  (0.2 to 2 mpy) at room temperature and from 76 to 203  $\mu\text{m}/\text{yr}$  (3 to 8 mpy) under agitated, aerated, and high-temperature conditions. The cupronickels are the most resistant of the copper alloys to alkaline solutions.

Most copper alloys are rapidly corroded by moist ammonia vapors and by ammonium hydroxide solutions containing more than a few parts per million (ppm) of ammonia because copper forms a complex ammonium ion. Substituted ammonia compounds, such as amines, are also corrosive to copper alloys. The cupronickels are the most resistant of the copper alloys.

#### 4-7.3.3 Pitting and Crevice Corrosion

The pitting of copper alloys in quiet seawater is shown in Fig. 4-18. Of the alloys shown, G bronze is resistant, aluminum brass is susceptible to some extent, as is copper, the cupronickels are mostly resistant, and manganese bronze dezincifies under these conditions.

Sulfide is a major pollutant in many estuaries and harbors. Several materials including high-copper alloys,



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Figure 4-18. Pitting (Immersed in Quiet Seawater Less Than 0.61 m/s (2 ft/s)) (Adapted from Ref. 87)

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Monels, and 316 stainless steel were exposed to seawater containing varying amounts of sulfide (Ref. 88). Flow velocity was typical pipe design flow of 2.4 m/s (7.9 ft/s). After exposures of 30, 60, and 120 days, corrosion rate and maximum thickness loss data were obtained by weight loss and pit depth measurements. The general conclusions are

1. All alloys tested, except 316 stainless steel, are susceptible to sulfide-induced corrosion in seawater at a 0.05-mg/litre ( $4.2 \times 10^{-7}$ -lb/gal) sulfide concentration. Most are susceptible at a 0.01-mg/litre ( $0.8 \times 10^{-7}$ -lb/gal) concentration. The results for the 120-day exposure are shown in Table 4-50.

2. Minor variations within an alloy class can result in large differences in corrosion behavior in seawater that contains sulfide. For example, the observed corrosion rates of cast nickel copper (Monel 411) are several orders of magnitude greater than those of the wrought alloy (Monel 400).

3. In seawater the copper alloy corrosion product films were brown or black depending upon the alloy.

Films in seawater that contains sulfide were always black and loosely adherent.

4. Selection of an alloy for service in seawater should include consideration of the amount of sulfide pollution likely to be encountered.

The corrosion characteristics in seawater of high-strength, chromium-containing (2.5%) 30% nickel-copper alloy have been compared with a 70:30 copper-nickel alloy (Ref. 89). The high-strength alloy (CA-719) is susceptible to shallow pitting in quiet and in slowly flowing seawater. The instantaneous pitting rates for beyond 4 yr are  $15 \mu\text{m/yr}$  (0.6 mpy) in quiet water and  $25 \mu\text{m/yr}$  (1 mpy) in slowly flowing seawater. The 70:30 copper-nickel alloy (CA-715) corrodes in a uniform manner ( $<25 \mu\text{m/yr}$  ( $<1$  mpy)) under the same conditions. However, in turbulent, rapidly flowing seawater CA 719 has excellent resistance to erosion and impingement, but CA 715 sustains serious damage.

The current corrosion allowance used in designing piping systems for CA of 1.3 mm (0.05 in.) is adequate for quiet or slowly flowing seawater but would not suffice

TABLE 4-50. RESULTS OF SULFIDE EXPOSURES (Ref. 88)

| ALLOY                  | 120 DAYS OF EXPOSURE                 |      |                         |      |  |       |                         |      |  |       |                         |      |
|------------------------|--------------------------------------|------|-------------------------|------|--|-------|-------------------------|------|--|-------|-------------------------|------|
|                        | 0.0 mg/l                             |      |                         |      | 0.01 mg/l ( $0.8 \times 10^{-7}$ lb/gal) |       |                         |      | 0.05 mg/l ( $4.2 \times 10^{-7}$ lb/gal) |       |                         |      |
|                        | CORROSION RATE, $\mu\text{m/yr}$ mpy |      | DEPTH OF ATTACK, mm mil |      | CORROSION RATE, $\mu\text{m/yr}$ mpy     |       | DEPTH OF ATTACK, mm mil |      | CORROSION RATE, $\mu\text{m/yr}$ mpy     |       | DEPTH OF ATTACK, mm mil |      |
| Ni-Al-bronze (wrought) | 106.3                                | 4.19 | 0.24                    | 9.45 | 202.3                                    | 7.96  | 1.27                    | 50.0 | 517.1                                    | 20.36 | 1.17                    | 46.1 |
| Ni-Al-bronze (cast)    | 101.0                                | 3.98 | 0.51                    | 20.1 | 223.4                                    | 8.80  | 1.12                    | 44.1 | 381.1                                    | 15.00 | 1.39                    | 54.7 |
| Mn-Ni-Al-bronze (cast) | 18.1                                 | 0.71 | 0.08                    | 3.15 | 27.7                                     | 1.09  | 0.10                    | 3.94 | 84.1                                     | 3.31  | 0.37                    | 14.6 |
| Mn bronze              | 87.6                                 | 3.45 | 1.06                    | 41.7 | 91.7                                     | 3.61  | 0.67                    | 26.4 | 301.9                                    | 11.89 | 0.64                    | 25.2 |
| Bronze comp M          | 160.6                                | 6.32 | 0.49                    | 19.3 | 185.2                                    | 7.29  | 0.66                    | 26.0 | 351.6                                    | 13.84 | 1.18                    | 46.5 |
| Bronze comp G          | 124.1                                | 4.89 | 0.52                    | 20.5 | 205.2                                    | 8.08  | Perf*                   | —    | 474.7                                    | 18.69 | Perf                    | —    |
| 90-10                  | 91.9                                 | 3.62 | 0.24                    | 9.45 | 126.6                                    | 4.98  | 0.56                    | 22.0 | 268.7                                    | 10.58 | 1.20                    | 47.2 |
| 90-10 + Sn             | 79.0                                 | 3.11 | 0.12                    | 4.72 | 143.8                                    | 5.66  | 0.39                    | 15.4 | 220.2                                    | 8.67  | 0.86                    | 33.9 |
| 70-30                  | 190.0                                | 7.48 | 0.39                    | 15.4 | 137.9                                    | 5.43  | 0.55                    | 21.7 | 569.2                                    | 22.41 | 1.49                    | 58.7 |
| 70-30 + Cr (CA719)     | 53.1                                 | 2.09 | 0.28                    | 11.0 | 302.2                                    | 11.90 | 0.87                    | 34.3 | 610.7                                    | 24.04 | 1.74                    | 68.5 |
| Monel 411 (cast)       | 10.0                                 | 0.39 | 0.52                    | 20.5 | 344.5                                    | 13.56 | 1.08                    | 42.5 | 839.8                                    | 33.06 | Perf                    | —    |
| Monel 400 (wrought)    | 2.8                                  | 0.11 | 0.40                    | 15.7 | 25.9                                     | 1.02  | 0.49                    | 19.3 | 44.7                                     | 1.76  | 0.44                    | 17.3 |
| K-Monel                | 3.3                                  | 0.13 | 0.48                    | 18.9 | 22.5                                     | 0.89  | 0.84                    | 33.1 | 40.5                                     | 1.59  | 0.88                    | 34.6 |
| 316 Stainless steel    | 0                                    | 0    | 0                       | 0    | 0.5                                      | 0.02  | 0.12                    | 4.72 | 0.1                                      | 0.004 | 0                       | 0    |

\*Perf = Perforation



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where seawater velocities of 4.6 m/s (15 ft/s) and higher are encountered. A corrosion allowance for CA 719 may reasonably be based on its pitting behavior in quiet and slowly flowing seawater. For CA 719 pipe this allowance would be (Ref. 89)

$$A = 4R + R_i(t - 4), \mu\text{m (mil)} \quad (4-1)$$

where

$A$  = corrosion allowance,  $\mu\text{m (mil)}$

$R$  = maximum linear pitting rate,  $\mu\text{m/yr (mpy)}$

$R_i$  = maximum instantaneous pitting rate after 4 yr,  $\mu\text{m/yr (mpy)}$

$t$  = time in years greater than four, yr

and the number 4 in Eq. 4-1 has units of yr.

All of the copper alloys are susceptible to some degree to crevice corrosion. The relative susceptibility of several alloys to crevice attack in 3.5% salt solution is shown in Table 4-51.

#### 4-7.3.4 Stress-Corrosion Cracking

Ammonia-containing compounds are the principal environmental species that causes stress-corrosion cracking in copper alloys. Although not the only damaging environmental component, ammoniacal stress-corrosion cracking is the major cause of service failures because there are many potential sources of ammonia. The presence of any nitrogenous compound capable of forming complexes resembling the cupric-ammonium complex should be carefully monitored. The presence of carbon

dioxide is not necessary for ammoniacal stress-corrosion cracking, but it speeds up the process. Also corrosion pits or other stress intensifiers do not seem to be necessary for initiation of the cracking.

In addition to the presence of ammonia and a susceptible copper alloy, the conditions that are necessary for ammoniacal stress-corrosion cracking include an applied or residual stress, water or moisture, and oxygen or other depolarizers.

It is the residual stresses that are usually important to the cracking of structures or components made of copper alloys. These stresses may be removed by stress-relief annealing.

Moist air containing as little as 5 ppm of sulfur dioxide can cause stress-corrosion cracking. An industrial atmosphere (New Haven, CT) badly contaminated with sulfur dioxide but believed to be essentially free of ammonia caused the cracking of many copper alloys in a test exposure. In contrast, only a few of these alloys cracked in a marine environment (Daytona Beach, FL).

Chloride ions may have an inhibitive or protective effect (Ref. 90). The risk of stress-corrosion cracking is greatest in industrial atmospheres, intermediate in urban atmospheres, and least in marine atmospheres.

Certain liquid metals cause stressed copper to crack. Mercury is particularly damaging to copper alloys. Thus neither metallic mercury nor its compounds should be permitted to contact copper alloys. Also molten solder, molten tin, and molten sodium have caused cracking of stressed copper alloys.

**TABLE 4-51. RELATIVE CREVICE ATTACK OF VARIOUS ALLOYS IN 3.5% NaCl SOLUTION OF 40° C (104° F) 60-DAY EXPOSURE (Ref. 84)**

| ALLOY CDA NO. AND NOMINAL COMPOSITION, %      | RELATIVE RANKING* (10 IS WORST) | DEPTH OF ATTACK, $\mu\text{m (mil)}$ |
|---|---------------------------------|--------------------------------------|
| 110 Electrolytic copper; 100 Cu               | 10                              | Complete perforation                 |
| 194; 97.5 Cu, 2.35 Fe, 0.03 P, 0.122 Zn       | 5                               | 254 to 381 (10 to 15)                |
| 230 Red brass; 85 Cu, 15 Zn                   | 9                               | Complete perforation                 |
| 260 Cartridge brass; 70 Cu, 30 Zn             | 10                              | Complete perforation                 |
| 619; 86.8 Cu, 9.2 Al, 4 Fe                    | 3                               | Slight dealloying attack             |
| 638; 95 Cu, 2.8 Al, 1.88 Si, 0.4 Co           | 3                               | Slight dealloying attack             |
| 688; 73.5 Cu, 22.7 Zn, 3.4 Al, 0.4 Co         | 3                               | Slight dealloying attack             |
| 706; 86.5 Cu, 1 Zn, 9-11 Ni, 1.0-1.8 Fe, 1 Mn | 3                               | 76.2 to 101.6 (3 to 4)               |
| 770; 55 Cu, 27 Zn, 18 Ni                      | 9                               | Complete perforation                 |

\*Determined on a basis of depth and on the rapidity and severity of attack. These rankings may be altered if different conditions are used.

NOTE: Specimen thickness is approximately 0.762 mm (0.030 in.) gage.

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The relative susceptibility of copper alloys to ammoniacal stress-corrosion cracking is shown in Table 4-52, and the stress-corrosion cracking of wrought alloys in industrial and marine atmospheres is shown in Table 4-53.

**4-7.3.4.1 Copper-Zinc Alloys**

Brasses containing over 20% zinc are highly susceptible to ammoniacal stress-corrosion cracking, and this susceptibility increases with increased zinc content. The highly susceptible brasses include those with or without small amounts of Pb, Sn, Mn, or Al, such as leaded brass, naval brass, admiralty brass, manganese bronze, or aluminum brass. Brasses containing less than 20% zinc, such as red brass and commercial bronze, are less susceptible than the brasses containing more than 20% zinc.

Stress-corrosion cracking in atmospheric environments occurs in copper alloys containing 20% or more zinc. As with ammoniacal stress-corrosion cracking, the susceptibility of the alloys increases with increased zinc content. Stress-corrosion cracking of brasses is more likely in industrial and marine atmospheres than in rural atmospheres because the industrial and marine atmospheres

are characterized by high concentrations of sulfur dioxide and ammonia. The susceptibility of brasses to stress-corrosion cracking in marine environments is significantly lower. Stress-corrosion cracking is more likely in moist or humid atmospheres than in dry atmospheres. The likelihood of brasses cracking in heated dry storage is relatively small.

Manganese bronze and nickel-manganese bronze are very susceptible to stress-corrosion cracking in seawater. Examples of their application include high-tensile fasteners and castings, such as ship propellers. If castings contain residual stresses, they should be stress relieved before being placed in service.

Sulfuric acid in the concentrations used for cleaning can cause stress-corrosion cracking in brass condenser and heat exchanger tubes.

**4-7.3.4.2 Copper-Tin Alloys**

The copper-tin alloys such as phosphor bronze are somewhat susceptible to ammoniacal stress-corrosion cracking. They are less susceptible than the high-zinc brasses but more susceptible than copper. They are not susceptible to cracking in atmospheric environments.

**TABLE 4-52. RELATIVE SUSCEPTIBILITY OF COPPER ALLOYS TO AMMONIACAL STRESS-CORROSION CRACKING (Ref. 91)**

|                             |  |
|-----------------------------|--|
| Very low susceptibility     | Cupronickels,* tough pitch copper, silicon bronze**  |
| Low susceptibility          | Phosphorized copper  |
| Intermediate susceptibility | Brasses containing less than 20% Zn, such as red brass, commercial bronze, aluminum bronze, nickel silver, phosphor bronze, and gilding metal  |
| High susceptibility         | Brass containing over 20% Zn, with or without small amounts of Pb, Sn, Mn, or Al (such as leaded brass, naval brass, admiralty brass, manganese bronze, or aluminum brass). The higher the amount of Zn, the higher the susceptibility |

\*For lowest susceptibility the iron in 90-10 cupronickel should be solutionized.

\*\*This alloy is highly susceptible to stress-corrosion cracking in high-temperature steam.

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**TABLE 4-53. STRESS-CORROSION CRACKING BEHAVIOR OF WROUGHT ALLOYS IN INDUSTRIAL AND MARINE ATMOSPHERES (Adapted from Ref. 92)**

|            |  |
|------------|--|
| Industrial | Alloys that cracked: C26000*, 353, 443, 672, 687, 688, 762, 766, 770, 782<br>Alloys that did not crack after exposure of 2.2 yr or longer: 110, 194, 195, 230, 405, 411, 422, 425, 510, 521, 619, 638, 706, 725, 752 |
| Marine     | Alloys that cracked: 672, 766, 770, 782<br>Alloys that did not crack after exposure of 2.2 yr or longer: 110, 194, 195, 230, 260, 353, 422, 443, 510, 521, 619, 638, 687, 688, 706, 725, 752, 762                    |

\*The prefix "C" and the suffix "00" are omitted hereafter.

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## 4-7.3.4.3 Copper-Aluminum Alloys

The susceptibility of copper-aluminum alloys to ammoniacal stress-corrosion cracking is similar to that of copper-tin alloys. Copper-aluminum alloys also are not susceptible to cracking in atmospheric environments.

## 4-7.3.4.4 Copper-Nickel Alloys

The susceptibility of copper-nickel alloys to ammoniacal cracking is very low. They are not susceptible to cracking in atmospheric environments.

## 4-7.3.5 High-Temperature Corrosion

Copper alloys are not considered high-temperature materials. They are used at temperatures up to 371°C (700°F); above this temperature range, material properties are degraded and oxidation occurs. Aluminum-bronze alloys have been used at temperatures around 399°C (750°F). Cupronickel (70 Cu-30 Ni) has good resistance to attack by fossil fuel combustion products at temperatures up to 316°C (600°F).

The resistance of copper alloys to corrosion in liquid metals is shown in Table 4-54. In general, copper alloys are not suitable materials for liquid metal service.

Fused caustic soda at 349° to 593°C (660° to 1100°F) is corrosive to copper.

## 4-7.3.6 Galvanic Corrosion

Copper alloys are cathodic to most common structural metals; therefore, they rarely undergo galvanic attack as a

result of contact with other metals. A galvanic series in seawater is shown in Fig. 4-19. Copper alloys are cathodic to iron, steel, aluminum, lead, tin, and zinc in many environments. Brasses can be coupled to iron in cold freshwater without serious galvanic attack. However, coupling brasses with iron in hot water and seawater results in significant attack on the iron. Coupling with stainless steel, tin, nickel, and Monel, all of which can be cathodic to brasses, is usually satisfactory. Joining aluminum, zinc, and magnesium with copper alloys results in galvanic attack on the more active aluminum, zinc, and magnesium. Generally, the copper alloys can be safely coupled to each other even though high-zinc brasses are slightly anodic to the high-copper alloys.

Galvanic corrosion problems often arise because of the use of a small amount of anodic material coupled to large amounts of cathodic material, such as in fasteners. Table 4-55 shows the galvanic compatibility of fasteners with base metal in seawater. For example, silicon-bronze fasteners are not compatible with Type 304 stainless steel but are compatible with steel and cast iron. Similarly, carbon steel fasteners are not compatible with 70:30 copper-nickel alloy, but Type 304 stainless steel fasteners are compatible.

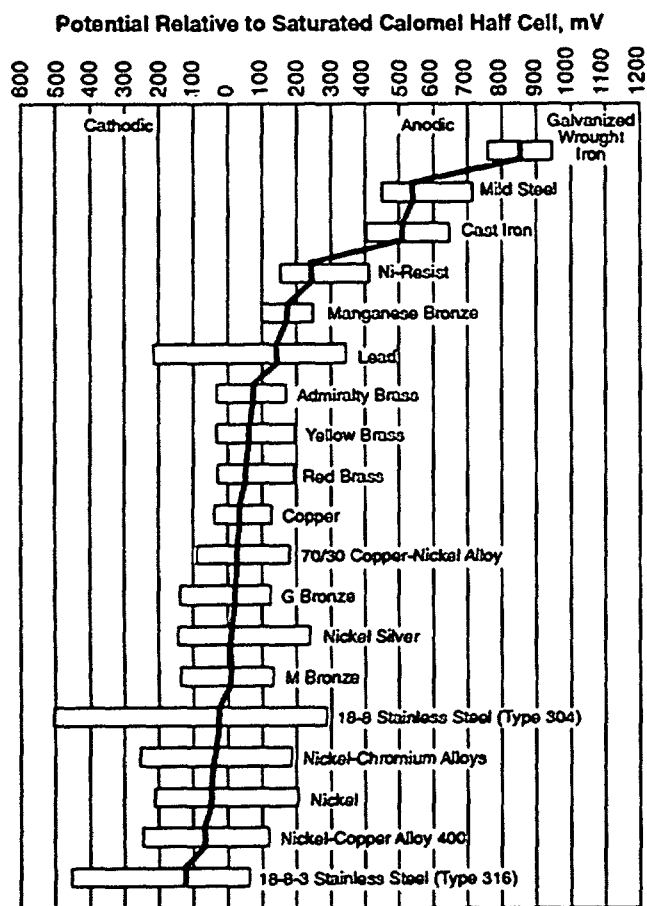
Table 4-56 shows the galvanic compatibility of pump and valve trim body material in seawater. The trim would be used in small amounts relative to the body, and the fluid velocities within the pump body or across the throat of a partially closed valve can be relatively high.

**TABLE 4-54. CORROSION RESISTANCE OF COPPER ALLOYS IN PRESENCE OF LIQUID METALS (Ref. 74)**

|                | CORROSION RESISTANCE             |                 |              |                             |                 |              |
|----------------|----------------------------------|-----------------|--------------|-----------------------------|-----------------|--------------|
|                | COPPER ALLOYS WITH Al, Si, OR Be |                 |              | COPPER ALLOYS WITH Zn OR Sn |                 |              |
|                | TEMPERATURE °C (°F)              |                 |              | TEMPERATURE °C (°F)         |                 |              |
|                | 300° (572°)                      | 600° (1112°)    | 799° (1471°) | 300° (572°)                 | 600° (1112°)    | 799° (1471°) |
| Na, K, and NaK | G                                | G               | P            | —                           | P               | —            |
| Lithium        | P                                | P               | P            | P                           | P               | —            |
| Magnesium      | —                                | P(651° (1204°)) | —            | —                           | P(651° (1204°)) | —            |
| Cadmium        | —                                | P               | —            | —                           | —               | —            |
| Mercury        | P                                | P               | —            | P                           | P               | —            |
| Aluminum       | —                                | P(660° (1220°)) | —            | —                           | P(660° (1220°)) | —            |
| Gallium        | P                                | P               | —            | P                           | P               | —            |
| Indium         | P                                | P               | —            | P                           | P               | —            |
| Thallium       | P(303° (577°))                   | P               | —            | P(303° (577°))              | P               | —            |
| Tin            | P                                | P               | —            | P                           | P               | —            |
| Lead           | L(327° (621°))                   | P               | P            | L(327° (621°))              | P               | P            |
| Bi-Pb alloy    | P                                | P               | P            | P                           | P               | —            |
| Antimony       | —                                | P(630° (1166°)) | —            | —                           | P(630° (1166°)) | —            |
| Bismuth        | L                                | P               | P            | L                           | P               | P            |

G = Good resistance  
L = Limited resistance  
P = Poor resistance

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Figure 4-19. Galvanic Series in Seawater (Ref. 87)

## 4-7.4 INTERFACE PROBLEMS

In electronic and electrical circuits solder flux is a source of corrosion of copper; therefore, the solder flux that has the lowest acid content possible should be used. Nonactivated rosin fluxes should be used if activated solder fluxes containing amines cause corrosion. Also solder flux should be completely removed after soldering. Care should be exercised, however, in removing solder flux because deterioration can result from contaminated cleaner, from too vigorous cleaning, or from reaction between the cleaner and the components.

Potting compounds, wire insulation and sleeving, conformal coatings, and paints and lacquers can result in corrosion of copper wires, leads, and circuit board conductors through two processes:

1. These organic-based materials can foster micro-organism growths in tropical environments. The metabolic products generated together with the damage done to the insulating materials can lead to corrosion.
2. These materials can emit potentially corrosive materials as a result of decomposition, reversion, outgassing, and leaching.

Table 4-57 lists military specifications for wire that does and does not use polyvinyl chloride (PVC) insulating material. According to MIL-STD-1568 (Ref. 94), non-PVC-insulated wire should be used.

Red plague corrosion is especially damaging to electrical wiring. The problem is galvanic and is most serious with small-diameter copper wire that is plated with silver and insulated with Teflon. Corrosion begins at pinholes or breaks in the silver and is caused by moisture introduced through or under the insulation. It seriously impairs the fatigue life and electrical conductivity of the copper wire. The problem may be reduced by using a dual-plated wire consisting of  $1.02 \mu\text{m}$  (0.04 mil) of silver plate over  $1.02 \mu\text{m}$  (0.04 mil) of nickel plate. The problem does not occur with tin-plated or nickel-plated wire.

When gold is plated over copper, the copper diffuses into the gold and the gold accelerates corrosion of the copper at pores and pinholes in the gold.

Copper can corrode in contact with woods that are highly acidic. The more corrosive woods include oak, sweet chestnut, western red cedar, and Douglas fir.

Also copper can lose  $0.1$  to  $0.2 \text{ mg}/\text{dm}^2\text{-day}$  ( $2 \times 10^{-6}$  to  $4 \times 10^{-6} \text{ lb}/\text{ft}^2\text{-day}$ ) in contact with wood treated with creosote.

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TABLE 4-55. GALVANIC COMPATIBILITY (SEAWATER FASTENERS) (Ref. 87)

| BASE METAL                  | FASTENER  |              |                  |         |                        |            |                         |            |
|-----------------------------|-----------|--------------|------------------|---------|------------------------|------------|-------------------------|------------|
|                             | ALUMINUM* | CARBON STEEL | SILICON BRONZE   | NICKEL  | NICKEL-CHROMIUM ALLOYS | TYPE 304   | NICKEL-COPPER ALLOY 400 | TYPE 316   |
| Aluminum                    | Neutral   | C**          | Unsatisfactory** | C**     | C                      | C          | C**                     | C          |
| Steel and cast iron         | NC        | Neutral      | C                | C       | C                      | C          | C                       | C          |
| Austenitic nickel cast iron | NC        | NC           | C                | C       | C                      | C          | C                       | C          |
| Copper                      | NC        | NC           | C                | C       | C                      | C          | C                       | C          |
| 70:30 Copper-nickel alloy   | NC        | NC           | NC               | C       | C                      | C          | C                       | C          |
| Nickel                      | NC        | NC           | NC               | Neutral | C†                     | C†         | C                       | C†         |
| Type 304                    | NC        | NC           | NC               | NC      | May vary††             | Neutral†   | C                       | C††        |
| Nickel-copper alloy 400     | NC        | NC           | NC               | NC      | May vary††             | May vary†† | Neutral                 | May vary†† |
| Type 316                    | NC        | NC           | NC               | NC      | May vary††             | May vary†† | May vary††              | Neutral††  |

NOTE: C = Compatible, protected

NC = Not compatible, preferentially corroded

\* Anodizing would change ratings as fastener.

\*\* Fasteners are compatible and protected but may lead to enlargement of bolt hole in aluminum plate.

† Cathodic protection afforded fastener by the base metal may not be enough to prevent crevice corrosion of fastener, particularly under head of bolt fasteners.

†† Crevice corrosion may occur under head of bolt fasteners.

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TABLE 4-56. GALVANIC COMPATIBILITY (SEAWATER PUMP AND VALVE TRIM) (Ref. 87)

| BODY MATERIAL                           | TRIM            |                         |            |
|---|-----------------|-------------------------|------------|
|   | BRASS OR BRONZE | NICKEL-COPPER ALLOY 400 | TYPE 316   |
| Cast iron                               | Protected       | Protected               | Protected  |
| Austenitic nickel cast iron             | Protected       | Protected               | Protected  |
| M or G bronze 70/30 copper-nickel alloy | May vary*       | Protected               | Protected  |
| Nickel-copper alloy 400                 | Unsatisfactory  | Neutral                 | May vary** |
| Alloy 20                                | Unsatisfactory  | May vary                | May vary   |

\* Bronze trim is commonly used. The trim may become anodic to the body if velocity and turbulence keep a stable protective film from forming on the seat.

\*\* Type 316 is so close to nickel-copper alloy 400 in potential that it does not receive enough cathodic protection to protect it from pitting under low velocity and crevice conditions.

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**MIL-HDBK-735(MR)****TABLE 4-57. WIRE SPECIFICATIONS (Ref. 93)***Non-PVC-Insulated Wire*

1. The list of military specifications that follows is for wiring whose jackets and insulation do not contain PVC; therefore, these specifications meet the requirements of MIL-STD-1568. These wires should be specified instead of wires that do contain PVC.

|   |  |
|---|--|
| MIL-C-17 (all types other than I, IIa, and IV)              | MIL-C-19547  |
| MIL-W-76 (other than types LW, MW, and HW)                  | MIL-W-22759  |
| MIL-C-442 (other than Class I jacket)                       | MIL-C-22931  |
| MIL-C-915 (other than thermoplastic jacket)                 | MIL-I-23053 (all types other than /2 and /3)   |
| MIL-C-3432 (other than jacket types O and D)                | MIL-W-25038  |
| MIL-C-7078 (other than /2 thru /7 or /23 thru /25 callouts) | MIL-C-27072 (other than cable sheath Styles 1 or 3 binder tape Type b or Class B jacket) |
| MIL-W-8777  | MIL-C-27500 (other than 01 or 51 jacket or symbol A, B, C, P, AA, AB, or AD)             |
| MIL-C-13777 (unsheathed)                                    | MIL-C-55021 (other than P or SP jacket)  |
| MIL-W-16878 (other than /1B, /2C, or /3D callouts)          | MIL-W-81044  |
| MIL-W-19150   | MIL-W-81381  |
|   | MIL-W-81822 (other than /1 or /7 callouts)   |

*PVC and/or Other Corrosive Insulated Wire*

2. The list of military specifications that follows is for wiring whose jacket or insulation material contains PVC or other potentially corrosive elements. This wire should not be called out in engineering data packages.

|   |   |
|---|---|
| MIL-C-17 (Types I, IIa, and IV)   | MIL-C-13777 (sheathed)  |
| MIL-W-76 (Types LW, MW, and HW)   | MIL-W-16878 (with /1B, /2C or /3D callouts)   |
| MIL-C-442 (Class I jacket only)   | MIL-C-21609 (par. 3.3.3.4)  |
| MIL-C-915 (thermoplastic jacket only, par. 3.3.3.1)   | MIL-I-23053 (sleeving /2 and /3)  |
| MIL-C-3432 (jacket types O or D)  | MIL-C-23437   |
| MIL-W-5086  | MIL-C-27072 (cable sheaths Styles 1 or 3 or binder tape Type b or Class B jacket)   |
| MIL-W-5088 (Appendix A, par 30.1.3; see restrictions for MIL-C-7078 and MIL-C-27500) (Appendix A, par. 30.1.4; see restrictions for MIL-C-17) | MIL-C-27500 (with 01 or 51 jacket or symbol A, B, C, P, AA, AB, or AD from Table I) |
| MIL-W-7072  | MIL-C-55021 (with jacket symbol P or SP)  |
| MIL-C-7078 (with /2 through /7 or /23 through /25 callouts)   | MIL-W-81822 (with /1 or /7 callouts)  |

**4-7.5 METHODS FOR PREVENTION OF CORROSION**

The appearance of corrosion on copper and many of its alloys is described in Table 4-58. In most cases, if copper is exposed to the atmosphere, tarnishing will be the most severe form of corrosion encountered. Tarnish can be prevented by coating copper with a clear lacquer.

A black oxide chemical conversion coating, described in MIL-F-495 (Ref. 96), provides a good base for adhesive bonding or for organic coatings. It is, however, primarily a decorative coating. Chemical conversion finishes for copper alloys are discussed in par. 3-6.1.2. Cadmium plate, described in QQ-P-416 (Ref. 97), and tin plate, described in MIL-T-10727 (Ref. 98), are suitable finishes for electrical bonding. Tin provides solderability and

corrosion protection. It may be applied by hot-dipping, or it may be electroplated and reflowed. Copper should not be used under a silver or gold plate. Instead nickel should be used under silver or gold or between copper and silver. Nickel plating for copper alloys is discussed in par. 3-7.1.6.

Normally, copper and copper alloys are not painted; however, they may be painted for decorative or other purposes, as indicated in par. 3-7.3.5.

General corrosion is not a problem in most of the environments in which copper and copper alloys are used. If general corrosion is a problem, however, one of the following prevention methods should be applied:

1. Increase the thickness of the cross section to obtain an adequate service life.

## MIL-HDBK-735(MR)

TABLE 4-58. APPEARANCE OF CORROSION ON VARIOUS COPPER ALLOYS (Ref. 95)

|                      |   |
|----------------------|---|
| Bare                 | Unfinished copper and its alloys normally take on a darkened copper color. Corroded copper is greenish-white. If the corrosion is caused by an acid environment, such as unremoved solder flux, the corrosion product tends to be more grayish-white and quite voluminous. Corrosion products of copper alloys form bluish-green coatings on the surface. |
| Primed and topcoated | When the coating system is damaged, the exposed copper will begin to darken. After a time, the exposed copper may turn black and be partly covered by a green corrosion product.  |
| Tin-plated           | As the tin corrodes, a white-yellow corrosion product appears on exposed copper. This corrosion is accelerated because tin is sacrificial to copper.  |
| Cadmium-plated       | If the cadmium plating is damaged or removed, the normal white corrosion product grows at a rapid rate on the exposed copper because cadmium is sacrificial to copper. The green-colored corrosion product of copper appears only when the cadmium plating is completely destroyed.   |

2. Choose a more resistant material or copper alloy.

3. Choose from the various types of coatings that may be useful.

Corrosion problems in the application of copper alloys are usually the result of crevice corrosion, stress-corrosion cracking, and dezincification.

All of the copper alloys are susceptible to some degree to crevice corrosion. Prevention of crevice corrosion is primarily a design consideration; therefore, during design, crevices and water traps should be eliminated or minimized. If crevices cannot be ruled out, a more resistant alloy should be chosen. Table 4-51 indicates a ranking of alloy susceptibility to crevice corrosion.

Many of the high-strength copper alloys, especially in the cold-worked condition, are susceptible to stress-corrosion cracking. The most susceptible alloys usually

contain zinc as an alloying element. Stress-relief annealing is effective for some alloys in some applications. However, the usual approach to eliminating the problem is to use a less susceptible or even immune alloy. Tables 4-52 and 4-53 show the relative stress-corrosion susceptibility of some common copper alloys. Table 4-59 shows typical stress-relief annealing temperatures for several copper alloys.

For a given cold-worked product, the exact minimum annealing temperature varies with such factors as composition, degree of cold work, and microstructure. As an alternative, overannealing can be performed if the resultant mechanical properties are adequate for the intended service. Overannealing softens the alloy enough so that hardness or microstructure can be used as an indicator of stress relief.

TYPE 4-59. TYPICAL STRESS-RELIEF ANNEALING TEMPERATURE (Ref. 99)

| ALLOY NAME            | ALLOY NUMBER* | TEMPERATURE** |      |
|-----------------------|---------------|---------------|------|
|                       |               | °C            | °F   |
| Commercial bronze     | C22000        | 204           | 400  |
| Cartridge brass       | C26000        | 260           | 500  |
| Muntz metal           | C28000        | 191           | 375  |
| Admiralty brass       | C44300        | 302           | 575  |
| Cupronickel (30%)     | C71500        | 427           | 800  |
| Phosphor bronze (5%)  | C51000        | 191           | 375  |
| Phosphor bronze (10%) | C52400        | 191           | 375  |
| Silicon bronze (3%)   | C65500        | 371           | 700  |
| Aluminum bronze D     | C61400        | 600           | 1112 |

\*ASTM-SAE Unified Numbering System (UNS) for metals and alloys. The first three digits are the Copper Development Association designations for the same alloys. *Unified Numbering System for Metals and Alloys* (1975), published by the Society of Automotive Engineers, shows the metals and alloy numbers assigned through July 1975 together with common designations for the same materials.

\*\*Suggested annealing time for Muntz metal is 0.5 h; for all other alloys listed the annealing time is 1 h.

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Dealloying attack can be prevented by using a resistant material. Brasses that contain at least 85% copper and admiralty brasses that contain 1% tin and inhibiting additions of arsenic, antimony, or phosphorus have high resistance to dezincification. Alloy 688 is a high-strength brass particularly suitable to severe environments. This alloy has unusual resistance to dezincification in seawater. Another type of copper alloy may be specified, such as a cupronickel, that has a high resistance to dealloying. Copper-aluminum alloys that contain about 4% nickel and a relatively low amount of aluminum have improved resistance to dealloying attack. The use of a temper-anneal heat treatment in the range of 649° to 704°C (1200° to 1300°F) reduces the susceptibility of these nickel-aluminum-bronze alloys to dealloying attack.

The copper-nickel alloys are susceptible to attack by sulfides in seawater at low concentrations. Sulfides as low as 0.007 ppm can induce pitting of 90:10 and 70:30 alloys. Accelerated attack occurs at higher concentrations of sulfide. If the copper-nickel alloy is likely to be exposed to polluted seawater for extensive periods, an alternative material should be specified.

### 4-7.6 EXAMPLES OF CORROSION PROBLEMS

#### 4-7.6.1 Missile Flare Motor

One of the small, hand-held antitank missiles of the Army has experienced corrosion problems. To prevent environmental corrosion, the missile is packed and sealed in its own disposable launch tube.

Testing of some missiles that have been stored for some time has revealed a problem with a small dc motor in the flare assembly. The motors from some of these missiles would not start, would not reach the required speed, or were slow in reaching the required speed. Examination of a failed motor revealed a green deposit on the commutator, the governor slip ring, and the brushes. The green material was analyzed and determined to be cupric acetate caused by the interaction of copper and acetic acid. Further study determined that the source of the acetic acid was RTV-732 sealant.

For the reaction to have occurred, acetic acid vapors and water vapor were transmitted through a silicone rubber boot. The rubber boot was intended as a seal against intrusion of water and dust to the interior of the launch tube. Time is required for the acetic acid vapors and water to be transmitted through the boot and the storage time was determined to be adequate. The pathway through the boot is illustrated in Fig. 4-20.

#### 4-7.6.2 Automotive Radiators

Motor vehicle radiators made of copper are often used with an ethylene glycol, i.e., antifreeze, and water solution as the coolant. Although commercial antifreeze and coolant solutions always contain an inhibitor, these inhibitors do not last indefinitely. Therefore, the solutions should be renewed or fresh inhibitor should be added periodically because copper can be significantly corroded by uninhibited ethylene glycol and water solutions at the usual operating temperatures and low pH.

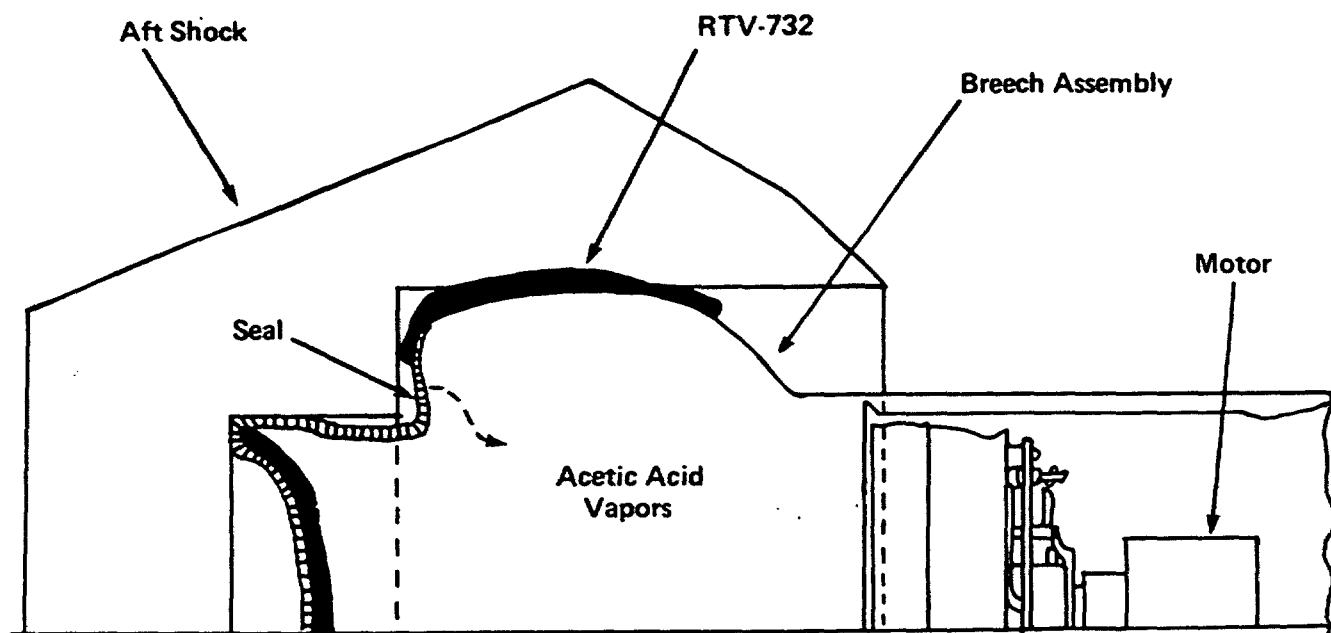


Figure 4-20. Round, Showing Location of RTV-732 and Motor (Ref. 100)



**MIL-HDBK-735(MR)****4-8 IRON AND IRON ALLOYS****4-8.1 TYPES OF ALLOYS**

Iron and its alloys (steel) are the most commonly used engineering metals in Army materiel. Commercially pure irons are designated as ingot iron and Armco iron. These materials are relatively weak and are not used in structural applications for which strength is a major requirement.

The useful forms of iron and steel contain carbon. Cast irons rarely contain less than 1% carbon, and the great majority of steels will not contain much more carbon than this.

No matter what its composition, steel is made by furnace refining pig iron, whereas cast irons are produced by melting pig iron and pouring it into molds that have been formed around prepared patterns. Some wrought iron products are available as are cast steels.

The useful properties of steel depend upon the addition of alloying elements and thermal and mechanical treatment. The categories of steel that follow are based upon the addition of alloying elements:

1. Cast irons, wrought irons, and carbon steels to which no alloying elements are deliberately added. Some alloying elements may result from the addition of scrap. Other elements that can be present in minute quantities are nitrogen, sulfur, and phosphorus.

2. Low-alloy steels contain small amounts of added alloying elements, such as chromium, nickel, manganese, molybdenum, copper, and vanadium. The high-strength steels are included in this category.

3. Stainless steels contain large amounts of alloying elements, such as chromium (greater than 12%) and nickel. These steels include low-strength austenitic and ferritic grades and the high-strength grades, such as martensitic, precipitation hardening, and maraging steels.

**4-8.2 CAST IRONS**

Cast iron is a generic term applied to iron alloys containing silicon and relatively high concentrations of carbon (around 3%). The principal forms of cast iron are gray cast iron, white cast iron, malleable cast iron, ductile or nodular cast iron, silicon cast iron, and alloy cast irons. The chemical compositions and mechanical properties of several cast irons are listed in Table 4-60.

Gray cast iron contains free graphite flakes in its microstructure. Because of their relatively low melting points and excellent fluidity in the molten state, gray cast irons can be readily cast into intricate shapes.

Practically all of the carbon in white cast irons is in the form of iron carbide. These irons are extremely hard and brittle. Graphite formation is related to the rate of cooling from the melt; therefore, rapid cooling by chilling can produce a white iron from one that would normally be gray. Silicon content is kept low because silicon promotes graphite formation.

Malleable cast irons are produced by high-temperature heat treatment of white cast irons. The graphite forms as rosettes or clusters instead of flakes. Malleable cast irons have improved ductility over the white cast irons.

Ductile cast irons exhibit ductility in the as-cast forms. Graphite is present as nodules or spheroids that result from special treatment in the molten state. The mechanical properties of ductile irons can be altered by heat treatments.

Increasing the silicon content of gray cast iron to over 14% renders it extremely resistant to many aggressive corrodents. A notable exception is hydrofluoric acid. High-silicon cast irons are inherently hard, which makes them resistant to erosion-corrosion. Their excellent corrosion resistance results from the formation of a passive silicon dioxide  $\text{SiO}_2$  surface layer upon exposure to the corrosive environment.

In addition to silicon, molybdenum, nickel, chromium, and copper are added to cast irons for improved corrosion-erosion resistance, heat resistance, and mechanical properties. High-nickel-chromium cast irons, with or without copper, are the most widely used of the alloy cast irons. These austenitic alloys, known as Ni-Resist, are the toughest of the gray cast irons. They are also produced as ductile cast irons. A white cast iron containing about 4% nickel and 2% chromium is very hard. It has a Brinell hardness of 550 to 725. This alloy, known as Ni-Hard, is used where erosion-corrosion resistance is needed.

**4-8.2.1 Types of Corrosion**

Because cast iron artifacts are usually made with thick sections, the corrosion that does occur does not usually present a structural problem in the environments commonly experienced.

**4-8.2.1.1 Uniform Corrosion****4-8.2.1.1.1 Weathering Corrosion**

Corrosion in the atmosphere is greater in a humid climate than in a dry climate. Corrosion is also greater in the presence of pollutants in an industrial atmosphere than in a rural atmosphere. Marine climates also result in increased rates of corrosion.

Fig. 4-21 shows the influence of site and length of exposure on the corrosion rate of malleable and ductile cast irons. State College, PA (rural), shows the mildest attack at the end of 7 yr of exposure. State College is followed by Newark, NJ (industrial-coastal), Point Reyes, CA (West Coast-marine), Whiting, IN (industrial-inland), and Kure Beach, NC (East Coast-marine) as the most aggressive sites. The sites are in the same ranking after a 3-yr exposure. The relatively high rates of attack at the two industrial sites after the first year declined on longer exposures.

**TABLE 4-60. CAST IRON ALLOYS (Ref. 2)**

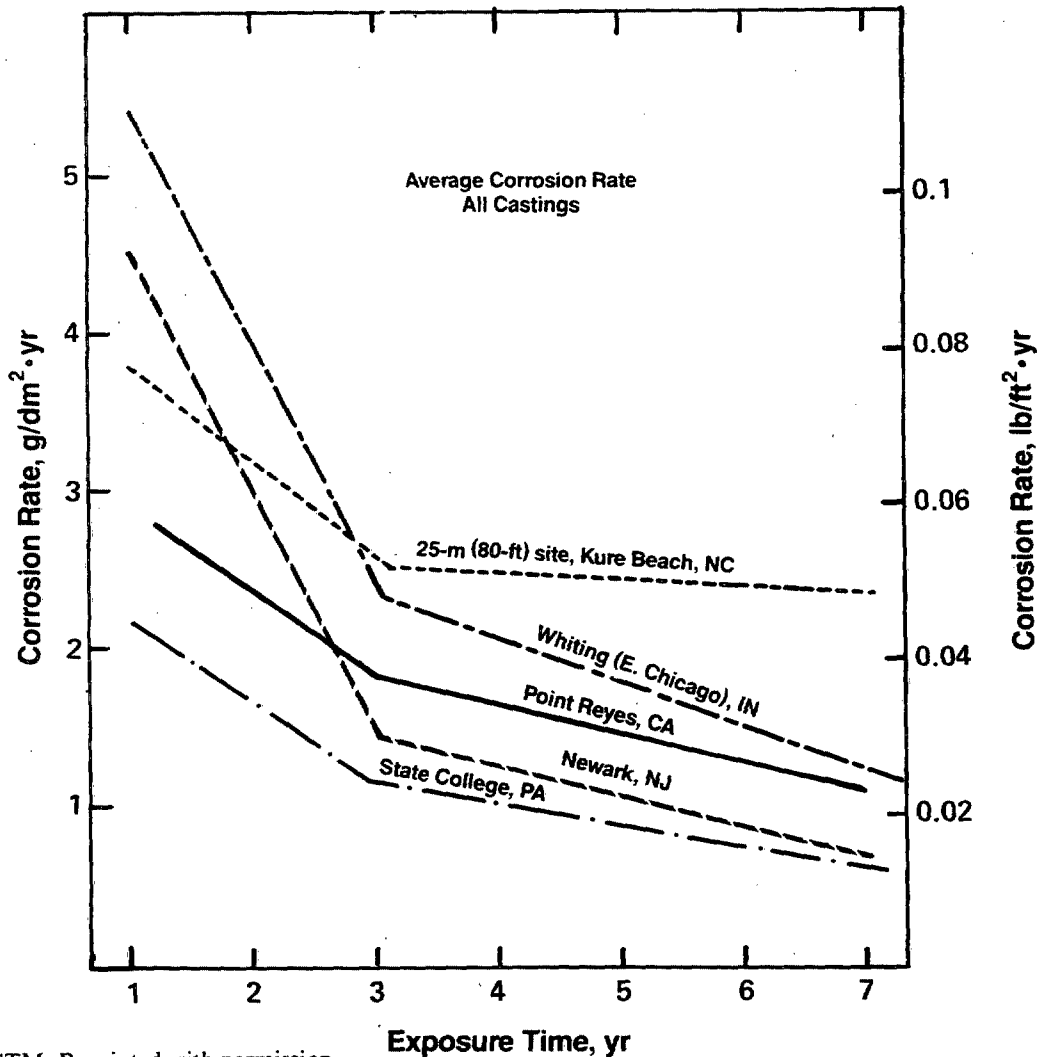
| ALLOY                           | ASTM               | UNS    | COMPOSITION, %*   | CONDITION | MECHANICAL PROPERTIES** |     |                   |     |            |            |
|---------------------------------|--------------------|--------|---|-----------|-------------------------|-----|-------------------|-----|------------|------------|
|                                 |                    |        |   |           | YIELD STRENGTH,         |     | TENSILE STRENGTH, |     | ELONGA-    | HARDNESS,  |
|                                 |                    |        |   |           | MPa                     | ksi | MPa               | ksi | TION,<br>% |            |
| Gray cast iron                  | A159<br>(G3000)    | F10006 | 3.1—3.4 C, 0.6—0.9 Mn,<br>1.9—2.3 Si                                      | As cast   | —                       | —   | 207               | 30  | —          | 187 to 241 |
| Malleable cast iron             | A602<br>(M3210)    | F20000 | 2.2—2.9 C, 0.15—1.25 Mn,<br>0.9—1.90 Si                                   | Annealed  | 221                     | 32  | 345               | 50  | 12         | 130        |
| Ductile cast iron               | A395<br>(60-40-18) | F32800 | (none specified)  | Annealed  | 276                     | 40  | 414               | 60  | 18         | 170        |
| Cast iron                       | A436(1)            | F41000 | 3.0 C, 1.5—2.5 Cr,<br>5.5—7.5 Cu, 0.5—1.5 Mn,<br>13.5—17.5 Ni, 1.0—2.8 Si | As cast   | —                       | —   | 172               | 25  | —          | 150        |
| Cast iron                       | A436(2)            | F41002 | 3.0 C, 1.5—2.5 Cr,<br>0.50 Cu, 0.5—1.5 Mn,<br>18—22 Ni, 1.0—2.8 Si        | As cast   | —                       | —   | 172               | 25  | —          | 145        |
| Cast iron                       | A436(5)            | F41006 | 2.4 C, 0.1 Cr, 0.5 Cu,<br>0.5—1.5 Mn, 34—36 Ni,<br>1.0—2.0 Si             | As cast   | —                       | —   | 138               | 20  | —          | 110        |
| Ductile austenitic<br>cast iron | A439<br>(D-2)      | F43000 | 3.0 C, 1.75—2.75 Cr,<br>0.7—1.25 Mn, 18—22 Ni,<br>1.5—3.0 Si              | As cast   | 207                     | 30  | 400               | 58  | —          | 170        |
| Ductile austenitic<br>cast iron | A439<br>(D-5)      | F43006 | 2.4 C, 0.1 Cr, 1.0 Mn,<br>34—36 Ni, 1.0—2.8 Si                            | As cast   | 207                     | 30  | 379               | 55  | —          | 155        |
| Silicon cast iron               | A518               | F47003 | 0.7—1.1 C, 0.5 Cr,<br>0.5 Cu, 1.50 Mn, 0.5 Mo,<br>14.2—14.75 Si           | As cast   | —                       | —   | 110               | 16  | —          | 520        |

\*Single values are maximum values.

\*\*Typical room temperature properties

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**Figure 4-21. Influence of Site and Length of Exposure on Corrosion of Malleable and Ductile Irons (Ref. 101)**

After a 12-yr exposure to the atmosphere, the corrosion rate of most cast irons is about one third to one quarter of that of steel (Ref. 102). Ductile iron shows a slightly higher corrosion rate than malleable iron. Gray iron has a slightly lower corrosion rate than the malleable iron at the Kure Beach 25-m (80-ft) site (Ref. 103).

Machining the malleable irons tends to result in one-eighth to one-quarter higher corrosion, but machining the ductile irons has the reverse effect. This reversal could be attributed to a thin layer of flaky graphite at the skin of the unmachined ductile iron castings. Graphite, being cathodic, accelerates the attack on the iron.

#### 4-8.2.1.1.2 Corrosion in Natural Waters

Cast iron pipes, usually buried in soil, are widely used in handling freshwater. Cast iron is a common material for underground structures.

In seawater white cast irons undergo uniform corrosion and gray cast irons undergo selective leaching. An increase in the flow velocity usually results in accelerated attack.

#### 4-8.2.1.1.3 Corrosion in Acid Solutions

Cast iron has better resistance to hot and very strong sulfuric acid than most materials, including carbon and stainless steels; however, the corrosion rates are relatively high. Gray cast iron should not be used to handle oleum. Oleum attacks the continuous network of graphite, and the expanding volume of corrosion products splits the iron. Malleable and nodular or ductile cast iron do not undergo this form of attack because the carbon is not continuous in the iron. High-silicon cast irons have high resistance to all concentrations of sulfuric acid at temperatures up to the boiling point.

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Ordinary cast irons are never used with hydrochloric acid. Ni-Resist, a nickel-containing cast iron, is suitable only for low concentrations of hydrochloric acid at room temperature. Durichlor is a high-silicon iron containing molybdenum that is used with all concentrations of hydrochloric acid at moderate temperatures. High-silicon cast irons, however, are not resistant to attack by hydrofluoric acid. Cast iron can withstand dry hydrogen chloride at temperatures below 204°C (400°F) and chlorine gas at temperatures below 177°C (350°F).

Ordinary and nickel cast irons are attacked by nitric acid, but high-silicon cast irons can handle nitric acid that is greater than 30% concentration to the boiling point and less than 30% concentration to 82°C (180°F). In concentrated solutions of mixed sulfuric and nitric acids, cast iron has a corrosion rate less than 508  $\mu\text{m}/\text{yr}$  (20 mpy), but silicon cast irons can be used with any concentration of mixed acid.

High-silicon cast irons are affected by hydrofluoric acid impurity in commercial phosphoric acid. They are, however, resistant to attack by pure phosphoric acid.

Duriron is used to handle acetic acid and is suitable for use with other organic acids. Cast irons are unaffected by organic solvents. However, water or acids in the solvents can cause corrosion.

### 4-8.2.1.1.4 Corrosion in Alkaline Solutions

Cast iron is resistant to attack by alkalis, such as caustic soda NaOH and caustic potash KOH. Moreover, as little as 2% nickel in cast iron improves corrosion resistance to alkalis.

### 4-8.2.1.2 Galvanic Corrosion

Gray cast iron has a relatively active potential in flowing seawater. When used as the body of a pump or valve, it tends to protect trim parts constructed of brass or bronze, nickel-copper alloy, and Type 316 stainless steel. However, as the cast iron corrodes, exposed graphite on the surface can shift the potential in a noble direction. In time the iron may achieve a potential to both low-alloy steels and mild steel. If the cast iron body should become cathodic to the trim parts, they are no longer protected and may corrode rapidly. Valve bodies made of cast steel do not undergo this shift in potential and may be a better choice for some applications.

### 4-8.2.1.3 Selective Leaching

White cast irons undergo uniform corrosion, and gray cast irons can undergo selective leaching in seawater and other mildly corrosive environments. In this phenomenon the iron or steel matrix is leached out and the graphite network is left. Graphite is cathodic to iron, and in mild environments an excellent galvanic cell is set up. Graphitization is a slow process. If the cast iron is in an environment that corrodes the metal rapidly, uniform corrosion occurs. Graphitization does not occur in modular or malleable

cast irons because no graphite network is present to hold the residue together. White cast iron has little free carbon and is not subject to graphitization.

### 4-8.2.1.4 Erosion-Corrosion

An increase in the flow velocity of a corrodent usually results in accelerated attack. In seawater, velocities in the 0.91- to 1.8-m/s (3- to 6-ft/s) range reduce fouling by marine organisms, and pitting of the more noble alloys slows down or even ceases. At higher velocities the protective film is stripped away from cast iron, carbon steel, and copper-base alloys, and corrosion rates increase dramatically. This occurrence is illustrated in Table 4-61. The stainless Type 316 and many nickel-base alloys remain passive.

In piping systems designed to operate at 1.8 m/s (6 ft/s), velocities in the eddy just downstream of a gate-valve seat, in the eddy downstream of a short-radius ell, or through the partially opened seat of a globe valve may be much greater than 1.8 m/s (6 ft/s). Should the velocities in these eddies exceed 30.5 m/s (100 ft/s), all of the velocity-limited metals, i.e., steel- and copper-base materials, could undergo high rates of metal loss.

### 4-8.2.1.5 Cavitation

Susceptibility of various metals to cavitation damage is shown in Table 4-62. Cast iron does not exhibit good resistance to cavitation damage relative to the other metals.

### 4-8.2.1.6 Fretting

The fretting resistances of various metal combinations is shown in Table 4-63.

## 4-8.2.2 Methods for Prevention of Corrosion

The cast irons are usually chosen for their mechanical properties and casting characteristics. Cast iron is normally cast in thick sections; thus it usually does not require corrosion prevention measures to maintain structural integrity unless it is used in aggressively corrosive environments. In aggressively corrosive environments, one of the corrosion-resistant grades, such as the Ni-Resist and the high-silicon alloys, should be considered.

Although the Ni-Resist alloys have relatively low tensile strength, their toughness is better than that of unalloyed gray cast iron. Furthermore, it is possible to obtain ductile or nodular Ni-Resist alloys.

The high-silicon alloys are very susceptible to thermal and mechanical shock; consequently, they cannot withstand any significant stress or impact and cannot be subjected to sudden fluctuations in temperature.

Many of the corrosion prevention methods appropriate to carbon and low-alloy steel are also suitable for cast iron and are mentioned in par. 4-8.3.3.

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**TABLE 4-61. CORROSION OF METALS BY SEAWATER MOVING AT DIFFERENT VELOCITIES (Ref. 104)**

| MATERIAL                 | TYPICAL CORROSION RATES, mdd (lb/ft <sup>2</sup> ·day) |                              |                              |
|--------------------------|--|------------------------------|------------------------------|
|                          | 0.305 m/s<br>(1 ft/s)*                                 | 1.22 m/s<br>(4 ft/s)**       | 8.23 m/s<br>(27 ft/s)†       |
| Carbon steel             | 34177 (0.70)   | 73 (1.5×10 <sup>-3</sup> )   | 254 (5.20×10 <sup>-3</sup> ) |
| Cast iron                | 44918 (0.92)   | —                            | 270 (5.53×10 <sup>-3</sup> ) |
| Silicon bronze           | 976 (0.02)   | 2 (0.04×10 <sup>-3</sup> )   | 343 (7.03×10 <sup>-3</sup> ) |
| Admiralty brass          | 1953 (0.04)  | 20 (0.41×10 <sup>-3</sup> )  | 170 (3.48×10 <sup>-3</sup> ) |
| Hydraulic bronze         | 3906 (0.08)  | 1 (0.02×10 <sup>-3</sup> )   | 339 (6.94×10 <sup>-3</sup> ) |
| G bronze                 | 6835 (0.14)  | 2 (0.04×10 <sup>-3</sup> )   | 280 (5.73×10 <sup>-3</sup> ) |
| Al bronze (10% Al)       | 4882 (0.10)  | —                            | 236 (4.83×10 <sup>-3</sup> ) |
| Aluminum brass           | 1953 (0.04)  | —                            | 105 (2.15×10 <sup>-3</sup> ) |
| 90-10 Cu Ni (0.8% Fe)    | 4882 (0.10)  | —                            | 99 (2.03×10 <sup>-3</sup> )  |
| 70-30 Cu Ni (0.05% Fe)   | 1953 (0.04)  | —                            | 199 (4.08×10 <sup>-3</sup> ) |
| 70-30 Cu Ni (0.5% Fe)    | <976 (<0.02)   | <1 (<0.02×10 <sup>-3</sup> ) | 39 (0.80×10 <sup>-3</sup> )  |
| Monel                    | <976 (<0.02)   | <1 (<0.02×10 <sup>-3</sup> ) | 4 (0.08×10 <sup>-3</sup> )   |
| Stainless steel Type 316 | 976 (0.02)   | 0 0                          | <1 (<0.02×10 <sup>-3</sup> ) |
| Hastelloy C              | <976 (<0.02)   | —                            | 3 (0.06×10 <sup>-3</sup> )   |
| Titanium                 | 0 0  | —                            | 0 0                          |

\*Immersed in tidal current

\*\*Immersed in seawater flume

†Attached to immersed rotating disk

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**TABLE 4-62. CAVITATION RESISTANCE (Ref. 87)**

| BASED ON FIELD EXPERIENCE        | RANKING† | BASED ON LABORATORY TEST                   |
|----------------------------------|----------|--|
| STELLITE*                        | 1        | STELLITE*                                  |
| 17-7 Cr-Ni stainless steel weld  | 2        | Two layers 17-7 Cr-Ni stainless steel weld |
| 18-8 Cr-Ni stainless steel weld  | 3        | 18-8 Cr-Ni stainless steel weld            |
| AMPCO** No. 10 weld              | 4        | AMPCO** No. 10 weld                        |
| 25-20 Cr-Ni weld                 | 5        | Cast AMPCO** No. 18 bronze                 |
| Eutectic-xyron 2-24 weld         | 6        | Nickel-aluminum bronze                     |
| AMPCO** bronze coatings          | 7        | 18-8 Cr-Ni cast stainless                  |
| 18-8 Cr-Ni cast stainless        | 8        | 13% Cr, cast stainless                     |
| Nickel-aluminum bronze, cast     | 9        | Manganese bronze, cast                     |
| 13% Cr, cast stainless           | 10       | Cast steel                                 |
| Manganese bronze, cast           | 11       | Bronze                                     |
| 18-8 Stainless spray metallizing | 12       | Cast iron                                  |
| Cast steel                       | 13       | Sprayed stainless 18-8 Cr-Ni               |
| Bronze                           | 14       | Rubber                                     |
| Rubber                           | 15       | Aluminum                                   |
| Cast iron                        | 16       |  |
| Aluminum                         | 17       |  |

\*Trademark Union Carbide Corporation

\*\*Trademark Ampco Metals, Inc.

†Ranking of 1 is best.

From "Resistance of Various Materials to Cavitation Damage" by W. M. Rheingans, published in *Report of the 1956 Cavitation Symposium*. Copyright © 1957. Reprinted with permission from The American Society of Mechanical Engineers.

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TABLE 4-63. FRETTING RESISTANCE OF VARIOUS MATERIALS (Ref. 105)

| POOR   | AVERAGE                                   | GOOD  |
|--|---|---|
| Aluminum on cast iron                          | Cast iron on cast iron                    | Laminated plastic on gold plating                       |
| Aluminum on stainless steel                    | Copper on cast iron                       | Hard tool steel on tool steel                           |
| Magnesium on cast iron                         | Brass on cast iron                        | Cold-rolled steel on cold-rolled steel                  |
| Cast iron on chrome plating                    | Zinc on cast iron                         | Cast iron on cast iron with phosphate coating           |
| Laminated plastic on cast iron                 | Cast iron on silver plating               | Cast iron on cast iron with coating of rubber cement    |
| Bakelite on cast iron                          | Cast iron on copper plating               | Cast iron on cast iron with coating of tungsten sulfide |
| Hard tool steel on stainless steel             | Cast iron on amalgamated copper plating   | Cast iron on cast iron with rubber gasket               |
| Chrome plating on chrome plating               | Cast iron on cast iron with rough surface | Cast iron on cast iron with Molykote lubricant          |
| Cast iron on tin plating                       | Magnesium on copper plating               | Cast iron on stainless with Molykote lubricant          |
| Cast iron on cast iron with coating of shellac | Zirconium on zirconium                    |   |

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## 4-8.2.3 Examples of Corrosion Problems

In an Army ammunition plant a cast Carpenter 20 pump impeller completely disappeared in service in 4 to 15%  $H_2SO_4$  (plus a small amount of  $HNO_3$ ). Many erosion-corrosion failures occur because turbulent flow conditions exist. Turbulence produces greater agitation of the liquid at the metal surface and more intimate contact between environment and metal. Impellers are typical components operating under turbulent conditions. Duriron, a high-silicon cast iron, appears to be a better candidate for this application. It possesses the best all-around corrosion resistance over a wide concentration range of  $H_2SO_4$ , is not affected by aeration, and is very

resistant to erosion-corrosion.

## 4-8.3 CARBON AND LOW-ALLOY STEELS

Carbon steel is alloyed with one or more of the following elements to produce low-alloy steels: chromium, nickel, copper, molybdenum, phosphorus, vanadium, and silicon. Alloying additions in the range of a few percent or less produce improved mechanical properties and hardenability. Heat treating and cold-working the low-alloy steels can produce extremely high strengths. The alloy designation system in use throughout the U.S. is given in Table 4-64. "High strength" refers to a steel having a yield strength of at least 896 MPa (130 ksi). The

TABLE 4-64. ALLOY DESIGNATION FOR CARBON AND LOW-ALLOY STEELS (Ref. 106)

Industrial carbon and low-alloy steels are generally designated by four numerical digits. \* The first two refer to the alloy type and the next two indicate the carbon content. Thus

10XX are plain carbon steels  
 11XX are carbon steels with higher than normal sulfur content for easier machining  
 13XX contain 1.75% Mn (manganese)  
 23XX contain 3% Ni (nickel)  
 25XX contain 5% Ni  
 31XX have 1% Ni and some Cr (chromium)  
 33XX have 3% Ni and some Cr  
 40XX contain 0.25% Mo (molybdenum)  
 41XX contain 0.25% Mo and 1% Cr  
 43XX contain 0.25% molybdenum, 0.75% Cr and 1.75% Ni

50XX contain 0.3% Cr

51XX contain 1.0% Cr

52XX contain 1.5% Cr

61XX contain 1% Cr and 0.15% V (vanadium)

86XX contain 0.5% Cr, 0.5% Ni, 0.2% Mo

92XX contain 2% Si (silicon)

The XX refers to percent carbon; thus a 4340 steel contains

| C    | Mo   | Cr  | Ni  |
|------|------|-----|-----|
| 0.40 | 0.25 | 0.8 | 1.8 |

as well as the usual minor elements

| Mn  | S     | P     | Si  |
|-----|-------|-------|-----|
| 0.7 | 0.040 | 0.040 | 0.3 |
|     | max   | max   |     |

\*This system, promoted by the American Iron and Steel Institute and the Society for Automotive Engineers, is used throughout the United States.

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various classes of high-strength steels are illustrated in Table 4-65, and the chemical composition and mechanical properties of some carbon and low-alloy steels are listed in Table 4-66.

**TABLE 4-65. SUMMARY OF TYPES OF HIGH-STRENGTH STEELS (Ref. 106)**

| GENERAL GROUP           | EXAMPLES OF TYPES                                    |
|-------------------------|--|
|                         | <b>HEAT TREATED</b>                                  |
| Low-alloy martensitic   | AISI 4130, AISI 4330, AISI 4340, 300 M               |
| Stainless martensitic   | AISI 403, AISI 410, AISI 416, AISI 431               |
| Precipitation hardening | Am-350, Almar 362, 17-4PH, PH13-8-Mo                 |
| Maraging steels         | 18% nickel grades 200, 250, and 300                  |
|                         | <b>COLD-WORKED</b>                                   |
| Unalloyed               | Piano wire, wire rope (cable, "improved plow steel") |
| Austenitic Stainless    | 18% manganese<br>AISI 301                            |

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#### 4-8.3.1 Types of Corrosion

##### 4-8.3.1.1 Uniform Corrosion

Iron shows active-passive corrosion behavior. In the passive condition iron can show pitting corrosion. The conditions that result in passivity are included in the discussion that follows.

##### 4-8.3.1.1.1 Weathering Corrosion

###### 4-8.3.1.1.1.1 Wrought Steels

Bare carbon steel is very susceptible to attack in atmospheric environments. In clean air, rusting begins on a clean surface when the relative humidity is greater than 70%, but if the air is contaminated with industrial pollutants or marine salts, the critical relative humidity for rust formation is lower.

In those atmospheres in which corrosion is accelerated by surface deposits of particulate matter, such as industrial or marine environments, corrosion attack is greater for the first several years and then decreases. When steel rusts, the corrosion products can be beneficial in stifling further attack. However, if the steel contains sulfides, the corrosion products do not develop completely over the surface; therefore, local corrosion can result.

Elements in minor amounts affect the corrosion resistance of steel. For example, trace amounts of copper and manganese can counteract the effects of sulfides in the steel. Extensive use of scrap in making carbon steels

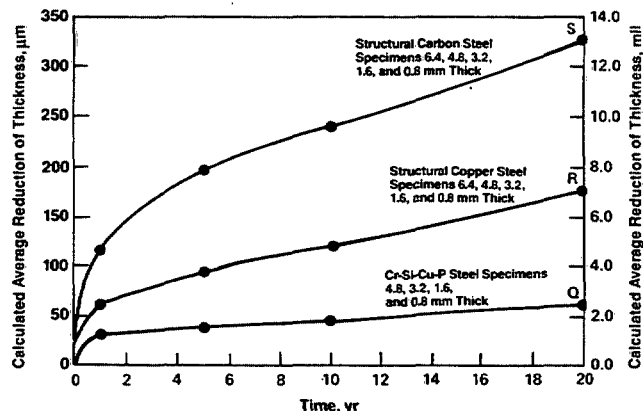
results in the presence of significant amounts of minor elements. In addition, alloying elements are added to improve physical and mechanical properties.

Low-alloy steels are more resistant to atmospheric corrosion than ordinary carbon steels. Among the low-alloy steels is a group of alloys that develop a high degree of corrosion resistance to the atmosphere by forming a protective rust coating. In an industrial atmosphere rust equivalent to 25- to 51- $\mu\text{m}$  (1- to 2-mil) penetration of the metal is protective. This degree of rust requires 1 to 2 yr to form. Typical weathering steels contain about 2% or more alloy content, and at least 0.2% of this is copper. Fig. 4-22 compares the corrosion of a weathering steel with carbon steel and a copper steel in an industrial atmosphere.

When copper is added to ordinary carbon steel, which normally contains some sulfur, the greatest reduction in corrosion results from the first 0.05% added. Some improvement does result from higher copper additions, especially after long-term exposure. Impurity amounts of copper in sulfur-free iron do not result in a significant improvement of corrosion resistance; however, adding phosphorus to a copper-bearing steel results in marked improvement in the corrosion resistance.

Adding nickel to a plain carbon steel can improve the corrosion resistance to the same extent as copper additions, but up to twice as much nickel content as copper content is needed to accomplish equivalent improvements.

Although adding chromium to a plain carbon steel significantly improves the corrosion resistance of the steel to atmospheric exposure, the chromium is more effective if at least 0.1% copper is present.



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**Figure 4-22. Comparison of Corrosion of Steels of Varying Thicknesses and Various Composition in an Industrial Atmosphere (Adapted from Ref. 107)**

TABLE 4-66. CARBON AND LOW-ALLOY STEELS (Ref. 2)

| STEEL TYPE    | ASTM                | UNS    | COMPOSITION, %*   | MECHANICAL PROPERTIES** |          |                    |                 |          |
|---------------|---------------------|--------|---|-------------------------|----------|--------------------|-----------------|----------|
|               |                     |        |   | YIELD STRENGTH,         |          | TENSILE STRENGTH,  |                 | ELONGA-  |
|               |                     |        |   | MPa                     | ksi      | MPa                | ksi             | TION, %  |
| C-Mn          | A53B                | K03005 | 0.30 C, 1.20 Mn   | 241                     | 35       | 414                | 60              | —        |
| C-Mn          | A106B               | K03006 | 0.30 C, 0.29—1.06 Mn,<br>0.10 min Si  | 241                     | 35       | 414                | 60              | 30       |
| C             | A285A               | K01700 | 0.17 C, 0.90 Mn   | 165                     | 24       | 310 to 379         | 45 to 55        | 30       |
| HSLA          | A517F               | K11576 | 0.08—0.22 C, 0.55—1.05 Mn,<br>0.13—0.37 Si, 0.36—0.78 Cr,<br>0.67—1.03 Ni, 0.36—0.64 Mo,<br>0.002—0.006 B, 0.12—0.53 Cu,<br>0.02—0.09 V | 689                     | 100      | 793 to 931         | 115 to 135      | 16       |
| HSLA          | A242(1)             | K11510 | 0.15 C, 1.00 Mn,<br>0.20 min Cu, 0.15 P   | 290 to 345              | 42 to 50 | 434 to 483         | 63 to 70        | 21       |
| 2.25 Cr-1 Mo  | A387(22)            | K21590 | 0.15 C, 0.30—0.60 Mn,<br>0.5 Si, 2.00—2.50 Cr,<br>0.90—1.10 Mo  | 207***                  | 30       | 414 to 586***      | 60 to 85        | 18***    |
| 4-6 Cr-0.5 Mo | A335(P5)            | K41545 | 0.15 C, 0.30—0.60 Mn,<br>0.5 Si, 4.00—6.00 Cr,<br>0.45—0.65 Mo  | 310†<br>207             | 45<br>30 | 517 to 689†<br>414 | 75 to 100<br>60 | 18†<br>— |
| 9 Cr-1 Mo     | A335 (P9)           | K81590 | 0.15 C, 0.30—0.6 Mn,<br>0.25—1.00 Si, 8.00—10.00 Cr,<br>0.90—1.10 Mo  | 207                     | 30       | 414                | 60              | —        |
| 9Ni           | A333(8),<br>A353(1) | K81340 | 0.13 C, 0.90 Mn,<br>0.13—0.32 Si, 8.40—9.60 Ni  | 517                     | 75       | 689 to 827         | 100 to 120      | 20       |
|               | AISI 4130           | G41300 | 0.28—0.33 C, 0.80—1.10 Mn,<br>0.15—0.3 Si, 0.8—1.10 Cr,<br>0.15—0.25 Mo   | 827††                   | 120      | 965††              | 140             | 22††     |
|               | AISI 4340           | G43400 | 0.38—0.43 C, 0.60—0.80 Mn,<br>0.15—0.3 Si, 0.70—0.90 Cr,<br>1.65—2.00 Ni, 0.20—0.30 Mo  | 862†††                  | 125      | 1020†††            | 148             | 20†††    |

\*Single values are maximum values unless otherwise indicated.

\*\*Room temperature properties. Single values are minimum values.

\*\*\*Class 1

†Class 2

†† 1-in. diameter bars water-quenched from 857°C (1575°F) and tempered at 649°C (1200°F)

††† 1-in. diameter bars oil-quenched from 843°C (1550°F) and tempered at 649°C (1200°F)

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Increasing the manganese content of some alloy combinations can improve atmospheric corrosion resistance. The amount of sulfur present affects the improvement obtained from manganese additions. Sulfide present as manganese sulfide results in improved corrosion resistance over its presence as ferrous sulfide.

The corrosivity of several tropical sites has been compared based upon the exposure of carbon steel and other metals (Ref. 109). Tropical rain forests showed extremely low corrosion rates and are generally less corrosive than northern US rural environments. The low rates of attack are attributed to the absence of air pollution, washing of the test panels by short, heavy showers of pure rainwater, the shading of the panels from solar radiation by trees, and small variations in temperature. Open inland tropical sites showed corrosion equal to or slightly higher than that for the northern US rural environment. Although tropical seashore sites can be highly corrosive, there is great variability among these sites.

### 4-8.3.1.1.1.2 Cast Steels

Steel castings have many applications. Principal uses include railroad wheels, couplers, and side frames; equipment for construction, mining activities, and motor vehicles; and valve bodies and machinery for the oil, gas, and process industries. Silicon, copper, chromium, nickel, phosphorus, and manganese additions improve the corrosion characteristics of cast steels in various environments.

Cast steels in general have better corrosion resistance than corresponding wrought alloys. The atmospheric corrosion of cast steels is independent of whether the surfaces are as-cast or machined (Ref. 110). The reason for this independence is that cast steels are more homogeneous than wrought steels and thus are less prone to form electrolytic cells at the microstructural scale (Ref. 111).

### 4-8.3.1.1.2 Corrosion in Natural Waters

The composition of iron or carbon and low-alloy steel has little effect upon the corrosion rate in natural waters. The corrosion of iron and steel in water depends upon the oxygen content of the water. Also the steady-state corrosion rate is higher in water that is moving relative to the iron than it is in still water. Because corrosion is controlled by the diffusion of oxygen to the metal surface, the corrosion rate is a function of the dissolved oxygen concentration (Ref. 112). The formation of a corrosion product film on the surface acts as a barrier to oxygen diffusion. Therefore, the initial corrosion rate in air-saturated water is about 10 mdd ( $2.0 \times 10^{-4}$  lb/ft<sup>2</sup>·day); however, the steady-state rate may be 10 to 25 mdd ( $2.0 \times 10^{-4}$  to  $5.1 \times 10^{-4}$  lb/ft<sup>2</sup>·day).

At a critical concentration of dissolved oxygen, the

corrosion rate falls off to a low value because of passivation of the iron, but if passivity breaks down locally, a passive-active cell is established that causes severe pitting and crevice corrosion.

In the range of oxygen concentration in which diffusion controls the corrosion rate, the rate increases with temperature. In an open system, however, oxygen concentration decreases as temperature increases.

The effect of  $4 \leq \text{pH} \leq 10$  on the corrosion rate is negligible. In the acid region of  $\text{pH} < 4$ , the surface film is dissolved, hydrogen is generated, and the corrosion rate increases. At a  $\text{pH} > 10$ , the corrosion rate decreases because the condition favors passivity. The pH of natural waters is usually between 4 and 10.

In freshwater, factors such as hardness, chloride content, and sulfur content of the water can influence corrosion, whereas in hard water, carbonates often deposit on the metal surface and protect it. However, if the coating is not complete, local corrosion, such as pitting, may occur at unprotected locations. Corrosion decreases with increasing purity of the water. Abnormally high corrosion rates of iron and steel in some natural waters can be traced to the presence of sulfate-reducing bacteria.

The typical seawater corrosion rate of 127  $\mu\text{m}/\text{yr}$  (5 mpy) can be much higher in the splash zone because of aeration and alternate wetting and drying. The corrosion rate in quiet seawater can increase sixfold at fluid velocities of 4.6 m/s (15 ft/s). Carbon steel is very susceptible to pitting in seawater and is highly susceptible to fouling by marine organisms. Fouling can create sites at which crevice corrosion can occur.

### 4-8.3.1.1.3 Corrosion in Acid Solutions

Ordinary carbon steel is used for sulfuric acid in concentrations greater than 70% and for oleum (sulfur trioxide in sulfuric acid). Less concentrated acid rapidly attacks steel. Carbon steel is unsuitable for all sulfuric acid concentrations at temperatures greater than 79°C (175°F).

Ordinary carbon steels are never used for hydrochloric acid service. In fact, inhibitors are necessary when steel is cleaned by pickling in hydrochloric acid. Carbon steel is suitable for dry hydrogen chloride gas below 260°C (500°F) and dry chlorine gas below 204°C (400°F).

Steel is suitable for handling aqueous hydrofluoric acid at concentrations greater than 60%. A few tenths of a percent of silicon increase the susceptibility of steel to attack by hydrofluoric acid. Ordinary carbon steel is used for anhydrous hydrofluoric acid and for dry fluorine gas. Moist fluorine or aqueous solutions of fluorine, however, can be extremely corrosive.

Ordinary low-alloy steels are rapidly attacked by most concentrations of nitric acid. Ordinary steel is suitable for mixed sulfuric and nitric acids when the water content is low. Steel exhibits poor resistance to phosphoric acid.

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### 4-8.3.1.1.4 Corrosion in Alkaline Solutions

Steel is suitable for most applications involving the common alkalis, such as caustic soda and caustic potash. Precautions should be taken to avoid concentrations and temperatures that can result in stress-corrosion cracking. The conditions necessary for stress-corrosion cracking are discussed in par. 4-8.3.1.3.

### 4-8.3.1.1.5 Corrosion in Salt Solutions

The corrosion rate declines at sodium chloride concentrations above 3% in air-saturated water. This decline occurs because the solubility of oxygen in water decreases as the sodium chloride concentration increases. Alkali metal salts, e.g., KCl, LiCl, Na<sub>2</sub>SO<sub>4</sub>, KI, and NaBr, affect the corrosion rate of iron and steel in approximately the same manner as sodium chloride. Alkaline earth salts, e.g., CaCl<sub>2</sub> and SrCl<sub>2</sub>, are slightly less corrosive than chlorides or sulfates at low concentrations (0.1 to 0.25N) but not necessarily at higher concentrations.

Acid salts react with water to form acid solutions. Therefore, acid salts cause corrosion at rates similar to the corresponding acids at the same pH. Examples of such salts are AlCl<sub>3</sub>, NiSO<sub>4</sub>, MnCl<sub>2</sub>, and FeCl<sub>2</sub>. Ammonium salts, e.g., NH<sub>4</sub>Cl, are also acid, but they produce a higher corrosion rate than that corresponding to the acid at a given pH. Ammonium nitrate in high concentrations is more corrosive than ammonium chloride or sulfate salts. In the presence of excess ammonia, the corrosion rate of iron in ammonium nitrate at room temperature may be as fast as 51 mm/yr (2 in./yr (ipy)).

Alkaline salts, which react with water to form solutions having a pH > 10, act as corrosion inhibitors in the presence of dissolved oxygen. Examples of such salts are trisodium phosphate (Na<sub>3</sub>PO<sub>4</sub>), sodium tetraborate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>), sodium silicate (Na<sub>2</sub>SiO<sub>3</sub>), and sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>).

Corrosive oxidizing salts include FeCl<sub>3</sub>, CuCl<sub>2</sub>, HgCl<sub>2</sub>, and sodium hypochlorite; all of which represent the most difficult class of chemicals to handle in metal equipment. Oxidizing salts that are efficient inhibitors include Na<sub>2</sub>CrO<sub>4</sub>, NaNO<sub>2</sub>, and KMnO<sub>4</sub>.

### 4-8.3.1.2 Galvanic Corrosion

Mild steel, which contains less than 0.18% carbon, is anodic to many metals in seawater, including passive stainless steels. Mild steel is not likely to be used in this environment without protection. Care should be exercised to insure that a paint coating does not expose small areas of steel coupled to large areas of a more noble metal.

A low-nickel, low-chromium steel is cathodic to mild steel in many natural environments. Therefore, welding rods and steel bolts and nuts used to couple mild steel should always be a low-nickel, low-chromium steel or a similar composition that is cathodic to a major area of the structure.

In corrosion tests of bimetallic couples in coastal and inland tropical environments in Panama, the corrosion of carbon steel was increased by about 130% by 316 stainless steel, 45% by Monel, and 35% by phosphor bronze.

The oxide scale on a steel that results from hot-rolling can be cathodic to the bare metal, but because the mill scale does not form a good protective coating, small areas of bare metal may be exposed. Therefore, mill scale should be completely removed from steel to be exposed to an aqueous electrolyte.

### 4-8.3.1.3 Stress-Corrosion Cracking

Ordinary carbon steels and low-alloy steels are subject to stress-corrosion cracking. The environments in which carbon steel may crack include sodium hydroxide, nitrate solutions, bicarbonate-carbonates, liquid ammonia, moist CO-CO<sub>2</sub> mixtures, and phosphates. The low-carbon steels that may be susceptible to the specific environments have a Rockwell Hardness number of 22C and a tensile yield strength of less than 517 MPa (75 ksi). Cracking has occurred in low-pressure boilers constructed by riveting, welded tanks containing hot, concentrated sodium hydroxide solutions, welded tanks containing agricultural ammonia, structures containing illuminating gas produced by the destructive distillation of coal, and tanks containing nitrates. Stress-corrosion cracking in low-carbon steels is primarily intergranular. These steels show good resistance to cracking when exposed to seawater and chloride solutions.

Low-alloy or medium-strength steels, including carbon steels, exhibit yield strengths below 1241 MPa (180 ksi). Generally these steels do not crack in rural, marine, or industrial environments; however, hydrogen gas can cause cracking. Cracking tendency increases with increasing hydrogen pressure, yield strength, and temperature. Hydrogen can be generated by the metal plating processes that are often employed to deposit a protective metal coating on low-alloy steels. Gaseous hydrogen sulfide is more aggressive than hydrogen, and solutions of hydrogen sulfide also are aggressive. Pressurized water containing carbon monoxide and carbon dioxide can cause stress-corrosion cracking. Steels in this strength range can crack in seawater and chloride solutions, particularly if a notch is present.

Very high-strength low-alloy steels, those possessing tensile strengths greater than 1241 MPa (180 ksi), are more susceptible than the low- or medium-strength steels, and susceptibility to cracking increases with strength level. The relative resistance of various high-strength steels to stress-corrosion cracking is given in Table 4-67. The susceptibility of several high-strength steels to stress-corrosion cracking is given in Ref. 113 in terms of fracture mechanics parameters.

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TABLE 4-67. RESISTANCE OF HIGH-STRENGTH STEELS TO STRESS-CORROSION CRACKING (Ref. 31)

| HIGH-STRENGTH STEELS WITH HIGH RESISTANCE TO STRESS-CORROSION CRACKING     |                                      |
|--|--------------------------------------|
| STEEL  | CONDITION                            |
| AM350 stainless steel  | SCT 1000 and above                   |
| AM355 stainless steel  | SCT 1000 and above                   |
| Almar 362 stainless steel  | H1000 and above                      |
| Custom 455 stainless steel   | H1000 and above                      |
| PH 13-8 Mo stainless steel   | H1000 and above                      |
| 15-5 PH stainless steel  | H1000 and above                      |
| 17-4 PH stainless steel  | H1000 and above                      |
| PH 14-8 Mo stainless steel   | CH900 and SRH950 and above           |
| PH 15-7 Mo stainless steel   | CH900                                |
| 17-7 PH stainless steel  | CH900                                |
| Carbon steel (1000 Series)   | Below 1241 MPa (180 ksi) YS          |
| Low-alloy steel (4130, 4340, D6AC, etc.)                                   | Below 1241 MPa (180 ksi) YS          |
| Music wire (ASTM 228)  | Cold drawn                           |
| HIGH-STRENGTH STEELS WITH MODERATE RESISTANCE TO STRESS-CORROSION CRACKING |                                      |
| STEEL  | CONDITION                            |
| Carbon steel (1000 series)   | 1241 to 1379 MPa (180 to 200 ksi) YS |
| Low-alloy steel (4130, 4340, D6AC, etc.)                                   | 1241 to 1379 MPa (180 to 200 ksi) YS |
| PH 13-8 Mo stainless steel   | Below H1000                          |
| 15-5 PH stainless steel  | Below H1000                          |
| 17-4 PH stainless steel  | Below H1000                          |
| HIGH-STRENGTH STEELS WITH LOW RESISTANCE TO STRESS-CORROSION CRACKING      |                                      |
| STEEL  | CONDITION                            |
| Carbon steel (1000 Series)   | Above 1379 MPa (200 ksi) YS          |
| Low-alloy steel (4130, 4340 D6AC, etc.)                                    | Above 1379 MPa (200 ksi) YS          |
| H-11 steel   | Above 1379 MPa (200 ksi) YS          |
| 440 stainless steel  | All                                  |
| 18 Ni maraging steel, 200 grade  | Aged at 482°C (900°F)                |
| 18 Ni maraging steel, 250 grade  | Aged at 482°C (900°F)                |
| 18 Ni maraging steel, 300 grade  | Aged at 482°C (900°F)                |
| 18 Ni maraging steel, 350 grade  | Aged at 482°C (900°F)                |
| AM 350 stainless steel   | Below SCT 1000                       |
| AM 355 stainless steel   | Below SCT 1000                       |
| Custom 455 stainless steel   | Below H1000                          |
| PH 15-7 Mo stainless steel   | All except CH900                     |
| 17-7 PH stainless steel  | All except CH900                     |

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## 4-8.3.1.4 Corrosion Fatigue

High-strength steel components subjected to cyclic loading are susceptible to corrosion-fatigue failure. Corrosion fatigue can be defined as the number of stress or strain cycles required to produce failure or as the rate of fatigue crack growth under given loading conditions. The number of stress or strain cycles to produce failure is not very useful for quantitative design purposes.

The crack growth rate per cycle  $da/dN$  is primarily controlled by the alternating stress intensity  $\Delta K$  through an expression of the form

$$da/dN = C(\Delta K)^n \quad (4-2)$$

where

- $a$  = crack growth
- $C$  = scaling constant
- $\Delta K$  = difference between the maximum and minimum stress intensities for each cycle, i.e.,  
 $\Delta K = K_{max} - K_{min}$
- $N$  = number of cycles
- $n$  = scaling constant.

Eq. 4-2 adequately describes behavior for the midrange of crack growth rates. This rate is typically  $10^{-6}$  to  $10^{-4}$  mm ( $4 \times 10^{-4}$  to  $4 \times 10^{-2}$  mil) per cycle. At higher crack growth rates, when  $K_{max}$  approaches fracture toughness  $K_{IC}$ , the rate expression often underestimates the true propagation rate. At lower growth rates, when  $\Delta K$  approaches the threshold stress intensity  $\Delta K_0$ , the true crack propagation rate is often overestimated.

The variation in crack growth rate with  $\Delta K$ , as shown in Fig. 2-60, can be divided into three regimes:

1. At low growth rates, i.e., Regime A, there is a strong influence of microstructure and mean stress and a variable influence of environment.

2. In the midrange of growth rates, i.e., Regime B, there is little influence of microstructure and mean stress on crack growth. Mean stress is characterized by the load ratio  $R = K_{min}/K_{max}$ . The slope in Regime B is the scaling constant  $n$ .

3. At higher growth rates, i.e., Regime C, growth rates become extremely sensitive to both microstructure and mean stress because static fracture modes become involved (Ref. 114).

Fatigue crack growth rate curves for various high-strength steels in different environments are given in Ref. 115.

## 4-8.3.1.5 High-Temperature Corrosion

## 4-8.3.1.5.1 Oxidation

Ordinary steels form a thick oxide film in high-temperature air or oxygen. However, because the film is brittle, it is subject to failure by mechanical action and thermal cycling. Iron is alloyed with chromium to obtain oxidation resistance at elevated temperatures.

## 4-8.3.1.5.2 Liquid Metal Corrosion

Although carbon steel has been successfully used to contain liquid mercury at temperatures of  $540^\circ\text{C}$  ( $1000^\circ\text{F}$ ), the use of low-alloy steels in mercury boilers has resulted in thermal-gradient mass transfer. Iron was dissolved at high temperatures and deposited on surfaces at cooler temperatures. The rate of attack can be reduced by adding 1 to 10 ppm of titanium to the mercury.

A similar mass transfer phenomenon occurs in a liquid sodium system. Carbon is transferred from carbon steel to a stainless steel. The driving force for concentration-gradient mass transfer is the difference in the carbon content of the two metals.

## 4-8.3.1.6 Biological Corrosion

Iron is corroded in some deaerated natural waters and in soils through the action of sulfate-reducing bacteria. The bacteria thrive only under conditions of little or no oxygen and in the range of  $5.5 \leq \text{pH} \leq 8.5$ . In the corrosion process 3 moles of ferrous hydroxide are formed for each mole of ferrous sulfide. Sulfate-reducing bacteria can cause severe damage in a short time.

## 4-8.3.2 Interface Problems

Poultice corrosion can occur when an absorptive material, such as paper, wood, asbestos, sacking, cloth, or mud, is in contact with a steel surface. Differential aeration cells form at adjacent wet and dry areas which lead to pitting corrosion. An example is fiber floor mats in vehicles that are subject to wetting through leaks in the body.

Marine organisms, such as barnacles, mussels, and algae, attach themselves to steel surfaces immersed in seawater or freshwater. The result is crevice corrosion at the point of attachment.

Problems can arise from interfaces with wood and other natural, treated, or manufactured materials that can release a corrosive. Some woods release organic acids and some plastics decompose or revert and release hydrogen chloride or other corrosive species.

Problems also arise from the chloride ion in the residue left by human handling.

## 4-8.3.3 Methods for Prevention of Corrosion

Almost all the methods for prevention of corrosion discussed in Chapter 3 are applicable to carbon and low-alloy steels.

There are many types of inhibitors, as discussed in par. 3-5. Most inhibitors are intended for application in aggressive solutions with which ferrous alloys might come in contact. Some inhibitors may be incorporated in different kinds of organic coatings. Vapor phase inhibitors are effective in protecting ferrous alloys in an enclosure, such as packaging.

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Chemical conversion coatings for ferrous alloys are discussed in par. 3-6.1.3. They are a very important class of ferrous metal treatments. Some are intended to be a base for organic coatings; others are intended to be the primary means of preventing corrosion.

Shot peening as a method of introducing surface compressive stresses is discussed in par. 3-6.4. Surface compressive stresses reduce the likelihood of corrosion fatigue and stress-corrosion cracking.

Ferrous alloys are commonly coated with other metals to prevent corrosion. The important coating metals are zinc, nickel, tin, and cadmium. However, many other metals may be applied to ferrous alloys. Metal coatings discussed in par. 3-7.1 are

1. Aluminum, par. 3-7.1.1
2. Chromium, par. 3-7.1.3
3. Lead, par. 3-7.1.5
4. Nickel, par. 3-7.1.6
5. Tin, par. 3-7.1.7
6. Zinc, par. 3-7.1.8
7. Noble metals, par. 3-7.1.9.

The various types of inorganic coatings are discussed in par. 3-7.2. The metal-ceramic coatings are important at elevated temperatures, but those metal-ceramic coatings that can be cured at relatively low temperatures can be used on the low-alloy ferrous metals.

Organic coatings are widely used on ferrous alloys as protection against corrosive environments. Paints and enamels are discussed in par. 3-7.3.1. Painting systems are comprised of a chemical conversion coating followed by a primer over which a topcoat is applied. The various sealants described in par. 3-7.3.2 are applicable to assemblies of ferrous alloys. Many of the rust-preventive compounds described in par. 3-7.3.3 are useful on ferrous alloys.

Cleaning of ferrous alloys in preparation for further treatment and coating is discussed in par. 3-7.3.4.1.

Susceptibility of low-alloy, high-strength steels to hydrogen cracking is a form of corrosion that is a serious problem. These materials are therefore often plated or given some other protective coating before use. During processing, such as pickling and coating by electroplating, they absorb hydrogen and are then subject to hydrogen embrittlement. Baking at moderate temperatures is widely employed for relief from hydrogen embrittlement. However, conventional bakeout procedures cannot remove more than a fraction of the hydrogen in a coated steel. In addition, the microstructure and composition of a steel have a strong influence on hydrogen uptake and release on baking.

Hydrogen behavior in Type 4340 series steels of different grades and tempers has been studied (Ref. 116). The results indicate that hydrogen outgassing procedures should be tailored to specific microstructures and steel grades. In this way the hydrogen content and, therefore,

the hydrogen embrittlement tendency can be better controlled.

A steel having no higher strength than needed should be selected to avoid stress-corrosion cracking. Cathodic protection and inhibitors can prevent pitting that forms the sites at which stress-corrosion cracking initiates.

### 4-8.3.4 Examples of Corrosion Problems

#### 4-8.3.4.1 Corrosion of the 1½-Ton Truck

A survey of 1½-ton trucks was conducted in 1979, only 3 yr after the vehicles had been released for field operations. Specific areas were selected for inspection for rust: cab floor pan, tailgate, cargo bed, front fenders, air intake plenum, fire wall gutter, and the fender-fire wall plenum junction. Rust on the floor pan and tailgate was recorded as either present or not. The severity of rust in other areas was assessed and recorded as none, slight, moderate, heavy, or perforated. The results are summarized in the paragraphs that follow. Vehicles indicated as LEAD were new unissued vehicles.

The conclusions of the investigation and resulting recommendations are quoted in the paragraphs that follow (Ref. 117) and summarized in Table 4-68:

#### *Rust Damage*

"There is a significant problem with rust in the . . . fleet. It is especially serious in Hawaii, and it will get progressively worse unless some corrective actions are taken immediately. As shown earlier, 87 percent of the vehicles surveyed had wet floor mats and 56 percent had rusted floor pans. If only those vehicles manufactured during 1977 are considered (less than 30 months old), 90 percent have wet mats and 63 percent have rusted floor pans. In the majority of these vehicles, the fiber floor mat has already begun to deteriorate and rot. Since this soggy mat is in constant contact with the floor pan, it is causing a serious rust problem there, which will result in the floor pan rusting through. When this occurs, the vehicle cannot be driven until the floor pan is repaired.

"In the other areas of the vehicle, considering only those conditions of Moderate, Heavy, or Perforated rust, there are serious problems in the fire wall gutter (35 percent of the sample) and the fenders (17 percent). In most vehicles, there was standing water in the fire wall gutter, which is creating the rust observed even though the gutter has been rustproofed. If this situation continues, the gutter seam will rust through and allow water to enter the cab area underneath the upper part of the floor mat."

#### *Rustproofing*

"Rustproofing of the fleet was not thoroughly done. More than 75 percent of the vehicles examined had no rustproofing under the hood reinforcement web, and approximately 13 percent were not rustproofed under the fenders, cargo bed, or cab floor. Furthermore, although this survey did not examine hidden areas, it is reasonable

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TABLE 4-68. RUST SUMMARY OF M880 TRUCKS (Ref. 117)

| Sample Size                     | ALL      | 0-2500 mi | <30 mo OLD | LEAD |
|---------------------------------|----------|-----------|------------|------|
|                                 | w/o LEAD | w/o LEAD  | w/o LEAD   | ONLY |
|                                 | 63.6*    | 34.0      | 18.6       | 36.4 |
| Floor Mat Wet                   | 87**     | 82**      | 90**       | 33** |
| Floor Pan Rusted                | 56       | 49        | 63         | 13   |
| Tailgate Rusted                 | 17       | 14        | 13         | 1    |
| Cargo Bed Rust (M, H, P)        | 8        | 5         | 2          | 0    |
| Fender Rust (M, H, P)           | 17       | 21        | 0          | 0    |
| Fire Wall Gutter Rust (M, H, P) | 35       | 34        | 16         | 7    |

M = moderate

H = heavy

P = perforated

\*Percent of total sample

\*\*Percent of vehicles in this column

to assume that some of these areas were not completely rustproofed, based on the condition of the hood web.

"This lack of adequate rustproofing may be the result of poor workmanship or failure of the manufacturer to properly inspect the vehicles after rustproofing. In either case, some action is required to improve the rustproofing treatment and prevent further damage. This is especially necessary if the vehicles are in areas having a salt-air environment or in areas where salt is used extensively during the winter on the highways."

*Water Leakage*

"Water is entering the cab around the door gaskets and through the inner door panel via the glass, because the deflector inside the door panel is not positioned correctly. There is also evidence that water may be coming into the cab through miscellaneous holes located where the door hinges are mounted to the cab body."

*Recommendations*

"To improve the condition of the vehicles still in depot storage and those already issued to field units, the following actions are recommended:

(1) For all vehicles:

- a. Remove and discard all fiber and rubber floor mats.
- b. Repair and repaint rusted cab floor pans.
- c. Repair or replace defective door gaskets and inner door panel water deflectors, and plug miscellaneous holes in the door hinge mounting area.

(2) Those vehicles that are in use where there is a salt-air environment or where salt is used extensively during the winter on the roads should be re-rustproofed. This can be accomplished either by unit maintenance personnel or by a commercial rustproofing contractor in the local area."

**4-8.3.4.2 Steel Membrane in Binary Chemical Munitions**

Binary chemical munitions are designed to produce toxic chemical agents by the reaction of relatively nontoxic ingredients at the time of use. In a binary projectile the two ingredients are separated by a 1010 cold-rolled steel membrane 0.25 mm (0.01 in.) thick. One of the reactants in the G-agent binary process is corrosive and is believed to be small quantities of hydrofluoric acid. One solution to the problem is to replace the steel membrane with a more corrosion-resistant material. Another is to use a chemical inhibitor in the corrosive reactant.

Tests were conducted in 0.59 N hydrofluoric acid with various inhibitors and metals (Ref. 118). Corrosion of steel was more rapid in the hydrofluoric acid than in the binary agent. However, inhibitors that proved effective in retarding corrosion in the hydrofluoric acid were not effective in the corrosive reactant. Although nickel and 321 stainless steel are more resistant to attack in the corrosive reagent than is steel, neither is considered sufficiently resistant.

**4-8.3.4.3 Helicopter Main Landing Gear Drag Strut**

Of several corrosion-related problems observed on a utility helicopter, this example is the only one considered to be serious (Ref. 119).

The drag-strut assembly of the main landing gear failed due to one of two brake line holes within the strut. The strut consists of 300-M steel hardened to Rockwell C53 to 56. The design also includes shot peening over the entire length of the drag strut, as well as vacuum cadmium plating, for corrosion protection. Stress-corrosion cracking is the primary cause of this failure.

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This failure developed because water collected on the strut, on top of the lower brake line hole, to a depth of about 25 mm (1 in.). Stress-corrosion cracking originated at the lower brake line hole from a corrosion pit of approximately 0.25 mm (0.010 in.) in depth. Also the plugs used to seal the brake line holes did not fill the entire cavity in the strut and permitted water to attack the poorly protected metal surface on the sides of the opening.

A solid plug for the brake line holes, i.e., a plug that completely fills the brake line hole, is one modification implemented for prevention of similar strut failures. Another solution includes designating the drag strut as a critical part, which means that the strut would be inspected completely on a specific requirement, such as shot peening, during the manufacturing process.

The corrosion problem also can be avoided through application of a better cadmium plate and by addition of a resin coating over the cadmium plating. In the future, installation of the brake line outside of the strut will not require holes in this part.

### 4-8.3.4.4 Missile Fuse Springs

An air defense missile fuse-boost and impact-switch springs are made of ASTM A 228 steel music wire and are plated with 1.27  $\mu\text{m}$  (0.05 mil) of 99% pure gold. Gold plate of this thickness has pores. Although the fuse is considered a hermetically sealed component, during periods of long storage moisture enters the component, the steel exposed at the pores becomes a small anode, and the gold becomes a large cathode. Thus the springs eventually fail (Ref. 120).

### 4-8.3.4.5 Gun Tube Erosion

Gun tube erosion is damage and enlargement of the bore caused by firing—a serious erosion-corrosion problem faced by the military. This damage results from the conditions created in the bore upon firing (Refs. 121, 122, and 69).

These conditions generate the processes that follow:

1. The bore surface is chemically and structurally altered.
2. The lands are swaged by the accelerating projectile.
3. Copper from the rotating band of the projectile is deposited on the bore.
4. Rapid expansion of the propellant reaction gases sweeps molten metal from the surface of the bore.
5. Unburned propellant particles and solid reaction products in the rapidly expanding gases cause mechanical abrasion of the bore.
6. Because there is incomplete closure of the bore by the projectile, high-velocity and high-temperature gases jet through the openings and melt, gouge, and scour the surface of the bore.

The net result of these processes is loss of material, enlargement of the bore, and damage to the bore surface. After repeated firing, the gun suffers a loss of muzzle velocity and accuracy.

Conventional gun barrels are, in general, made of low-alloy steel; large-caliber barrels are usually made of modified 4330 steel. The typical composition and mechanical properties of gun steel are given in Table 4-69.

### 4-8.3.4.6 Corrosion Fatigue Behavior of Tungsten-Carbide-Coated Type 4340 Steel Helicopter Blade Retention Bolts

Fretting-induced corrosion resulted in significant surface pitting on the 4340 steel main rotor blade retention bolts for the 540 helicopter rotor system after less than 500 h of service. Thus these cadmium-plated bolts have a service lifetime of 300 h. These bolts were replaced with chromium-plated reworked bolts having a service lifetime of 500 h. Based upon a similar application in another rotor system, a plasma-sprayed, tungsten-carbide-coated bolt had a projected lifetime of over 3000 h. However, the blade retention mechanism is subjected to fatigue conditions under operating conditions, and there was inadequate information on the fatigue strength of the tungsten-carbide-coated 4340 steel bolts.

Fatigue testing of bare and coated specimens in air and 3.5% sodium chloride solutions showed comparable fatigue behavior for the tungsten-carbide-coated and the chromium-plated specimens. However, full-scale fatigue tests in laboratory air produced no failures of the tungsten-carbide-coated specimens through the equivalent of four airframe lifetimes (about 14,000 h of flight loading) (Ref. 123).

**TABLE 4-69. COMPOSITION AND MECHANICAL PROPERTIES OF GUN STEEL (Ref. 121)**

| COMPOSITION, wt %   |                                  |
|---|----------------------------------|
| 0.37 C, 0.47 Mn, 0.006 P, 0.02 Si, 3.17 Ni,<br>0.85 Cr, 0.65 Mo, 0.10 V |                                  |
| MECHANICAL PROPERTIES   |                                  |
| Tensile strength  | ≈ 1241 MPa (≈180 ksi)            |
| Yield strength  | 965 to 1103 MPa (140 to 160 ksi) |
| V-notched Charpy impact strength  | ≈41 J (≈30 ft-lb)                |
| Hardness  | ≈ Rc                             |

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## 4-8.4 HIGH-ALLOY AND STAINLESS STEELS

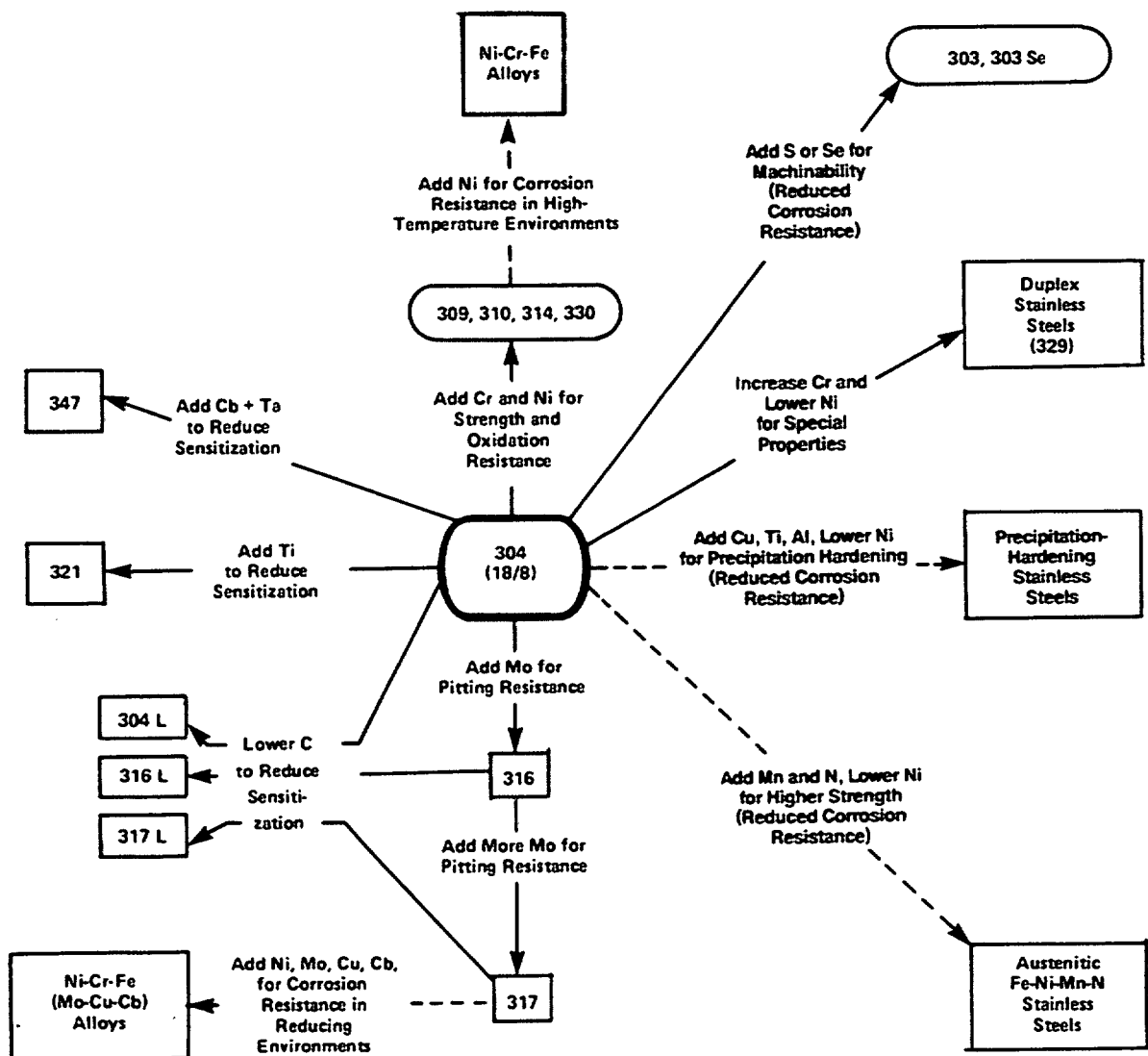
The stainless steels are a family of ferrous alloys containing at least 11% chromium. The effect of this amount of chromium in steel in reducing corrosion is dramatic.

## 4-8.4.1 Categories of Alloys

There are many grades of stainless steels. By varying the chemical composition, heat treating, and cold-working, a wide range of properties is achieved. Wrought stainless steels are designated by a three-digit number. The numbering system is applied by the American Iron

and Steel Institute (AISI). The symbols designating cast stainless steels are defined by the Alloy Casting Institute (ACI). Corrosion-resistant grades have designations with the prefix C; heat-resistant grades have designations with the prefix H.

The austenitic grades of wrought stainless steel are designated by numbers in the 200 and 300 series. The 300 series is based upon the classic 18% chromium and 8% nickel stainless steel. Certain modifications of the composition affect the corrosion resistance, whereas other modifications of the composition are made to achieve mechanical properties. The modifications of the composition and their effects are illustrated in Fig. 4-23.



Dashed lines show compositional links to other alloy systems.

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Figure 4-23. Some Composition Modifications of 18/8 Austenitic Stainless Steel to Produce Special Properties (Ref. 124)



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In the 200 series of austenitic stainless steel, some of the nickel in the basic 18/8 composition is replaced with manganese and nitrogen.

Duplex stainless steels contain both austenite and ferrite phases and about 28% chromium and 6% nickel. The compositions and mechanical properties of some 200 series, 300 series, and duplex stainless steels are given in Tables 4-70 through 4-75.

Some of the 400 series stainless steels have a ferritic structure, and some alloys have a martensitic structure. The composition and mechanical properties of some 400 series ferrite stainless steels are given in Table 4-76.

Martensitic stainless steels in the 400 series have chromium concentrations in the range of 11.5 to 18%, and they have an austenitic structure at high temperature that is transformed into martensite upon cooling to room temperature. The compositions and mechanical properties of the 400 series martensitic stainless steels are given in Table 4-77. Stainless steels hardened by transformation to martensite are tempered to give the desired engineering properties. This tempering can influence corrosion susceptibility. For example, corrosion susceptibility of type 420 stainless steel is at its maximum when the alloy is

tempered at temperatures in the range of 450° to 600°C (842° to 1112°F).

Precipitation-hardening stainless steels are usually designated by a trade name rather than by their AISI 600 series designations. There are three types of precipitation-hardening stainless steels:

1. Martensitic types, which are supplied in the martensitic condition, are hardened by a simple aging treatment of the fabricated part.

2. Semiaustenitic types, which are supplied in the austenitic condition, are transformed to martensite by special heat treatment before precipitation hardening.

3. The austenite in the austenitic types is precipitation hardened directly.

The heat treatments of precipitation-hardening stainless steels are chosen to optimize mechanical properties. Precipitation hardening generally results in a slight increase in corrosion susceptibility and an increased susceptibility to hydrogen embrittlement. The chemical composition and typical mechanical properties of some precipitation-hardening stainless steels are given in Tables 4-78 through 4-80.

**TABLE 4-70. COMPOSITIONS OF THE 200 SERIES OF AUSTENITIC STAINLESS STEELS (Refs. 125 and 126)**

| AISI<br>GRADE | COMPOSITION*, % |         |      |         |     |       |       |      |          |
|---------------|-----------------|---------|------|---------|-----|-------|-------|------|----------|
|               | Cr              | Ni      | C    | Mn      | Si  | P     | S     | N    | OTHER    |
| 201           | 16-18           | 3.5-5.5 | 0.15 | 5.5-7.5 | 1.0 | 0.060 | 0.030 | 0.25 | —        |
| 202           | 17-19           | 4-6     | 0.15 | 7.5-10  | 1.0 | 0.060 | 0.030 | 0.25 | —        |
| 205           | 16.5-18         | 1-1.75  | 0.25 | 14-15.5 | 1.0 | 0.060 | 0.030 | 0.40 | 1-1.75Mo |
| 216**         | 17.5-22         | 5-7     | 0.08 | 7.5-9   | 1.0 | 0.045 | 0.030 | 0.50 | 3Mo      |
| 216L**        | 17.5-22         | 5-7     | 0.08 | 7.5-9   | 1.0 | 0.045 | 0.030 | 0.50 | 3Mo      |

\*Balance iron. Single values are maximum values unless otherwise noted.

\*\*Not standard AISI grades

**TABLE 4-71. TYPICAL MECHANICAL PROPERTIES OF THE 200 SERIES OF AUSTENITIC STAINLESS STEELS\* (Refs. 125 and 126)**

| AISI<br>GRADE | TENSILE STRENGTH |     | YIELD STRENGTH<br>(0.2% offset) |     | ELONGA-<br>TION, % | HARDNESS<br>ROCKWELL B |
|---------------|------------------|-----|---------------------------------|-----|--------------------|------------------------|
|               | MPa              | ksi | MPa                             | ksi |                    |                        |
| 201           | 793              | 115 | 379                             | 55  | 55                 | 90                     |
| 202           | 724              | 105 | 379                             | 55  | 55                 | 90                     |
| 205           | 827              | 120 | 476                             | 69  | 58                 | 98                     |
| 216**         | 689              | 100 | 379                             | 55  | 45                 | 92                     |

\*Annealed sheet and strip

\*\*Not standard AISI grade

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TABLE 4-72. COMPOSITIONS OF THE 300 SERIES OF AUSTENITIC STAINLESS STEELS (Ref. 125)

| AISI<br>GRADE | COMPOSITION,* % |         |      |     |          |       |        |   |
|---------------|-----------------|---------|------|-----|----------|-------|--------|---|
|               | Cr              | Ni      | C    | Mn  | Si       | P     | S      | OTHER   |
| 301           | 16-18           | 6-8     | 0.15 | 2.0 | 1.0      | 0.045 | 0.030  | —   |
| 302           | 17-19           | 8-10    | 0.15 | 2.0 | 1.0      | 0.045 | 0.030  | —   |
| 302B          | 17-19           | 8-10    | 0.15 | 2.0 | 2-3      | 0.045 | 0.030  | —   |
| 303           | 17-19           | 8-10    | 0.15 | 2.0 | 1.0      | 0.20  | 0.15** | Mo 0.60†                                      |
| 303Se         | 17-19           | 8-10    | 0.15 | 2.0 | 1.0      | 0.20  | 0.060  | Se 0.15**                                     |
| 304           | 18-20           | 8-10.5  | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  | —   |
| 304L          | 18-20           | 8-12    | 0.03 | 2.0 | 1.0      | 0.045 | 0.030  | —   |
| 304N          | 18-20           | 8-10.5  | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  | N 0.10-0.16                                   |
| 305           | 17-19           | 10.5-13 | 0.12 | 2.0 | 1.0      | 0.045 | 0.030  | —   |
| 308           | 19-21           | 10-12   | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  | —   |
| 309           | 22-24           | 12-15   | 0.20 | 2.0 | 1.0      | 0.045 | 0.030  | —   |
| 309S          | 22-24           | 12-15   | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  | —   |
| 310           | 24-26           | 19-22   | 0.25 | 2.0 | 1.5      | 0.045 | 0.030  | —   |
| 310S          | 24-26           | 19-22   | 0.08 | 2.0 | 1.5      | 0.045 | 0.030  | —   |
| 314           | 23-26           | 19-22   | 0.25 | 2.0 | 1.5-3.0  | 0.045 | 0.030  | —   |
| 316           | 16-18           | 10-14   | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  | Mo 2.0-3.0                                    |
| 316F          | 16-18           | 10-14   | 0.08 | 2.0 | 1.0      | 0.20  | 0.10** | Mo 1.75-2.50                                  |
| 316L          | 16-18           | 10-14   | 0.03 | 2.0 | 1.0      | 0.045 | 0.030  | Mo 2.0-3.0                                    |
| 316N          | 16-18           | 10-14   | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  | Mo 2-3, N 0.1-0.16                            |
| 317           | 18-20           | 11-15   | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  | Mo 3.0-4.0                                    |
| 317L          | 18-20           | 11-15   | 0.03 | 2.0 | 1.0      | 0.045 | 0.030  | Mo 3.0-4.0                                    |
| 321           | 17-19           | 9-12    | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  | Ti 5XC**                                      |
| 330           | 17-20           | 34-37   | 0.08 | 2.0 | 0.75-1.5 | 0.040 | 0.030  | —   |
| 347           | 17-19           | 9-13    | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  | Cb+Ta, 10XC**                                 |
| 348           | 17-19           | 9-13    | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  | Cb+Ta, 10XC**but<br>0.10 Ta max,<br>Co 0.20†† |
| 384           | 15-17           | 17-19   | 0.08 | 2.0 | 1.0      | 0.045 | 0.030  |   |

\*Balance iron. Single values are maximum values unless otherwise noted.

\*\*Minimum

†Optional

††Maximum

NOTE: ASTM Specification A213-75 designates the carbon content of 304L and 346L, as 0.035% maximum.

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TABLE 4-73. TYPICAL MECHANICAL PROPERTIES OF THE 300 SERIES OF AUSTENITIC STAINLESS STEELS\* (Ref. 125)

| AISI<br>GRADE | TENSILE STRENGTH |     | YIELD STRENGTH<br>(0.2% offset) |     | ELONGA-<br>TION, % | HARDNESS,<br>ROCKWELL B |
|---------------|------------------|-----|---------------------------------|-----|--------------------|-------------------------|
|               | MPa              | ksi | MPa                             | ksi |                    |                         |
| 301           | 758              | 110 | 276                             | 40  | 60                 | 85                      |
| 302           | 621              | 90  | 276                             | 40  | 50                 | 85                      |
| 302B          | 655              | 95  | 276                             | 40  | 55                 | 85                      |
| 303**         | 621              | 90  | 241                             | 35  | 50                 | 76                      |
| 303Se**       | 621              | 90  | 241                             | 35  | 50                 | 76                      |
| 304           | 586              | 85  | 241                             | 35  | 55                 | 80                      |
| 304L          | 517              | 75  | 193                             | 28  | 55                 | 79                      |
| 304N          | 621              | 90  | 331                             | 48  | 50                 | 85                      |
| 305           | 586              | 85  | 262                             | 38  | 50                 | 80                      |
| 308           | 586              | 85  | 241                             | 35  | 50                 | 80                      |
| 309           | 621              | 90  | 310                             | 45  | 45                 | 85                      |
| 309S          | 621              | 90  | 310                             | 45  | 45                 | 85                      |
| 310           | 655              | 95  | 310                             | 45  | 45                 | 85                      |
| 310S          | 655              | 95  | 310                             | 45  | 45                 | 85                      |
| 314           | 621              | 90  | 345                             | 50  | 40                 | 85                      |
| 316           | 621              | 90  | 276                             | 40  | 50                 | 79                      |
| 316F          | 586              | 85  | 241                             | 35  | 60                 | 85                      |
| 316L          | 517              | 75  | 221                             | 32  | 50                 | 79                      |
| 316N          | 621              | 90  | 331                             | 48  | 48                 | 85                      |
| 317           | 621              | 90  | 276                             | 40  | 45                 | 85                      |
| 317L          | 586              | 85  | 241                             | 35  | 55                 | 85                      |
| 321           | 621              | 90  | 241                             | 35  | 45                 | 80                      |
| 330           | 586              | 85  | 310                             | 45  | 40                 | 80                      |
| 347           | 655              | 95  | 276                             | 40  | 45                 | 85                      |
| 348           | 655              | 95  | 276                             | 40  | 45                 | 85                      |
| 384           | 517              | 75  | 241                             | 35  | 55                 | 70                      |

\*Annealed sheet and strip

\*\*Annealed bars

TABLE 4-74. COMPOSITIONS OF SOME DUPLEX STAINLESS STEELS

| DESIGNATION    | TYPICAL COMPOSITION,* % |     |      |      |      |      |      |                            |
|----------------|-------------------------|-----|------|------|------|------|------|----------------------------|
|                | Cr                      | Ni  | C    | Mn   | Si   | P    | S    | OTHER                      |
| AISI Type 329  | 28.0                    | 6.0 | 0.10 | 2.00 | 1.0  | 0.04 | 0.03 | Mo 1.5                     |
| 326**          | 26.0                    | 6.5 | 0.05 | 1.00 | 0.6  | 0.01 | 0.01 | Ti 0.25                    |
| Sandvik 3RE60  | 18.5                    | 4.5 | 0.02 | 1.50 | 1.6  | 0.01 | 0.01 | Mo 2.5                     |
| Ferrallium 255 | 26.0                    | 5.5 | 0.04 | 0.80 | 0.45 |      |      | Mo 3.3<br>Cu 1.7<br>N 0.17 |

\*Balance iron

\*\*Earlier version known as developmental alloy IN-744; commercially available since 1970 under proprietary designations of UNILOY 326, AL 326, and H-326.

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**TABLE 4-75. TYPICAL MECHANICAL PROPERTIES OF SOME DUPLEX STAINLESS STEELS\* (Ref. 124)**

| DESIGNATION   | TENSILE STRENGTH |     | YIELD STRENGTH<br>(0.2% offset) |     | ELONGA-<br>TION, % | HARDNESS,<br>ROCKWELL B |
|---------------|------------------|-----|---------------------------------|-----|--------------------|-------------------------|
|               | MPa              | ksi | MPa                             | ksi |                    |                         |
| AISI Type 329 | 724              | 105 | 552                             | 80  | 25                 | 98                      |
| 326           | 689              | 100 | 517                             | 75  | 35                 | 95                      |
| Sandvik 3RE60 | 717              | 104 | 483                             | 70  | 48                 | 92                      |
| Ferralium 255 | 855              | 124 | 648                             | 94  | 25                 |                         |

\*Mill-annealed condition

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TABLE 4-76. STANDARD WROUGHT FERRITIC STAINLESS STEELS (Ref. 2)

| ANSI<br>TYPE | UNS    | COMPOSITION, %* |      |      |     |       |       |                               | MECHANICAL PROPERTIES |     |                      |     |                  |               |
|--------------|--------|-----------------|------|------|-----|-------|-------|-------------------------------|-----------------------|-----|----------------------|-----|------------------|---------------|
|              |        | Cr              | C    | Mn   | Si  | P     | S     | OTHER                         | YIELD<br>STRENGTH,    |     | TENSILE<br>STRENGTH, |     | ELON-<br>GATION, | HARD-<br>NESS |
|              |        |                 |      |      |     |       |       |                               | MPa                   | ksi | MPa                  | ksi | %                | HB            |
| 405          | S40500 | 11.5-14.5       | 0.08 | 1.0  | 1.0 | 0.04  | 0.03  | 0.1-0.3Al                     | 276                   | 40  | 448                  | 65  | 30               | 150           |
| 409          | S40900 | 10.5-11.75      | 0.08 | 1.0  | 1.0 | 0.045 | 0.045 | (6×C)Ti†                      | 241                   | 35  | 448                  | 65  | 25               | 137           |
| 429          | S42900 | 14-16           | 0.12 | 1.0  | 1.0 | 0.04  | 0.03  | —                             | 276                   | 40  | 483                  | 70  | 30               | 163           |
| 430          | S43000 | 16-18           | 0.12 | 1.0  | 1.0 | 0.04  | 0.03  | —                             | 276                   | 40  | 517                  | 75  | 30               | 160           |
| 430F         | S43020 | 16-18           | 0.12 | 1.25 | 1.0 | 0.06  | 0.15† | 0.6 Mo                        | 379                   | 55  | 552                  | 80  | 25               | 170           |
| 430FSe       | S43023 | 16-18           | 0.12 | 1.25 | 1.0 | 0.06  | 0.06  | 0.15 Se††                     | 379                   | 55  | 552                  | 80  | 25               | 170           |
| 434          | S43400 | 16-18           | 0.12 | 1.0  | 1.0 | 0.04  | 0.03  | 0.75-1.25 Mo                  | 365                   | 53  | 531                  | 77  | 23               | 160           |
| 436          | S43600 | 16-18           | 0.12 | 1.0  | 1.0 | 0.04  | 0.03  | 0.75-1.25 Mo<br>(5×C)(Cb+Ta)† | 365                   | 53  | 531                  | 77  | 23               | 160           |
| 442          | S44200 | 18-23           | 0.20 | 1.0  | 1.0 | 0.04  | 0.03  | —                             | 310                   | 45  | 552                  | 80  | 20               | 185           |
| 446          | S44600 | 23-27           | 0.20 | 1.5  | 1.0 | 0.04  | 0.03  | 0.25N                         | 379                   | 55  | 586                  | 85  | 25               | 160           |

\*Single values are maximum values unless otherwise noted.

\*\*Typical room temperature properties of annealed plates

†0.70 max

††Minimum

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**TABLE 4-77. STANDARD WROUGHT MARTENSITIC STAINLESS STEELS (Ref. 2)**

| ANSI<br>TYPE | UNS    | COMPOSITION, %* |          |           |           |                           | MECHANICAL PROPERTIES** |     |                      |     |                       |                     |
|--------------|--------|-----------------|----------|-----------|-----------|---------------------------|-------------------------|-----|----------------------|-----|-----------------------|---------------------|
|              |        | Cr              | Ni       | Mo        | C         | OTHER                     | YIELD<br>STRENGTH,      |     | TENSILE<br>STRENGTH, |     | ELON-<br>GATION,<br>% | HARD-<br>NESS<br>HB |
|              |        |                 |          |           |           |                           | MPa                     | ksi | MPa                  | ksi |                       |                     |
| 403          | S40300 | 11.5-13.0       | —        | —         | 0.15      | —                         | 276                     | 40  | 517                  | 75  | 35                    | 155                 |
| 410          | S41000 | 11.5-13.5       | —        | —         | 0.15      | —                         | 241                     | 35  | 483                  | 70  | 30                    | 150                 |
| 414          | S41400 | 11.5-13.5       | 1.25-2.5 | —         | 0.15      | —                         | 621                     | 90  | 793                  | 115 | 20                    | 235                 |
| 416          | S41600 | 12-14           | —        | 0.6       | 0.15      | 0.15S†                    | 276                     | 40  | 517                  | 75  | 30                    | 155                 |
| 416Se        | S41623 | 12-14           | —        | —         | 0.15      | 0.15Se†                   | 276                     | 40  | 517                  | 75  | 30                    | 155                 |
| 420          | S42000 | 12-14           | —        | —         | 0.15      | —                         | 345                     | 50  | 655                  | 95  | 20                    | 195                 |
| 420F         | S42020 | 12-14           | —        | 0.6       | 0.15†     | 0.155S†                   | 379                     | 55  | 655                  | 95  | 22                    | 220                 |
| 422          | S42200 | 11-13           | 0.5-1.0  | 0.75-1.25 | 0.20-0.25 | 0.15-0.30V,<br>0.75-1.25W | 862                     | 125 | 1000                 | 145 | 18                    | 320                 |
| 431          | S43100 | 15-17           | 1.25-2.5 | —         | 0.20      | —                         | 655                     | 95  | 862                  | 125 | 20                    | 260                 |
| 440A         | S44002 | 16-18           | —        | 0.75      | 0.6-0.75  | —                         | 414                     | 60  | 724                  | 105 | 20                    | 210                 |
| 440B         | S44003 | 16-18           | —        | 0.75      | 0.75-0.95 | —                         | 427                     | 62  | 738                  | 107 | 18                    | 215                 |
| 440C         | S44004 | 16-18           | —        | 0.75      | 0.95-1.20 | —                         | 448                     | 65  | 758                  | 110 | 14                    | 220                 |
| 501          | S50100 | 4-6             | —        | 0.40-0.65 | 0.10†     | —                         | 207                     | 30  | 483                  | 70  | 28                    | 160                 |
| 502          | S50200 | 4-6             | —        | 0.40-0.65 | 0.10      | —                         | 172                     | 25  | 448                  | 65  | 30                    | 150                 |

\*Single values are maximum values unless noted otherwise.

\*\*Typical room temperature properties of annealed plates

†Minimum

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**TABLE 4-78. TYPICAL COMPOSITIONS OF THE PRECIPITATION-HARDENING STAINLESS STEELS (Ref. 124)**

| TRADE DESIGNATION     | COMPOSITION,* % |       |      |      |      |      |      |      |      |              |
|-----------------------|-----------------|-------|------|------|------|------|------|------|------|--------------|
|                       | Cr              | Ni    | C    | Mn   | Si   | Cu   | Mo   | Ti   | Al   | OTHER        |
| <b>MARTENSITIC</b>    |                 |       |      |      |      |      |      |      |      |              |
| Stainless W**         | 16.75           | 6.75  | 0.07 | 0.50 | 0.50 | —    | —    | 0.80 | 0.20 | —            |
| 17-4 PH               | 16.50           | 4.25  | 0.04 | 0.40 | 0.50 | 3.60 | —    | —    | —    | Cb + Ta 0.25 |
| 15-5 PH (XM-12)††     | 15.00           | 4.60  | 0.04 | 0.25 | 0.40 | 3.50 | —    | —    | —    | Cb + Ta 0.35 |
| CROLOY 16-6 PH        | 15.75           | 7.50  | 0.03 | 0.80 | 0.45 | —    | —    | 0.60 | 0.40 | —            |
| CUSTOM 450 (XM-25)    | 14.90           | 6.50  | 0.03 | 0.30 | 0.25 | 1.50 | 0.80 | —    | —    | Cb + Ta 0.75 |
| CUSTOM 455 (XM-16)    | 11.75           | 8.50  | 0.03 | 0.20 | 0.20 | 2.25 | —    | 1.20 | —    | Cb + Ta 0.30 |
| PH 13-8 Mo (XM-13)    | 13.00           | 8.00  | 0.04 | 0.05 | 0.05 | —    | 2.25 | —    | 1.00 | —            |
| ALMAR 362 (XM-9)      | 14.50           | 6.50  | 0.03 | 0.30 | 0.20 | —    | —    | 0.80 | —    | —            |
| IN-736                | 10.00           | 10.00 | 0.02 | 0.10 | 0.10 | —    | 2.00 | 0.20 | 0.30 | —            |
| <b>SEMIAUSTENITIC</b> |                 |       |      |      |      |      |      |      |      |              |
| 17-7 PH               | 17.00           | 7.00  | 0.07 | 0.70 | 0.40 | —    | —    | —    | 1.15 | —            |
| PH 15-7 Mo            | 15.00           | 7.00  | 0.07 | 0.70 | 0.40 | —    | 2.25 | —    | 1.15 | —            |
| AM-350                | 16.50           | 4.25  | 0.10 | 0.75 | 0.35 | —    | 2.75 | —    | —    | N 0.10       |
| AM-355                | 15.50           | 4.25  | 0.13 | 0.85 | 0.35 | —    | 2.75 | —    | —    | N 0.12       |
| PH 14-8 Mo† (XM-24)   | 15.50           | 8.75  | 0.05 | 0.10 | 0.10 | —    | 2.50 | —    | 1.35 | —            |
| <b>AUSTENITIC</b>     |                 |       |      |      |      |      |      |      |      |              |
| 17-10 P               | 17.0            | 10.50 | 0.12 | 0.75 | 0.50 | —    | —    | —    | —    | P 0.28       |
| HNM                   | 18.5            | 9.50  | 0.30 | 3.50 | 0.50 | —    | —    | —    | —    | P 0.25       |
| A-286                 | 15.0            | 25.0  | 0.06 | 1.20 | 0.50 | —    | 1.20 | 2.00 | 0.25 | V 0.30       |

\*Balance iron

\*\*Predominantly ferritic

† Vacuum induction melted, maximum values

†† Designations in parentheses are ASTM designations.

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TABLE 4-79. TYPICAL MECHANICAL PROPERTIES OF THE SEMIAUSTENITIC AND AUSTENITIC PRECIPITATION-HARDENING STAINLESS STEELS (Ref. 124)

| DESIGNATION    | CONDITION                               | TENSILE STRENGTH, |     | YIELD STRENGTH,<br>(0.2% offset) |     | ELONGA-<br>TION, % | HARDNESS<br>ROCKWELL<br>B or C |
|----------------|---|-------------------|-----|----------------------------------|-----|--------------------|--------------------------------|
|                |   | MPa               | ksi | MPa                              | ksi |                    |                                |
| SEMIAUSTENITIC |   |                   |     |                                  |     |                    |                                |
| 17-7 PH        | A*                                      | 896               | 130 | 276                              | 40  | 35                 | B 85                           |
|                | SZC** + PH*** 510°C (950°F)             | 1620              | 235 | 1517                             | 220 | 6                  | C 48                           |
|                | T† 760°C (1400°F),<br>PH 566°C (1051°F) | 1379              | 200 | 1276                             | 185 | 9                  | C 43                           |
| PH 15-7 Mo     | A                                       | 896               | 130 | 379                              | 55  | 35                 | B 88                           |
|                | SZC + PH 510°C (950°F)                  | 1655              | 240 | 1551                             | 225 | 6                  | C 48                           |
|                | T 760°C (1400°F),<br>PH 566°C (1051°F)  | 1448              | 210 | 1379                             | 200 | 7                  | C 44                           |
| AM-350         | A                                       | 1103              | 160 | 379                              | 55  | 40                 | B 95                           |
|                | T 732°C (1350°F),<br>PH 455°C (851°F)   | 1344              | 195 | 1069                             | 155 | 10.5               | C 41                           |
|                | SZC + PH 455°C (851°F)                  | 1379              | 200 | 1172                             | 170 | 15                 | C 43                           |
| AM-355         | A                                       | 1207              | 175 | 448                              | 65  | 30                 | B 95                           |
|                | T 732°C (1350°F),<br>PH 455°C (851°F)   | 1344              | 195 | 1069                             | 155 | 10                 | C 41                           |
|                | SZC + PH 455°C (851°F)                  | 1517              | 220 | 1310                             | 190 | 13                 | C 45                           |
| PH 14-8 Mo††   | A                                       | 862               | 125 | 379                              | 55  | 25                 | B 88                           |
|                | SZC + PH 510°C (950°F)                  | 1586              | 230 | 1482                             | 215 | 6                  | C 48                           |
|                | SZC + PH 566°C (1051°F)                 | 1448              | 210 | 1379                             | 200 | 6                  | C 45                           |
| AUSTENITIC     |   |                   |     |                                  |     |                    |                                |
| 17-10 P        | A                                       | 614               | 89  | 255                              | 37  | 70                 | B 82                           |
|                | PH 705°C (1301°F)                       | 986               | 143 | 676                              | 98  | 20                 | C 32                           |
| HNM            | A                                       | 800               | 116 | 386                              | 56  | 57                 | B 92                           |
|                | PH 732°C (1350°F)                       | 1151              | 167 | 855                              | 124 | 19                 | C 38                           |
| A-286          | A                                       | 621               | 90  | 241                              | 35  | 45                 | B 81                           |
|                | PH 718°C (1324°F)                       | 1007              | 146 | 689                              | 100 | 25                 | C 34                           |

\*A = Solution annealed

\*\*SZC = Subzero cooled to -73°C (-99°F)

\*\*\*PH = Precipitation hardened at indicated temperature

†T = Tempered at indicated temperature

†† Vacuum induction melted

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TABLE 4-80. TYPICAL MECHANICAL PROPERTIES OF THE MARTENSITIC PRECIPITATION-HARDENING STAINLESS STEELS (Ref. 124)

| DESIGNATION    | CONDITION | TENSILE STRENGTH |     | YIELD STRENGTH<br>(0.2% offset) |     | ELONGA-<br>TION, % | HARDNESS,<br>ROCKWELL<br>C |
|----------------|-----------|------------------|-----|---------------------------------|-----|--------------------|----------------------------|
|                |           | MPa              | ksi | MPa                             | ksi |                    |                            |
| Stainless W    | A*        | 827              | 120 | 517                             | 75  | 7                  | 30                         |
|                | PH**      | 1344             | 195 | 1241                            | 180 | 7                  | 46                         |
| 17-4 PH        | A         | 1034             | 150 | 758                             | 110 | 10                 | 33                         |
|                | PH        | 1379             | 200 | 1227                            | 178 | 12                 | 44                         |
| 15-5 PH        | A         | 862              | 125 | 586                             | 85  | 10                 | 27                         |
|                | PH        | 1379             | 200 | 1276                            | 185 | 14                 | 44                         |
| Croloy 16-6 PH | A         | 924              | 134 | 758                             | 110 | 16                 | 28                         |
|                | PH        | 1303             | 189 | 1276                            | 185 | 16                 | 40                         |
| Custom 450     | A         | 972              | 141 | 814                             | 118 | 13                 | 28                         |
|                | PH        | 1344             | 195 | 1282                            | 186 | 14                 | 43                         |
| Custom 455     | A         | 1000             | 145 | 793                             | 115 | 14                 | 31                         |
|                | PH        | 1724             | 250 | 1689                            | 245 | 10                 | 49                         |
| PH 13-8 Mo     | A         | 896              | 130 | 586                             | 85  | 12                 | 28                         |
|                | PH        | 1551             | 225 | 1379                            | 200 | 13                 | 48                         |
| ALMAR 362      | A         | 827              | 120 | 724                             | 105 | 13                 | 25                         |
|                | PH        | 1296             | 188 | 1276                            | 185 | 15                 | 41                         |
| IN-736         | A         | 958              | 139 | 738                             | 107 | 16                 | 28                         |
|                | PH        | 1310             | 190 | 1282                            | 186 | 14                 | 38                         |

\*A = Solution annealed

\*\*PH = Precipitation-hardened maximum values

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Cast stainless steels can also be described as austenitic, ferritic, martensitic, and precipitation hardening. The austenitic cast stainless steels can exhibit poor resistance to intergranular corrosion because of chromium depletion in the vicinity of precipitated carbides. This is the same phenomenon as sensitization in the wrought stainless steel alloys. The cast martensitic alloys can be hardened and tempered to give a wide range of mechanical properties, but the ferritic cast alloys cannot be hardened. Their high chromium content gives good resistance to oxidizing

acids. Precipitation-hardening, cast alloys combine high strength, good toughness, and moderate corrosion resistance. The cast stainless steels usually have higher silicon content than the corresponding wrought product, which improves castability. The corrosion resistance of cast and the corresponding wrought stainless steels are equivalent in most environments. The chemical composition and mechanical properties of some cast stainless steels are shown in Tables 4-81 through 4-84.

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TABLE 4-81. COMPOSITIONS OF CORROSION-RESISTANT, CAST MARTENSITIC, FERRITIC, AND PRECIPITATION-HARDENING STAINLESS STEELS (Refs. 2 and 125)

| ACI DESIGNATION         | NEAREST WROUGHT COMPARATIVE | COMPOSITION*, % |     |      |     |     |                   |
|-------------------------|-----------------------------|-----------------|-----|------|-----|-----|-------------------|
|                         |                             | Cr              | Ni  | C    | Mn  | Si  | OTHER             |
| MARTENSITIC             |                             |                 |     |      |     |     |                   |
| CA-15                   | 410                         | 11.5-14         | 1.0 | 0.15 | 1.0 | 1.5 | Mo 0.5**          |
| CA-40                   | 420                         | 11.5-14         | 1.0 | 0.40 | 1.0 | 1.5 | Mo 0.5**          |
| CA-6NM                  | —                           | 11.5-14         | 4.0 | 0.06 | 1.0 | 1.5 | Mo 0.7            |
| CA-6N                   | —                           | 11.5-14         | 7.0 | 0.06 | 1.0 | 1.5 | Al, Ti            |
| FERRITIC                |                             |                 |     |      |     |     |                   |
| CB-30                   | 442                         | 18-22           | 2.0 | 0.30 | 1.0 | 1.0 | —                 |
| CC-50                   | 446                         | 26-30           | 4.0 | 0.50 | 1.0 | 1.0 | —                 |
| CD-4MCu†,††             | 329                         | 26              | 5.0 | 0.04 | 1.0 | 1.0 | Cu 3.0,<br>Mo 2.0 |
| PRECIPITATION-HARDENING |                             |                 |     |      |     |     |                   |
| CB-7Cu-1†               | 17-4 PH                     | 16              | 4.0 | 0.05 | —   | —   | Cu 3.0            |
| CB-7Cu-2†               | 15-5 PH                     | 15              | 5.0 | 0.05 | —   | —   | Cu 3.0, Cb        |

\*Balance iron. Single values are maximum values unless otherwise noted.

\*\*Not intentionally added

†Typical compositions

††Duplex, predominantly ferritic

TABLE 4-82. TYPICAL MECHANICAL PROPERTIES OF CORROSION-RESISTANT, CAST MARTENSITIC, FERRITIC, AND PRECIPITATION-HARDENING STAINLESS STEELS\* (Refs. 2 and 125)

| ACI DESIGNATION         | NEAREST WROUGHT COMPARATIVE | TENSILE STRENGTH, |     | YIELD STRENGTH (0.2% offset), |     | ELONGATION IN 2 in., % | HARDNESS, BRINELL |
|-------------------------|-----------------------------|-------------------|-----|-------------------------------|-----|------------------------|-------------------|
|                         |                             | MPa               | ksi | MPa                           | ksi |                        |                   |
| MARTENSITIC             |                             |                   |     |                               |     |                        |                   |
| CA-15                   | 410                         | 1379              | 200 | 1034                          | 150 | 7                      | 390               |
| CA-40                   | 420                         | 1517              | 220 | 1138                          | 165 | 1                      | 470               |
| CA-6NM                  | —                           | 827               | 120 | 689                           | 100 | 14                     | 300               |
| CA-6N                   | —                           | 965               | 140 | 931                           | 135 | 15                     | —                 |
| FERRITIC                |                             |                   |     |                               |     |                        |                   |
| CB-30                   | 431                         | 655               | 95  | 414                           | 60  | 15                     | 195               |
| CC-50                   | 446                         | 669               | 97  | 448                           | 65  | 18                     | 210               |
| CD-4MCu**               | 329                         | 745               | 108 | 558                           | 81  | 25                     | 260               |
| PRECIPITATION-HARDENING |                             |                   |     |                               |     |                        |                   |
| CB-7Cu-1                | 17-4 PH                     | —                 | —   | 1076                          | 156 | 3                      | 418               |
| CB-7Cu-2                | 15-5 PH                     | 1241              | 180 | 1034                          | 150 | 6                      | —                 |

\*After heat treatment for optimum properties

\*\*Can be precipitation hardened. Properties noted here are for the solution-annealed condition.

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**TABLE 4-83. COMPOSITIONS OF CORROSION-RESISTANT, CAST AUSTENITIC STAINLESS STEELS (Adapted from Ref. 2)**

| ACI DESIGNATION | NEAREST WROUGHT COMPARATIVE | COMPOSITION, %* |           |      |     |     |                     |
|-----------------|-----------------------------|-----------------|-----------|------|-----|-----|---------------------|
|                 |                             | Cr              | Ni        | C    | Mn  | Si  | OTHER               |
| CF-3            | 304L                        | 17-21           | 8-12      | 0.03 | 1.5 | 2.0 | —                   |
| CF-8            | 304                         | 18-21           | 8-11      | 0.08 | 1.5 | 2.0 | —                   |
| CF-20           | 302                         | 18-21           | 8-11      | 0.20 | 1.5 | 2.0 | —                   |
| CF-3M           | 316L                        | 17-21           | 9-13      | 0.03 | 1.5 | 1.5 | Mo 2.0-3.0          |
| CF-8M           | 316                         | 18-21           | 9-12      | 0.08 | 1.5 | 1.5 | Mo 2.0-3.0          |
| CF-8C           | 347                         | 18-21           | 9-12      | 0.08 | 1.5 | 2.0 | Cb**                |
| CF-16F          | 303                         | 18-21           | 9-12      | 0.16 | 1.5 | 2.0 | Mo 1.5, Se 0.2-0.35 |
| CH-20           | 309                         | 22-26           | 12-15     | 0.20 | 1.5 | 2.0 | —                   |
| CK-20           | 310                         | 23-27           | 19-22     | 0.20 | 1.5 | 2.0 | —                   |
| CN-7M           | —                           | 19-22           | 27.5-30.5 | 0.07 | 1.5 | 1.5 | Cu 3-4, Mo 2.0-3.0  |

\*Balance iron. Single values are maximum values unless otherwise noted.

\*\*Cb 8×C min, 1.0% max.

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**TABLE 4-84. TYPICAL MECHANICAL PROPERTIES OF CORROSION-RESISTANT, CAST AUSTENITIC STAINLESS STEELS (Adapted from Ref. 2)**

| ACI DESIGNATION | NEAREST WROUGHT COMPARATIVE | TENSILE STRENGTH, |     | YIELD STRENGTH (0.2% offset), |     | ELONGATION, % | HARDNESS, BRINELL |
|-----------------|-----------------------------|-------------------|-----|-------------------------------|-----|---------------|-------------------|
|                 |                             | MPa               | ksi | MPa                           | ksi |               |                   |
| CF-3            | 304L                        | 531               | 77  | 248                           | 36  | 60            | 140               |
| CF-8            | 304                         | 531               | 77  | 255                           | 37  | 55            | 140               |
| CF-20           | 302                         | 531               | 77  | 248                           | 36  | 50            | 163               |
| CF-3M           | 316L                        | 552               | 80  | 262                           | 38  | 55            | 150               |
| CF-8M           | 316                         | 552               | 80  | 290                           | 42  | 50            | 163               |
| CF-8C           | 347                         | 531               | 77  | 262                           | 38  | 39            | 149               |
| CF-16F          | 303                         | 531               | 77  | 276                           | 40  | 52            | 150               |
| CH-20           | 309                         | 607               | 88  | 345                           | 50  | 38            | 190               |
| CK-20           | 310                         | 524               | 76  | 262                           | 38  | 37            | 144               |
| CN-7M           | —                           | 476               | 69  | 221                           | 32  | 48            | 130               |

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#### 4-8.4.2 Types of Corrosion

##### 4-8.4.2.1 Pitting Corrosion

Pitting may result from the interaction of chloride ions with the passive surface of stainless steel, or it may be the result of anodic surface defects such as inclusions and second phases. Pitting is propagated by the dissolution of metal and maintenance of a high degree of acidity in the bottom of the pit. This is described in par. 2-2.3.3. All of the stainless steels are subject to pitting. Chromium, nickel, and molybdenum increase resistance to pitting.

Most pitting is caused by chloride and chloride-containing ions. Bromine may also cause pitting, but fluoride and iodide solutions show little pitting tendency.

Cupric, ferric, and mercuric ions are strong pitting agents in chloride solution. Increasing temperature increases the pitting tendency, and stagnant solution conditions favor pitting. Surface conditions, such as inclusions and contaminants, can influence pitting tendency by acting as initial sites for pitting.

##### 4-8.4.2.2 Crevice Corrosion

Crevice corrosion occurs within shielded crevices or shielded surfaces if a stagnant solution is present. Examples of crevices are metal-to-metal or metal-to-nonmetal interfaces, such as those associated with rivets, bolts, gaskets, valve seats, loose surface deposits, and

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marine growths. Crevice corrosion usually occurs in gaps a few micrometers wide. It does not occur in grooves or slots where circulation of the fluid is possible.

Of all the alloying elements in stainless steel, molybdenum provides the greatest improvement in crevice corrosion resistance.

The importance of the cathode (bold) to anode (crevice) area ratio on the probability of initiating crevice corrosion for three alloys is illustrated in Fig. 4-24. Type 304 stainless steel is much more susceptible to crevice corrosion than Type 316 or the Incoloy Alloy 825.

#### 4-8.4.2.3 Intergranular Corrosion

Sensitization of austenitic stainless steel is the usual cause of intergranular corrosion of stainless steel. Sensitization results from chromium depletion in the vicinity of carbides precipitated at grain boundaries. Specific combinations of temperature, time, and composition are required for sensitization. These conditions readily result from welding.

The stabilized grades of stainless steel, such as 321 and 347, are not susceptible to sensitization, but when they are welded, the temperature in a very narrow zone immediately adjacent to the weld exceeds 1150°C (2102°F). This heating puts carbon into solid solution within the narrow zone. If the subsequent cooling rate is slow through the range 480° to 760°C (896° to 1400°F) or if the weld is reheated to temperatures in the chromium carbide precipitation range, a very thin zone of sensitized material may develop immediately adjacent to the weld.

Sensitization of the 400 series of ferritic stainless steels results from chromium depletion in the vicinity of

precipitated chromium carbides and nitrides in the grain boundaries. The temperature range at which this occurs and the speed of the process differ from those of austenitic stainless steels.

Susceptibility of austenitic stainless steel to sensitization is reduced by lowering the carbon content. However, the levels of carbon (plus nitrogen) required to reduce susceptibility to intergranular attack in ferritic stainless steel are much lower than they are for austenitic stainless steels.

Duplex stainless steels, which contain both austenite and delta ferrite, exhibit high resistance to intergranular corrosion.

Nonsensitized austenitic stainless steels are resistant to intergranular attack in almost all environments. An exception is oxidizing nitric acid containing certain metallic ions in their higher valence states. These metal ions include Cr<sup>+6</sup> (Cr<sub>2</sub>O<sub>7</sub><sup>-2</sup>), Mn<sup>+7</sup> (MnO<sub>4</sub><sup>-</sup>), Fe<sup>+3</sup>, Ce<sup>+4</sup>, and V<sup>+5</sup>.

#### 4-8.4.2.4 Stress-Corrosion Cracking

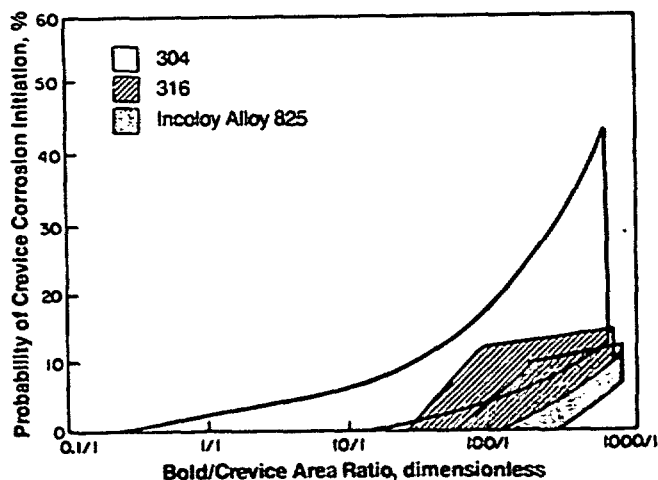
The requirements for stress-corrosion cracking are a sustained tensile stress and a specific corrodent. Chloride, caustic, and oxygen designate specific aqueous environments in which stainless steels are susceptible to cracking. Hydrogen embrittlement is facilitated by the entry of hydrogen in the metal. In sulfide cracking, sulfide ions poison the recombination of hydrogen ions that are generated in a corrosion process. Therefore, hydrogen is available at the surface for entry into the metal. Austenitic, ferritic, and duplex stainless steels are subject to chloride stress corrosion. Most service failures with high-strength martensitic and precipitation-hardening stainless steels occur as a result of hydrogen embrittlement.

##### 4-8.4.2.4.1 Chloride Cracking

The contributing factors, in addition to sustained-tensile stress, in chloride stress-corrosion cracking are

1. Chloride ions in aqueous solutions
2. Oxygen or other oxidizer
3. Favorable electrochemical potential
4. Elevated temperature
5. Opportunity for local breakdown of passivity
6. Opportunity to develop local acidity
7. Existence of a stress-raiser such as a notch or a pit.

The chloride ion may originate from many sources. Some common sources are seawater, the marine atmosphere, river water, sweaty hands, human waste, salted food-stuffs, soluble contaminants in thermal insulation, hydrochloric acid or other chloride-containing chemicals, lubricants, sealants, and decomposition products of polyvinyl chloride. The minimum concentration of chloride ions that can cause cracking may range from 1 ppm to a few thousand ppm depending upon many other factors; however, the likelihood of cracking increases with increas-



NOTE: Exposure Conditions: 30 days in Flowing Ambient Temperature Seawater

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Figure 4-24. Probability of Crevice Corrosion Initiation as a Function of Bold/Crevice Area Ratio (Ref. 127)

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ing chloride ion concentration. Chloride-concentrating mechanisms such as alternate wetting and drying should be avoided.

Stresses responsible for chloride cracking are usually the result of fabrication, fit-up, welding, or differential heating. Design stresses or stresses resulting from metal heat treatments add to these stresses but taken alone they are not the principle causes of most service failures. Relatively low stresses can cause cracking, e.g., stresses even lower than 69 MPa (10 ksi) can cause cracking in a steel having an ultimate tensile strength of 621 MPa (90 ksi). Decreasing the applied stress increases the time to failure as indicated in Fig. 4-25. The increase in fracture time is of practical significance on the relatively flat portion of the curve. A threshold stress below which cracking does not occur is also indicated on this figure and may be estimated from the scale on the left vertical axis. The threshold stress intensity for precracked fracture mechanics specimens is designated  $K_{Isc}$ .

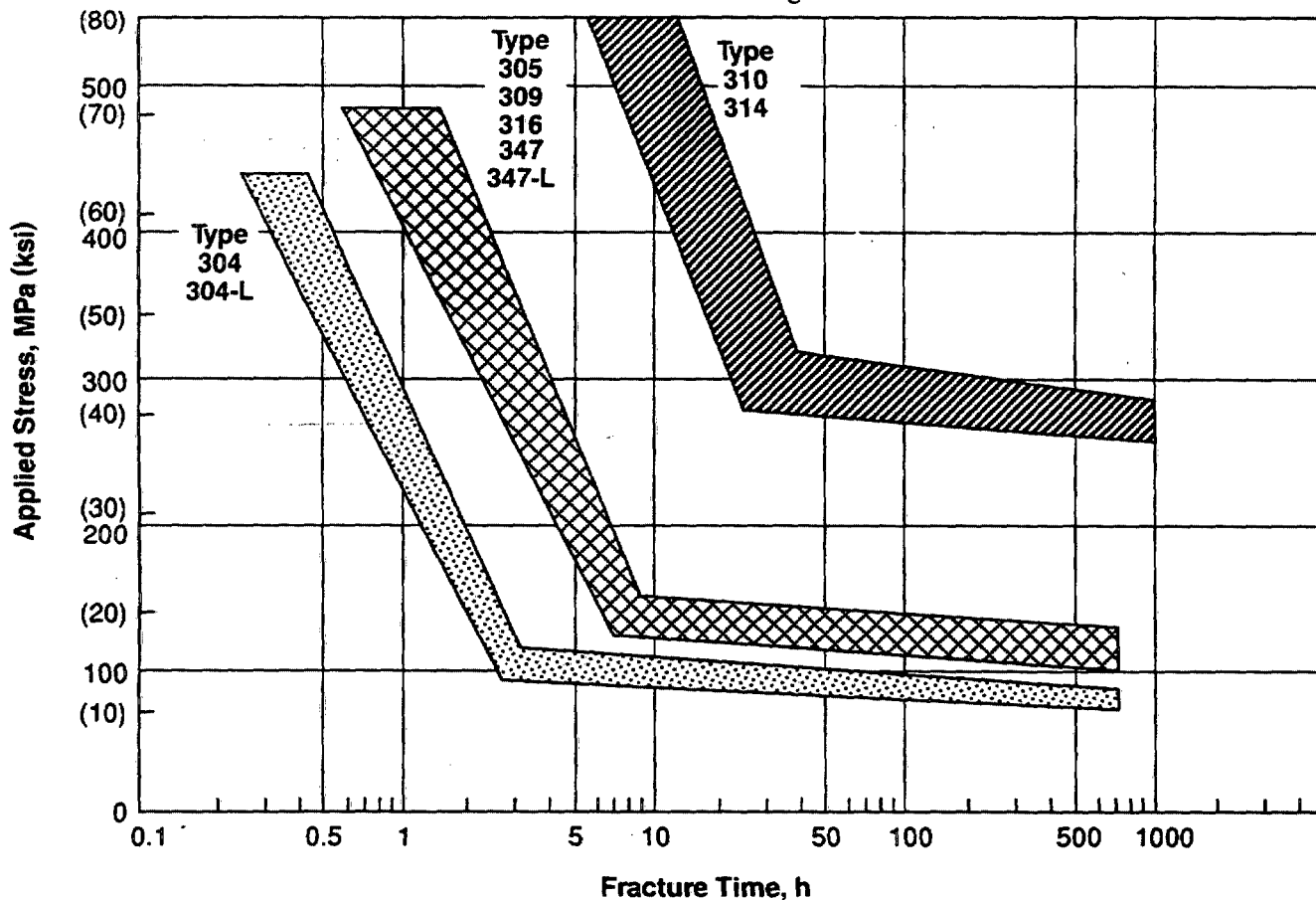
All of the austenitic stainless steels are subject to chloride stress-corrosion cracking. The relative susceptibilities are

1. Highest Susceptibility. Sulfur-bearing 303, 301, and sensitized 304
2. Intermediate Susceptibility. Nonsensitized 304, 304L
3. Lower Susceptibility. 316, 316L, 347, 347L
4. Lowest Susceptibility. 310, 314, USS 18-18-2.

The presence of oxygen or an oxidizer is important in chloride cracking in neutral solutions. Oxygen is not necessary for cracking in slightly acid solutions, however, introducing oxygen into such solutions accelerates cracking.

Chloride cracking of austenitic stainless steels seldom occurs except at elevated temperatures—above about 60°C (140°F). Chloride cracking of austenitic stainless steel does not occur below a critical electrochemical potential. Therefore, cathodic protection can be achieved by impressed currents or by coupling with a more anodic material such as carbon steel, aluminum, or lead.

A corrosion pit may be the precursor of stress-corrosion cracking. Increasing the bulk pH of a solution increases pitting resistance, and a similar improvement occurs in the resistance to chloride stress-corrosion cracking.



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**Figure 4-25. Relative Stress-Corrosion Cracking Behavior of Major Types of Austenitic Steel in Boiling Magnesium Chloride (Ref. 128)**

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Silicates, nitrates, phosphates, carbonates, iodides, and sulfides are all effective inhibitors of cracking if they are present in sufficient concentrations.

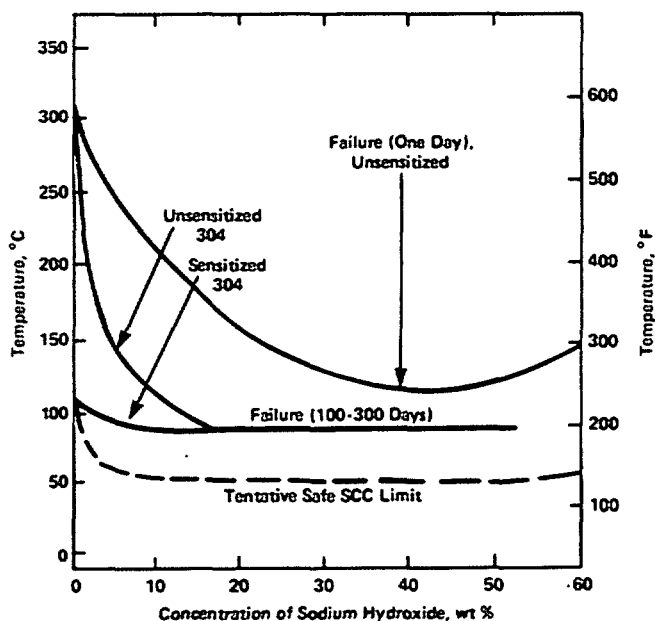
Ferritic stainless steels (AISI 400 series) usually exhibit uniform corrosion or pitting attack in chloride solutions. However, cracking can also occur under some conditions.

In the annealed condition duplex stainless steels are more resistant to chloride cracking than the common austenitic grades, such as Types 304 and 316. Welding may result in continuous regions of sensitized ferrite in the heat-affected zone, which can be susceptible to chloride cracking.

#### 4-8.4.2.4.2 Caustic Cracking

Hot caustic solutions, e.g., sodium hydroxide or potassium hydroxide, over a range of concentration from less than 1 to 100% can cause cracking of stainless steels. The temperature and concentration limits necessary for caustic cracking of several types of austenitic stainless steels to occur are shown in Fig. 4-26. Although oxygen is not necessary for caustic cracking, its presence can increase the caustic cracking susceptibility of an alloy. High levels of nickel and chromium provide resistance to caustic cracking in aerated solutions of sodium hydroxide.

The caustic cracking behaviors of ferritic, duplex, and martensitic stainless steels under one set of environmental conditions are compared in Table 4-85. As is evident, the environmental conditions were not sufficiently severe to



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**Figure 4-26. Temperature and Concentration Limits for Caustic Cracking of Types 304, 347, 316, and 321 Stainless Steels (Ref. 124)**

crack Type 304 austenitic stainless steel in the given metallurgical condition within the exposure period.

#### 4-8.4.2.4.3 Oxygen Cracking

Sensitized Type 304 stainless steel can crack in high-temperature, high-purity water in which the oxygen content of the water is at least 0.2 ppm. This action occurs most readily in the presence of a crevice, although this is not necessary for cracking of sensitized Type 304 stainless steel.

#### 4-8.4.2.4.4 Other Cracking Environments

There are three additional groups of aqueous chemical environments that can cause stress-corrosion cracking at room temperature:

1. Polythionic acids can crack sensitized steels at room temperature.
2. Dilute fluoride solutions have caused cracking of sensitized Type 304 in components having high residual stress.
3. Any strong acid containing a trace of chloride may cause cracking at room temperature.

#### 4-8.4.2.4.5 Hydrogen Embrittlement

Yield strength is the dominant characteristic that correlates with the susceptibility of stainless steel to hydrogen embrittlement. Cracking can readily occur in most high-strength steels irrespective of their composition or structure. Martensitic and precipitation-hardening stainless steels having yield strengths above 1034 MPa (150 ksi) can crack in marine atmospheres, and notched specimens may crack at lower yield strengths. Although tempering martensitic stainless steels and overaging precipitation-hardening stainless steels improve cracking resistance, these processes lower yield strength. Stainless steels and higher alloys having high resistance to hydrogen cracking are listed in Table 4-86.

The pH of the environment can influence hydrogen cracking resistance. Time-to-failure is lowest at low pH, and the acidification that occurs within crevices could lead to unanticipated cracking under bulk solution conditions.

The presence of hydrogen sulfide in various environments decreases the cracking resistance of high-strength steels. A minimum hardness exists below which cracking does not occur at a given applied stress. This minimum hardness increases with decreasing hydrogen sulfide concentration. Cracking is facilitated by such factors as low pH, elevated temperature, galvanic coupling to anodic materials, and cold-working. Stainless steels considered acceptable for hydrogen sulfide environments are listed in Table 4-87.

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**TABLE 4-85. CRACKING BEHAVIOR OF VARIOUS STAINLESS STEELS IN DEAERATED 10% NaOH SOLUTION AT 332° C (630° F) (C-RING SPECIMENS STRESSED AT 90% OF THE YIELD STRENGTH) (Ref. 130)**

| STAINLESS STEEL                 | CONDITION                           | OBSERVATION* |
|---------------------------------|-------------------------------------|--------------|
| Type 304 (austenitic)           | <i>Mill Annealed</i>                | NC           |
|                                 | 10 h at 648° C (1199° F)            | NC           |
| Type 405 (ferritic)             | <i>Mill Annealed</i>                | NC, GC       |
|                                 | 1 h at 1010° C (1850° F)/FC         | NC, GC       |
| Fe-18%Cr-2%Mo-0.5%Ti (ferritic) | <i>Mill Annealed</i>                | NC, IGA      |
|                                 | 1 h at 1010° C (1850° F)/FC         | C            |
|                                 | 3 h at 475° C (887° F)              | C            |
|                                 | 20 h at 475° C (887° F)             | C            |
| E-Brite 26-1 (ferritic)         | <i>Mill Annealed</i>                | NC           |
|                                 | 1 h at 1010° C (1850° F)/FC         | C            |
|                                 | 100 h at 475° C (887° F)            | NC           |
|                                 | 300 h at 475° C (887° F)            | C            |
| 3RE60 (duplex)                  | <i>Mill Annealed</i>                | NC, GC, IGA  |
|                                 | 10 h at 643° C (1190° F)            | NC, GC, IGA  |
|                                 | 100 h at 475° C (887° F)            | C            |
|                                 | 300 h at 475° C (887° F)            | C            |
| Type 410 (martensitic)          | <i>Mill Annealed</i>                | NC, GC       |
|                                 | tempered 648° C (1199° F) (Rc = 28) | NC, GC       |
|                                 | tempered 566° C (1050° F) (Rc = 41) | NC, GC       |
|                                 | tempered 482° C (900° F) (Rc = 50)  | C            |

\*NC = No cracking in 4800 h

C = Cracking during 4800 h

GC = Heavy general corrosion

IGA = Intergranular attack

FC = Furnace-cooled

Rc = Hardness on Rockwell C Scale

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**TABLE 4-86. STAINLESS STEELS AND HIGHER ALLOYS REGARDED AS HAVING HIGH RESISTANCE TO HYDROGEN EMBRITTLEMENT BY MARSHALL SPACE FLIGHT CENTER (Ref. 31)**

| ALLOY   | CONDITION                  |
|---|----------------------------|
| AISI 300 Series Stainless Steel (Unsensitized)* | All                        |
| 21-6-9 Stainless Steel                          | All                        |
| Carpenter 20Cb                                  | All                        |
| Carpenter 20Cb3                                 | All                        |
| A286  | All                        |
| AM350   | SCT 1000 and above         |
| AM355   | SCT 1000 and above         |
| ALMAR 362                                       | H1000 and above            |
| Custom 455                                      | H1000 and above            |
| 15-5 PH   | H1000 and above            |
| PH 14-8 Mo                                      | CH900 and SRH950 and above |
| PH 15-7 Mo                                      | CH900                      |
| 17-7 PH   | CH900                      |
| Nitronic 33**                                   | All                        |
| Hastelloy alloy C                               | All                        |
| Hastelloy alloy X                               | All                        |
| Incoloy alloy 800                               | All                        |
| Incoloy alloy 901                               | All                        |
| Incoloy alloy 903                               | All                        |
| Inconel alloy 600**                             | Annealed                   |
| Inconel alloy 625                               | Annealed                   |
| Inconel alloy 718**                             | All                        |
| Inconel alloy X-750                             | All                        |
| Monel alloy K-500**                             | All                        |
| NI-Span-C alloy 902                             | All                        |
| René 41   | All                        |
| Unitemp 212                                     | All                        |
| Waspalloy                                       | All                        |

\*Including weldments of 304L, 316L, 321 and 347

\*\*Including weldments



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**TABLE 4-87. STAINLESS STEELS LISTED IN NACE STANDARD MR0175\* AS ACCEPTABLE FOR HYDROGEN SULFIDE ENVIRONMENTS\*\* (Ref. 268)**

| AUSTENITIC          | FERRITIC              | MARTENSITIC     | PRECIPI-<br>TATION<br>HARDENING | DUPLEX<br>(AUSTENITIC/<br>FERRITIC)†  |
|---------------------|-----------------------|-----------------|---------------------------------|---|
| AISI                | AISI                  | AISI            | ASTM                            | UNS S31803  |
| 302                 | 405                   | 410             | A 453 Gr 660††                  | UNS S32550  |
| 304                 | 430                   | 501             | A 638 Gr 660††                  | UNS S32404  |
| 304L                |                       |                 |                                 |   |
| 305                 |                       |                 |                                 |   |
| 308                 |                       |                 |                                 |   |
| 309                 |                       |                 |                                 |   |
| 310                 |                       |                 |                                 |   |
| 316                 |                       |                 |                                 |   |
| 316L                |                       |                 |                                 |   |
| 317                 |                       |                 |                                 |   |
| 321                 |                       |                 |                                 |   |
| 347                 |                       |                 |                                 |   |
| ASTM                | ASTM                  | ASTM            | UNS S17400                      | Cast Duplex<br>(Austenitic/Ferritic)<br>stainless steel<br>Z6CNDU20.28M, NF A<br>320-55 French National<br>Standard |
| A 182               | A 268                 | A 217 Gr CA 15  | UNS S45000                      |   |
| A 193†††            | GR TP 405, TP 430, TP | A 268 Gr TP 410 | UNS S66286                      |   |
| Gr B8R, B8RA, B8,   | XM 27, TP XM 33       | A 743 Gr CA 15M |                                 |   |
| B8M, B8MA           |                       | A 487 CI CA 15M |                                 |   |
| A 194†††            |                       | A 487 CI CA6NM  |                                 |   |
| Gr 8R, 8RA, 8A, 8MA |                       | UNS S42400      |                                 |   |
| A320†††             |                       |                 |                                 |   |
| Gr B8, B8M          |                       |                 |                                 |   |
| A 351               |                       |                 |                                 |   |
| Gr CF3, CF8, CF3M,  |                       |                 |                                 |   |
| CF8M                |                       |                 |                                 |   |
| B 463               |                       |                 |                                 |   |
| B 473               |                       |                 |                                 |   |
| UNS S20910          |                       |                 |                                 |   |
| UNS N08020          |                       |                 |                                 |   |
| UNS S31254          |                       |                 |                                 |   |

\*Caution: NACE Standard MR0175 is updated annually. It is the responsibility of the user of this table to consult the National Association of Corrosion Engineers (NACE) for the most current edition of MR0175.

\*\*Materials listed in this table should be used only under the conditions noted in the text of MR0175.

†Wrought condition only. Aging over 260°C (500°F) may reduce low-temperature toughness and reduce resistance to environmental cracking.

††Austenitic precipitation hardening stainless steel with chemical composition in accordance with UNS S66286 is acceptable at 35 HRC maximum hardness provided it is either in the solution annealed and aged or in the solution annealed and double aged condition.

†††Carbide solution treated.

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## 4-8.4.2.5 Corrosion Fatigue

The effect of the environment is shown by comparing the variation of fatigue-fracture stress with the number of stress cycles applied in air and in the environment of interest. The corrosion-fatigue strength is the stress at which no failure occurs after  $10^7$  or  $10^8$  cycles or some other experimentally feasible number of cycles; this value is not the corrosion-fatigue limit. It is, however, a convenient approximation of the stress level below which no failure can occur. If the test specimen contains a notch that acts as a stress raiser, the fatigue limits in air and in the test environment are reduced. Pitting, intergranular corrosion, and stress corrosion can produce stress raisers.

For stainless steels and higher alloys tensile strength is the most important property relating to resistance to corrosion fatigue. For example, increasing tensile strength by precipitation hardening improves corrosion-fatigue strength.

The factors that follow have a detrimental effect on corrosion-fatigue strength:

1. Sensitizing heat treatments of both austenitic and martensitic stainless steels
2. A surface stress raiser
3. A  $\text{pH} \leq 3$  which results in a 50% reduction of the corrosion-fatigue strength of cold-worked Type 316L.

## 4-8.4.2.6 Galvanic Corrosion

Guidelines relating to the galvanic coupling of stainless steels with other metals in aqueous solutions are given in Table 4-88, and the galvanic corrosion potentials of various materials in flowing seawater are given in Fig. 4-27. The corrosion potentials of the stainless steels are noble in this environment. In the presence of crevices, however, stainless steels may exhibit less noble potentials due to oxygen depletion within the crevice. Therefore, coupling a relatively large area with the small-area characteristic of a crevice may result in rapid attack of the material within the crevice. Another example of poor practice is to use mild steel fasteners (small anodes) to assemble stainless steel plates (large cathode). Under

TABLE 4-88. DEGREE OF CORROSION AT BIMETALLIC CONTACTS IN AQUEOUS ENVIRONMENTS (Ref. 131)

| METAL<br>CONSIDERED | CONTACT METAL                            |   |   |  |        |                                   |                        |
|---------------------|--|---|---|--|--------|-----------------------------------|------------------------|
|                     | GOLD,<br>PLATINUM,<br>RHODIUM,<br>SILVER | MONEL(1),<br>INCONEL(2),<br>NICKEL-<br>MOLYBDENUM<br>ALLOYS | CUPRONICKELS,<br>SILVER SOLDER,<br>ALUMINUM-<br>BRONZES,<br>TIN-BRONZES,<br>GUNMETALS | COPPER,<br>BRASSES,<br>"NICKEL<br>SILVERS" | NICKEL | LEAD, TIN,<br>AND SOFT<br>SOLDERS | STEEL AND<br>CAST IRON |
| Stainless steels    |  |   |   |  |        |                                   |                        |
| Type 304            | A*                                       | A   | A   | A  | A      | A                                 | A                      |
| Type 431            | C  | A or C(s)   | A or C(s)   | A or C(s)                                  | A      | A                                 | A                      |
| Type 410            | C  | C   | C   | C  | B or C | A                                 | A                      |

| METAL<br>CONSIDERED | CONTACT METAL |      |  |                  |             |             |          |          |                                       |
|---------------------|---------------|------|--|------------------|-------------|-------------|----------|----------|---------------------------------------|
|                     | CADMIUM       | ZINC | MAGNESIUM<br>AND<br>MAGNESIUM<br>ALLOYS<br>(CHROMATED) | STAINLESS STEELS |             |             | CHROMIUM | TITANIUM | ALUMINUM<br>AND<br>ALUMINUM<br>ALLOYS |
|                     |               |      |  | TYPE<br>304      | TYPE<br>431 | TYPE<br>410 |          |          |                                       |
| Stainless steels    |               |      |  |                  |             |             |          |          |                                       |
| Type 304            | A             | A    | A  | —                | A           | A           | A        | A        | A                                     |
| Type 431            | A             | A    | A  | A                | —           | A           | A        | (0)      | A                                     |
| Type 410            | A             | A    | A  | C                | C           | —           | C        | C        | A                                     |

\*A = The corrosion of the "metal considered" is not increased by the "contact metal".

B = The corrosion of the "metal considered" may be slightly increased by the "contact metal".

C = The corrosion of the "metal considered" may be markedly increased by the "contact metal". (Acceleration is likely to occur only when the metal becomes wet by moisture containing an electrolyte, e.g., salt, acid, or combustion products. In ships, acceleration may be expected to occur under in-board conditions because salinity and condensation are frequently present. Under less severe conditions the acceleration may be slight or negligible.)

s = Serious acceleration of corrosion of Type 431 stainless steel in contact with copper or nickel alloys may occur at crevices where the oxygen supply is low.

0 = No data available

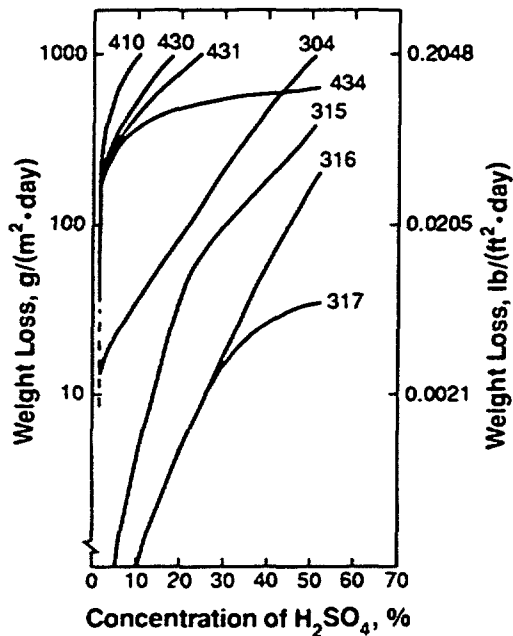
1 = Monel Alloy 400

2 = Inconel Alloy 600

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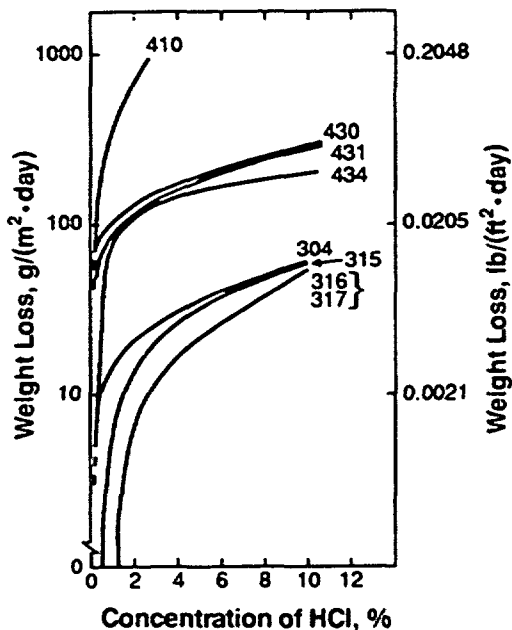


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**Figure 4-28. Corrosion Rates of Various Stainless Steels in Different Concentrations of Un-aerated Sulfuric Acid at 20° C (68° F) (Ref. 133).**



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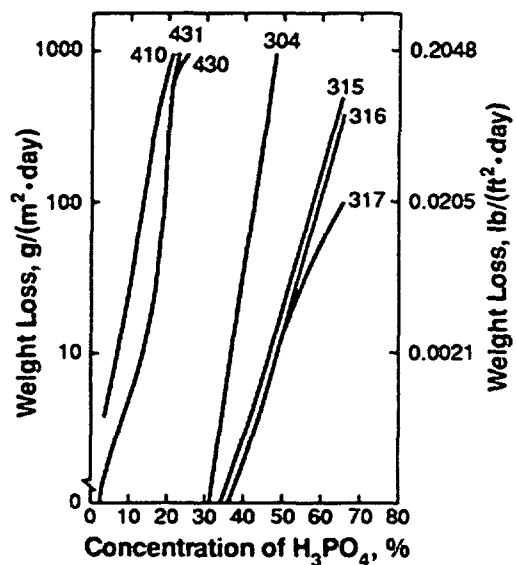
**Figure 4-29. Corrosion Rates of Various Stainless Steels in Hydrochloric Acid Solutions at 20° C (68° F) (Ref. 133)**

corrosion potential. The corrosion rates of stainless steels in boiling solutions of phosphoric acid are shown in Fig. 30. Phosphoric acid used in industry is often impure; therefore, testing in the service environment is desirable.

Stainless steels containing 18% chromium generally exhibit passive behavior toward nitric acid over a wide range of temperatures and pressures. The corrosion rates of some stainless steels in boiling nitric acid solutions are shown in Fig. 4-31. Type 304L is widely used for handling nitric acid. The corrosion rates of Type 304L are given in Fig. 4-32 as a function of nitric acid concentration and temperature. High-silicon stainless steels have been used for highly oxidizing conditions or for conditions under which aggressive corrosion products, such as hexavalent chromium ions, can accumulate and cause intergranular attack (Ref. 122).

Stainless steels have limited resistance to hydrofluoric acid. Sulfurous acid—generated by the dissolution of sulfur dioxide in water—can be handled by the grades of stainless steel containing molybdenum. Boric acid and carbonic acids do not corrode stainless steels.

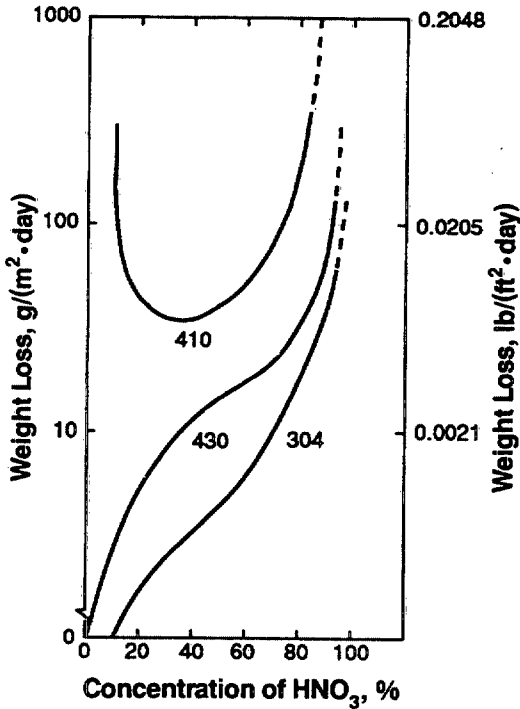
Organic acids can corrode stainless steel. Passive behavior is shown in the presence of oxidizers; however, increasing temperature favors active behavior. Some typical corrosion rates of stainless steels in organic acids are shown in Table 4-89. Higher alloy materials are preferred for handling concentrated hot solutions of formic acid contaminated with chlorides, which may cause pitting. Acetic acid at high temperatures may be handled by Type 304L, whereas acetic acid at low temperatures may be handled by Type 316L.



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**Figure 4-30. Corrosion Rates of Various Stainless Steels in Phosphoric Acid Solutions at Their Boiling Points (Ref. 133)**

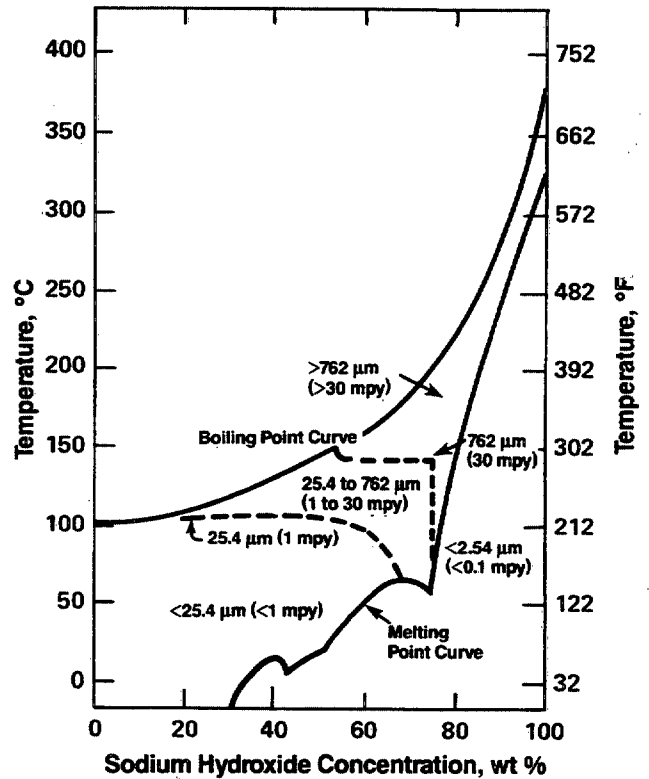
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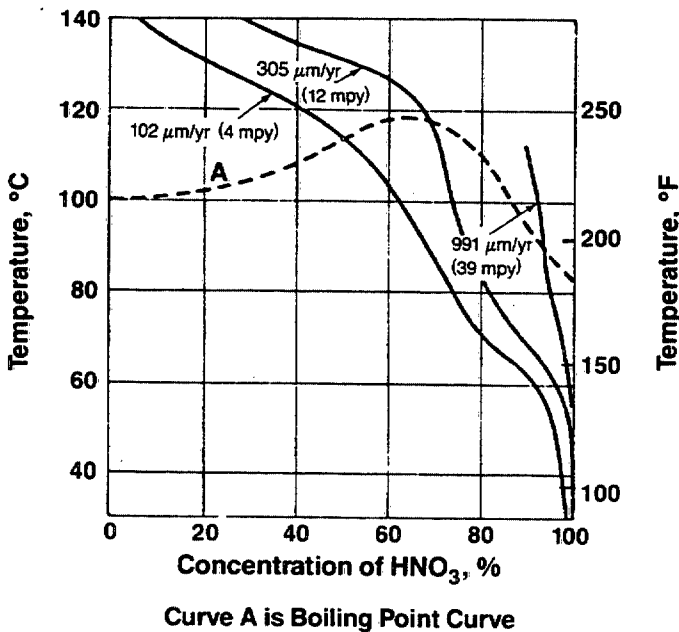
Figure 4-31. Corrosion Rates of Various Stainless Steels in Boiling Nitric Acid Solutions (Ref. 133)

Stainless steels exhibit active-passive behavior in sodium and potassium hydroxide solutions. Increasing concentrations and temperatures result in the active condition. Types 304 and 316 exhibit low corrosion rates over a wide range of temperatures and concentrations, as indicated in Fig. 4-33, caustic cracking may occur at elevated temperatures, as indicated in par. 4-8.4.2.4.2.



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Figure 4-33. Isocorrosion Chart for Types 304 and 316 Stainless Steels in Sodium Hydroxide (Ref. 135)



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Figure 4-32. Corrosion Behavior of Type 304L Stainless Steel in Nitric Acid Solutions of Various Concentrations and Temperatures (Ref. 124)

TABLE 4-89. CORROSION OF STAINLESS STEELS BY ORGANIC ACIDS (Ref. 134)

| ACID                 | CONCENTRATION | TEMPERATURE |     | CORROSION RATE   |          |                  |          |                  |          |                  |          |                  |     |
|----------------------|---------------|-------------|-----|------------------|----------|------------------|----------|------------------|----------|------------------|----------|------------------|-----|
|                      |               |             |     | 410              |          | 430              |          | 304              |          | 316              |          | 20Cb-3           |     |
|                      |               |             |     | $\mu\text{m/yr}$ | mpy      | $\mu\text{m/yr}$ | mpy      | $\mu\text{m/yr}$ | mpy      | $\mu\text{m/yr}$ | mpy      | $\mu\text{m/yr}$ | mpy |
| Acetic<br>(air-free) | 50%           | 24          | 75  | >1270            | >50      | 508 to 1270      | 20 to 50 | <508             | <20      | <51              | <2       | <51              | <2  |
|                      | 50%           | 100         | 212 | >1270            | >50      | 508 to 1270      | 20 to 50 | 508 to 1270      | 20 to 50 | <51              | <2       | <51              | <2  |
|                      | Glacial       | 24          | 75  | <508             | <20      | <508             | <20      | <51              | <2       | 508 to 1270      | 20 to 50 | <51              | <2  |
|                      | Glacial       | 100         | 212 | >1270            | >50      | >1270            | >50      | >1270            | >50      | >508             | >20      | <508             | <20 |
| Acetic<br>(aerated)  | 50%           | 24          | 75  | >1270            | >50      | <508             | <20      | <51              | <2       | <51              | <2       | <51              | <2  |
|                      | 50%           | 100         | 212 | >1270            | >50      | <508             | <20      | <51              | <2       | <51              | <2       | <51              | <2  |
|                      | Glacial       | 24          | 75  | >1270            | >50      | 508 to 1270      | 20 to 50 | <51              | <2       | <51              | <2       | <51              | <2  |
|                      | Glacial       | 100         | 212 | >1270            | >50      | >1270            | >50      | 508 to 1270      | 20 to 50 | 508 to 1270      | 20 to 50 | <508             | <20 |
| Formic               | 50%           | 24          | 75  | 508 to 1270      | 20 to 50 | 508 to 1270      | 20 to 50 | <51              | <2       | >1270            | >50      | <51              | <2  |
|                      | 50%           | 100         | 212 | >1270            | >50      | >1270            | >50      | <51              | <2       | >1270            | >50      | <51              | <2  |
|                      | 80%           | 24          | 75  | >1270            | >50      | 508 to 1270      | 20 to 50 | <51              | <2       | >1270            | >50      | <51              | <2  |
|                      | 80%           | 100         | 212 | >1270            | >50      | >1270            | >50      | <51              | <2       | >1270            | >50      | <51              | <2  |

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## 4-8.4.2.10 Corrosion by Hot Gases

The formation of an oxide scale on stainless steels by hot gases is a common form of corrosion. Oxidation can occur in oxygen, air, carbon dioxide, steam, and mixtures of these gases. Iron is alloyed with chromium to obtain oxidation resistance at elevated temperatures. The resistance of stainless steels to oxidation is associated with the formation of chromic oxide ( $\text{Cr}_2\text{O}_3$ ) scale. A thin, tenacious protective scale is formed at a chromium concentration of about 18 wt%, as shown in Fig. 4-34. Formation of the protective chromic oxide scale involves selective oxidation of chromium at the metal surface and depletes the chromium at the metal-to-oxide interface. Bulk chromium contents of about 25% in commercial stainless steels, such as Type 310, are required for good oxidation resistance.

Generally accepted maximum service temperatures in air are shown in Table 4-90 for wrought alloys and in Table 4-91 for cast stainless steels. Intermittent or cyclic service that involves thermal cycling can cause the scales to crack and spall and expose the alloy surface to the service environment.

The presence of water vapor decreases the resistance of stainless steels to oxidation in air. The temperature limits in moist air should be adjusted downward by 56 to 83 deg C (100 to 149 deg F) from those shown in Tables 4-90 and 4-91. In carbon dioxide service the temperature limits listed in Table 4-90 should be revised downward by 56 to 111 deg C (100 to 200 deg F) for the lower chromium alloys, such as Types 410, 430, 302, 321, 316, and 317. The higher chromium alloys, such as Types 309, 310, and 330, may be used at temperatures close to those listed for air in Table 4-90.

Attack by high-temperature oxidizing gases containing sulfur dioxide and air can form a mixed-oxide-plus-sulfide scale on the metal surface. Sulfide scales are formed in reducing gases such as hydrogen-hydrogen sulfide mixtures.

Rates of scale formation by high-chromium stainless steels are higher in dry sulfur dioxide than in air. Water vapor in an air-sulfur dioxide atmosphere accelerates attack. The generally accepted maximum service temperatures for stainless steels in sulfur dioxide are shown in Table 4-92.

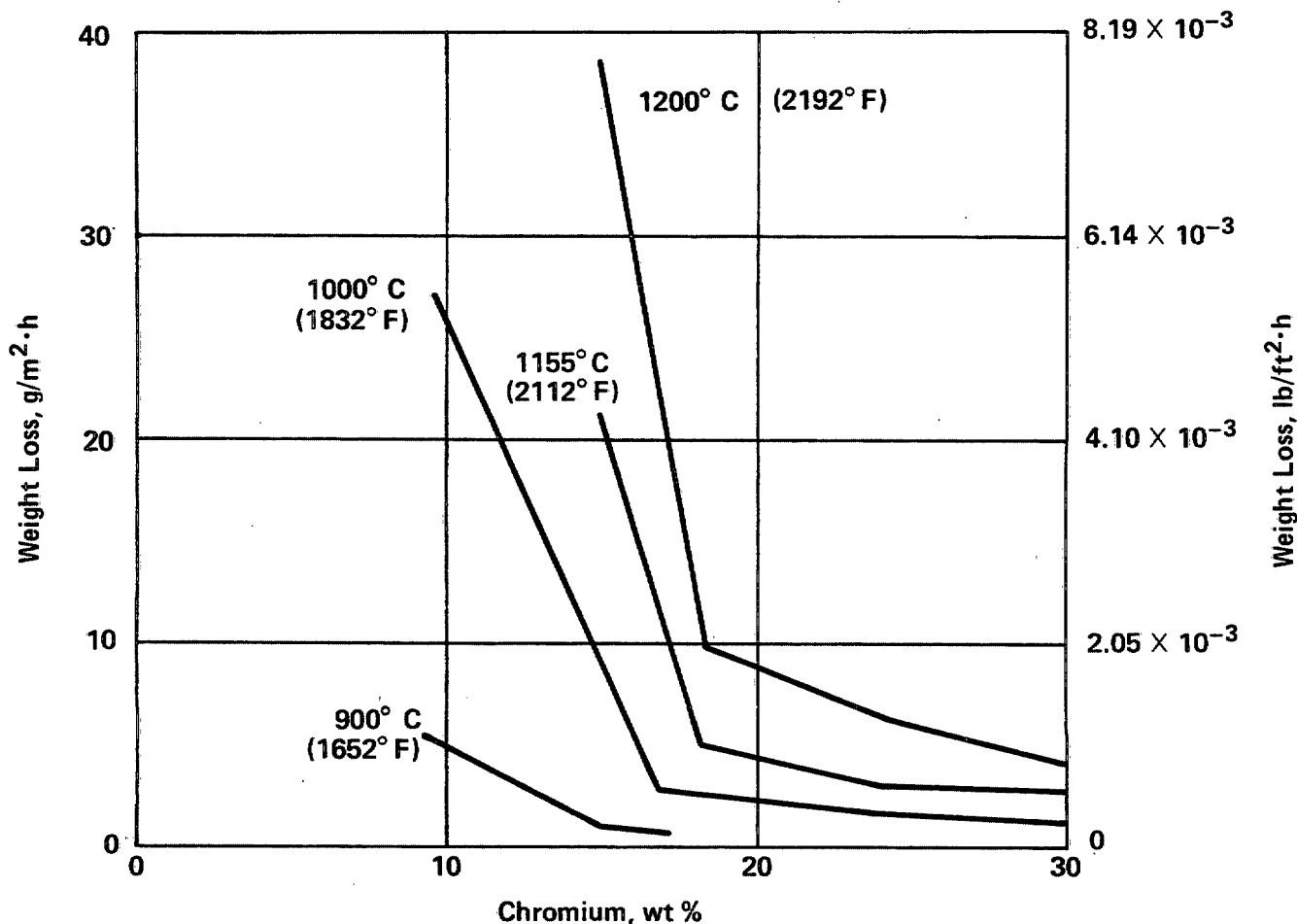


Figure 4-34. Effect of Alloyed Chromium on Oxidation of Steels Containing 0.5% C, 220 h

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TABLE 4-90. GENERALLY ACCEPTED MAXIMUM SERVICE TEMPERATURES IN AIR FOR WROUGHT STAINLESS STEELS (Ref. 136)

| MATERIAL    | INTERMITTENT SERVICE |      | CONTINUOUS SERVICE |      |
|-------------|----------------------|------|--------------------|------|
|             | °C                   | °F   | °C                 | °F   |
| AUSTENITIC  |                      |      |                    |      |
| 201         | 815                  | 1499 | 845                | 1553 |
| 202         | 815                  | 1499 | 845                | 1553 |
| 301         | 840                  | 1544 | 900                | 1652 |
| 302         | 870                  | 1598 | 925                | 1697 |
| 304         | 870                  | 1598 | 925                | 1697 |
| 308         | 925                  | 1697 | 980                | 1796 |
| 309         | 980                  | 1796 | 1095               | 2003 |
| 310         | 1035                 | 1895 | 1150               | 2102 |
| 316         | 870                  | 1598 | 925                | 1697 |
| 317         | 870                  | 1598 | 925                | 1697 |
| 321         | 870                  | 1598 | 925                | 1697 |
| 330         | 1035                 | 1895 | 1150               | 2102 |
| 347         | 870                  | 1598 | 925                | 1697 |
| MARTENSITIC |                      |      |                    |      |
| 406         | 815                  | 1499 | 1035               | 1895 |
| 410         | 815                  | 1499 | 705                | 1301 |
| 416         | 760                  | 1400 | 675                | 1247 |
| 420         | 735                  | 1355 | 620                | 1148 |
| 440         | 815                  | 1499 | 760                | 1400 |
| FERRITIC    |                      |      |                    |      |
| 405         | 815                  | 1499 | 705                | 1301 |
| 430         | 870                  | 1598 | 815                | 1499 |
| 442         | 1035                 | 1895 | 980                | 1796 |
| 446         | 1175                 | 2147 | 1095               | 2003 |

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**TABLE 4-91. GENERALLY ACCEPTED MAXIMUM SERVICE TEMPERATURES IN AIR FOR CAST STAINLESS STEELS (Ref. 136)**

| MATERIAL | WROUGHT COMPARATIVE | COMPOSITIONS PREFERRED FOR CYCLIC SERVICE | CONTINUOUS SERVICE |      |
|----------|---------------------|---|--------------------|------|
|          |                     |   | °C                 | °F   |
| HA       | —                   |   | 650                | 1202 |
| HC       | 446                 | Good                                      | 1120               | 2048 |
| HD       | —                   |   | 1065               | 1949 |
| HE       | —                   |   | 1065               | 1949 |
| HF       | 302B                |   | 900                | 1652 |
| HH       | 309                 |   | 1065               | 1949 |
| HI       | —                   |   | 1120               | 2048 |
| HK       | 310                 |   | 1095               | 2003 |
| HL       | —                   |   | 1150               | 2102 |
| HN       | —                   | Good                                      | 1095               | 2003 |
| HT       | 330                 | Very good                                 | 1035               | 1895 |
| HU       | —                   | Very good                                 | 1095               | 2003 |
| HW       | —                   | Excellent                                 | 1095               | 2003 |
| HX       | —                   | Excellent                                 | 1150               | 2102 |

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The corrosion rates of austenitic stainless steels in the reducing hydrogen-hydrogen sulfide environments are illustrated in Fig. 4-35. High-chromium Type 310 is favored for high-temperature hydrogen sulfide environments.

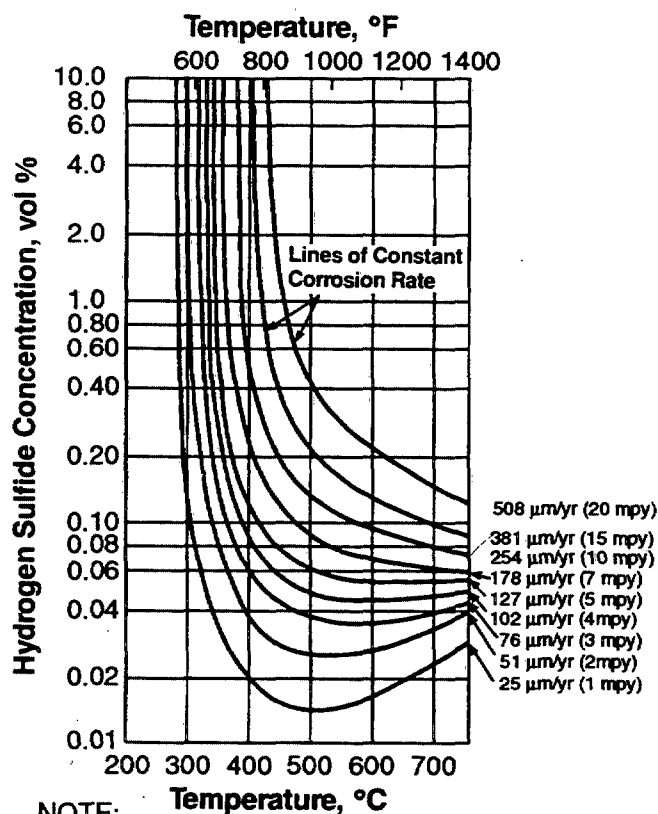
Stainless steels are attacked by sulfur vapor at elevated temperatures. Higher chromium types, such as Type 310, show the greatest resistance to attack.

The combustion products of most fossil fuels contain sulfur compounds. Oxidizing flue gases generally contain sulfur dioxide, carbon dioxide, nitrogen, water vapor, and oxygen. Reducing flue gases contain hydrogen sulfide, hydrogen, water vapor, carbon monoxide, carbon

**TABLE 4-92. GENERALLY ACCEPTED MAXIMUM SERVICE TEMPERATURES IN SULFUR DIOXIDE FOR SELECTED STAINLESS STEELS (Ref. 136)**

| MATERIAL | TEMPERATURE |      |
|----------|-------------|------|
|          | °C          | °F   |
| 304      | 800         | 1472 |
| 321      | 800         | 1472 |
| 347      | 800         | 1472 |
| 310      | 1050        | 1922 |
| 410      | 700         | 1292 |
| 430      | 800         | 1472 |
| 446      | 1025        | 1877 |

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NOTE:  
Pressure range 1.2 to 3.4 MPa (175 to 495 psi)  
and exposure times greater than 150 h.

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**Figure 4-35. Effect of Temperature and Hydrogen Sulfide Content on Corrosion Rate of Austenitic Stainless Steels (Ref. 137)**

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dioxide, and nitrogen. A high-chromium-content stainless steel has improved corrosion resistance in flue gases.

Stainless steels can form carbides of chromium and iron in high-temperature gases containing carbon compounds, such as carbon monoxide or hydrocarbons. These carbides may reduce ductility and toughness and thus cause failure. Large volume changes associated with carbide formation can generate high local stresses and result in cracking of the material below the carburized layer. Chromium imparts the greatest resistance to carburization. Other beneficial alloying elements are nickel, silicon, columbium, and titanium.

Atomic nitrogen produced by the dissociation of ammonia at elevated temperatures can form brittle nitride surface layers in stainless steel. High nickel content increases resistance to attack.

At high temperatures, e.g., 600°C (1112°F), stainless steels react with chlorine and hydrogen chloride gases to form a volatile chloride scale. Because nickel forms one of the least volatile chlorides, the maximum operating temperature is governed by the nickel content of the alloy. The upper temperature limit for stainless steel in dry chlorine and hydrogen chloride is about 320°C (608°F).

Low-melting sulfates and vanadates are generated by burning solid and liquid fuels containing sulfur, sodium, and vanadium. These compounds can react with the surface oxide scales on stainless steel to form liquid eutectics. Thus the presence of vanadates can result in very severe attack on the stainless steel.

### 4-8.4.3 Interface Problems

#### 4-8.4.3.1 Metal-to-Metal

Common metal-to-metal interface problems that can affect the corrosion of stainless steel include

1. Formation of crevices resulting in crevice corrosion, as described in par. 4-8.4.2.2
2. Fit-up between structural members creating tensile stresses necessary for stress-corrosion cracking
3. Dissimilar metals at joints between structural members and between a fastener and the structural member, as illustrated in Table 4-93, for exposure in quiet seawater for 6 mo and discussed in par. 4-8.4.2.6
4. Sensitization in which a metal zone is modified creating interfaces at the micro level as discussed in par. 4-8.4.2.3.

#### 4-8.4.3.2 Metal-to-Nonmetal

Metal-to-nonmetal interfaces may also create crevices and fit-up stresses in the metal member. However, the most serious problems in stainless steel-to-nonmetal interfaces are the creation and maintenance of a moist environment that contains chloride ions. The pitting corrosion that can result is discussed in par. 4-8.4.2.1.

### 4-8.4.4 Methods for Prevention of Corrosion

A stainless steel usually is selected for its resistance to corrosion in a particular environment even though less expensive alternative materials are available that possess comparable mechanical properties. Therefore, selection of the proper material is the primary defense against corrosion. For example, various kinds of coatings would not be considered to protect stainless steel against corrosion. If coatings were to be necessary, they could be applied to a less expensive material.

Pitting and crevice corrosion of austenitic steel in chloride solutions, such as seawater, can be suppressed by cathodic protection. However, cathodic protection causes hydrogen blistering if attempted on martensitic, e.g., Type 410, and ferritic, e.g., Type 430, stainless steels in seawater. Certain ions—sulfate, hydroxyl, chlorate, carbonate, chromate, and nitrate—tend to inhibit pitting in chloride solution. A pH greater than about 10 has an inhibiting effect on pitting, and flowing conditions reduce pitting. Surface inclusions and contaminants that may act as sites for initiation of pitting can be removed by chemical treatment.

Passive films that may form on corrosion-resistant steels are described in par. 3-6.1.3.

Sensitization to intergranular attack can be avoided by using low-carbon grades of austenitic stainless steels, by using stabilized grades of stainless steels, by avoiding the specific combinations of temperature and time required for sensitization of a specific composition, and by annealing to modify the sensitized microstructure.

Damage from hydrogen embrittlement can be avoided or reduced by avoiding the conditions that favor hydrogen generation or by baking the assembly to reduce the embrittling hydrogen species. Cracking is promoted by the presence of crevices, pitting and other stress raisers, hydrogen sulfide in the environment, low pH, elevated temperature, galvanic coupling to anodic materials, and cold-working.

Factors that have a detrimental effect on corrosion fatigue strength and that therefore should be avoided or minimized are sensitization of both austenitic and martensitic stainless steels, surface stress raisers, and a low pH.

In those environments in which stainless steels exhibit active-passive behavior, general corrosion can be minimized by adding oxidizers, which put the corrosion potential in the passive range. For example, nitric acid or cupric ions added to sulfuric acid and ferric and cupric ions added to phosphoric acid solutions maintain stainless steel in the passive range. Reduced temperatures and the concentration of some environmental species tend to promote passive behavior.

**TABLE 4-93. SUMMARY OF MARINE EXPOSURE RESULTS  
OF COUPLED METALS (Ref. 138)**

| BOLT             | PANEL                               |  |   |  |  |
|------------------|-------------------------------------|--|---|--|--|
|                  | Fiberglass<br>Type G-10             | Aluminum 5456  | HY-130 Steel                            | Titanium 6Al-4V                        | 17-4PH Stainless   |
| Aluminum 2024-T4 | no attack                           | mild pits and edge<br>corr; very<br>int galv<br>corr   | very mild galv<br>corr; general<br>corr | no attack                              | very int crev corr<br>and tunneling;<br>mild pits and<br>tunneling     |
| Without sealant  | pits in crev; *<br>pits in bolt end | no attack  | mild galv corr head                     | very int galv corr                     | very int galv corr   |
| With sealant     | no attack                           | very mild pits and<br>edge corr; very<br>int galv corr | general corr                            | no attack                              | very int tunneling   |
|                  | pits on entire<br>bolt              | corr exposed<br>threads                                | galv corr<br>exposed surfaces           | very int galv corr                     | galv corr head and end   |
| Anodized Steel   | no attack                           | no attack  | general corr                            | no attack                              | int tunneling  |
| Without sealant  | mild corr<br>exposed threads        | no attack  | int galv corr;<br>exposed surfaces      | missing;<br>prob very int<br>galv corr | missing;<br>prob very int<br>galv corr                                 |
| With sealant     | no attack                           | very mild pits and edge<br>corr; int galv<br>corr      | general corr                            | no attack                              | int galv corr under<br>sealant; mild<br>pits and very<br>int tunneling |
|                  | mild corr<br>exposed threads        | no attack  | int galv corr;<br>exposed surfaces      | missing;<br>prob very int<br>galv corr | missing;<br>prob very int<br>galv corr                                 |

\*corr = corrosion, crev = crevice, galv = galvanic, int = intense, prob = probably

(cont'd on next page)

**TABLE 4-93. (cont'd)**

| BOLT            | PANEL                |   |                                   |  |   |
|-----------------|----------------------|---|-----------------------------------|--|---|
|                 | Fiberglass Type G-10 | Aluminum 5456                               | HY-130 Steel                      | Titanium 6Al-4V  | 17-4PH Stainless  |
| 304 SS          | no attack            | mild pits and edge corr; galv corr          | very mild galv corr; general corr | no attack  | very int crev corr and tunneling; tunneling               |
| Without sealant | mild crev corr*      | no attack                                   | no attack                         | very int galv corr; very int pits and tunneling on threads | mild crev corr  |
| With sealant    | no attack            | very mild edge corr; galv corr              | general corr                      | no attack  | very int crev corr and tunneling; tunneling and mild pits |
|                 | mild crev corr       | no attack                                   | no attack                         | int crev corr; very int pits on threads                    | very int crev corr  |
| 316 SS          | no attack            | mild pits and edge corr; galv corr          | very mild galv corr; general corr | no attack  | very int crev corr and tunneling; tunneling and mild pits |
| Without sealant | very mild crev corr  | no attack                                   | no attack                         | crev corr  | no attack   |
| With sealant    | no attack            | mild pits and edge corr; very int galv corr | very mild galv corr; general corr | no attack  | very int tunneling and mild pits                          |
|                 | no attack            | no attack                                   | no attack                         | crev corr; pits on threads                                 | no attack   |
| A286            | no attack            | galv corr; mild edge corr                   | general corr                      | no attack  | very int crev corr and tunneling                          |
| Without sealant | very mild crev corr  | no attack                                   | no attack                         | int crev corr; pits on exposed surfaces                    | no attack   |

\*corr = corrosion, crev = crevice, galv = galvanic, int = intense, prob = probably

(cont'd on next page)

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TABLE 4-93. (cont'd)

| BOLT            | PANEL                   |  |   |   |  |
|-----------------|-------------------------|--|---|---|--|
|                 | Fiberglass<br>Type G-10 | Aluminum 5456  | HY-130 Steel                            | Titanium 6Al-4V                                     | 17-4PH Stainless                                       |
| A286 (cont'd)   |                         |  |   |   |  |
| With sealant    | no attack               | mild pits;<br>mild edge corr<br>*                    | general corr                            | no attack   | very int tunneling                                     |
|                 | no attack               | no attack  | no attack                               | int crev<br>corr;<br>int pits on<br>exposed threads | no attack  |
| MP35N           |                         |  |   |   |  |
| Without sealant | no attack               | pits and edge corr;<br>int galv corr                 | very mild galv corr;<br>general corr    | no attack   | very int crev corr<br>and tunneling;<br>mild tunneling |
| With sealant    | no attack               | very mild pits and<br>edge corr                      | very mild galv<br>corr; general<br>corr | no attack   | very int crev corr<br>and tunneling;<br>mild tunneling |
|                 | no attack               | no attack  | no attack                               | no attack   | missing;<br>prob no attack                             |
| Titanium        |                         |  |   |   |  |
| Without sealant | no attack               | very mild pits and<br>edge corr;<br>int galv<br>corr | general corr                            | no attack   | very int crev corr<br>and tunneling;<br>mild tunneling |
| With sealant    | no attack               | very mild pits and<br>edge corr;<br>int galv<br>corr | very mild galv corr;<br>general corr    | no attack   | very int crev corr<br>and tunneling; mild<br>tunneling |
|                 | no attack               | no attack  | no attack                               | no attack   | no attack  |

\*corr = corrosion, crev = crevice, galv = galvanic, int = intense, prob = probably

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**MIL-HDBK-735(MR)****4-8.4.5 Examples of Corrosion Problems****4-8.4.5.1 Intergranular Corrosion in Stainless Steel Components Handling Strong Nitric Acid**

Several instances of intergranular corrosion of stainless steel occurred in welded components handling strong nitric acid in the production of trinitrotoluene (TNT) (Ref. 139). The problems and potential solutions are shown in Table 4-94. In general, poor welding practice was the cause of these failures, although some operational practices could have contributed to them.

**4-8.4.5.2 Application of Type 304L Stainless Steel for Sulfuric Acid Handling in Ammunition Plants**

This use is described in par. 4-13.5.2. The summary of the results of electrochemical studies are that Type 304L stainless steel is suitable for use in the low-, middle-, and high-stage distillate environments. However, Type 304 stainless steel should not be used in H<sub>2</sub>SO<sub>4</sub> media in the 40 to 80% concentration range because the material shows unstable passivity.

**4-9 LEAD AND LEAD ALLOYS**

The utility of lead is determined by its physical and mechanical properties and by its corrosion resistance in various natural and chemical environments. Lead has a high density: 11339 kg/m<sup>3</sup> (707.9 lb/ft<sup>3</sup>). It has low strength and poor creep resistance. Lead is soft, easily formed, and has a low melting point, i.e., 327.5°C

(621.5°F). It is amphoteric, i.e., soluble in both acids and bases. Trace amounts of lead salts are toxic. Also lead is relatively inexpensive.

The uses of lead include

1. Roofing, fascia, and other architectural applications
2. Piping and vessels in the chemical process industry
3. Electrical cable sheathing
4. Shielding for ionizing radiation
5. Storage battery grids
6. Solders
7. Type metals for the printing industry
8. Bearings
9. Coatings for other metals
10. Ammunition.

The chemical composition and mechanical properties of some lead alloys are shown in Table 4-95. Small amounts of antimony or tin are added to lead to improve its corrosion resistance in the atmosphere. For example, overhead telephone cable sheathing containing 0.8% antimony is frequently used. Hard leads contain 3% to 18% antimony. A 10% antimonial alloy, for example, has greatly improved tensile strength and hardness. Antimonial lead and lead-calcium-tin alloys are used for grids in lead-acid battery plates. Lead and lead-tin compositions, including terne alloys, are used as protective coatings for other metals. Soft solders contain 50% lead and 50% tin. Chemical lead, such as that specified for sulfuric acid processing equipment, contains 0.06% copper. Tellurium lead is a work-hardening alloy that has high resistance to fatigue failure.

**TABLE 4-94. PROBLEMS AND POTENTIAL SOLUTIONS (Ref. 139)**

| COMPONENT ALLOY                             | PROBLEM   | SOLUTION<br>IMPROVE WELD TECHNIQUE  |
|---|---|---|
| Storage tank<br>316L SS*                    | Intergranular corrosion<br>Epitaxial solidification                     | Use A1 3003 or 5454   |
| Transfer line<br>316L SS                    | Intergranular corrosion<br>Epitaxial solidification                     | Extra-low carbon SS<br>Preweld shot peen<br>Postweld heat treat or use type<br>321/347 SS |
| Tubeturn flange<br>316L SS                  | Intergranular corrosion<br>Weld beading                                 | Extra-low carbon SS<br>Weld integrity   |
| American flange<br>Japanese pipe<br>304L SS | Intergranular corrosion<br>Epitaxial nucleation<br>Welding alloy filler | Extra-low carbon SS<br>Compatible weld filler   |
| German alloy<br>4541 (321 SS) condenser     | Weld and tube corrosion   | Use A1 3003, 5454   |

\*SS = stainless steel

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TABLE 4-95. LEAD ALLOYS (Ref. 2)

| ALLOY           | COMPOSITION, %                | CONDITION | MECHANICAL PROPERTIES     |                             |               |              |
|-----------------|-------------------------------|-----------|---------------------------|-----------------------------|---------------|--------------|
|                 |                               |           | YIELD STRENGTH, MPa (ksi) | TENSILE STRENGTH, MPa (ksi) | ELONGATION, % | HARDNESS, HB |
| Chemical lead   | 99.9 min Pb                   | Rolled    | 13 (1.9)                  | 17 (2.5)                    | 50            | 5            |
| Antimonial lead | 90 Pb, 10 Sb                  | Rolled    | —                         | 28 (4.1)                    | 47            | 13           |
| Tellurium lead  | 99.85 Pb, 0.04 Te,<br>0.06 Cu | Rolled    | 15 (2.2)                  | 21 (3.0)                    | 45            | 6            |
| 50-50 Solder    | 50 Pb, 50 Sn,<br>0.12 max Sb  | Cast      | —                         | 47 (6.8)                    | 50            | 14           |

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As a coating, lead provides an excellent corrosion barrier as long as it is pore-free. Lead does not provide appreciable sacrificial protection to steel. Lead corrosion products, however, do tend to plug scratches or pores and thereby protect the underlying metal. Lead coatings can be produced in several ways including hot dipping, electroplating, thermal spraying, and cladding. Sprayed coatings tend to be porous, whereas electrodeposited coatings can be pore-free if they are sufficiently thick. It is difficult to bond lead to steel; therefore, lead coatings often contain 2% tin to increase their bonding strength.

#### 4-9.1 TYPES OF CORROSION

The corrosion resistance of lead in many environments results from the formation of insoluble corrosion product films. The corrosion resistance of lead in many media can

be gaged by the solubility of the lead compounds that are formed. The solubility of various lead compounds in cold water is given in Table 4-96.

##### 4-9.1.1 Galvanic Corrosion

Lead is midway in the seawater galvanic series; therefore, it is cathodic to iron and anodic to copper. The galvanic behavior of lead depends to a large extent on the protective films that may be present on its surface. Protective films make the lead more cathodic than it would otherwise be. Iron coupled to lead is preferentially attacked in acid solutions, whereas in alkaline solutions lead-iron couples produce accelerated corrosion of the lead. Galvanic couples of lead and copper are common in equipment used to handle sulfuric, phosphoric, and sulfurous acids. The corrosion product film on the lead is

TABLE 4-96. SOLUBILITY OF LEAD COMPOUNDS (Ref. 140)

| COMPOUND       | SOLUBILITY,           |                             |
|----------------|-----------------------|-----------------------------|
|                | g/100 cm <sup>3</sup> | (lb/gal)                    |
| Lead acetate   | 44.3                  | (3.70)                      |
| Lead carbonate | 0.00011               | (9.2 × 10 <sup>-6</sup> )   |
| Lead chloride  | 0.99                  | (8.3 × 10 <sup>-2</sup> )   |
| Lead chromate  | 0.0000058             | (4.8 × 10 <sup>-7</sup> )   |
| Lead fluoride  | 0.064                 | (5.3 × 10 <sup>-3</sup> )   |
| Lead formate   | 1.6                   | (1.3 × 10 <sup>-1</sup> )   |
| Lead iodide    | 0.044                 | (3.7 × 10 <sup>-3</sup> )   |
| Lead nitrate   | 56.6                  | (4.72)                      |
| Lead oxalate   | 0.00016               | (1.3 × 10 <sup>-5</sup> )   |
| Lead oxide     | 0.0017                | (1.4 × 10 <sup>-4</sup> )   |
| Lead hydroxide | 0.016                 | (1.3 × 10 <sup>-3</sup> )   |
| Lead phosphate | 0.000014              | (1.2 × 10 <sup>-6</sup> )   |
| Lead sulfate   | 0.0044                | (3.7 × 10 <sup>-4</sup> )   |
| Lead sulfide   | 0.01244               | (1.038 × 10 <sup>-3</sup> ) |
| Lead sulfite   | Insoluble             |                             |

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highly protective in these acids. Aluminum-lead couples lead to severe galvanic attack on aluminum.

Because lead does not possess sufficient strength, it must be supported in many applications. In these cases, care should be taken to avoid galvanic attack. The protective films that normally form in atmospheric corrosion are electrically insulating, so they afford resistance against galvanic attack. However, if the corroding environment is such that the film is electrically conductive, local galvanic cells are created and cause localized attack. Lead sulfide is a conducting film that forms in the presence of hydrogen sulfide.

Lead and lead-tin coatings for steel are useful for atmospheric applications but not for immersion in aqueous solutions or in soil. Both lead and tin are cathodic to iron and accelerate corrosive action on steel at bare points, pores, and other discontinuities in a coating. In the atmosphere these bare points tend to become blocked with corrosion products, and this blockage stifles further attack. However, this sequence may not occur in an aqueous medium.

#### 4-9.1.2 Uniform Corrosion

##### 4-9-1.2.1 Weathering Corrosion

In the atmosphere the most resistant films are developed in industrial areas. In these areas sulfur compounds, such as sulfur dioxide and hydrogen sulfide, form surface films of sulfates and sulfides. Oxides and carbonates may predominate where there is less pollution. In marine locations chlorides are found in the corrosion product film; these chlorides are slightly soluble. However, the sulfates and carbonates present in sea salt would normally assist in the formation of a protective film.

The corrosion of lead in several atmospheres is shown in Table 4-97. Depending on location, these rates indicate that it would take 35 to 80 yr in most atmospheres for the average depth of penetration to reach 25.4  $\mu\text{m}$  (1 mil).

On steel panels with electroplated lead coatings, the corrosion attack on the steel is a function of the thickness

of the lead coating. The behavior in industrial, rural, and marine atmospheres is illustrated in Fig. 4-36. The protective corrosion film on the lead surface has provided better protection in the presence of the polluted New York City atmosphere (sulfur dioxide) than in the pollution-free atmosphere of State College, PA. The heaviest coatings are required for protection at the marine sites. Lead coatings are discussed in par. 3-7.1.5.

Terneplate is a lead-containing coating with superior characteristics. It is applied to steel, which has first been fluxed, by hot dipping. The molten bath contains 80% to 85% lead and 12% to 25% tin. The tin not only acts as a bonding agent but insures a smooth, continuous coating. Normally terneplate is not exposed to the atmosphere without painting, and it is readily painted without any surface preparation other than cleaning.

##### 4-9.1.2.2 Corrosion in Natural Water

Lead carbonate and lead oxide are the usual corrosion products in neutral aqueous solutions. The oxide itself, however, is not particularly protective. Aerated distilled water is moderately corrosive to lead in the absence of carbon dioxide. Lead is not attacked by pure distilled water that is free from dissolved gases, and lead is resistant to attack in nonpotable waters except for acid mine drainage. Natural runoff is likely to contain organic acids that dissolve sufficient lead to be dangerous for drinking. The presence of small amounts of nitrates in ground water also increases the corrosive attack on lead. The toxic properties of trace amounts of lead salts make it mandatory to exclude use of lead (and its alloys) in soft potable waters, carbonated beverages, and all food products. (Soft potable waters are those low in calcium salt content.)

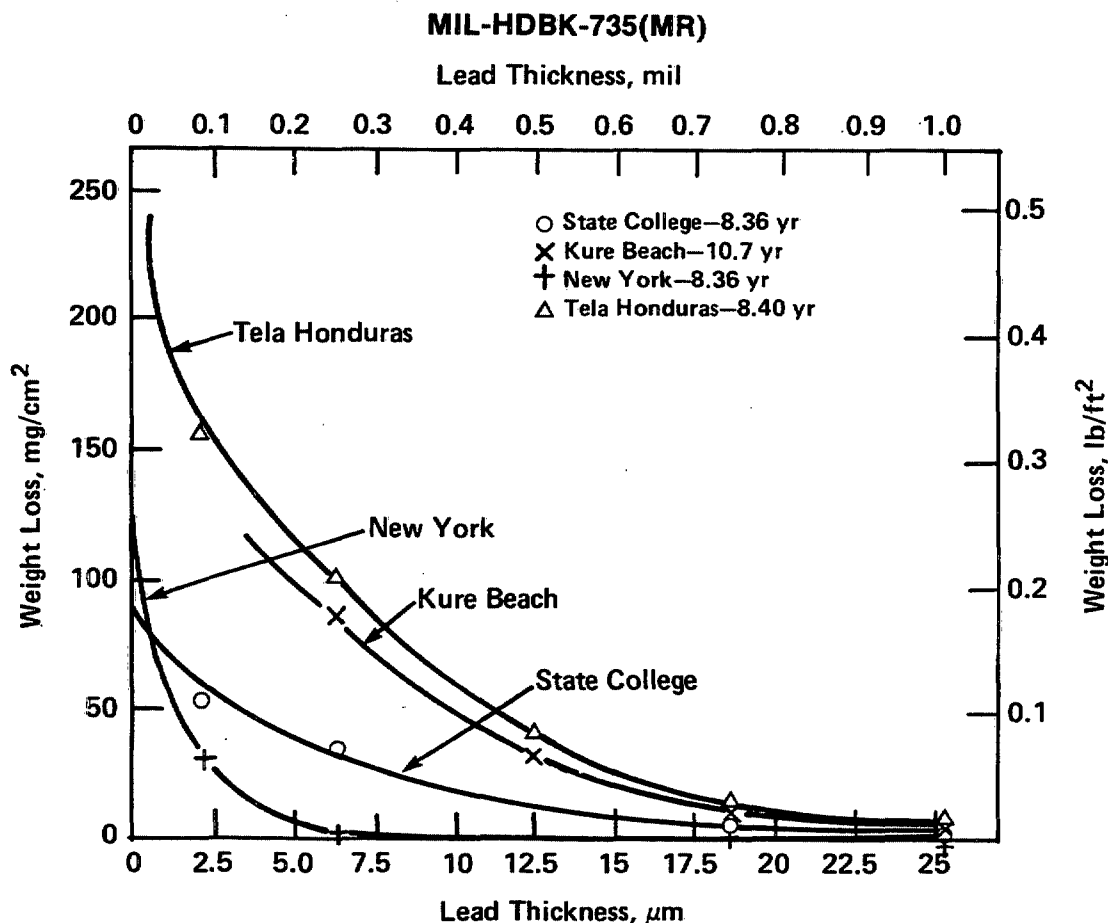
Lead and lead alloys are used in saltwater service as protective coatings on copper and other metals used for pipe, sheet, etc. In tests at Port Hueneme, CA, 99.5% sheet lead specimens were exposed for 30 mo at 0.6 m (2 ft) below the mean low tide level. The average corrosion rate was 5  $\mu\text{m}/\text{yr}$  (0.2 mpy) (Ref. 143).

TABLE 4-97. CORROSION PENETRATION OF LEAD (Ref. 141)

| TEST LOCATION     | CHEMICAL LEAD           |          | ANTIMONIAL LEAD         |          |
|-------------------|-------------------------|----------|-------------------------|----------|
|                   | $\mu\text{m}/\text{yr}$ | (mpy)    | $\mu\text{m}/\text{yr}$ | (mpy)    |
| Altoona, PA       | 0.734*                  | (0.0289) | 0.587*                  | (0.0231) |
| New York, NY      | 0.384                   | (0.0151) | 0.333                   | (0.0131) |
| Sandy Hook, NJ    | 0.538                   | (0.0212) | 0.511*                  | (0.0201) |
| Key West, FL      | 0.589*                  | (0.0232) | 0.559*                  | (0.0220) |
| LaJolla, CA       | 0.526                   | (0.0207) | 0.582                   | (0.0229) |
| State College, PA | 0.318                   | (0.0125) | 0.358                   | (0.0141) |
| Phoenix, AZ       | 0.104                   | (0.0041) | 0.305                   | (0.0120) |

\*10-yr rate used because 20-yr panels were missing  
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**Figure 4-36. Weight Loss of Steel vs Thickness of Lead Coating (Ref. 142)**

Lead alloys exhibit resistance to seawater. Babbit metal (80% lead, 15% antimony, and 5% tin) corrodes at a rate of  $152 \mu\text{m}/\text{yr}$  (6 mpy) in seawater, and solder (50% tin and 50% lead) corrodes at a rate of  $53 \mu\text{m}/\text{yr}$  (2.1 mpy).

#### 4-9.1.2.3 Corrosion in Acid Solutions

Lead has excellent resistance to sulfuric acid over a wide range of concentrations. The isocorrosion chart shown in Fig. 4-37 summarizes the corrosion resistance of lead to sulfuric acid within a concentration range of 50% to 100% and from  $24^\circ\text{C}$  ( $75^\circ\text{F}$ ) to the boiling point. Between 50% and 5%, the corrosion rate is less than  $127 \mu\text{m}/\text{yr}$  (5 mpy). Below 5% acid, however, a marked increase in corrosion occurs. The use of 3% antimonial lead is recommended in this range because antimonial lead (6%) has better resistance to sulfuric acid corrosion than chemical lead, even at high acid concentration.

Lead is not generally used in hydrochloric acid solutions. In cold, dilute acid (less than 1%), the rate of attack is about  $254$  to  $330 \mu\text{m}/\text{yr}$  (10 to 13 mpy). In quiet, 5% to 20% solutions at room temperature, the rate of attack is  $508 \mu\text{m}/\text{yr}$  (20 mpy). Agitation and aeration can greatly increase the corrosion rate. Antimony in lead greatly improves the resistance to attack by hydrochloric acid.

Lead is not resistant to hydrobromic acid.

Lead is resistant to hydrofluoric acid. The upper concentration limit for successful use is 60% to 65%, depending on temperature. At  $80^\circ\text{C}$  ( $176^\circ\text{F}$ ) the corrosion rate in 48% acid is  $3 \mu\text{m}/\text{yr}$  (0.12 mpy).

Lead cannot be used safely for handling nitric acid below concentrations of about 80%. The reduced solubility of lead nitrate in nitric acid at high concentrations does not extend to lower concentrations.

Lead is commonly used with the impure phosphoric acid solutions obtained by leaching phosphate rock with sulfuric acid. The pure acid is moderately corrosive, whereas hot or cold, impure acid is not.

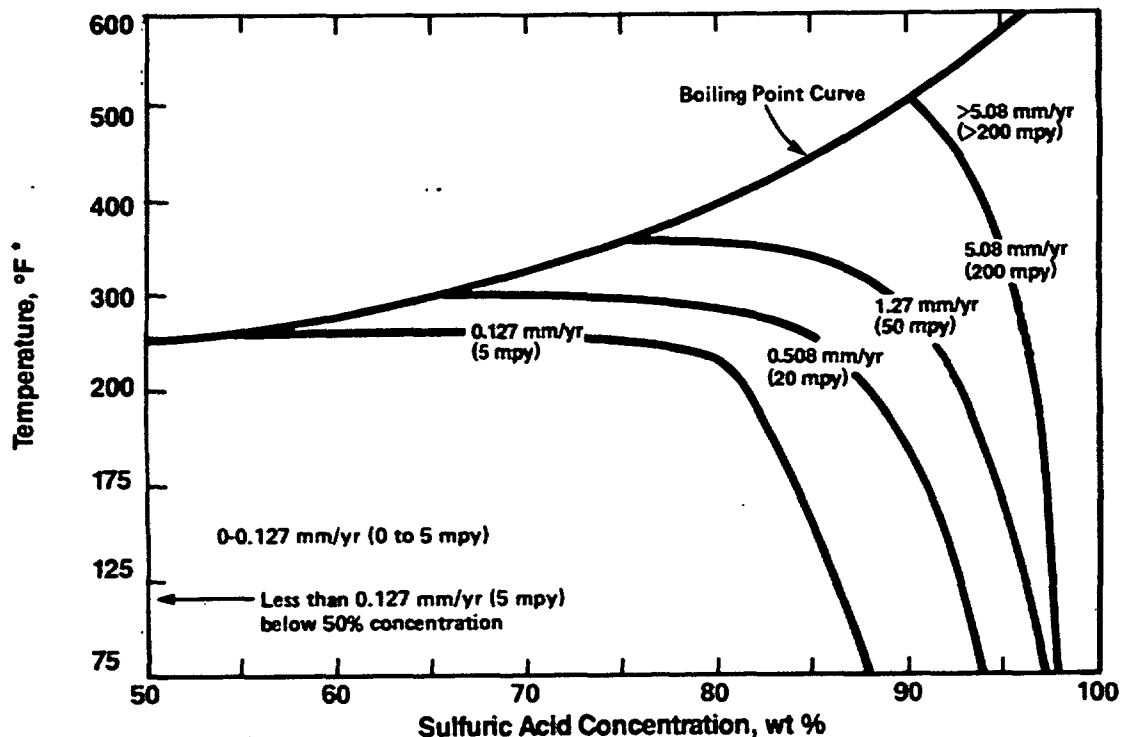
Chromic acid solutions, such as chromium-plating baths, are handled very satisfactorily with lead—lead chromate has extremely low solubility. Antimonial lead is particularly useful for handling electroplating solutions.

Mixtures of hydrochloric or nitric acid with sulfuric acid are highly corrosive to lead.

#### 4-9.1.2.4 Corrosion in Alkaline Solutions

Lead is amphoteric. The plumbates resulting from the reaction of lead with alkalis are very soluble; strong caustic solutions attack lead rapidly. Lead has moderate

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\*No temperature conversions were tried because of the unusual vertical scale.

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Figure 4-37. Corrosion of Lead by Sulfuric Acid as a Function of Temperature (Ref. 144)

resistance to dilute alkalis such as sodium and potassium hydroxide, i.e., up to 30% concentrations at room temperature. Ammonium hydroxide is much less corrosive than sodium hydroxide.

#### 4-9.1.2.5 Corrosion in Salt Solutions

Lead is resistant to most types of salt solutions. Lead and lead alloys have good resistance to neutral solutions in which lead carbonate and the oxide are formed on the surface. Lead will form protective films in the pH range of

about 3 to 11. The protective films that form become less protective in strongly acidic or alkaline solutions. Table 4-98 shows the corrosion of lead in several salt solutions.

#### 4-9.1.2.6 Corrosion in Organic Compounds

Lead is resistant to most organic compounds except the organic acids. Dilute acetic, formic, and most of the other organic acids—such as propionic, succinic, and lactic acids—corrode lead rapidly.

TABLE 4-98. CORROSION OF LEAD IN VARIOUS SALT SOLUTIONS (Ref. 145)

| SALT               | CONCENTRATION,<br>wt % | CORROSION RATE*  |             |
|--------------------|------------------------|------------------|-------------|
|                    |                        | $\mu\text{m/yr}$ | mpy         |
| Water (no salt)    | —                      | <2.5             | <0.1        |
| Sodium chloride    | 0.25 to 5.7            | 5.1 to 30.5      | 0.2 to 1.2  |
| Potassium chloride | 0.25 to 1.5            | 10.2 to 22.9     | 0.4 to 0.9  |
|                    | 3.8 to 7.4             | <2.5 to 2.5      | <0.1 to 0.1 |
| Potassium nitrate  | 0.5 to 9.2             | 22.9 to 76.2     | 0.9 to 3    |
| Sodium sulfate     | 0.25 to 2.0            | <2.5             | <0.1        |
|                    | 4.8 to 16.7            | <2.5             | <0.1        |
| Potassium sulfate  | 0.25 to 7.4            | <2.5 to 2.5      | <0.1 to 0.1 |

\*Based on 200-day test at 8°C (46°F)

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Some of the organic compounds that have little or no effect on lead are acetaldehyde, acetone, carbon tetrachloride, crude chlorosulfonic acid, and glycerin. Lead is resistant to most sulfonated organic compounds such as benzene sulfonic acid, naphthalene sulfonic acid, and sulfonated oils. Benzaldehyde and nitrophenols corrode lead.

**4-9.1.2.7 Corrosion in Gases**

Lead is resistant to wet or dry chlorine at temperatures under 100°C (212°F) and to dry bromine at lower temperatures.

Lead is not resistant to gaseous hydrogen fluoride.

**4-9.1.3 High-Temperature Corrosion**

Lead and high-lead alloys are not useful at very high temperatures because melting points are low and strength drops off rapidly above room temperature. However, lead is used at temperatures up to 232°C (450°F) when the lead is metallurgically bonded to steel.

**4-9.1.4 Pitting Corrosion in Soils**

The performance of lead and lead alloys underground depends to a large extent on the characteristics of the soil. In most soils the average corrosion rate is low; it ranges from 2.5 to 13  $\mu\text{m}/\text{yr}$  (0.1 to 0.5 mpy). The depth of pitting is the most important factor. In soils containing film-forming substances, such as silicates, sulfates, or carbonates, pitting is usually slight. However, in soils that are high in organic acids or nitrates or low in oxygen, pitting can be severe.

**4-9.1.5 Crevice Corrosion**

A metal such as lead that relies on the formation of an insoluble film for its corrosion resistance is subject to crevice corrosion attack. For example, a nonconducting substance pressed against the metal forms a crevice in which replenishment of the film-forming substances takes place slowly. Therefore, the protective film cannot be maintained within the crevice because the composition of the electrolyte within the crevice changes. Accordingly, the metal within the crevice is anodic to the protected surface adjacent to the crevice. In underground installations of lead pipe, crevice corrosion results from the chemical inhomogeneity of the soil or local changes in the environment. The local changes in the environment may be caused by aeration, moisture content, stray electrical currents, packing, backfill, and bacteria.

**4-9.1.6 Corrosion Fatigue**

Lead sheet and cable sheathing can fail by cracking as a result of fatigue. Hardening lead with alloying elements raises the fatigue limits.

**4-9.2 INTERFACE PROBLEMS**

Gold is used extensively to promote the solderability of electrical contacts. However, gold dissolves in tin-lead solder and forms a brittle intermetallic compound. This intermetallic compound looks and acts like a cold solder joint. The pickup of gold by solder is enhanced by thick gold, high impurity content of the gold, long soldering times, and high soldering temperatures.

If solder is applied to copper at a high temperature, a noble copper-tin phase is formed, and this noble phase can accelerate the galvanic attack of adjacent copper.

Lead is corroded by several dilute, aerated organic acids, e.g., formic and acetic acids. In contact with certain green woods, e.g., Douglas fir or oak, that slowly exude volatile acids, corrosion damage to lead can be serious. Woods that do not cause damage in this respect are seasoned cedar or hemlock. On setting certain plastics, e.g., room temperature vulcanizing (RTV) silicone rubbers, generate potentially corrosive organic acids.

Lead is attacked by waters that have become alkaline. For example, waters that have been in contact with wet portland cement can corrode lead.

Lead is widely used as a shield against penetrating ionizing radiation. Severe atmospheric corrosion of lead is a result of the interaction of the radiation with the environment. Radiation results in the formation of oxides of nitrogen in the atmosphere. The oxides of nitrogen in the air react with moisture in the air to form nitric acid, which readily attacks lead. However, high humidity in the air is necessary to produce the attack.

**4-9.3 METHODS FOR PREVENTION OF CORROSION**

Many applications of lead and lead alloys use the inherent corrosion resistance of the surface films that form in the environment to which the lead or the alloys are exposed. In some applications lead is a barrier that can be selected for its corrosion resistance on one side and yet can present a corrosion problem on the other, e.g., lead piping that is placed underground. Other applications employ lead for its properties not related to corrosion resistance, such as high density, malleability, lubricity, and low melting point. In some of these applications the inherent corrosion resistance to an environment is a collateral benefit. In others, if lead is to be used, it must be protected against corrosion attack.

Lead may be protected with organic coatings. For example, terneplate has good paint retention and will last almost indefinitely in any atmosphere if painted occasionally. Lead pipes buried in aggressive soil may be coated with an asphaltic compound that is then wrapped with paper while hot. Other forms of wrapping may also be used. Solder joints in electrical circuits are protected with conformal coatings.

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Babbit metal used in bearings is protected from corrosion by the lubricating oils present.

Cathodic protection may be applied to buried lead pipe. However, the cathodic protection process creates an alkaline environment, and lead tends to be sensitive to alkali attack. If excessive protective potentials are maintained, the environment can become so alkaline that the lead will corrode faster than if not cathodically protected. In addition, even if protection is maintained at an acceptable potential, interruption of the current for an extended period can result in attack of the lead surface by the alkaline environment.

### 4-9.4 EXAMPLES OF CORROSION PROBLEMS

The presence of lead in solders, braze alloys, free-machining steel, bearing surfaces, antifretting inserts, etc., should always be ascertained before a component is subjected to a potentially aggressive corrodent. Corrosion problems have occurred because the presence of lead was not ascertained before cleaning or pickling operations.

## 4-10 MAGNESIUM AND MAGNESIUM ALLOYS

Elemental magnesium has a density of  $1738.0 \text{ kg/m}^3$  ( $108.50 \text{ lb/ft}^3$ ), a melting point of  $649^\circ\text{C}$  ( $1200^\circ\text{F}$ ), and a boiling point of  $1091^\circ\text{C}$  ( $1995^\circ\text{F}$ ). Several characteristics of magnesium are exploited in applications. These characteristics include

1. High strength-to-weight ratio in castings
2. High stiffness-to-weight ratio in wrought forms
3. Ease of fabrication into assemblies that includes good hot formability and excellent machinability
4. A low elastic modulus that contributes to the high stiffness-to-weight ratio, gives good resistance to denting, and also results in a high damping factor. (The damping capacity of a material in vibration is the ratio of the energy absorbed per cycle to the total energy per cycle.)

Other properties of magnesium, such as those that follow, may be detrimental to some applications:

1. Relatively high notch sensitivity, which can be compensated for by proper design that minimizes the effects of stress concentrations
2. Low hardness values
3. Potential corrosion hazards
4. Potential fire hazard, particularly in the finely divided state.

The properties of magnesium have led to a wide range of applications; most of which use the high strength- and high stiffness-to-weight ratios. Some examples of magnesium applications are airframe and missile components; gear cases and machinery housings; road wheels and landing gears; instrument components, frames, and cases; shipping containers; and portable ramps and ladders.

In spite of its positive mechanical properties, the corrosion characteristics of magnesium have resulted in severe restrictions on its use in Army materiel. For example, guidance on the use of magnesium in air vehicles (Ref. 18) states,

"Magnesium alloys shall be used only with specific approval of the procuring activity. Use of magnesium shall be restricted to noncorrosion prone areas where adequate protection systems can be maintained with ease and high reliability. Magnesium alloys shall not be used in primary flight control systems, for landing gear wheels, for primary structures or other areas subject to abuse, foreign object damage, or to abrasion. Magnesium alloys also are forbidden in any location where fluid or moisture entrapment is possible."

### 4-10.1 TYPES OF ALLOYS

Commercially pure magnesium is the starting point for producing magnesium alloys. However, commercially pure magnesium produced in the United States is contaminated with various elements, especially iron, and these contaminants are highly detrimental to corrosion resistance. For example, the corrosion rate of commercially pure magnesium in 3% sodium chloride solution is 100 to 500 times greater than that of chemically pure magnesium ( $99.95 + \% \text{ Mg}$ ) containing less than 10 ppm of iron, nickel, and copper combined. Because the corrosion rate of chemically pure magnesium in 3% sodium chloride solution is about  $250 \mu\text{m/yr}$  (10 mpy), a rate 100 to 500 times greater is unacceptable. Therefore, commercially pure magnesium has little direct application. Alloying with various elements, however, improves the corrosion resistance and the mechanical properties of commercially pure magnesium.

The corrosion rate of chemically pure magnesium is greatly increased when it is alloyed with the following elements in excess of the concentrations listed: 2% zinc, 0.3% calcium, 0.5% silver, 0.1% copper, 0.017% iron, and 0.0005% nickel. These concentrations are the magnesium tolerance limits. The increase in corrosion rate when the tolerance limit is exceeded is gradual with zinc, more rapid with calcium and silver, and precipitous with copper, iron, and nickel.

Addition of up to 5% lead, tin, or aluminum has little effect on the corrosion rate of chemically pure magnesium in saltwater. Sodium, silicon, manganese, thorium, zirconium, cerium, praseodymium, and neodymium also have little effect on corrosion resistance in salt water even when these elements are alloyed in excess of their maximum solubilities.

The addition of 1% manganese increases the tolerance limit for nickel to nearly 0.010% but has little effect on the tolerance limit for copper.

Although the addition of 1% zinc does not appreciably

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affect the tolerance limits for iron, copper, and nickel, it does make the increase in corrosion rate more gradual when the tolerance limit is exceeded.

Much, but not all, of the alloying of magnesium is done to overcome the adverse corrosion effects of iron, copper, and nickel contaminants in the commercially pure magnesium.

The cast and wrought magnesium may be considered in two categories:

1. Alloys based upon aluminum as the principal alloying component. These alloys can be heat-treated in the cast form to achieve good strength properties, although ductility of fully heat-treated alloys is low. The cast forms tend to show microporosity. However, adding aluminum to magnesium reduces the tolerance limit for iron. Adding 0.2% manganese tends to counteract the tolerance-reducing effect of aluminum. Adding 3% zinc to magnesium-aluminum-manganese alloys improves the tolerance limits for iron, copper, and nickel. Furthermore, the harmful effect of exceeding the zinc tolerance level of 2% does not occur when 3% zinc is added to magnesium-aluminum-manganese alloys. Both manganese and zinc are added to nearly all domestic commercial magnesium-aluminum alloys because of their ability to reduce the effect of contaminants in the commercially pure aluminum.

2. Alloys that depend upon the grain-refining effect of zirconium. These alloys show good ductility, but little increase in strength. The magnesium-zirconium matrix is strengthened in various ways, such as by adding zinc. Zirconium is a scavenging element that removes iron, aluminum, silicon, and some other elements to low levels. The removal of these elements results in high-purity alloys.

Thorium is added to improve creep resistance at temperatures up to 300°C (572°F) and to reduce porosity. Rare earth elements also improve creep resistance and reduce microporosity in magnesium alloys.

Table 4-99 gives the composition of several magnesium alloys. Tempers of the alloys are designated by the letters and numbers that follow the letter and numbers designating the composition. The temper code is essentially that applied to aluminum alloys which is given in Table 4-5. The temper and composition designations are separated by a hyphen. The mechanical properties of some magnesium alloys are shown in Table 4-100.

### 4-10.2 TYPES OF CORROSION

There is no distinction between the corrosion responses of alloys containing aluminum or zirconium. From a corrosion perspective both types attempt to overcome the presence of corrosion-enhancing contaminants.

#### 4-10.2.1 Uniform Corrosion

##### 4-10.2.1.1 Weathering Corrosion

Magnesium is highly reactive chemically; therefore, it is not highly resistant to corrosion. Nevertheless, it does have good resistance to atmospheric environments, which is attributed to the formation of a protective surface film. Susceptibility to weathering corrosion depends on how the atmosphere affects the protective film. The film may be converted to soluble bicarbonates, sulfites, and sulfates, which are washed away by rain, or the film may break down under the influence of chloride ion.

Magnesium alloys containing aluminum have somewhat better resistance to atmospheric corrosion than the other alloys. Aluminum concentrates in the protective film as the magnesium is leached away. Exposure tests of magnesium alloys demonstrate the beneficial effect of aluminum in rural and industrial sites, but not at seacoast locations (Ref. 147). In atmospheric exposure tests that included an alloy that was specially treated to reduce the iron content, the corrosion of the low-iron alloy was about one third that of the high-iron alloy at a marine location (Ref. 146).

The corrosion behavior of magnesium alloys in weathering environments is usually below 51  $\mu\text{m}/\text{yr}$  (2 mpy) with few exceptions. The corrosion rate of two magnesium alloys, AZ80A and ZK61A, in various atmospheric environments has been compared to the rate of low-carbon steel (Ref. 148). The corrosion of the zirconium-containing ZK61A alloy was similar to that of low-carbon steel, whereas the rate of corrosion of the aluminum-containing AZ80A alloy was generally much less.

Magnesium alloys exposed to weathering environments show fine pitting. The percent loss in strength by corrosion, however, is only slightly greater than the percent reduction in metal cross section calculated from weight loss data. Also the ductility of these alloys can be significantly reduced by exposure to weathering environments.

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TABLE 4-99. COMPOSITION OF MAGNESIUM ALLOYS  
(AS DESIGNATED BY ASTM) (Ref. 146)

| ALLOY                 | Al, %    | Zn, %    | Mn, %    | Zr, %    | Th, %   | RARE<br>EARTHS,<br>% | MAXIMUM |       |       |           |
|-----------------------|----------|----------|----------|----------|---------|----------------------|---------|-------|-------|-----------|
|                       |          |          |          |          |         |                      | Si, %   | Cu, % | Ni, % | Others, % |
| <i>Wrought Alloys</i> |          |          |          |          |         |                      |         |       |       |           |
| AZ31B*,**             | 2.5-3.5  | 0.6-1.4  | 0.20 min | —        | —       | —                    | 0.10    | 0.05  | 0.005 | 0.30      |
| AZ31C                 | 2.4-3.6  | 0.50-1.5 | 0.15 min | —        | —       | —                    | 0.10    | 0.10  | 0.03  | 0.30      |
| AZ61A*                | 5.8-7.2  | 0.40-1.5 | 0.15 min | —        | —       | —                    | 0.10    | 0.05  | 0.005 | 0.30      |
| AZ80A*                | 7.8-9.2  | 0.20-0.8 | 0.12 min | —        | —       | —                    | 0.10    | 0.05  | 0.005 | 0.30      |
| HK31A                 | —        | —        | —        | 0.40-1.0 | 2.5-4.0 | —                    | —       | 0.10  | 0.01  | 0.30      |
| HM21A                 | —        | —        | 0.45-1.1 | —        | 1.5-2.5 | —                    | —       | —     | —     | 0.30      |
| HM31A                 | —        | —        | 1.2 min  | —        | 2.5-3.5 | —                    | —       | —     | —     | 0.30      |
| M1A                   | —        | —        | 1.2 min  | —        | —       | —                    | 0.10    | 0.05  | 0.01  | 0.30      |
| ZE10A                 | —        | 1.0-1.5  | —        | —        | —       | 0.12-0.22            | —       | —     | —     | 0.30      |
| ZK60A                 | —        | 4.8-6.2  | —        | 0.45 min | —       | —                    | —       | —     | —     | 0.30      |
| <i>Cast Alloys</i>    |          |          |          |          |         |                      |         |       |       |           |
| AM100A                | 9.3-10.7 | 0.30 max | 0.10 min | —        | —       | —                    | 0.30    | 0.10  | 0.01  | 0.30      |
| AZ63A                 | 5-3-6.7  | 2.5-3.5  | 0.15 min | —        | —       | —                    | 0.30    | 0.25  | 0.01  | 0.30      |
| AZ81A                 | 7.0-8.1  | 0.40-1.0 | 0.13 min | —        | —       | —                    | 0.30    | 0.10  | 0.01  | 0.30      |
| AX91A                 | 8.3-9.7  | 0.35-1.0 | 0.13 min | —        | —       | —                    | 0.50    | 0.10  | 0.03  | —         |
| AZ91B                 | 8.3-9.7  | 0.35-1.0 | 0.13 min | —        | —       | —                    | 0.50    | 0.35  | 0.03  | —         |
| AZ91C                 | 8.1-9.3  | 0.40-1.0 | 0.13 min | —        | —       | —                    | 0.30    | 0.10  | 0.01  | 0.30      |
| AZ92A                 | 8.3-9.7  | 1.6-2.4  | 0.10 min | —        | —       | —                    | 0.30    | 0.25  | 0.01  | 0.30      |
| EZ33A                 | —        | 2.0-3.1  | —        | 0.50-1.0 | —       | 2.5-4.0              | —       | 0.10  | 0.01  | 0.30      |
| HK31A                 | —        | —        | —        | 0.40-1.0 | 2.5-4.0 | —                    | —       | 0.10  | 0.01  | 0.30      |
| HZ32A                 | —        | 1.7-2.5  | —        | 0.50-1.0 | 2.5-4.0 | 0.10 max             | —       | 0.10  | 0.01  | 0.30      |
| K1A                   | —        | —        | —        | 0.40-1.0 | —       | —                    | —       | —     | —     | 0.30      |
| QE22A†,††             | —        | —        | —        | 0.40-1.0 | —       | 1.8-2.5              | —       | 0.10  | 0.01  | 0.30      |
| ZE41A                 | —        | 3.5-5.0  | 0.15 max | 0.40-1.0 | —       | 0.75-1.75            | —       | 0.10  | 0.01  | 0.30      |
| ZH62A                 | —        | 5.2-6.2  | —        | 0.50-1.0 | 1.4-2.2 | —                    | —       | 0.10  | 0.01  | 0.30      |
| ZK51A                 | —        | 3.6-5.5  | —        | 0.50-1.0 | —       | —                    | —       | 0.10  | 0.01  | 0.30      |
| ZK61A                 | —        | 5.5-6.5  | —        | 0.60-1.0 | —       | —                    | —       | 0.10  | 0.01  | 0.30      |

\*0.005% Fe maximum

\*\*0.04% Ca maximum

†2.0 to 3.5% Ag

††Rare earth elements in the form of didymium

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TABLE 4-100. MECHANICAL PROPERTIES OF SOME MAGNESIUM ALLOYS (Ref. 2)

| ALLOY         | DESIG-NATION | UNS    | COMPOSITION, %                      | CONDI-TION                   | MECHANICAL PROPERTIES     |                             |                                  |               |
|---------------|--------------|--------|-------------------------------------|------------------------------|---------------------------|-----------------------------|----------------------------------|---------------|
|               |              |        |                                     |                              | YIELD STRENGTH, MPa (ksi) | TENSILE STRENGTH, MPa (ksi) | ELON-GATION IN 51 mm, (2 in.), % | HARD-NESS, HB |
| Wrought alloy | AZ31B        | M11311 | 2.5-3.5 Al, 0.20 min Mn, 0.6-1.4 Zn | Annealed                     | 103 to 124 (15 to 18)     | 221 (32)                    | 9 to 12                          | 56            |
| Cast alloy    | AZ91C        | M11914 | 8.1-9.3 Al, 0.13 min Mn, 0.4-1.0 Zn | As cast                      | 76 (11)                   | 159 (23)                    | —                                | 60            |
| Cast alloy    | EZ33A        | M12330 | 2.0-3.1 Zn, 0.5-1.0 Zr              | Aged                         | 97 (14)                   | 138 (20)                    | 2                                | 50            |
| Wrought alloy | HK31A        | M13310 | 0.3 Zn, 2.5-4.0 Th, 0.4-1.0 Zr      | Strain-hardened and annealed | 165 to 179 (24 to 26)     | 228 to 234 (33 to 34)       | 4                                | 57            |

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#### 4-10.2.1.2 Corrosion in Natural Waters

##### 4-10.2.1.2.1 Freshwaters

Magnesium alloys rapidly form a protective film in stagnant distilled water at room temperature. However, the film is dissolved if the magnesium alloy is exposed to continuously refreshed, rapidly flowing demineralized water.

The susceptibility of magnesium alloys to corrosion in deionized water increases greatly as the temperature increases. For example, AZ31B has a corrosion rate of 432  $\mu\text{m}/\text{yr}$  (17 mpy) in water at 100°C (212°F) compared to 30,480  $\mu\text{m}/\text{yr}$  (30.48 mm/yr (1200 mpy)) at 150°C (302°F).

Corrosion of magnesium alloys by water can be inhibited by the addition of fluoride ion. For example, the corrosion of AZ31B alloy in stagnant deionized water at 150°C (302°F) was reduced from 27,940  $\mu\text{m}/\text{yr}$  (27.94 mm/yr (1100 mpy)) to 7112  $\mu\text{m}/\text{yr}$  (7.1 mm/yr (280 mpy)) by the addition of 10 ppm sodium fluoride (Ref. 149).

Waters that contain acid gases  $\text{CO}_2$  and  $\text{SO}_2$  from the atmosphere increase the corrosion rate of magnesium alloys. In the presence of dissolved  $\text{CO}_2$ , a soluble magnesium bicarbonate film forms that is not protective. About 0.25 g/l ( $2.1 \times 10^{-3}$  lb/gal) magnesium will dissolve in water equilibrated with air that contains its normal 300-ppm concentration of  $\text{CO}_2$ . If the solution is not changed, it becomes saturated with magnesium carbonate, and the apparent corrosion rate decreases.

Waters that have high temporary hardness are corrosive to magnesium alloys because the bicarbonate ion reacts with the protective magnesium hydroxide film. Pits that

are formed will not grow to appreciable depth if the temporary hardness of the water is low and if the sum of the chloride and sulfate concentrations is less than about 100 ppm.

##### 4-10.2.1.2.2 Seawater

The corrosion rate of magnesium alloys in seawater is about 250  $\mu\text{m}/\text{yr}$  (10 mpy). If unprotected, magnesium alloys are not suitable for service in seawater.

#### 4-10.2.1.3 Corrosion in Acid Solutions

With the exceptions of hydrofluoric acid and chromic acid, all of the mineral acids vigorously attack magnesium and its alloys. The corrosion of magnesium alloys decreases with an increasing concentration of hydrofluoric acid.

Magnesium is highly resistant to fluorine-containing chemicals because of the formation of an insoluble surface film of crystalline magnesium fluoride. This corrosion resistance includes liquid fluorine, hot fluorine gas, chlorine trifluoride, and perchloryl fluoride.

Boiling 20% chromic acid is widely used for cleaning corrosion products from magnesium alloys without attacking the metal itself. However, the passive film produced by chromic acid can be destroyed by traces of chloride in the corrosion products being removed. Therefore, a small amount of a silver salt, such as silver chromate, is usually added to the chromic acid to remove any chloride contamination as insoluble silver chloride.

Aqueous solutions of organic acids attack magnesium, so dilute acetic acid inhibited by sodium nitrite is used as a pickling treatment for magnesium alloys.

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### 4-10.2.1.4 Corrosion in Alkaline Solutions

Magnesium has good resistance to corrosion in strong alkalis at temperatures less than 60°C (140°F).

### 4-10.2.1.5 Corrosion in Aqueous Solutions

In solutions of alkaline metal salts or alkaline earth metal salts, anions with oxidizing power or those capable of forming insoluble magnesium salts result in less attack than anions that form soluble magnesium salts. For example, magnesium suffers little attack from alkalis, chromates, fluorides, nitrates, or phosphates. However, vigorous corrosion occurs in solutions of chlorides, bromides, iodides, or sulfates because soluble magnesium salts form on the surface.

Neutral solutions of heavy-metal salts, such as iron, copper, and nickel, generally cause severe attack of magnesium alloys.

In those neutral solutions in which there is normally little corrosion, lowering the pH increases the solubility of the surface films and causes attack. For example, chromate solutions that stifle attack at higher pH levels become corrosive if made acidic. However, if either chromic or hydrofluoric acid is used to lower the pH, the acid attack will not occur.

Solutions combining film-forming salts with salts that cause film breakdown produce deep, localized pitting. Chromate solutions containing chlorides in minor amounts are of this type.

### 4-10.2.1.6 Corrosion in Organic Chemicals

Magnesium and its alloys are not affected by aliphatic and aromatic hydrocarbons, ketones, ether, glycols, or alcohols with the exception of methyl alcohol. The reaction with methyl alcohol is inhibited by the presence of water in the alcohol.

Most alkyl halides, when dry, cause little corrosion of magnesium; however, wet, boiling alkyl halides usually hydrolyze to yield acids that corrode magnesium.

### 4-10.2.2 Galvanic Corrosion

Magnesium is highly active in the electromotive force (EMF) series, and it has little tendency to polarize in most environments. Therefore, magnesium and magnesium alloys are also highly active in the galvanic series.

The dissimilar metals most frequently involved in structures with magnesium alloys are

1. Aluminum alloys
2. Iron, copper, and nickel alloys.

Very pure aluminum (alloy 1099) is almost completely compatible with magnesium alloys in chloride solutions. Aluminum containing magnesium, manganese, or silicon alloying elements has equivalent compatibility. Zinc, however, has a small adverse effect; iron, copper, and nickel can have large adverse effects as alloying elements

in aluminum. Nevertheless, the adverse effect of these elements on galvanic compatibility with magnesium alloy may be mitigated by magnesium in the aluminum alloy or magnesium ion in the electrolyte solution. Rivets of Type 5056 aluminum, which contains about 5% magnesium, have been used extensively in magnesium alloy structures without causing significant galvanic attack. Series 5XXX and 6XXX aluminum alloys are the most compatible in magnesium-aluminum galvanic couples.

Corroding couples of magnesium alloys and aluminum alloys often generate an alkaline environment that may result in corrosion of the aluminum alloy and in galvanic corrosion of the more reactive magnesium.

Iron alloys, copper alloys, and nickel alloys are incompatible with magnesium alloys. There is little significant difference among these metal alloys in the galvanic attack they can cause on magnesium alloys. Titanium-base alloys are only slightly less cathodic to magnesium alloys. When these metals are constituents of the magnesium alloy, they may be considered to react galvanically with magnesium resulting in high rates of uniform corrosion in electrolyte solutions. Magnesium alloys are widely used as sacrificial anodes in the cathodic protection of steel.

Steel is frequently electroplated with cadmium to reduce its severe galvanic attack on magnesium. Electroplates of chromium, lead, silver, and manganese on steel are roughly comparable to cadmium plate in compatibility with magnesium. Tin is rapidly gaining favor as being superior to cadmium. Zinc is approximately equal to tin in compatibility, but in severe marine environments zinc coatings rapidly bare the steel substrate. Copper, nickel, gold, and platinum electroplates are incompatible with magnesium.

Because high-purity aluminum is much more compatible with magnesium than tin, aluminum coatings on steel are potentially useful in preventing galvanic attack on magnesium alloys. The coating, however, must be extremely sound. If underlying steel is exposed through a pore, the alkaline environment generated at the surface of the steel will rapidly strip the adjacent aluminum coating.

### 4-10.2.3 Stress-Corrosion Cracking

A limitation in the structural application of some magnesium alloys is susceptibility to stress-corrosion cracking in moist air. Susceptibility of an alloy to stress-corrosion cracking is determined by exposing stressed specimens to the weathering atmosphere. Resistance to stress-corrosion cracking is not appreciably influenced by the direction of applied stress relative to the direction of rolling or working.

Most stress-corrosion failures in magnesium alloy structures are caused by residual stresses introduced during fabrication. Sources of such failures are restrained weldments, interference fits, and casting inserts.



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Susceptible magnesium alloys, especially those containing aluminum, are usually stress relieved after welding.

Of the commercial alloys listed in Table 4-99, only wrought ZK60A and the alloys containing more than approximately 1.5% aluminum are sufficiently susceptible to stress-corrosion cracking to warrant concern.

Castings are generally much less susceptible to stress-corrosion cracking than wrought products of similar composition. Although AZ61A alloy sheet and extrusions and AZ80A alloy extrusions and forgings are highly susceptible to stress-corrosion cracking, the casting alloys containing 6% to 10% aluminum are only slightly susceptible. AZ31B sheet and extrusions and ZK60A extrusions and forgings are moderately susceptible, whereas, cast AZ31B alloy and cast ZK51A alloy seem to be immune.

### 4-10.2.4 Corrosion Fatigue

Fatigue tests conducted on specimens of AZ31B alloy indicate the following characteristics (Ref. 146):

1. The fatigue strength in air decreases as the humidity increases.
2. The fatigue strength in distilled water is greater than it is in condensing humidity.
3. Water, CO<sub>2</sub>, and SO<sub>2</sub>, but not oxygen and nitrogen, are the principal contributors to atmospheric corrosion fatigue of magnesium.
4. The effect of corrosion on the fatigue strength of magnesium can be virtually nullified by cathodic protection.
5. Working of the surface to create compressive stresses has a favorable effect on resistance to both dry and wet fatigue.
6. The dry fatigue strength can be preserved in the presence of condensing humidity by coatings.

Some coatings that provided substantial preservation of the dry fatigue strength included petroleum jelly, vinyl organosol over vinyl primer (0.1 mm (0.004 in.) total), and polyurethane (MIL-C-83286) over epoxy-polyamide primer (MIL-P-23377) (0.05 mm (0.002 in.) total).

Surface sealing with epoxy resin (Araldite 985E) rendered cast and wrought magnesium-zinc-zirconium alloys resistant to corrosion fatigue in another series of experiments (Ref. 150).

A study of the fatigue strength of AZ91, EZ33, and ZE41 cast magnesium alloys determined that fatigue strength is enhanced by HAE heavy anodic coating, which also mitigates corrosion effects on fatigue failure (Ref. 151). HAE coating is described as Class A, Types I and II, in MIL-M-45202 (Ref. 152).

### 4-10.2.5 High-Temperature Corrosion

Poor creep strength at elevated temperatures, rather than a corrosion reaction, usually limits the usefulness of a magnesium alloy.

Magnesium-zirconium alloys have adequate oxidation resistance to dry air up to 399°C (750°F), to wet air up to 349°C (660°F), to dry CO<sub>2</sub> up to 499°C (930°F), and to wet CO<sub>2</sub> up to 449°C (840°F). Magnesium alloys containing small amounts of beryllium adequately resist oxidation in wet air at temperatures in excess of 499°C (930°F). Excessive oxidation during heat treatment of magnesium alloys at temperatures above 349°C (660°F) can be prevented by the addition of at least 0.5% SO<sub>2</sub> to the furnace environment.

Magnesium will ignite in dry air at 645°C (1193°F). The ignition temperature in moist air is somewhat lower.

### 4-10.2.6 Local Corrosion

Cathodic impurities and surface contamination such as mill scales from rolling; carbonaceous lubricant residues from forming, forging, or impact extrusion; and flux dust or fly ash can result in severe pitting in magnesium alloys exposed to strong electrolytes. Pitting may occur in magnesium alloys exposed to freshwater, and magnesium alloys exposed to marine atmospheres often develop fine pits.

Painted magnesium alloys can undergo filiform corrosion when exposed to humid air and even when immersed in chloride solution. Any soluble salt having an anion that forms a soluble magnesium salt can initiate filiform corrosion. Filiform corrosion of painted magnesium is most likely to occur where the paint film is thin. Therefore, its likelihood of occurrence is greatly reduced by good paint pretreatment and by the presence of inhibitive chromate pigments in the paint. Instances of filiform corrosion under paint are more common with die castings than with wrought products. Although it is unsightly, filiform corrosion normally does not impair the mechanical function of a part because the corrosion tracks are much less than 25 μm (1 mil) deep.

Crevice and poutices should be avoided in magnesium structures; they are potential reservoirs for electrolytes. Crevice corrosion has been observed on unprotected faying surfaces of magnesium and magnesium alloy assemblies.

### 4-10.3 INTERFACE PROBLEMS

Fretting is a problem that occurs in the shipping of wrought products if magnesium surfaces are in contact. However, in normal shipping the fretting is usually superficial and affects only the appearance of the metal.

Wood, paper, cardboard, open cell foams, sponge rubbers, and other absorbers of moisture and wicking materials should not contact magnesium directly. They can result in pitting and crevice corrosion.

Magnesium alloys should not be used for parts on which deterioration of the protective finish can occur as the result of erosion or wear. Such parts in aircraft include leading edges, parts subject to engine exhaust impinge-

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ment and rocket blast, doors, steps, wheels, and flooring (Ref. 18). The fatty acid glycerides in animal fats and some vegetable oils react with magnesium hydroxide surface films. This reaction results in superficial staining.

**4-10.4 METHODS FOR PREVENTION OF CORROSION**

The severe restrictions on the use of magnesium alloys in Army air vehicles, quoted in par. 4-10, counsel careful assessment of potential magnesium alloy applications. Furthermore, if a magnesium alloy is chosen, effective methods for preventing corrosion should be specified.

**4-10.4.1 Design Considerations**

Magnesium assemblies should be designed so that

1. Open sections and concave surfaces are arranged so that moisture cannot collect in them.
2. Cavities are well sealed or can drain freely. The minimum drain hole size is 3.175 mm (0.125 in.) to prevent plugging.
3. There are no narrow gaps between components into which moisture could be drawn by capillary action. Use epoxy and vinyl tapes and coatings, wax, or latex for protective barriers.
4. There are no sharp corners, edges, bends, or notches.
5. Magnesium alloy parts should be readily accessible for inspection, application of protective finish, and replacement.

The following precautions should be followed in assembling magnesium components to avoid galvanic attack:

1. Steel fasteners should be tin- or cadmium-plated (Ref. 18).
2. Bolts should have pure aluminum or plastic washers large enough to extend 6.35 mm (0.25 in.) beyond the nut or bolt head. These washers seal the thread from the corroding environment and spread any galvanic corrosion over a wider area. This tends to prevent deep notch development in the interface.
3. Bolt heads and nuts should also be covered with a sealing compound to provide fillets so that water is not trapped.
4. All surfaces should be assembled wet, and a compatible sealant used. Sealants containing zinc chromate are effective with magnesium.

In Army aircraft the sealant for fastener installation should conform to the requirements in MIL-S-81733 (Ref. 27) in areas having an operating temperature below 107°C (225°F). An epoxy primer conforming to the requirements in MIL-P-23377 (Ref. 26) should be used in areas in which the operating temperature will exceed this limit (Ref. 18).

**4-10.4.2 Chemical and Anodic Treatments**

When magnesium alloys are used in Army materiel, a protective system is required. Possible systems are discussed in par. 3-6.1.4:

A study of the effectiveness of protective systems for three cast magnesium alloys—AZ91C, EZ33A, and ZE41A—has been conducted (Ref. 151). The surface preparation and finishing systems used in this study are shown in Table 4-101. The details of the cleaning and surface-treating procedures are shown in Table 4-102.

The effectiveness of surface treatments, including chromate and anodic coatings, with regard to reducing corrosion are

1. The influence of as-cast or machined surfaces on the behavior of subsequent surface treatments is either nil or short-lived.
2. Acid pickling does not change the inherent susceptibility of cast magnesium alloys to corrosion.
3. Steel shot peening does not increase the corrosion susceptibility of AZ91 or ZE41 alloys, and its adverse effect on alloy EZ33 is of short duration.
4. Virtually no protective effect results from styrene monomer resin impregnation of magnesium castings. The opinions that peening leads to heightened corrosion susceptibility and that resin impregnating results in lowered corrosion propensity are strongly held. Based on one-day salt fog tests, these views might be supported. They are, however, rendered invalid by results obtained with the longer exposures of the studies described in Ref. 151.
5. Superior protection is afforded magnesium castings by the anodic base coatings. Optimum for AZ91 alloy is the HAE heavy coating when applied to an as-cast surface. For EZ33 and ZE41 alloys, HAE heavy and thin and Dow 17 heavy and thin are highly effective; the longest protection is provided by the HAE coating.
6. Dow 7 chromate treatment is as protective as anodic coatings for AZ91 but is only half as protective for EZ33 and ZE41. These specimens were given a surface treatment after peening, which included pickling, chromating, and anodizing. Sufficient depth of peen-altered metal (at least 1.3 mm (0.05 in.)) was retained after surface treatment so that the effects of peening on the corrodibility of the metal could be ascertained.

**4-10.4.3 Paint Systems**

Chemical and anodic treatments usually form the base for a paint system. Magnesium alloys in Army aircraft should be treated prior to painting in accordance with MIL-M-45202 (Ref. 152) or MIL-M-3171 (Ref. 153). Holes drilled subsequent to the finish application should be treated in accordance with MIL-M-3171, Type VI (Ref. 153) (Ref. 18).

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TABLE 4-101. SURFACE PREPARATIONS AND FINISHING SYSTEMS USED IN CORROSION EXAMINATIONS (Ref. 151)

| TREATMENT LETTER | TREATMENT—FINISH   | TEST ENVIRONMENT |         |               |          |           |      |    |                    |        |
|------------------|--|------------------|---------|---------------|----------|-----------|------|----|--------------------|--------|
|                  |  | SURFACE          |         | SALT SOLUTION | SALT FOG | WATER FOG | PCZ* |    | LUBRICATING FLUIDS |        |
|                  |  | CAST             | MACHINE |               |          |           | M    | OF | MIN†               | SYN    |
| A                | Alkaline clean   | x                | x       | x             | x        | x         |      |    |                    |        |
| B                | A + acid pickle  | x                | x       |               | x        | x         |      |    |                    |        |
| C                | B + resin impregnate                                     | x                | x       |               | x        | x         |      |    |                    |        |
| D                | C + steel-shot peen (Almen 5A)                           | x                | x       |               | x        | x         |      |    |                    |        |
| E                | D + acid pickle  | x                | x       |               | x        | x         |      |    |                    |        |
| F                | A + Dow 20 (AZ91), Dow 1 (EZ33, ZE41)                    | x                | x       |               | x        | x         | x    | x  |                    |        |
| G                | A + Dow 7  | x                | x       |               | x        | x         | x    | x  | x                  | x      |
| H                | A + HAE (heavy), IIA3                                    | x                | x       |               | x        | x         | x    | x  | (AZ91)             | (AZ91) |
| I                | A + HAE (light), IA2                                     | x                | x       |               | x        | x         | x    | x  |                    |        |
| J                | A + Dow 17 (heavy) IID                                   | x                | x       |               | x        | x         | x    | x  |                    |        |
| K                | A + Dow 17 (light) IC                                    | x                | x       |               | x        | x         | x    | x  |                    |        |
| L                | H + epoxy primer, acrylic lacquer                        |                  | x       |               | x        | x         | x    | x  |                    |        |
| M                | H + epoxy primer, alkyd enamel                           |                  | x       |               | x        | x         | x    | x  |                    |        |
| N                | H + epoxy seal, chromate primer, urethane top coating    |                  | x       |               | x        | x         | x    | x  |                    |        |
| O                | H + epoxy primer, flexible primer, urethane top coating  |                  | x       |               | x        | x         | x    | x  |                    |        |
| P                | H + chloro-rubber, chromate primer, urethane top coating |                  | x       |               | x        | x         | x    | x  |                    |        |
| Q                | G (AZ91) Mineral oil—inhibitor CI1**                     | x                |         |               |          |           |      |    | x                  |        |
| R                | G (AZ91) Mineral oil—inhibitor CI2**                     | x                |         |               |          |           |      |    | x                  |        |
| S                | G (AZ91) Mineral oil—inhibitor CI3**                     | x                |         |               |          |           |      |    | x                  |        |
| T                | G (AZ91) Mineral oil—inhibitor CI4**                     | x                |         |               |          |           |      |    | x                  |        |
| U                | G (AZ91) Synthetic fluid—inhibitor CI1                   | x                |         |               |          |           |      |    |                    | x      |
| V                | G (AZ91) Synthetic fluid—inhibitor CI2                   | x                |         |               |          |           |      |    |                    | x      |
| W                | G (AZ91) Synthetic fluid—inhibitor CI3                   | x                |         |               |          |           |      |    |                    | x      |
| X                | G (AZ91) Synthetic fluid—inhibitor CI4                   | x                |         |               |          |           |      |    |                    | x      |

\*PCZ = Panama Canal Zone; M = marine; OF = open field

\*\*CI1 = dinonyl naphthalene sulfonate, sodium salt; CI2 = isopropyl monooleate; CI3 = ammonium stearate; CI4 = benzotriazole

†MIN = mineral; SYN = synthetic

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TABLE 4-102. CLEANING AND SURFACE TREATING PROCEDURES (Ref. 151)

| TREATMENT                                     | PROCEDURE  | REMARKS   |
|---|--|---|
| Alkaline cleaning                             | Solution—sodium orthosilicate (60 g/l + 3 g NACCONAL 40), 30°C (86°F) 15 min   |   |
| Pickling                                      | Solution—nitric acid (concentration 8% vol.) + sulfuric acid (concentration 2% vol.), 28°C (82°F), 10 s  | Approxiamtely 0.025 mm (0.001 in.) surface of specimen (cast skin) removal; desmuted solution 180 g/l CrO <sub>3</sub> , 28°C (82°F)  |
| Impregnating                                  | Styrene monomer (RC-2 Impco Corp.), vacuum, pressure 0.6 MPa (90 psi), 30 min  | Clean with solution—Oakrite 61B (43 g/l), 38°C (100°F); cold water rinse, alkaline clean in Oakrite 94 (43 g/l), 80°C (176°F), water rinse, dry, cure at 149°C (300°F), 3 h |
| Shot peening                                  | Alloy steel balls (C-1018), 3.2 mm (0.125 in.) diameter, Rc64, peen to Almen 5A intensity, 200% coverage   | Depth of peening effect determined by X ray for each alloy  |
| Chromating (Conforms to MIL-M-3171, Ref. 153) | Type 1 (Dow 1) — 180 g/l NaCr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O + 188 ml/l HNO <sub>3</sub> (70%), 1 min at 27°C (81°F), rinse, drain dry   | Applied to EZ33 and ZE41 alloys   |
| Chromating (Conforms to MIL-M-3171, Ref. 153) | Type I Dow 20 (Dow 1 modification) 15 g/l NH <sub>4</sub> HF <sub>2</sub> + 180 g/l Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O + 10 g/l Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> ·18H <sub>2</sub> O + 126 ml/l HNO <sub>3</sub> (70%); 1 min at 27°C (81°F), rinse, drain dry | Applied to AZ91   |
| Chromating (Conforms to MIL-M-3171, Ref. 153) | Type III (Dow 7)<br>a. 230 ml/l H <sub>2</sub> F <sub>2</sub> (49%), 5 min at 25°C (77°F), cold water rinse;<br>b. 150 g/l Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> ·2H <sub>2</sub> O + 2.5 g CaF <sub>2</sub> , 30 min, 98°C (208°F), hot rinse, drain dry   |   |
| Anodizing (Conforms to MIL-M-45202, Ref. 152) | Type IA2—HAE, light; thickness 0.005 to 0.00 mm (0.2 to 0.00 mil)<br>Type IIA3—HAE, heavy; thickness 0.02 to 0.03 mm (0.8 to 1.2 mil)<br>Type Ic)—Dow 17, light; thickness 0.005 to 0.01 mm (0.2 to 0.4 mil)<br>Type IID—Dow 17, heavy; thickness 0.02 to 0.03 mm (0.8 to 1.2 mil)                           | Specification procedures followed   |

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The paint systems usually consist of one or two coats of a zinc-chromate-pigmented primer plus two or more coats of enamel or lacquer. Because the corrosion of magnesium results in the formation of magnesium hydroxide, the paint should be alkali resistant, and there are many paints based on vinyl, epoxy, acrylic, alkyl, and urethane resins that have excellent resistance to alkali. These paints can effectively protect magnesium in severe service. Paint systems for Army aircraft shall be MIL-C-46168 (Ref. 25) aliphatic polyurethane topcoat over MIL-P-23377 (Ref. 26) epoxy polyamide primer (Ref. 18).

In the study of protective systems for cast magnesium alloys referred to in par. 4-10.4.2, the following conclusions were reached concerning organic coatings (Ref. 151):

1. The anodizing of magnesium castings prior to finishing with an organic system insures a system of maximum protection.

2. Coating Systems M, N, and O offered enhanced protection over the coatings currently specified or in use (similar to System L). Table 4-103 contains descriptions of the coating systems tested.

3. The protection afforded AZ91 alloy by the coating systems is about 50% of that afforded EZ33 alloy and about 35% of that afforded ZE41 alloy. These differences indicate the influence of the inherent corrodibility of each alloy.

4. Void-free specimens representing each coating system and alloy combination are equally corrosion-resistant in salt fog over 48 days of exposure.

**4-10.4.4 Oils, Greases, and Waxes**

Petroleum-base oils, greases, and waxes; lanolin grease; carnauba wax; and petroleum sulfonate rust preventives protect magnesium for a time from corrosion in mild environments.

**4-10.4.5 Inhibitors**

Chromates, e.g., such as zinc chromate, are generally effective in inhibiting the corrosion of magnesium, and they have been used extensively for this purpose.

The corrosion of magnesium alloys by water and in some aqueous solutions can be inhibited by the addition of fluoride ion.

**TABLE 4-103. COATING SYSTEMS FOR MAGNESIUM ALLOYS (Ref. 151)**

| SYSTEM | COMPONENTS   | SOURCE  | THICKNESS PER SIDE                       |
|--------|--|---|--|
| L      | Epoxy primer (MIL-P-23377)                                     | DeSoto, Inc., Garland, TX   | $6.4 \times 10^{-2}$ mm (2.5 mil)        |
|        | Acrylic lacquer (MIL-L-81352) with aluminum pigment (TT-P-320) | Materials Research Laboratory, Ft. Belvoir, VA<br>Aluminum Company of America, Alcoa Center, PA | $6.4 \times 10^{-2}$ mm (2.5 mil)        |
|        |  |   | $12.8 \times 10^{-2}$ mm (5.0 mil) TOTAL |
| M      | Epoxy primer (MIL-P-52192)                                     | Con-Lux Coatings, Inc., Edison, NJ  | $7.1 \times 10^{-2}$ mm (2.8 mil)        |
|        | Alkyd topcoat (TT-E-529)                                       | Atlas Paint Co., Irvington, NJ  | $6.9 \times 10^{-2}$ mm (2.7 mil)        |
|        |  |   | $14.0 \times 10^{-2}$ mm (5.5 mil) TOTAL |
| N      | Epoxy seal (Hysol CG 4226)                                     | Hysol Division, Olean, NY   | $3.6 \times 10^{-2}$ mm (1.4 mil)        |
|        | Chromate primer (TT-P-1757)                                    | Glidden Paint Co., Reading, PA  | $4.3 \times 10^{-2}$ mm (1.7 mil)        |
|        | Alkyd topcoat (TT-E-529)                                       | Atlas Paint Co., Irvington, NJ  | $5.3 \times 10^{-2}$ mm (2.1 mil)        |
|        |  |   | $13.2 \times 10^{-2}$ mm (5.2 mil) TOTAL |
| O      | Epoxy primer (MIL-P-23377)                                     | DeSoto, Inc., Garland, TX   | $4.1 \times 10^{-2}$ mm (1.6 mil)        |
|        | Flexible primer (PR-1432-GP)                                   | Products Research Corporation, Burbank, CA  | $5.8 \times 10^{-2}$ mm (2.3 mil)        |
|        | Urethane topcoat (MIL-C-83286)                                 | Deft, Inc., Torrance, CA  | $3.8 \times 10^{-2}$ mm (1.5 mil)        |
|        |  |   | $13.7 \times 10^{-2}$ mm (5.4 mil) TOTAL |
| P      | Chloro-rubber (Alloprene X-10)                                 | ICI, US Corporation, Wilmington, DE   | $6.9 \times 10^{-2}$ mm (2.7 mil)        |
|        | Chromate primer (TT-P-1757)                                    | Glidden Paint Co., Reading, PA  | $3.6 \times 10^{-2}$ mm (1.4 mil)        |
|        | Urethane topcoat (MIL-C-83286)                                 | Deft, Inc., Torrance, CA  | $3.0 \times 10^{-2}$ mm (1.2 mil)        |
|        |  |   | $13.5 \times 10^{-2}$ mm (5.3 mil) TOTAL |

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**MIL-HDBK-735(MR)****4-10.4.6 Electroplating**

Magnesium can be electroplated by processes employing the conventional sequence of copper, nickel, and then chromium. Tin, silver, and gold electroplates are used on magnesium in electronic applications for protection and to prevent the rapid formation of insulating films that interfere with soldering and electrical grounding.

Experience indicates that decorative copper-nickel-chromium plating offers about the same protection to magnesium as it does to zinc and aluminum.

The electroplating process involves the following steps:

1. Surface cleaning and activation
2. Zinc immersion coating
3. Copper strike
4. Standard nickel-chromium plating.

Corrosion tests on electroplated magnesium pressure die castings indicate that a total plate thickness of 51  $\mu\text{m}$  (2 mil) is required for adequate weathering resistance for 1 yr.

Nickel can also be deposited on magnesium by a chemical reduction, or electroless, process.

**4-10.5 EXAMPLES OF CORROSION PROBLEMS**

Severe pitting corrosion has been experienced on the differential housing of the steering control of some Army vehicles (Ref. 154). This component is made from cast magnesium approximately 25.4 mm (1 in.) thick. It rests near the bottom of the vehicle hull—a location that allows the component to contact water, dirt, fuel, oil, and other liquids that collect in the lower hull well.

Helicopter gear housings of AZ91C-T6 alloy have been used within the restrictions of ADS-13C (Ref. 18) because an adequate protection system can be maintained. These housings are chromated overall. The external finish is a chromate primer under an acrylic lacquer. The internal finish is a proprietary epoxy resin over the Dow 7 chromate pretreatment. Other alloys, such as EZ35A-T5

and ZE41A-T5, are of interest in this application because of better weldability and potentially lower susceptibility to general corrosion (Ref. 151).

**4-11 MOLYBDENUM**

Molybdenum has a density of 10219  $\text{kg}/\text{m}^3$  (637.95  $\text{lbm}/\text{ft}^3$ ), which is 1.30 times that of iron. It has a melting point of 2610°C (4730°F), which is high; it does, however, form a volatile oxide (molybdenum oxide,  $\text{MoO}_3$ ) that melts at 795°C (1463°F). This oxide forms in air at temperatures above approximately 704°C (1300°F).

Molybdenum is more abundant domestically than some of the other refractory metals. It is widely used as an alloying component because it improves the strength of both low- and high-alloy steels. Molybdenum also has a high modulus of elasticity, 310,264 MPa ( $45 \times 10^6$  psi), which means it is very stiff. Thus it deflects much less than steel of equivalent cross section under a given load. Molybdenum retains useful strength up to 1200°C (2192°F).

Examples of commercial alloys of molybdenum are TZM (0.5 Ti, 0.08 Zr, 0.015 C, Balance Mo) and Mo-30W, which is a completely solid solution. The alloy TZM retains useful strength to 1650°C (3002°F).

**4-11.1 TYPES OF CORROSION****4-11.1.1 Uniform Corrosion****4-11.1.1.1 Weathering Corrosion**

The corrosion of molybdenum based on 7 yr of exposure to three types of atmospheres is shown in Table 4-104. The corrosion rates, which are expressed as uniform weight loss or penetration, as well as the pit depth parameters are very small. Corrosion at the Kure Beach, NC, 25-m (80-ft) site (marine) is greater than that experienced at Newark, NJ (industrial). The smallest corrosion rate was experienced at State College, PA (rural).

**TABLE 4-104. ATMOSPHERIC CORROSION OF MOLYBDENUM (Ref. 147)**

| DESIGNA-<br>TION | DENSITY           |                    | SITE              | CORROSION RATE                       |                         |          | PIT DEPTH, $\mu\text{m}$ (mil) |          |          | ULTIMATE STRENGTH,<br>MPa (ksi) |                  | ELONGATION IN<br>51mm (2 in.), % |         |
|------------------|-------------------|--------------------|-------------------|--------------------------------------|-------------------------|----------|--------------------------------|----------|----------|---------------------------------|------------------|----------------------------------|---------|
|                  | kg/m <sup>3</sup> | lb/ft <sup>3</sup> |                   | mdd<br>(lb/ft <sup>2</sup> -day)     | $\mu\text{m}/\text{yr}$ | (mpy)    | 4 DEEPEST<br>AVERAGE           | MAXIMUM  |          | CONTROL                         | EXPOSED          | CONTROL                          | EXPOSED |
|                  |                   |                    |                   |                                      |                         |          |                                | SKY      | GROUND   |                                 |                  |                                  |         |
| Molybdenum 10200 | 637               |                    | Kure Beach, NC    | 0.4782<br>( $9.794 \times 10^{-6}$ ) | 1.71                    | (0.0674) | 41 (1.6)                       | 56 (2.2) | 61 (2.4) | 704.6<br>(102.2)                | 685.3<br>(99.4)  | 15.2                             | 17.0    |
|                  |                   |                    | Newark, NJ        | 0.3101<br>( $6.351 \times 10^{-6}$ ) | 1.11                    | (0.0437) | 38 (1.5)                       | 71 (2.8) | 76 (3.0) |                                 | 692.2<br>(100.4) |                                  | 17.5    |
|                  |                   |                    | State College, PA | 0.1261<br>( $2.583 \times 10^{-6}$ ) | 0.45                    | (0.0178) | 43 (1.7)                       | 94 (3.7) | 84 (3.3) |                                 | 685.3<br>(99.4)  |                                  | 15.4    |

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**MIL-HDBK-735(MR)****4-11.1.1.2 Corrosion in Acid Solutions**

Molybdenum shows good resistance to nonaerated, reagent grade hydrochloric, hydrofluoric, phosphoric, and sulfuric acids. Exposures in 71°C (160°F) nonaerated hydrochloric acid of concentrations varying between 1% and 20% show a maximum corrosion rate of 28  $\mu\text{m}/\text{yr}$  (1.1 mpy). The corrosion rate in 110°C (230°F) concentrated hydrochloric acid is about 8  $\mu\text{m}$  (0.3 mpy), and oxidizing agents and longer test periods increase the corrosion rates. Many of the alloys that are used for service in hydrochloric acid contain significant amounts of molybdenum. Molybdenum shows good resistance to hydrofluoric acid. Exposures in 25% and 49% hydrofluoric acid at 100°C (212°F) for 48 h give a maximum corrosion rate of 79  $\mu\text{m}/\text{yr}$  (3.1 mpy). All concentrations of phosphoric acid inflict only slight attack on molybdenum either at room temperature or boiling.

Molybdenum shows less than 25.4- $\mu\text{m}/\text{yr}$  (1-mpy) corrosion in 10% to 95% sulfuric acid at 71°C (160°F). The corrosion rates follow:

1. Less than 127  $\mu\text{m}/\text{yr}$  (5 mpy) in up to 50% boiling sulfuric acid
2. Less than 25.4  $\mu\text{m}/\text{yr}$  (1 mpy) in 10% sulfuric acid
3. Less than 102  $\mu\text{m}/\text{yr}$  (4 mpy) in 20% acid at 204°C (400°F).

However, the combination of higher concentrations and higher temperatures can result in severe attack. For example, resistance to 75% sulfuric acid at 204°C (400°F) is only fair, whereas resistance to 62% acid at 316°C (600°F) is poor. Aeration of the sulfuric acid has no significant effect on the corrosion rate of molybdenum.

Oxidizing conditions severely reduce the corrosion resistance of molybdenum in acid solutions. These conditions include aeration of the nonoxidizing acids, with the exception of sulfuric acid; oxidizing acids, such as nitric acid; and reducing acids containing oxidizers, such as nitric acid and ferric chloride.

Molybdenum and its alloys are readily corroded by nitric acid. For example, both concentrated boiling nitric acid and 25% dilute acid at room temperature readily attack molybdenum. At room temperature, however, concentrated nitric acid forms a protective film on molybdenum that stifles further attack. The alloys TZM and Mo-30W both corrode faster than molybdenum in 6.1% nitric acid.

The corrosion rates of molybdenum in some organic acids at 100°C (212°F) are 254  $\mu\text{m}/\text{yr}$  (10 mpy) in 10% acetic acid, 203  $\mu\text{m}/\text{yr}$  (8 mpy) in 10% formic acid, and 254  $\mu\text{m}/\text{yr}$  (10 mpy) in 0.25% benzoic acid.

**4-11.1.1.3 Corrosion in Alkaline Solutions**

Molybdenum is moderately resistant to aerated solutions of ammonia but is inert to deaerated ammonia. It shows fair resistance in 1% sodium hydroxide at 35°C (95°F) and 60°C (140°F), but in a 10% sodium hydroxide

solution, it shows better resistance to corrosion at both temperatures. At 35°C (95°F) molybdenum is severely corroded in sodium hypochlorite at pH  $\geq$  11.

**4-11.1.1.4 Corrosion in Salt Solutions**

Molybdenum shows good resistance to 3% sodium chloride, 10% aluminum chloride, and 10% ammonium chloride solutions at temperatures up to 100°C (212°F). The alloys TZM and Mo-30W are resistant to synthetic seawater at 60°C (140°F).

Molybdenum is severely corroded by 20% ferric chloride and 20% cupric chloride solutions at 35°C (95°F).

Molybdenum undergoes pinhole-type pitting in mercuric chloride solutions. TZM is susceptible to a type of crevice corrosion in mercuric chloride solutions.

**4-11.1.1.5 Corrosion in Halogen Gases**

Molybdenum undergoes vigorous attack by fluorine at room temperature. It is, however, resistant to attack by chlorine up to 230°C (446°F), bromine up to 449°C (840°F), and iodine up to 788°C (1450°F). Wet bromine and chlorine attack molybdenum at room temperature.

**4-11.1.2 High-Temperature Corrosion****4-11.1.2.1 Oxidation**

The relatively low melting point of the volatile oxide MoO<sub>3</sub> results in poor resistance to oxidation in air at high temperatures. Oxidation in air begins at 300°C (572°F), it is rapid at 500°C (932°F), and it is very rapid by 1200°C (2192°F). The relative corrosion rates of several metals in air at 1204°C (2200°F) are compared in Table 4-105.

**TABLE 4-105. AIR CORROSION AT 1204°C (2200°F) (Ref. 72)**

| METAL                     | RELATIVE CORROSION RATES* |
|---------------------------|---------------------------|
| Silicon                   | small                     |
| 81 Ni-12.5Cr-6.5 Al       | 0.4                       |
| 310 Stainless (25Cr-20Ni) | 1.0                       |
| 67Cr-33Ni                 | 1.9                       |
| Chromium                  | 5.0                       |
| Titanium                  | 29.6                      |
| Zirconium                 | 59                        |
| 93Cb-7Mo                  | 89                        |
| Tungsten                  | 114                       |
| Columbium                 | 696                       |
| Tantalum                  | 1140                      |
| Molybdenum                | 1600                      |

\*Refers to Type 310 steel

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The reactions of several gases with molybdenum at elevated temperatures are shown in Table 4-106.

**4-11.1.2.2 Reaction With Metallic Elements**

The corrosion of molybdenum in liquid metals is shown in Table 4-107. Mo-30W alloy is almost inert to attack by zinc at normal zinc casting temperatures.

**4-11.1.2.3 Reaction With Nonmetallic Elements**

Molybdenum forms a boride at high temperatures, a carbide above 1100°C (2012°F), and a silicide above 1000°C (1832°F). It does not react with phosphorus.

**4-11.1.2.4 Hot Corrosion of Alloys Containing Molybdenum**

A form of hot corrosion occurs with alloys containing molybdenum. Type 316 stainless steel, i.e., 18 chromium, 12 nickel, and 3 molybdenum, and alloys containing larger amounts of molybdenum have corroded at extremely high rates in high-temperature air. In other situations, the rate of attack was not exceptional. The explanation for these high corrosion rates may be that low-melting-point, volatile MoO<sub>3</sub> accumulates on the alloy surface so that the surface oxide loses its protective qualities. However, if the ventilation is sufficient to dissipate the volatile oxide, the normal high-melting oxide scale remains and provides protection to the alloy. Alloys with more than 40% chromium have been developed for use in situations during which MoO<sub>3</sub> hot corrosion might occur.

**4-11.2 METHODS FOR PREVENTION OF CORROSION**

Several coatings have been developed that give reliable protection at very high temperatures (exceeding 1371°C (2500°F)) to both molybdenum and columbium (Ref. 78). These coatings include

1. Layers of molybdenum disilicide (MoSi<sub>2</sub>)
2. Metallic chromium or nickel chromium subsequently sprayed with alumina Al<sub>2</sub>O<sub>3</sub> or other refractory material
3. Metallic aluminum, plus chromium, plus silicon
4. Titanium and titanium compounds, such as oxides, nitrides, carbides, and silicides and various combinations of these materials.

Several techniques are used to apply these coatings: plasma spraying, pack cementation, vapor plating, dipping in molten metal or cold slurry, electroplating, and cladding. Pack cementation develops excellent coatings of molybdenum disilicide.

Producing coatings that adhere to the base metal under thermal cycling conditions and that resist abrasion or mild surface impacts under handling and service conditions is extremely important. Experience with a molybdenum test specimen coated with a protective silicide coating shows that molybdenum oxidizes to MoO<sub>3</sub> and vaporizes through a pinhole defect in the coating.

**TABLE 4-106. REACTION OF MOLYBDENUM WITH GASES AT ELEVATED TEMPERATURES (Ref. 57)**

| GAS                               | TEMPERATURE, °C (°F) | CORROSION REACTION                 |
|-----------------------------------|----------------------|------------------------------------|
| Oxygen-deficient combustion gases | 1427 (2600)          | Tolerable in specific applications |
| Carbon dioxide                    | <1093 (<2000)        | Slight                             |
| Hydrogen                          | <2593 (<4700)        | Slight                             |
| Nitrogen                          | <2399 (<4350)        | Slight                             |
|                                   | >2399 (>4350)        | Nitriding                          |
| Nitric oxide                      | <1127 (<2060)        | Little effect                      |
|                                   | >1127 (>2060)        | Reacts readily                     |
| Nitrous oxide                     | 649 (1200)           | Oxidizing                          |
| Hydrogen sulfide                  | 899 (1650)           | Little effect                      |
| Sulfur dioxide                    | 899 (1650)           | Attacks readily                    |
| Water vapor                       | 649 (1200)           | Attacks                            |
| Dry fluorine                      | >21 (>70)            | Attacks                            |
| Bromine or chlorine               | <799 (<1470)         | Light weight loss                  |

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TABLE 4-107. CORROSION OF MOLYBDENUM IN LIQUID METALS (Ref. 37 and 155)

| LIQUID METAL              | TEMPERATURE, °C (°F)     | CORROSION  |
|---------------------------|--------------------------|--|
| Aluminum                  | 660 (1220)               | Rapid attack                                     |
| Bismuth                   | <1429 (<2605)            | Unattacked                                       |
| Bismuth lead              | 1093 (2000) for 24 h     | Attacks sintered molybdenum 4.9 cm/yr (1935 mpy) |
| Bismuth-lead-tin eutectic | 799 (1470)               | Tolerable  |
| Copper                    | <1300 (<2372)            | Good resistance                                  |
| Gallium                   | 299 (570)                | Unattacked                                       |
|                           | >538 (>1000)             | Severely attacked                                |
| Gold                      | —                        | Good resistance                                  |
| Lead                      | 1093 (2000) for 500 h    | No visible attack                                |
| Lithium                   | <999 (<1830)             | Good resistance                                  |
| Magnesium                 | 1000 (1832)              | Excellent resistance                             |
| Mercury                   | <599 (<1110)             | Good resistance in static and dynamic tests      |
|                           | 599 (1110) to 699 (1290) | Moderate attack                                  |
| Potassium                 | <899 (<1650)             | Excellent resistance                             |
| Silver                    | —                        | Good resistance                                  |
| Sodium                    | <899 (<1650)             | Suitable for long-term service                   |
| Sodium potassium          | 593 (1110)               | Good resistance                                  |
| Tin                       | <599 (<1110)             | Resists attack                                   |
|                           | >599 (>1110)             | Subject to attack                                |
|                           | 999 (1830) for 338 h     | 1.7% weight loss                                 |
|                           | 1499 (2730) for 2 h      | 0.7% weight loss                                 |
| Zinc                      | 446 (835)                | 0.16 cm/yr (65 mpy)                              |
|                           | 699 (1290)               | 1.84 cm/yr (725 mpy)                             |

#### 4-11.3 EXAMPLE OF CORROSION PROBLEM

Molybdenum is a potentially suitable material for future high-temperature, hypervelocity gun-tube liners. For this application, molybdenum shows good erosion resistance and good chemical resistance to propellant gases (Ref. 57). Molybdenum, however, has a higher elastic modulus than steel; thus it is stiffer than steel. At the strain developed during firing, molybdenum experiences much higher stress than steel. Accordingly, a molybdenum liner does not effectively transfer the load to the steel gun-tube jacket, and this ineffective transfer can damage the liners. Liners of molybdenum can perform successfully only if they are placed initially under compressive stress. The problem of transferring stress to the load-bearing steel jacket can be complicated by differences in thermal expansion between the liner and the jacket.

Hot hardness is another critical requirement of gun-tube liners. Refractory alloys, such as TZM (0.5 Ti, 0.08 Zr, 0.015 C, balance Mo), maintain hardness to high temperatures.

Most of the refractory metals considered for use as gun-tube liners are either expensive (Ta and Cb) or imported. Only molybdenum is available in good supply from domestic sources; it is also less expensive.

#### 4-12 NICKEL AND NICKEL ALLOYS

Nickel has a density of 8900 kg/m<sup>3</sup> (555.6 lb/ft<sup>3</sup>) and a melting point of 1453°C (2647°F). Nickel is an alloying element in the austenitic stainless steels, and a series of alloys based upon nickel is used extensively. Nickel is moderately expensive, i.e., the nickel-base alloys are more costly than the austenitic stainless steels. Many of these alloys are used in high-temperature environments such as gas turbine engines, but many are used by the chemical process industry for service in aqueous solutions.

Nickel-base alloys include

1. Commercially pure nickel
2. Nickel-copper alloys
3. Nickel-molybdenum alloys
4. Nickel-chromium-iron alloys
5. Nickel-chromium-iron-copper alloys
6. Nickel-chromium-molybdenum-iron alloys
7. Nickel-chromium-molybdenum alloys.

Additives used in significant amounts include aluminum, titanium, columbium, cobalt, tungsten, and tantalum. The compositions and physical properties of some nickel-base alloys are given in Table 4-108.

Nickel alloys are better known by trade names than by their UNS designations. The UNS designation, however, incorporates the commercial alloy number designation as the last three digits. Accordingly, Monel alloy 400 is

TABLE 4-108. NICKEL ALLOYS (Ref. 2)

| ALLOY | UNS    | COMPOSITION, %* |           |         |         |           |  | CONDITION                         | MECHANICAL PROPERTIES†    |                             |                |              |
|-------|--------|-----------------|-----------|---------|---------|-----------|--|-----------------------------------|---------------------------|-----------------------------|----------------|--------------|
|       |        | Ni(+Co)**       | Cr        | Fe††    | Mo      | C         | OTHER  |                                   | YIELD STRENGTH, MPa (ksi) | TENSILE STRENGTH, MPa (ksi) | ELON-GATION, % | HARDNESS, HB |
|       |        |                 |           |         |         |           |  |                                   |                           |                             |                |              |
| 200   | N02200 | 99.             | —         | 0.4     | —       | 0.15      | —  | Ann.                              | 103-207<br>(15-30)        | 379-552<br>(55-80)          | 55-40          | 90-120       |
| 201   | N02201 | 99.             | —         | 0.4     | —       | 0.02      | —  | Ann.                              | 69-172<br>(10-25)         | 345-414<br>(50-60)          | 60-40          | 75-102       |
| 400   | N04400 | 63.-70.         | —         | 1.0-2.5 | —       | 0.3       | 28.-34 Cu                                      | Ann.                              | 172-345<br>(25-50)        | 483-621<br>(70-90)          | 60-35          | 110-149      |
| K-500 | N05500 | 63.-70.         | —         | 2.0     | —       | 0.25      | 2.3-3.15 Al<br>0.35-0.85 Ti, 30 Cu             | Age Hdn.                          | 586-827<br>(85-120)       | 896-1138<br>(130-165)       | 35-20          | 250-315      |
| 600   | N06600 | 72.             | 14.-17.   | 6.-10.  | —       | 0.15      | —  | Ann.                              | 207-345<br>(30-50)        | 552-689<br>(80-100)         | 55-35          | 120-170      |
| 601   | N06601 | 58.-63.         | 21.-25.   | Bal     | —       | 0.10      | 1.0-1.7 Al                                     | Ann.                              | 207-414<br>(30-60)        | 552-793<br>(80-115)         | 70-40          | 110-150      |
| 625   | N06625 | Bal             | 20.-23.   | 5.      | 8.-10.  | 0.10      | 3.15-4.15 (Cb + Ta)                            | Ann.                              | 476-655<br>(69-95)        | 827-1034<br>(120-150)       | 60-30          | 145-220      |
| 706   | N09706 | 39.-44.         | 14.5-17.5 | Bal     | —       | 0.06      | —  | Soln Treat<br>and Aged<br>Spec HT | 1110<br>(161)             | 1331<br>(193)               | 20.            | 371.         |
| 718   | N07718 | 50.-55.         | 17.-21.   | Bal     | 2.8-3.3 | 0.08      | 4.75-5.5 (Cb + Ta)<br>0.65-1.15 Ti, 0.2-0.8 Al | Spec HT                           | 1179<br>(171)             | 1351<br>(196)               | 17.            | 382.         |
| X-750 | N07750 | 70.             | 14.-17.   | 5.-9.   | —       | 0.08      | 0.7-1.2 (Cb + Ta)<br>2.25-2.75 Ti, 0.4-1.0 Al  | Spec HT                           | 793-979<br>(115-142)      | 1117-1331<br>(162-193)      | 30-15          | 300-390      |
| 800   | N08800 | 30.-35.         | 19.-23.   | Bal     | —       | 0.10      | 0.15-0.6 Al, 0.15-0.6 Ti                       | Ann.                              | 207-414<br>(30-60)        | 517-689<br>(75-100)         | 60-30          | 120-184      |
| 800H  | N08800 | 30.-35.         | 19.-23.   | Bal     | —       | 0.05-0.10 | 0.15-0.6 Al, 0.15-0.6 Ti                       | Soln Treat                        | 138-345<br>(20-50)        | 448-655<br>(65-95)          | 50-30          | 100-184      |
| 801   | N08801 | 30.-34.         | 19.-22.   | Bal     | —       | 0.10      | 0.75-1.5 Ti                                    | Spec HT                           | 548<br>(79.5)             | 889<br>(129)                | 29.5           |              |
| 825   | N08825 | 38.-46.         | 19.5-23.5 | Bal     | 2.5-3.5 | 0.05      | 1.5-3.0 Cu, 0.6-1.2 Ti                         | Ann.                              | 241-448<br>(35-65)        | 586-724<br>(85-105)         | 50-30          | 120-180      |
| B-2   | N10665 | Bal             | 1.0       | 2.      | 26.-30. | 0.02      | —  | Ann.                              | 524<br>(76)               | 958<br>(139)                | 53.            | 210.         |
| C-276 | N10276 | Bal             | 14.5-16.5 | 4.-7.   | 15.-17. | 0.02      | 3.0-4.5 W                                      | Ann.                              | 359<br>(52)               | 793<br>(115)                | 61.            | 194.         |
| C-4   | N06455 | Bal             | 14.-18.   | 3.      | 14.-17. | 0.015     | 0.7 Ti   | Ann.                              | 421<br>(61)               | 800<br>(116)                | 54.            | 194.         |
| G     | N06007 | Bal             | 21.-23.   | 18.-21. | 5.5-7.5 | 0.05      | 1.0-2.0 Mn, 1.5-2.5 Cu<br>1.75-2.5 (Cb + Ta)   | Ann.                              | 317<br>(46)               | 703<br>(102)                | 61.            | 161.         |
| X     | N06002 | Bal             | 20.5-23.  | 17.-20. | 8.-10.  | 0.05-0.15 | 0.2-1.0 W                                      | Ann.                              | 386<br>(56)               | 758<br>(110)                | 45.            | 178.         |

\*Single values are maximums unless otherwise stated.

\*\*Single values are minimums.

†Typical room temperature properties

††Bal = Balance

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NO4400, but Hastelloy X is NO6002. The common generic names of nickel-base alloys include the Monels, the Inconels, and the Hastelloys. (Monel and Inconel are registered trademarks of the International Nickel Company, Inc. Hastelloy and Haynes are registered trademarks of Haynes International, Inc.)

**4-12.1 TYPES OF NICKEL ALLOYS****4-12.1.1 Commercially Pure Nickel**

Nickel alloys 200 and 201 are commercially pure nickels. Nickel 201 has a lower carbon content; therefore, it is preferred for applications at temperatures greater than 316°C (600°F). The low carbon content prevents the loss of ductility that can result from graphitization.

**4-12.1.2 Nickel-Copper Alloys**

The Monel alloys contain at least 30% copper. Monel alloy 400 shares many characteristics with commercially pure nickel; however, it is an improvement in some characteristics. Monel alloy K-500 is age-hardenable. It possesses increased strength and hardness over alloy 400 and the corrosion-resistant characteristics of alloy 400.

**4-12.1.3 Nickel-Molybdenum Alloys**

Hastelloy alloy B-2 is the major nickel-molybdenum alloy. This alloy contains no chromium.

**4-12.1.4 Nickel-Chromium-Iron Alloys**

Inconel alloy 600 is a nickel-base alloy used in corrosive environments at elevated temperatures. It combines good mechanical properties with workability and is readily welded.

Incoloy alloy 800 is used for its oxidation resistance and strength at high temperatures. Incoloy alloy 825 also has improved aqueous corrosion resistance compared to alloy 800.

**4-12.1.5 Nickel-Chromium-Iron-Copper Alloys**

Hastelloy alloy G is a columbium-stabilized, nickel-base alloy. Alloy G-3 is an improved version of alloy G with lower carbon (0.015% maximum versus 0.05% maximum), lower columbium plus tantalum (0.3% typical versus 2.0%), and increased molybdenum (7.0% nominal versus 6.5% nominal). Alloy G-30 is a high-chromium nickel-base alloy (29.5% chromium versus 21.0 to 23.5% in alloy G-3). Compared to alloy G-3, the chemical composition of G-30 includes increased carbon (0.03% maximum), increased columbium plus tantalum (0.7%) and decreased molybdenum (5.0%).

Because it is stabilized, alloy G can be used in the as-welded condition. Alloys G-3 and G-30 both exhibit greater general corrosion resistance than alloy G, excellent weldability, and are suitable for use in most chemical process applications in the as-welded condition.

**4-12.1.6 Nickel-Chromium-Molybdenum-Iron Alloys**

Hastelloy alloy X is a heat-resistant alloy that has good high-temperature strength and exceptional resistance to oxidizing atmospheres. Alloy X is used in the hot section of gas turbine engines on parts such as burner cans and transition ducts. In an oxidizing environment alloy X forms a complex chromium-oxide spinel scale on its surface, which provides good resistance up to temperatures of 1177°C (2150°F).

**4-12.1.7 Nickel-Chromium-Molybdenum Alloys**

Inconel alloy 625 has high strength and toughness from cryogenic temperatures to 1093°C (2000°F). Its strength results from the stiffening effect of molybdenum and columbium on the nickel-chromium matrix. The alloy has good oxidation resistance and it resists attack by many acidic environments. The high nickel content of the alloy provides good resistance to chloride stress-corrosion cracking. The stabilization provided by columbium and tantalum renders the alloy suitable for service in corrosive media in the as-welded condition.

Alloy 625 has been used as sheet metal in high-temperature gas turbine applications. Such applications include ducting systems, thrust reversers, and after-burners. After long aging in the 593° to 760°C (1100° to 1400°F) temperature range, however, the room temperature ductility of the alloy is significantly reduced.

Hastelloy alloy C-276 is an improved wrought version of Hastelloy C. The low-carbon (0.01% maximum), low-silicon (0.08%) version was developed to overcome the severe intergranular corrosion attack of as-welded Hastelloy C in many oxidizing and chloride-containing environments. The alloy is widely used in the process industries.

Hastelloy alloy C-4 has excellent high-temperature stability, and its corrosion resistance and mechanical properties in the thermally aged condition are similar to its properties in the annealed condition. With the exceptions of lower iron concentration and no tungsten in alloy C-4, the composition is similar to alloy C-276. The corrosion resistance of the two alloys is also similar.

**4-12.2 TYPES OF CORROSION OF NICKEL ALLOYS****4-12.2.1 Commercially Pure Nickel****4-12.2.1.1 Uniform Corrosion****4-12.2.1.1.1 Weathering Corrosion**

The weathering corrosion rates of alloy 200 in several locations are shown in Table 4-109. The highest corrosion rate occurred in an industrial atmosphere. Nevertheless, the average corrosion rate for a 7-yr exposure was 1.78 µm/yr (0.070 mpy). This is not considered excessive.

TABLE 4-109. CORROSION AND PIT DEPTH DATA ON TEST PANELS (Ref. 156)

| MATERIAL           | LOCATION                           | AVERAGE WEIGHT LOSS                      |                            | AVERAGE CORROSION RATE       |                            |                               |         | AVERAGE OF 4 DEEPEST PITS, $\mu\text{m}$ (mil) |       |
|--------------------|------------------------------------|--|----------------------------|------------------------------|----------------------------|-------------------------------|---------|--|-------|
|                    |                                    | mg/dm <sup>2</sup> (lb/ft <sup>2</sup> ) |                            | mdd (lb/ft <sup>2</sup> day) |                            | $\mu\text{m}/\text{yr}$ (mpy) |         | 2 yr   | 7 yr  |
|                    |                                    | 2 yr                                     | 7 yr                       | 2 yr                         | 7 yr                       | 2 yr                          | 7 yr    |  |       |
| Nickel 200         | Kure Beach (24-m (80-ft) site), NC | 55.0                                     | 150.8                      | 0.075                        | 0.059                      | 0.305                         | 0.025   | <25.4  | <25.4 |
| Incoloy alloy 800  |                                    | (1.1 × 10 <sup>-3</sup> )                | (3.1 × 10 <sup>-3</sup> )  | (1.54 × 10 <sup>-6</sup> )   | (1.2 × 10 <sup>-6</sup> )  | (0.012)                       | (0.010) | (<1)   | (<1)  |
| Inconel alloy 600  |                                    | 23.4                                     | 33.6                       | 0.032                        | 0.013                      | 0.152                         | 0.051   | <25.4  | <25.4 |
| Monel alloy 400    |                                    | (0.48 × 10 <sup>-3</sup> )               | (0.69 × 10 <sup>-3</sup> ) | (0.66 × 10 <sup>-6</sup> )   | (0.27 × 10 <sup>-6</sup> ) | (0.006)                       | (0.002) | (<1)   | (<1)  |
| Incoloy alloy 825* |                                    | 22.9                                     | 27.6                       | 0.031                        | 0.011                      | 0.127                         | 0.051   | <25.4  | <25.4 |
| Nickel 200         | Newark, NJ                         | (0.47 × 10 <sup>-3</sup> )               | (0.57 × 10 <sup>-3</sup> ) | (0.63 × 10 <sup>-6</sup> )   | (0.23 × 10 <sup>-6</sup> ) | (0.005)                       | (0.002) | (<1)   | (<1)  |
| Incoloy alloy 825* |                                    | 77.0                                     | 224.6                      | 0.106                        | 0.088                      | 0.432                         | 0.356   | <25.4  | <25.4 |
| Nickel 200         |                                    | (1.6 × 10 <sup>-3</sup> )                | (4.6 × 10 <sup>-3</sup> )  | (2.17 × 10 <sup>-6</sup> )   | (1.80 × 10 <sup>-6</sup> ) | (0.017)                       | (0.014) | <1   | (<1)  |
| Incoloy alloy 825* |                                    | 25.1                                     | 18.9                       | 0.034                        | 0.007                      | 0.152                         | 0.025   | <25.4  | <25.4 |
| Nickel 200         |                                    | (0.51 × 10 <sup>-3</sup> )               | (0.39 × 10 <sup>-3</sup> ) | (0.70 × 10 <sup>-6</sup> )   | (0.14 × 10 <sup>-6</sup> ) | (0.006)                       | (0.001) | (<1)   | (<1)  |
| Incoloy alloy 800  | Point Reyes, CA                    | 355.0                                    | 1095.0                     | 0.484                        | 0.428                      | 2.007                         | 1.778   | <25.4  | <25.4 |
| Inconel alloy 600  |                                    | (7.3 × 10 <sup>-3</sup> )                | (22.4 × 10 <sup>-3</sup> ) | (9.91 × 10 <sup>-6</sup> )   | (8.77 × 10 <sup>-6</sup> ) | (0.079)                       | (0.070) | (<1)   | (<1)  |
| Monel alloy 400    |                                    | 16.3                                     | 11.7                       | 0.022                        | 0.005                      | 0.102                         | 0.025   | <25.4  | <25.4 |
| Incoloy alloy 825* |                                    | (0.33 × 10 <sup>-3</sup> )               | (0.24 × 10 <sup>-3</sup> ) | (0.45 × 10 <sup>-6</sup> )   | (0.10 × 10 <sup>-6</sup> ) | (0.004)                       | (0.001) | (<1)   | (<1)  |
| Nickel 200         |                                    | 19.4                                     | 16.6                       | 0.027                        | 0.006                      | 0.102                         | 0.025   | <25.4  | <25.4 |
| Incoloy alloy 825* | State College, PA                  | (0.40 × 10 <sup>-3</sup> )               | (0.34 × 10 <sup>-3</sup> ) | (0.55 × 10 <sup>-6</sup> )   | (0.12 × 10 <sup>-6</sup> ) | (0.004)                       | (0.001) | (<1)   | (<1)  |
| Monel alloy 400    |                                    | 161.0                                    | 505.5                      | 0.214                        | 0.196                      | 0.889                         | 0.813   | <25.4  | <25.4 |
| Incoloy alloy 825* |                                    | (3.3 × 10 <sup>-3</sup> )                | (10.4 × 10 <sup>-3</sup> ) | (4.38 × 10 <sup>-6</sup> )   | (4.01 × 10 <sup>-6</sup> ) | (0.035)                       | (0.032) | (<1)   | (<1)  |
| Nickel 200         |                                    | 18.9                                     | 11.0                       | 0.026                        | 0.004                      | 0.127                         | 0.025   | <25.4  | <25.4 |
| Incoloy alloy 825* |                                    | (0.39 × 10 <sup>-3</sup> )               | (0.23 × 10 <sup>-3</sup> ) | (0.53 × 10 <sup>-6</sup> )   | (0.08 × 10 <sup>-6</sup> ) | (0.005)                       | (0.001) | (<1)   | (<1)  |
| Incoloy alloy 800  | State College, PA                  | 30.4                                     | **                         | 0.042                        | **                         | 0.178                         | **      | <25.4  | **    |
| Inconel alloy 600  |                                    | (0.62 × 10 <sup>-3</sup> )               | **                         | (0.86 × 10 <sup>-6</sup> )   | **                         | (0.007)                       | **      | (<1)   | **    |
| Monel alloy 400    |                                    | 21.4                                     | **                         | 0.029                        | **                         | 0.152                         | **      | <25.4  | **    |
| Incoloy alloy 825* |                                    | (0.44 × 10 <sup>-3</sup> )               | **                         | (0.59 × 10 <sup>-6</sup> )   | **                         | (0.006)                       | **      | (<1)   | **    |
| Nickel 200         |                                    | 19.4                                     | **                         | 0.027                        | **                         | 0.102                         | **      | <25.4  | **    |
| Incoloy alloy 825* | State College, PA                  | (0.40 × 10 <sup>-3</sup> )               | **                         | (0.55 × 10 <sup>-6</sup> )   | **                         | (0.004)                       | **      | (<1)   | **    |
| Monel alloy 400    |                                    | 50.1                                     | **                         | 0.069                        | **                         | 0.279                         | **      | <25.4  | **    |
| Incoloy alloy 825* |                                    | (1.0 × 10 <sup>-3</sup> )                | **                         | (1.41 × 10 <sup>-6</sup> )   | **                         | (0.011)                       | **      | (<1)   | **    |
| Nickel 200         |                                    | 29.3                                     | **                         | 0.040                        | **                         | 0.178                         | **      | <25.4  | **    |
| Incoloy alloy 825* |                                    | (0.60 × 10 <sup>-3</sup> )               | **                         | (0.82 × 10 <sup>-6</sup> )   | **                         | (0.007)                       | **      | (<1)   | **    |
| Nickel 200         | State College, PA                  | 51.5                                     | 141.5                      | 0.070                        | 0.058                      | 0.305                         | 0.229   | <25.4  | <25.4 |
| Incoloy alloy 800  |                                    | (1.1 × 10 <sup>-3</sup> )                | (2.9 × 10 <sup>-3</sup> )  | (1.43 × 10 <sup>-6</sup> )   | (1.19 × 10 <sup>-6</sup> ) | (0.012)                       | (0.009) | (<1)   | (<1)  |
| Inconel alloy 600  |                                    | 15.6                                     | 11.7                       | 0.021                        | 0.005                      | 0.102                         | 0.025   | <25.4  | <25.4 |
| Monel alloy 400    |                                    | (0.32 × 10 <sup>-3</sup> )               | (0.24 × 10 <sup>-3</sup> ) | (0.43 × 10 <sup>-6</sup> )   | (0.10 × 10 <sup>-6</sup> ) | (0.004)                       | (0.001) | (<1)   | (<1)  |
| Incoloy alloy 825* |                                    | 11.8                                     | 13.4                       | 0.016                        | 0.005                      | 0.076                         | 0.025   | <25.4  | <25.4 |
| Nickel 200         | State College, PA                  | (0.24 × 10 <sup>-3</sup> )               | (0.27 × 10 <sup>-3</sup> ) | (0.33 × 10 <sup>-6</sup> )   | (0.10 × 10 <sup>-6</sup> ) | (0.003)                       | (0.001) | (<1)   | (<1)  |
| Incoloy alloy 800  |                                    | 52.0                                     | 125.4                      | 0.071                        | 0.051                      | 0.279                         | 0.203   | <25.4  | <25.4 |
| Monel alloy 400    |                                    | (1.1 × 10 <sup>-3</sup> )                | (2.6 × 10 <sup>-3</sup> )  | (1.45 × 10 <sup>-6</sup> )   | (1.04 × 10 <sup>-6</sup> ) | (0.011)                       | (0.008) | (<1)   | (<1)  |
| Incoloy alloy 825* |                                    | 18.1                                     | 11.8                       | 0.024                        | 0.005                      | 0.102                         | 0.025   | <25.4  | <25.4 |
| Incoloy alloy 825* |                                    | (0.37 × 10 <sup>-3</sup> )               | (0.24 × 10 <sup>-3</sup> ) | (0.49 × 10 <sup>-6</sup> )   | (0.10 × 10 <sup>-6</sup> ) | (0.004)                       | (0.001) | (<1)   | (<1)  |

\*Formerly Ni-o-nel alloy 825

\*\*Lost due to vandalism at Point Reyes

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### 4-12.2.1.1.2 Corrosion in Acid Solutions

Nickel will corrode in dilute sulfuric, hydrochloric, and phosphoric acids containing oxidizers, such as air and metal salts.

### 4-12.2.1.1.3 Corrosion in Alkaline Solutions

Nickel is suitable for service in practically all alkaline concentrations and temperatures. Anhydrous ammonia or aqueous ammonium hydroxide solutions of less than 1% concentration do not attack nickel. However, nickel forms a soluble nickel-ammonium complex corrosion product and thus is attacked by stronger solutions of ammonia or aqueous ammonium hydroxide.

### 4-12.2.1.2 Pitting Corrosion

Nickel exhibits a noble galvanic potential in seawater; however, nickel is quite susceptible to pitting in quiet seawater—508 to 1270  $\mu\text{m}/\text{yr}$  (0.508 to 1.27 mm/yr (20 to 50 mpy)). Nickel is immune to pitting in seawater at very high velocities (6.1 m/s (20 ft/s)). Also nickel is attacked by strong alkaline hypochlorite solutions, from which pitting results, but a small amount of sodium silicate will inhibit this attack.

### 4-12.2.1.3 Stress-Corrosion Cracking

Nickel may be susceptible to stress-corrosion cracking in aqueous or fused caustic conditions if it is severely stressed. However, it is not susceptible to stress-corrosion cracking in chloride environments.

### 4-12.2.1.4 High-Temperature Corrosion

The high-temperature oxidation of pure nickel follows a parabolic relationship with time. The oxidation resistance of nickel, however, can be greatly improved by adding large quantities of chromium. Nickel forms a eutectic with nickel sulfide that melts at 646°C (1194°F), which is much less than the melting point of nickel (1453°C) (2647°F). Therefore, nickel can be severely damaged by sulfidation.

Nickel does not form a stable nitride at elevated temperatures, but commercially pure nickel corroded in a 3-month test in a chemical plant ammonia line operating at 499°C (930°F) (Ref. 157). The corrosion was the result of manganese-nitride formation. Manganese is an impurity in commercially pure wrought nickel.

Pure nickel does not form a stable carbide at elevated temperatures; therefore, graphite may form in a carburizing atmosphere and result in embrittlement.

Nickel is a superior material for service at elevated temperatures in dry chlorine, fluorine, and hydrogen chloride.

### 4-12.2.2 Nickel-Copper Alloys

#### 4-12.2.2.1 Uniform Corrosion

##### 4-12.2.2.1.1 Weathering Corrosion

Monel alloy 400 roofing sheets off the old Penn Station in New York City were examined when the building was torn down (Ref. 158). The sheets were roughly 0.43 mm (0.017 in.) thick after 54 yr of exposure. This corresponds to a corrosion rate of 0.322 mdd ( $6.60 \times 10^{-6}$  lb/ft<sup>2</sup>-day). For comparison, the Monel 400 specimens exposed in an industrial atmosphere in Newark, NJ, showed a corrosion rate of 0.196 mdd ( $4.01 \times 10^{-6}$  lb/ft<sup>2</sup>-day) over a 7-yr period.

##### 4-12.2.2.1.2 Corrosion in Acid Solutions

Alloy 400 has improved corrosion resistance compared to that of commercially pure nickel in nonoxidizing acids, such as sulfuric, hydrochloric, and phosphoric. The presence of oxidizers, such as air and metal salts, increases the corrosion susceptibility. Alloy 400 is also not resistant to oxidizing media, such as nitric acid, ferric chloride, chromic acid, wet chlorine, sulfur dioxide, or ammonia.

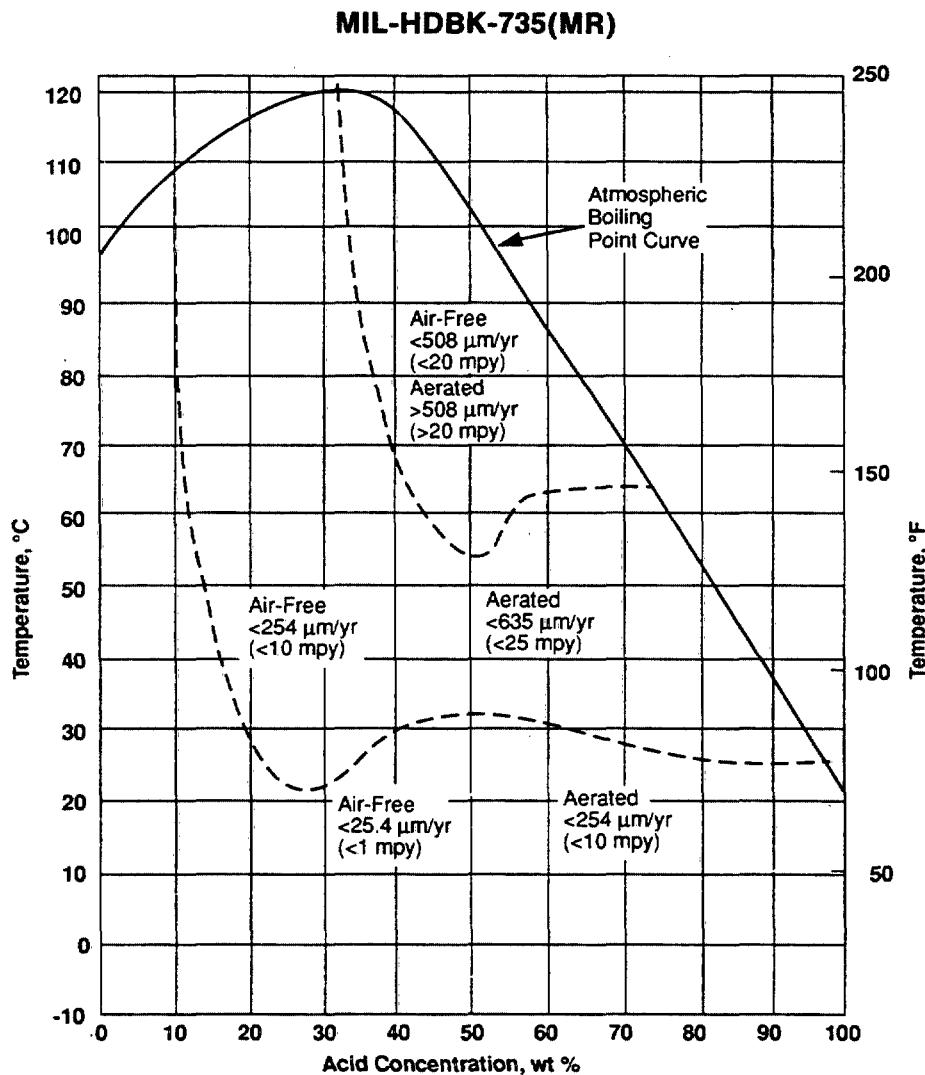
Alloy 400 does, however, have excellent resistance to hydrofluoric acid solutions at all temperatures and pressures. Fig. 4-38 is an isocorrosion diagram for Monel alloy 400 in hydrofluoric acid. Aeration or the presence of oxidizing salts increases corrosion rates.

##### 4-12.2.2.2 Pitting and Crevice Corrosion

The pitting penetration rate of alloy 400 in quiet seawater is from 76 to 381  $\mu\text{m}/\text{yr}$  (3 to 15 mpy). Alloy 400 shows some susceptibility to crevice corrosion attack. On a scale of 100 (Hastelloy C = 0, pure copper = 100), alloy 400 has a resistance of 10 to fouling organisms in quiet seawater. Above a velocity of about 0.91 m/s (3 ft/s), it is increasingly difficult for fouling organisms to attach themselves to the surface of the alloy. At seawater velocities above 1.8 m/s (6 ft/s), the pitting of alloy 400 is less than 25.4  $\mu\text{m}/\text{yr}$  (1 mpy), and at very high velocities, i.e., greater than 6.1 m/s (20 ft/s), the corrosion rate of alloy 400 is nil.

##### 4-12.2.2.3 Stress-Corrosion Cracking

Alloy 400 is not subject to chloride stress-corrosion cracking. When it contains residual stresses, it is cracked by warm (49°C (120°F)) hydrofluorosilic acid, mercury, and mercury salts (Ref. 160). Alloy 400 has cracked when in contact with hydrofluoric acid vapor, air, and moisture (Ref. 161), but it does not crack when it is fully immersed in the acid.



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**Figure 4-38. Isocorrosion Diagram for Monel Alloy 400 in Hydrofluoric Acid (Ref. 159)**

#### 4-12.2.2.4 High-Temperature Corrosion

Nickel-copper alloys are not used in high-temperature oxidizing and sulfidizing atmospheres. The corrosion of Monel in dry chlorine and fluorine at high temperatures is somewhat greater than that of nickel, but its corrosion rate in dry hydrogen chloride is much greater than that of nickel.

#### 4-12.2.3 Nickel-Molybdenum Alloys

##### 4-12.2.3.1 Uniform Corrosion in Acid Solutions

Hastelloy B-2 is suited for equipment handling hydrochloric acid at all concentrations and temperatures including the boiling point, as indicated in Fig. 4-39. Its corrosion behavior, however, is affected by oxidizing chemicals. The presence of ferric or cupric ions in solution greatly accelerates corrosion attack. Dissolved oxygen also increases the corrosion rate.

Alloy B-2 has good resistance to pure sulfuric acid at all

concentrations below 60% acid at temperatures up to the boiling point. It also has good resistance below 100°C (212°F) at concentrations above 60% acid. Fig. 4-40 is an isocorrosion diagram of Hastelloy alloy B-2 in sulfuric acid. The presence of oxidizing salts, such as ferric chloride, ferric sulphate, or cupric chloride, can accelerate corrosion in sulfuric acid.

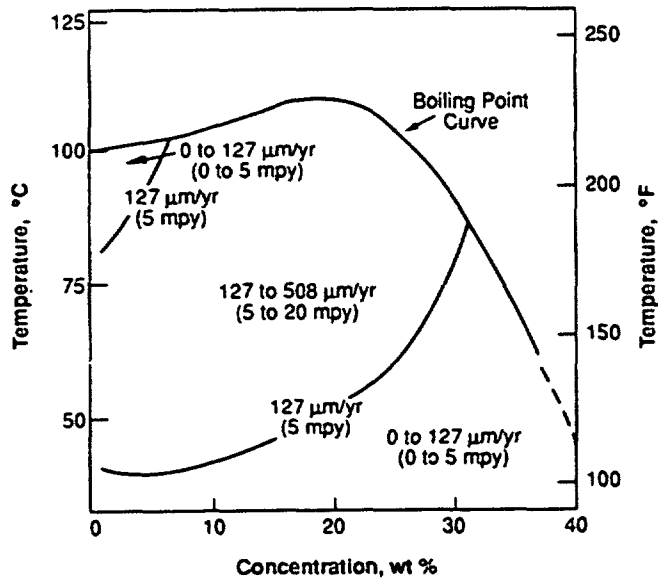
Alloy B-2 has acceptable corrosion resistance in most concentrations and temperatures of reagent grade phosphoric acid and is resistant to attack by hydrofluoric acid and many organic acids, such as acetic, formic, and cresylic.

Alloy B-2 is not suitable for use in oxidizing acids, such as nitric and chromic, nor in oxidizing salts, such as ferric chloride and cupric chloride.

##### 4-12.2.3.2 Pitting Corrosion

Alloy B-2 is highly resistant to pitting in most acid-chloride environments, and it is resistant to many dry,

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NOTE: All test specimens were solution heat-treated and in the unwelded condition.

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**Figure 4-39. Isocorrosion Diagram for Hastelloy Alloy B-2 in Hydrochloric Acid (Ref. 162)**

chloride-bearing salts, including aluminum chloride, magnesium chloride, antimony chloride, ammonium chloride, and zinc chloride.

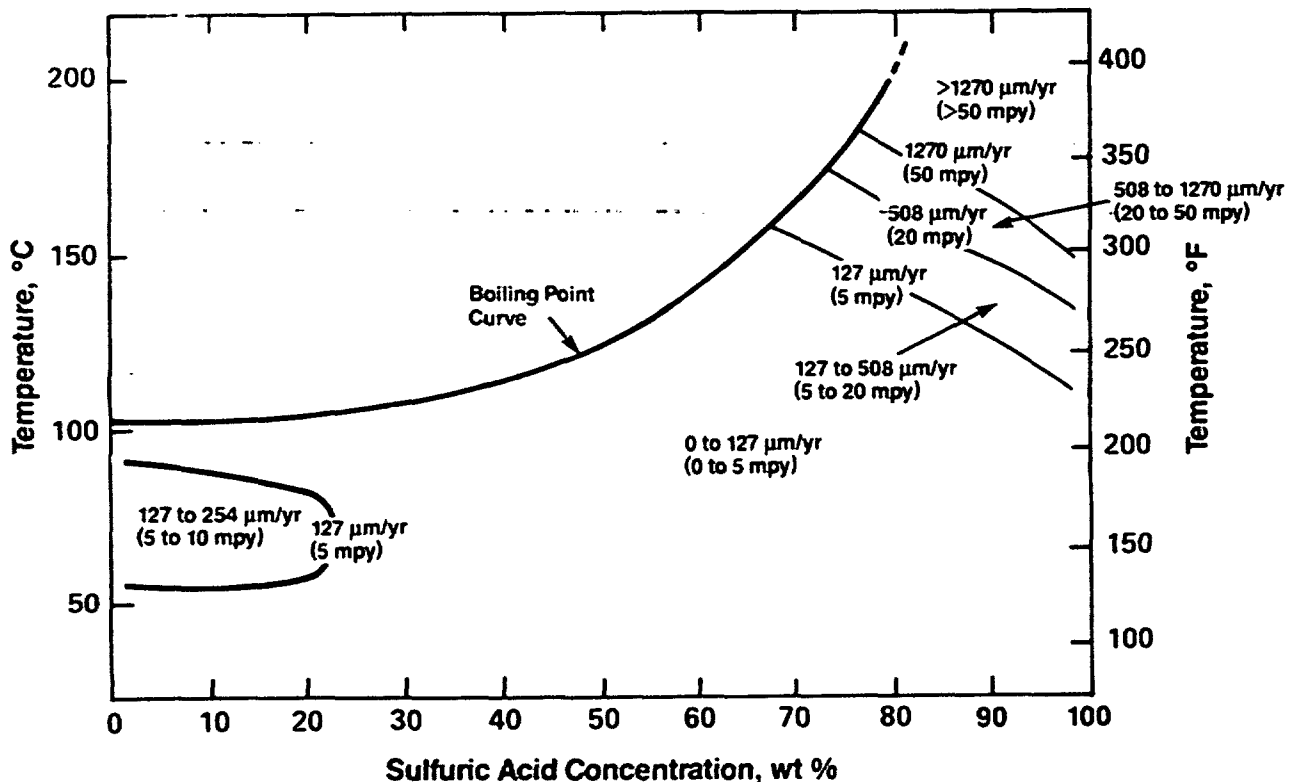
#### 4-12.2.3.3 Stress-Corrosion Cracking

Alloy B-2 is resistant to chloride stress-corrosion cracking.

#### 4-12.2.3.4 High-Temperature Corrosion

Alloy B-2 has limited use in elevated temperature environments. Because it contains no chromium, B-2 does not form a protective scale in air. Alloy B-2 does, however, have good resistance to dry chlorine and dry hydrogen at elevated temperatures.

Alloy B-2 is used in reducing environments and vacuum furnaces because it has good mechanical properties at elevated temperatures. In the temperature range of 599° to 849°C (1110° to 1560°F), however, intermetallic phases form upon aging. Therefore, alloy B-2 should not be used in any environment for long periods in this temperature range.



NOTE: All test specimens were solution heat-treated and in the unwelded condition.

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**Figure 4-40. Isocorrosion Diagram for Hastelloy Alloy B-2 in Sulfuric Acid (Ref. 162)**



**MIL-HDBK-735(MR)****4-12.2.4 Nickel-Chromium-Iron Alloys****4-12.2.4.1 Uniform Corrosion****4-12.2.4.1.1 Weathering Corrosion**

The nickel-chromium-iron alloys show much less weathering corrosion than the nickel or the nickel-copper alloys.

**4-12.2.4.1.2 Corrosion in Acid Solutions**

Alloy 800 is not used much in aqueous environments; its resistance to corrosion is between that of Types 304 and 316 stainless steels. Alloy 825 has good resistance in pure sulfuric acid up to concentrations of 40% at temperatures up to boiling, and it has good resistance at all concentrations up to 66°C (150°F). Oxidizing salts, such as cupric and ferric compounds, lower the corrosion rate in dilute sulfuric acid. Alloy 825 has good resistance to attack in phosphoric acid but has limited resistance in hydrochloric or hydrofluoric acid.

**4-12.2.4.1.3 Corrosion in Ammonia Solutions**

Alloy 600 is very resistant to attack by ammonia solutions over the full range of concentrations and temperatures.

**4-12.2.4.2 Pitting and Crevice Corrosion**

Alloy 600 is subject to pitting and crevice corrosion because of its lack of molybdenum. Although alloy 825 has better resistance to pitting and crevice corrosion than alloy 800 because of its higher nickel content, other commercially available alloys have higher resistances.

**4-12.2.4.3 Stress-Corrosion Cracking**

Alloy 600 is susceptible to stress-corrosion cracking in high-temperature, concentrated alkalis as well as in molten anhydrous hydroxides. Alloy 600 cracked in hydrofluoric acid vapor over 48% hydrofluoric acid at 60°C (140°F), but it did not crack after several thousand hours in simulated boiler water (Ref. 161). However, tests at high stress levels and high temperatures have demonstrated stress-corrosion cracking of alloy 600 in high-purity water, as well as in the presence of caustic or lead compounds (Ref. 163). Thus, avoiding high stress levels is essential for avoiding stress-corrosion cracking in alloy 600.

Sensitized alloy 800 cracks in polythionic acid (Ref. 161), but the stress-corrosion cracking behavior of alloy 800 is better than that of the 300 series stainless steels.

Although alloy 825 cracks in boiling magnesium chloride solution, it has good resistance to stress-corrosion cracking in neutral chloride solutions.

In general, nickel alloys are resistant to stress-corrosion cracking in environments, including nitrate and ammonia solutions and sulfides, that cause cracking in other metals.

**4-12.2.4.4 High-Temperature Corrosion**

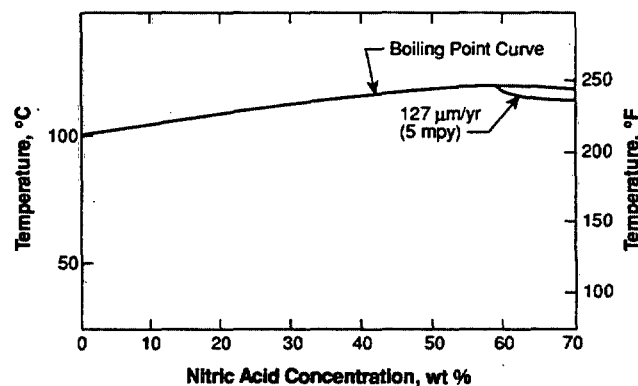
Alloy 600 can be used in air up to about 1093°C (2000°F), but the presence of sulfur reduces the maximum-use temperature to about 316°C (600°F). Alloy 600 has excellent resistance to dry halogens at elevated temperatures.

Although alloy 800 can be used in oxidizing gases up to about 1093°C (2000°F), it cannot be used in strong reducing mixtures of hydrogen sulfide and hydrogen.

The nickel-chromium-iron alloys can undergo sensitization at elevated temperatures. The source of carbon could be the alloy itself or graphite that precipitates in a carbon-containing gas. This sensitization can result in intergranular corrosion as well as in oxidation and sulfidation. Alloy 825 resists intergranular attack after being heated in the sensitizing range.

**4-12.2.5 Nickel-Chromium-Iron-Copper Alloys****4-12.2.5.1 Uniform Corrosion in Acid Solutions**

Hastelloy alloy G-30 has only limited usefulness in hydrochloric acid. Alloy G-30 has excellent resistance to nitric acid, as shown in Fig. 4-41, over a wide range of acid concentrations and temperatures and has demonstrated excellent resistance to a wide range of phosphoric acid compositions presumably because of the high chromium content of the alloy. Alloy G-30 has acceptable corrosion rates over a wide range of sulfuric acid compositions and a limited temperature range, as shown in Fig. 4-42. Although many alloys resist pure sulfuric acid, alloy G-30 resists combinations of sulfuric acid and chlorides. Alloy G-30 is used in phosphoric acid production and in processing organic chemicals, especially when chlorides are present.

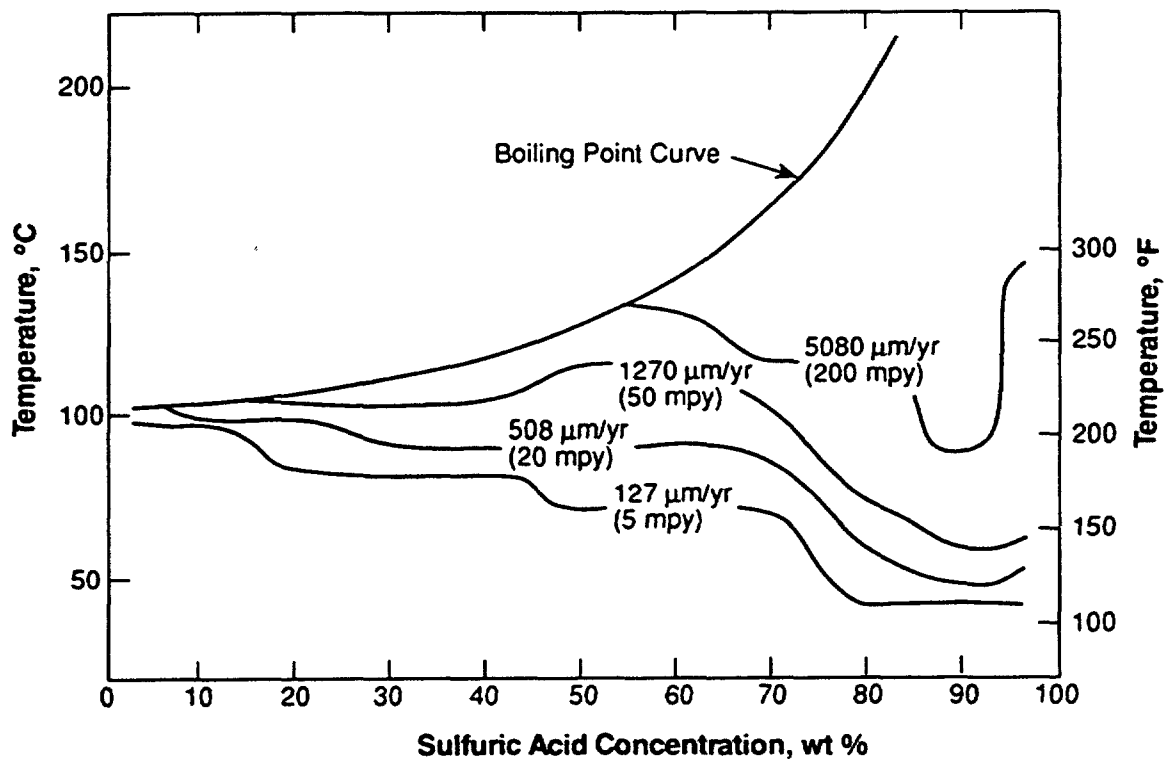


NOTE: All test specimens were solution heat-treated and in the unwelded condition.

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**Figure 4-41. Isocorrosion Diagram for Hastelloy Alloy G-30 in Nitric Acid (Ref. 162)**

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NOTE: All test specimens were solution heat-treated and in the unwelded condition.

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Figure 4-42. Isocorrosion Diagram for Hastelloy Alloy G-30 in Sulfuric Acid (Ref. 162)

#### 4-12.2.5.2 Pitting and Crevice Corrosion

Alloys G, G-3, and G-30 are resistant to pitting and crevice corrosion. Alloy G is susceptible to this type of corrosion in solutions with high chloride levels containing oxidizing ions, however, alloy G-30 has demonstrated resistance to pitting in such solutions.

#### 4-12-2.5.3 Stress-Corrosion Cracking

Alloys G, G-3, and G-30 are resistant to stress-

corrosion cracking.

#### 4-12.2.6 Nickel-Chromium-Molybdenum-Iron Alloys

##### 4-12.2.6.1 High-Temperature Oxidation

The oxidation of Hastelloy alloy X is compared to another nickel-base alloy and a cobalt-base alloy in Table 4-110.

TABLE 4-110. COMPARATIVE OXIDATION RESISTANCE IN FLOWING AIR\* (Ref. 164A)

| TEST TEMPERATURE, |      | AVERAGE METAL AFFECTED** IN |         |                    |         |                   |         |
|-------------------|------|-----------------------------|---------|--------------------|---------|-------------------|---------|
| °C                | °F   | 1008 HOURS, † μm (mil)      |         |                    |         |                   |         |
|                   |      | Hastelloy Alloy S           |         | Haynes Alloy 188†† |         | Hastelloy Alloy X |         |
| 980               | 1800 | 13                          | (0.5)   | 15                 | (0.6)   | 23                | (0.9)   |
| 1095              | 2000 | 33                          | (1.3)   | 33                 | (1.3)   | 69                | (2.7)   |
| 1150              | 2100 | 43                          | (1.7)   | 203                | (8.0)   | 147               | (5.8)   |
| 1205              | 2200 | >805                        | (>31.7) | >551               | (>21.7) | >899              | (>35.4) |

\*Flowing air at a velocity of 2134 mm/min (7.0 ft/min) in a tube furnace; samples cycled to room temperature once a week

\*\*Metal loss plus average depth of internal penetration; large internal voids not included

†All figures shown as greater than stated value represent extrapolation of tests for which samples were consumed in less than 1008 h.

††Haynes alloy No. 188 is a cobalt-base alloy.

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## 4-12-2.6.2 Hot Corrosion

The hot corrosion of Hastelloy alloy X is shown in Table 4-111. This information is compared to the information for two other nickel-base alloys and a cobalt-base alloy in Table 4-112.

Continued temperature cycling of alloy X eventually reduces its room temperature ductility. As a result, repair welding becomes difficult without solution annealing, and solution annealing may not be possible on large parts.

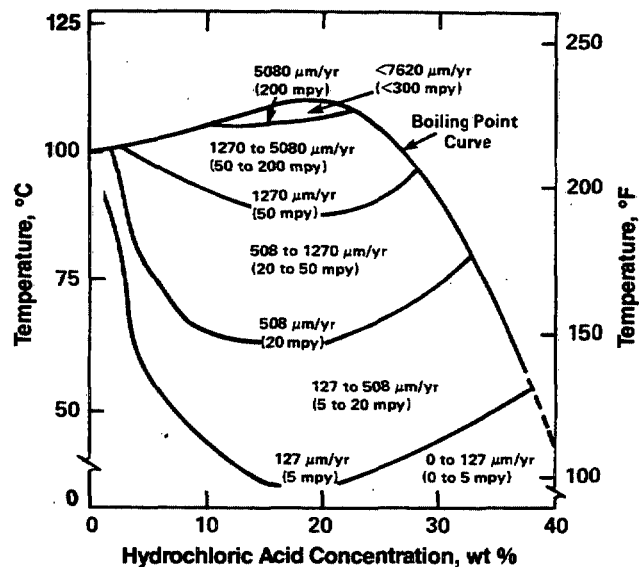
## 4-12.2.7 Nickel-Chromium-Molybdenum Alloys

## 4-12.2.7.1 Uniform Corrosion

## 4-12.2.7.1.1 Corrosion in Acid Solutions

Hastelloy alloy C-276 is resistant to all concentrations of hydrochloric acid at room temperature and is used successfully up to about 49°C (120°F). Such usage is illustrated in the isocorrosion diagram of Fig. 4-43. Alloy C-276 is only marginally more resistant than alloy C-4, and the presence of oxygen increases the corrosion rate significantly. Alloy 625 is resistant to aqueous solutions of hydrochloric acid at temperatures below 66°C (150°F).

Hastelloy alloy C-276 has only limited resistance to nitric acid. The resistance of alloy C-4, which is shown in the isocorrosion diagram of Fig. 4-44, is somewhat better,



NOTE: All test specimens were solution heat-treated and in the unwelded condition.

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Figure 4-43. Isocorrosion Diagram for Hastelloy Alloy C-276 in Hydrochloric Acid (Ref. 162)

TABLE 4-111. HOT CORROSION OF HASTELLOY ALLOY X\* (Ref. 165)

| TEST TEMPERATURE,<br>°C | TEST TEMPERATURE,<br>°F | TEST PERIOD,<br>h | METAL LOSS/SIDE,<br>mm (mil) | MAXIMUM                           | TOTAL METAL                |
|-------------------------|-------------------------|-------------------|------------------------------|-----------------------------------|----------------------------|
|                         |                         |                   |                              | PENETRATION/<br>SIDE,<br>mm (mil) | AFFECTED/SIDE,<br>mm (mil) |
| 899                     | 1650                    | 200               | 0.03 (1.2)                   | 0.05 (1.8)                        | 0.08 (3.0)                 |
| 899                     | 1650                    | 1000              | 0.03 (1.2)                   | 0.14 (5.6)                        | 0.17 (6.8)                 |
| 954                     | 1750                    | 200               | 0.03 (1.3)                   | 0.08 (3.0)                        | 0.11 (4.3)                 |
| 1010                    | 1850                    | 200               | 0.04 (1.6)                   | 0.08 (3.3)                        | 0.12 (4.8)                 |

\*All tests performed by exposure to the combustion products of No. 2 diesel oil (0.4% sulfur) and 5 ppm of sea salt. Gas velocity over samples was 4 m/s (13 ft/s). Thermal shock frequency was 1/h.

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TABLE 4-112. COMPARATIVE AVERAGE HOT CORROSION RESISTANCE FOR 1000 HOURS AT 900°C (1650°F)\* (Ref. 164B)

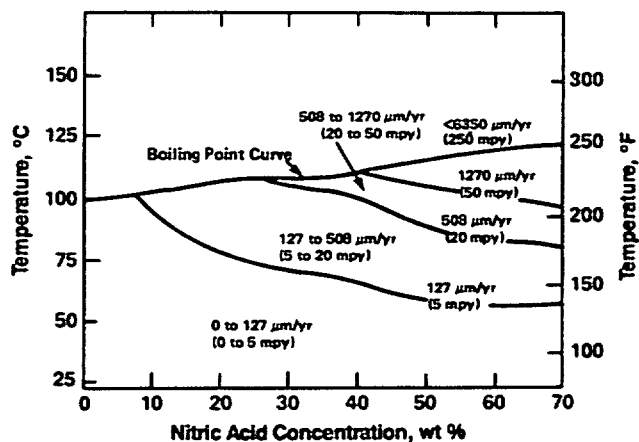
|                                  | ALLOY               |                       |                     |                      |
|----------------------------------|---------------------|-----------------------|---------------------|----------------------|
|                                  | Haynes Alloy<br>230 | Haynes Alloy<br>188** | Haynes Alloy<br>625 | Hastelloy<br>Alloy X |
| Metal Loss, μm (mil)             | 30 (1.2)            | 20 (0.8)              | 46 (1.8)            | 41 (1.6)             |
| Average Metal Affected, μm (mil) | 130 (5.1)           | 69 (2.7)              | 132 (5.2)           | 140 (5.5)            |

\*Tests were conducted in a low-velocity burner rig burning No. 2 fuel oil with 0.4% sulfur. Air:fuel ratio was 30:1. Artificial seawater was injected at a rate equivalent to 5 ppm salt. Samples were cycled out of the gas stream once an hour and cooled to near ambient temperature. Gas velocity was 4 m/s (13 ft/s).

\*\*Haynes alloy 188 is a cobalt-base alloy.

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NOTE: All test specimens were solution heat-treated and in the unwelded condition.

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**Figure 4-44. Isocorrosion Diagram for Hastelloy Alloy C-4 in Nitric Acid (Ref. 162)**

whereas alloy 625 is resistant to mixtures of nitric and hydrofluoric acids.

Alloys C-276 and C-4 have acceptable corrosion resistance in most concentrations and temperatures of reagent grade phosphoric acid, but commercial grades of phosphoric acid contain fluorides and ferric salts as impurities

that can accelerate the corrosion attack. Alloy 625 has excellent resistance to phosphoric acid solutions, including the commercial grades of phosphoric acid.

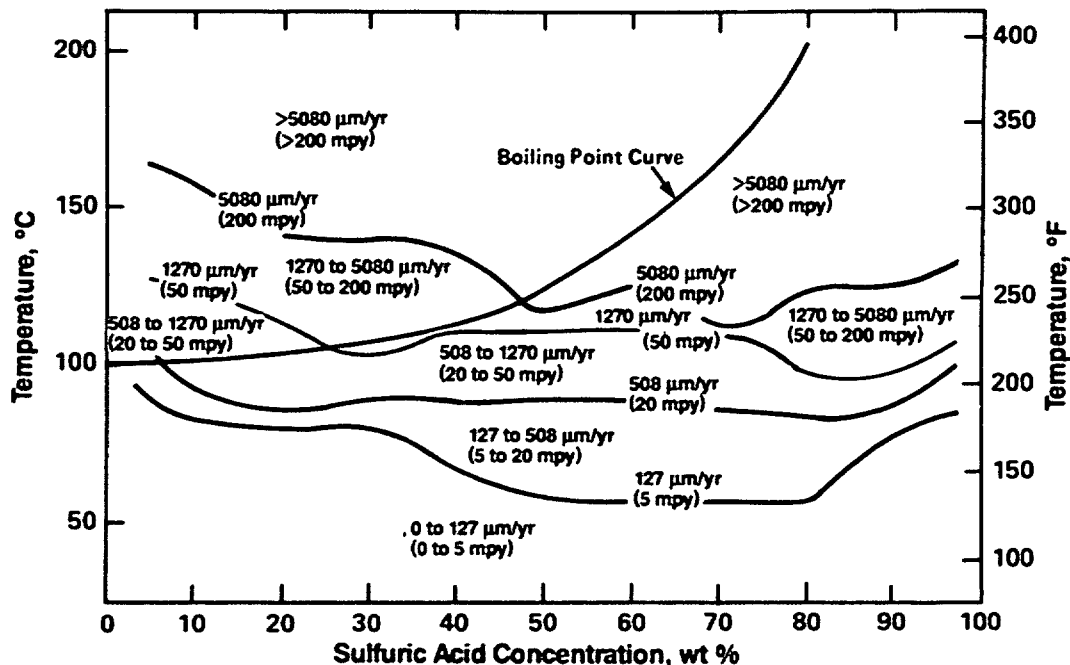
Alloys C-276 and C-4 have acceptable corrosion rates in sulfuric acid over a relatively wide range of concentrations and temperatures. The isocorrosion diagram of alloy C-276 in sulfuric acid is Fig. 4-45. Chloride contamination of sulfuric acid tends to increase the corrosion attack of alloys C-276 and C-4 at all acid concentrations. Alloy 625 is resistant to aqueous sulfuric acid solutions at temperatures below 66°C (150°F).

Alloy 625 and alloy C-276 have satisfactory resistance to sulfuric acid, fluorspar, and hydrogen fluoride in hydrofluoric acid generators.

Alloys C-276 and C-4 have good resistance to acetic and formic acids at temperatures to their boiling points in all concentrations. Alloy 625 is also resistant to organic acids below 66°C (150°F).

#### 4-12.2.7.1.2 Corrosion in Acid Salts

Alloys C-276 and C-4 are highly resistant to acid chlorides, such as ammonium chloride or zinc chloride. Alloy C-276 resists acid sulfates, such as aluminum or ammonium sulfates, and acid phosphates, and it resists ferric chloride at room temperature and can be used safely in concentrations up to 40% at 66°C (150°F).



NOTE: All test specimens were solution heat-treated and in the unwelded condition.

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**Figure 4-45. Isocorrosion Diagram for Hastelloy Alloy C-276 in Sulfuric Acid (Ref. 162)**

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## 4-12.2.7.1.3 Corrosion in Chlorine

Hastelloy alloy C-276 has good resistance to room temperature chlorine dioxide and other solutions containing free chlorine in appreciable concentrations, such as those used for bleaching purposes. However, the alloy may be attacked in solutions above room temperature, especially at temperatures over 66°C (150°F). At room temperature the rate of penetration in wet chlorine gas is less than 25.4 μm/yr (1 mpy); at higher temperatures, local attack may occur.

## 4-12.2.7.2 Pitting and Crevice Corrosion

Inconel alloy 625 and Hastelloy C are inert to crevice corrosion in quiet seawater. Hastelloy C does not pit in quiet seawater and has a relatively low resistance to fouling organisms in quiet seawater. At very high velocities, i.e., from 0.9 to 1.8 m/s (3 to 6 ft/s), the corrosion rate of Hastelloy C is nil.

Alloy C-276 has excellent resistance to pitting and crevice corrosion. The resistance of alloy 625 and alloy C-4 is less than alloy C-276 but better than alloy G.

## 4-12.2.7.3 Stress-Corrosion Cracking

Alloys 625, C-276, and C-4 have excellent resistance to chloride stress-corrosion cracking.

## 4-12.2.7.4 High-Temperature Corrosion

## 4-12.2.7.4.1 Oxidation

Alloy 625 has good resistance to oxidation at elevated temperatures. However, it loses room temperature

ductility after long aging in the 593° to 760°C (1100° to 1400°F) temperature range.

Hastelloy alloy S was developed primarily for gas turbine applications. It has good alloy stability and oxidation resistance and a low coefficient of thermal expansion. Its composition is similar to alloys C-276 and C-4. The oxidation rate of alloy S is compared to Hastelloy X and a cobalt-base alloy, Haynes alloy 188, in Table 4-110. The oxidation rate for alloy C-276, which is shown in Table 4-113, is significantly higher than that for alloy S. Therefore, alloy C-276 should not be used as a high-temperature alloy, and alloy S should not be used for low-temperature corrosion resistance.

## 4-12.2.7.4.2 Hot Corrosion

The hot corrosion resistances of alloy S and alloy 625 are compared with Hastelloy X and Haynes alloy 188 in Table 4-112. The resistances of alloy S and alloy X are similar but are not as good as the cobalt-base alloy 188, and the resistance of alloy 625 is not as good as that of alloy S and alloy X.

## 4-12.3 INTERFACE PROBLEMS

## 4-12.3.1 Metal-to-Metal

The seawater galvanic series shown in Fig. 4-27 indicates the relative nobility of nickel and nickel-base alloys. This is put into practical terms in Table 4-114, which shows the compatibility of various metals as fasteners and base metals. It is important to note that some of the stainless steels can be anodic or cathodic to nickel and its alloys

TABLE 4-113. OXIDATION OF HASTELLOY ALLOY C-276 (Ref. 166)

| AVERAGE OXIDATION RATE PER 100-h TEST PERIOD |      |                      |      |                         |      |
|--|------|----------------------|------|-------------------------|------|
| TEST TEMPERATURE,                            |      | 100 h,<br>CONTINUOUS |      | 100 h,<br>INTERMITTENT* |      |
| °C   | °F   | μm                   | mil  | μm                      | mil  |
| 982  | 1800 | 2.8                  | 0.11 | 2.8                     | 0.11 |
| 1038   | 1900 | 5.6                  | 0.22 | 4.6                     | 0.18 |
| 1093   | 2000 | 41.1                 | 1.62 | 73.2                    | 2.88 |

| AVERAGE OXIDATION EFFECTS OF TIME AT CONSTANT TEMPERATURE |      |  |   |                                   |      |
|---|------|--|---|-----------------------------------|------|
| TEST TEMPERATURE,   |      | DURATION<br>OF TEST PERIOD<br>(CONTINUOUS) | WEIGHT CHANGE                             | OXIDATION RATE<br>PER TEST PERIOD |      |
| °C  | °F   |  | mg/cm <sup>2</sup> (lb/in. <sup>2</sup> ) | μm                                | mil  |
| 1177  | 2150 | 15 min                                     | 5.2 ( 7.4 × 10 <sup>-5</sup> )            | 7.9                               | 0.31 |
| 1177  | 2150 | 30 min                                     | 9.0 (12.8 × 10 <sup>-5</sup> )            | 12.4                              | 0.49 |
| 1177  | 2150 | 1 h  | 13.3 (18.9 × 10 <sup>-5</sup> )           | 17.5                              | 0.69 |
| 1177  | 2150 | 2 h  | 18.4 (26.2 × 10 <sup>-5</sup> )           | 24.4                              | 0.96 |
| 1177  | 2150 | 6 h  | 23.6 (33.6 × 10 <sup>-5</sup> )           | 31.2                              | 1.23 |

\*Eight periods of 3 h and four periods of 19 h

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TABLE 4-114. GALVANIC COMPATIBILITY (SEA WATER FASTENERS) (Ref. 87)

| BASE METAL<br>↓             | FASTENER              |                  |                                    |                  |                            |                            |                            |                            |
|-----------------------------|-----------------------|------------------|------------------------------------|------------------|----------------------------|----------------------------|----------------------------|----------------------------|
|                             | Aluminum <sup>1</sup> | Carbon Steel     | Silicon Bronze                     | Nickel           | Nickel-Chromium Alloys     | Type 304                   | Nickel-Copper Alloy 400    | Type 316                   |
| Aluminum                    | Neutral               | C <sup>(2)</sup> | Unsatis- <sup>(2)</sup><br>factory | C <sup>(2)</sup> | C                          | C                          | C <sup>(2)</sup>           | C                          |
| Steel and Cast Iron         | NC                    | Neutral          | C                                  | C                | C                          | C                          | C                          | C                          |
| Austenitic Nickel Cast Iron | NC                    | NC               | C                                  | C                | C                          | C                          | C                          | C                          |
| Copper                      | NC                    | NC               | C                                  | C                | C                          | C                          | C                          | C                          |
| 70/30 Copper-Nickel Alloy   | NC                    | NC               | NC                                 | C                | C                          | C                          | C                          | C                          |
| Nickel                      | NC                    | NC               | NC                                 | Neutral          | C <sup>(3)</sup>           | C <sup>(3)</sup>           | C                          | C <sup>(3)</sup>           |
| Type 304                    | NC                    | NC               | NC                                 | NC               | May <sup>(4)</sup><br>Vary | Neutral <sup>(3)</sup>     | C                          | C <sup>(4)</sup>           |
| Nickel-Copper Alloy 400     | NC                    | NC               | NC                                 | NC               | May <sup>(4)</sup><br>Vary | May <sup>(4)</sup><br>Vary | Neutral                    | May <sup>(4)</sup><br>Vary |
| Type 316                    | NC                    | NC               | NC                                 | NC               | May <sup>(4)</sup><br>Vary | May <sup>(4)</sup><br>Vary | May <sup>(4)</sup><br>Vary | Neutral <sup>(4)</sup>     |

(1) Anodizing would change ratings as fastener.

(2) Fasteners are compatible and protected but may lead to enlargement of the bolt hole in aluminum plate.

(3) Cathodic protection afforded the fastener by the base metal may not be enough to prevent crevice corrosion of the fastener particularly under the head of bolt fasteners.

(4) Crevice corrosion may occur under head of bolt fasteners.

NOTE: C = compatible, protected

NC = not compatible, preferentially corroded

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and that those alloys that are susceptible to crevice corrosion may show corrosion under the head of a bolt when the galvanic potential between the bolt and the base metal is small.

Table 4-115 shows the recommended welding materials for joining the various nickel alloys.

#### 4-12.3.2 Metal-to-Nonmetal

Hot corrosion is attributed to the formation of sodium sulfate on alloys in high-temperature gas turbines. The sodium sulfate reacts to form a metal sulfide. This action usually occurs on the nozzle guide vanes and the first row of rotor blades. Hot corrosion resistance is directly related to the chromium content of the alloy. Aluminum and titanium are added to increase the strength of the nickel-chromium alloy. This change also usually means reducing the chromium content, which increases the susceptibility to hot corrosion. The compositions of some

nickel-base, high-temperature alloys are shown in Table 4-116. Some of these alloys contain less than 10% chromium. Testing in a burner rig using JP-4R fuel gave results that indicate that at least 12% chromium is necessary for reasonable resistance to hot corrosion (Ref. 168).

Lower cost distillates, residual oils, and certain crude oils may contain organovanadium compounds, which, during combustion, are converted to vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>). This is a low-melting oxide that can cause problems in the hot corrosion of nickel-base superalloys. If the turbine metal components are cooler than the hot turbine gases and the metal temperature is below the temperature of condensation of V<sub>2</sub>O<sub>5</sub>, V<sub>2</sub>O<sub>5</sub> can continuously condense onto the turbine components. Because of the ability of condensed V<sub>2</sub>O<sub>5</sub> to dissolve oxide scales, the effect of continuously condensing V<sub>2</sub>O<sub>5</sub> on turbine parts may be catastrophic.

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TABLE 4-115. RECOMMENDED WELDING MATERIALS (Ref. 159)

| ALLOY                 | BARE WIRE (GTMA)<br>(AWS A5.14)       | COATED ELECTRODES (SMA)<br>(AWS A5.11)       |
|-----------------------|---------------------------------------|--|
| Nickel 200            | Nickel filler metal 61<br>(ERNi-3)    | Nickel welding electrode 141<br>(ENi-1)      |
| Nickel 201            | Nickel filler metal 61<br>(ERNi-3)    | Nickel welding electrode 141<br>(ENi-1)      |
| Monel alloy 400       | Monel filler metal 60<br>(ERNiCu-7)   | Monel welding electrode 190<br>(ENiCu-2)     |
| Monel alloy K-500     | Monel filler metal 64<br>(ERNiCu-8)   | Monel welding electrode 134<br>(ENiCuAl-1)   |
| Hastelloy alloy B-2   | Alloy B-2 (ERNiMo-7)                  | Alloy B-2 electrodes                         |
| Inconel alloy 600     | Inconel filler metal 82<br>(ERNiCr-3) | Inconel welding electrode 182<br>(ENiCrFe-3) |
| Incoloy alloy 800     | Inconel filler metal 82<br>(ERNiCr-3) | Inconel welding electrode 132<br>(ENiCrFe-1) |
| Incoloy alloy 825     | Incoloy filler metal 65               | Inco-weld A electrode<br>(ENiCrFe-2)         |
| Hastelloy alloy G     | Alloy G (ERNiCrMo-1)                  | Incoloy welding electrode 135                |
| Hastelloy alloy X     | Alloy X (ERNiCrMo-2)                  | Alloy G electrodes (ENiCrMo-1)               |
| Inconel alloy 625     | Inconel filler metal 625              | Alloy X electrodes (ENiCrMo-2)               |
| Hastelloy alloy C-276 | Alloy C-276 (ERNiCrMo-4)              | Inconel welding electrode 112                |
| Hastelloy alloy C-4   | Alloy C-4 (ERNiCrMo-7)                | Alloy C-276 electrodes<br>(ENiCrMo-4)        |
| Hastelloy alloy S     | Alloy S                               | Alloy C-4 electrodes                         |

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Several nickel-base materials have been subjected to conditions that explore the effect of vanadium pentoxide on the accelerated oxidation of these alloys (Ref. 169). The conclusions are

1. "Under the conditions imposed in the study, nickel and nickel-chromium alloys form protective scales in the presence of  $V_2O_5$ . The apparent rate of dissolution of the vanadates formed in liquid  $V_2O_5$  deposited onto the vanadium-oxide-coated substrate do not increase the rates of oxidation of the substrates."

2. "Initial, rapid rates of oxidation between  $V_2O_5$  and a metal substrate are due to reduction of  $V_2O_5$  by the substrate."

3. "Alloys based upon the intermetallic systems  $Ni_3Al$ ,  $NiAl$ , and  $NiTi$  are particularly susceptible to  $V_2O_5$  corrosion."

4. "The product of the reaction between  $V_2O_5$  and alloys that tend to form aluminum or titania-rich scales in simple oxidation is glass-like or amorphous."

#### 4-12.4 METHODS FOR PREVENTION OF CORROSION

The fundamental method for preventing corrosion of nickel and nickel-base alloys is to select the proper composition for the service environment. Corrosion testing may be required for environments for which there

is little experience. It is not likely that a nickel alloy would be protected by paint. If a paint film could be relied upon for corrosion protection, a much cheaper structural base metal could be specified.

Coatings are being developed for nickel alloys used in the high-temperature oxidation and hot corrosion environment of jet engines. These coatings range from simple diffusion-aluminide coatings to complex multicomponent, multilayered overcoats.

Overlay coatings of the  $NiCrAlY$  or  $NiCoCrAlY$  type result in significant improvements in oxidation and hot corrosion resistance. Platinum overlays on these coatings can improve oxidation and hot corrosion resistance.

Ceramic thermal barrier coatings for use on cooled hot section components of gas turbine engines could improve efficiency and/or component durability (Refs. 170, 171, and 172). The thermal barrier coat—a zirconia-yttria or a calcium-oxide-silica mixture—is applied over a  $NiCrAlY$ -type bond coat.

The thermal barrier coats tend to be porous and are subject to failure by sodium sulfate and vanadium deposition. Accordingly, dense overcoats have been tested that might extend the life of the thermal barrier coat (Ref. 173). These range from metals, such as  $AlPt_3$  and  $ZrPt_3$ , to ceramics, such as zirconia-yttria mixtures, and to glasses and glass mixtures.

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TABLE 4-116. NOMINAL COMPOSITIONS OF SOME NICKEL-BASE HIGH-TEMPERATURE ALLOYS (Ref. 167)

| ALLOYS           | COMPOSITION, wt % |         |         |       |         |       |      |   |
|------------------|-------------------|---------|---------|-------|---------|-------|------|---|
|                  | Cr                | Al      | Ti      | Co    | Mo      | W     | Ni†  | Other*  |
| B-1900           | 8.0               | 6.0     | 1.0     | 10.0  | 6.0     | 0.1** | Bal  | 4.3 Ta  |
| G.64             | 11.0              | 6.0     | —       | —     | 3.0     | 3.5   | Bal  | 5.0 Fe**, 2.0 Cb  |
| GMR235           | 15.5              | 3.0     | 2.0     | —     | 5.25    | —     | Bal  | 10 Fe   |
| Hastelloy X      | 22.0              | —       | —       | 1.5   | 9.0     | 0.6   | Bal  | 18.5 Fe   |
| IN-100           | 10.0              | 5.5     | 4.7     | 15.0  | 3.0     | —     | Bal  | 1.0 V   |
| INCO 700         | 15.0              | 3.0     | 2.2     | 28.5  | 3.75    | —     | 46.0 | —   |
| Alloy 713 C      | 12.5              | 6.1     | 0.8     | —     | 4.2     | —     | Bal  | 2.5 Fe**, 2.0 Cb  |
| INCO 718         | 19.0              | 0.5     | 0.9     | —     | 3.05    | —     | 52.5 | 18.5 Fe, 5.13 Cb††  |
| IN-738           | 16.0              | 3.4     | 3.4     | 8.5   | 1.75    | 2.6   | Bal  | 1.75 Ta, 0.9 Cb   |
| INCO X-750       | 15.5              | 0.7     | 2.5     | —     | —       | —     | 73.0 | 7.0 Fe, 0.95 Cb††   |
| INCO 751         | 15.5              | 1.2     | 2.3     | —     | —       | —     | 72.5 | 7.0 Fe, 0.95 Cb††   |
| MAR-M 200        | 9.0               | 5.0     | 2.0     | 10.0  | —       | 12.5  | Bal  | 1.0 Cb  |
| MAR-M 421        | 15.8              | 4.25    | 1.75    | 9.5   | 2.0     | 3.8   | Bal  | 2.0 Cb  |
| Nicrotung        | 12.0              | 4.0     | 4.0     | 10.0  | —       | 8.0   | Bal  | —   |
| Nimonic 75       | 20.0              | —       | 0.4     | —     | —       | —     | Bal  | 5.0 Fe**, 1.0 Mn**, 1.0 Si**                                |
| Nimonic 80A      | 18/21             | 0.5/1.8 | 1.8/2.7 | 2.0** | —       | —     | Bal  | 5.0 Fe**, 1.0 Mn**, 1.0 Si**                                |
| Nimonic 90       | 18/21             | 0.8/2.0 | 1.8/3.0 | 15/21 | —       | —     | Bal  | 5.0 Fe**, 1.0 Mn**, 1.0 Si**                                |
| Nimonic 100      | 10/12             | 4.0/6.0 | 1.0/2.0 | 18/22 | 4.5/5.5 | —     | Bal  | 2.0 Fe**  |
| Nimonic 105      | 13.5/16           | 4.2/4.8 | 0.9/1.5 | 18/22 | 4.5/5.5 | —     | Bal  | 1.0 Fe**, 1.0 Mn**, 1.0 Si**                                |
| Nimonic 115      | 15.0              | 5.0     | 4.0     | 15.0  | 3.5     | —     | Bal  | —   |
| RA-333           | 25.0              | —       | —       | 3.0   | 3.0     | 3.0   | Bal  | 18.0 Fe, 1.5 Mn, 1.25 Si                                    |
| TRW 1800         | 13.0              | 6.0     | 0.6     | —     | —       | 9.0   | Bal  | 1.5 Cb  |
| TRW 1900         | 10.3              | 6.3     | 1.0     | 10.0  | —       | 9.0   | Bal  | 1.5 Cb  |
| TRW-NASA VI<br>A | 6.1               | 5.4     | 1.0     | 7.5   | 2.0     | 5.5   | Bal  | 9.0 Ta, 0.5 Cb, 0.3 Rh,<br>0.43 Hf, 0.13 C, 0.02 B, 0.13 Zr |
| U-500            | 19.0              | 2.9     | 2.9     | 18.0  | 4.0     | —     | Bal  | 4.0 Fe**  |
| U-520            | 19.0              | 2.0     | 3.0     | 12.0  | 6.0     | 1.0   | Bal  | —   |
| U-700            | 15.0              | 4.25    | 3.5     | 18.5  | 5.2     | —     | Bal  | 1.0 Fe**  |
| Unitemp 1753     | 16.2              | 1.9     | 3.2     | 7.2   | 1.6     | 8.4   | Bal  | 9.5 Fe  |
| Waspaloy         | 19.5              | 1.4     | 3.0     | 13.5  | 4.3     | —     | Bal  | 2.0 Fe**  |

\*Common elements present in quantities less than 1.0% are not generally listed in this column.

\*\*Maximum

†Bal = Balance

††Includes Ta

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### 4-13 TANTALUM AND TANTALUM ALLOYS

Tantalum has a high melting point of 2996°C (5424°F) and a density of 16,598 kg/m<sup>3</sup> (1036.2 lbm/ft<sup>3</sup>). It is very ductile and can be cold-worked into a fine wire or thin foil. A thin foil 330 μm (13 mil) thick can be applied as cladding to structural metals; this fact permits the use of tantalum in many applications despite its high cost.

Of all metals, tantalum is one of the most inert; it is inert to a large variety of chemicals at temperatures below approximately 149°C (300°F). As the exposure temperature rises, however, tantalum reacts with a variety of reagents. The rate of attack increases as the temperature increases, but the specific conditions under which the reaction occurs can vary markedly depending on the reagents involved. At temperatures of several hundred degrees centigrade and higher, tantalum becomes extremely reactive in many environments, including air.

#### 4-13.1 TANTALUM ALLOYS

Various alloys have been formulated that use the excellent corrosion resistance or high melting point of tantalum and at the same time improve mechanical properties and decrease costs. Alloying elements include tungsten, columbium, titanium, and molybdenum although tantalum-tungsten alloys appear to be the most commercially advanced.

At room temperature an alloy containing 2.5% tungsten and 0.15% columbium has strength properties that are 50% higher than those of pure tantalum and only a slight decrease in ductility. At 1000°C (1832°F), however, the strength of the alloy is almost identical with that of pure tantalum. The tantalum-tungsten alloy is widely used in the process industry, and an alloy containing 10% tungsten is a candidate material for applications in gas turbine engines that operate at inlet temperatures between 1260° and 1649°C (2300° and 3000°F).

#### 4-13.2 TYPES OF CORROSION

The corrosion resistance of tantalum depends on the presence of a thin surface layer of tantalum pentoxide Ta<sub>2</sub>O<sub>5</sub>. The underlying substrate is attacked when the film is penetrated. A thin, continuous oxide film can be formed on tantalum by electrolytic anodizing in solutions such as phosphoric acid. The film has a high dielectric value, and it prevents the flow of current from tantalum to an electrolyte when the metal is made anodic.

##### 4-13.2.1 Galvanic Corrosion

A galvanic couple in which tantalum is the cathode results in the evolution of atomic hydrogen that is absorbed by tantalum and results in hydrogen embrittlement. However, if tantalum is the anode in a galvanic

couple, it anodizes so readily that the galvanic current drops to a very low level and no damage occurs.

In 0.1 normal sulfuric acid tantalum is more noble than zinc and aluminum but is anodic to platinum, silver, copper, bismuth, molybdenum, nickel, lead, and tin. However, the galvanic current rapidly decreases as tantalum spontaneously anodizes.

In hydrofluoric acid tantalum dissolves instead of spontaneously anodizing. Therefore, couples in which tantalum is the more active metal result in a steady-state current.

The polarity of galvanic couples with tantalum as the anode has been observed to reverse after some time. If this reversal occurs with any couple, given sufficient time, the tantalum becomes cathodic and hydrogen embrittlement can occur.

##### 4-13.2.2 Uniform Corrosion

###### 4-13.2.2.1 Corrosion in Natural Waters

Tantalum is not attacked by freshwater, acid mine waters, or seawater, either cold or hot. In the case of boiler waters and steam condensates, the alkalinity must be controlled; the pH should be less than 9. Tantalum is considered resistant to steam below 250°C (482°F).

###### 4-13.2.2.2 Corrosion in Acid Solutions

Tantalum is not attacked by such agents as sulfuric acid, nitric acid, hydrochloric acid, aqua regia, perchloric acid, hydrobromic acid, phosphoric acid when it is free of the fluoride ion, nitric oxides, chlorine oxides, hypochlorous acid, organic acids including monochloroacetic, and hydrogen peroxide at ordinary temperatures. It is attacked, however, even at room temperature, by hydrofluoric acid and free sulfur trioxide as in fuming sulfuric acid.

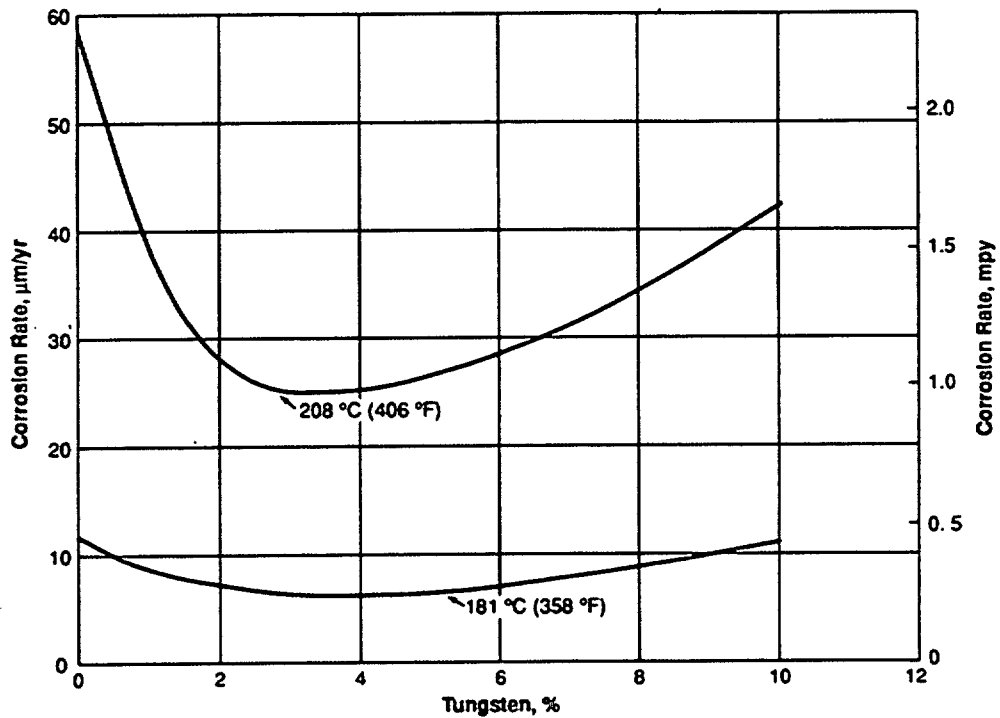
The corrosion rates of tantalum-tungsten alloys exposed to concentrated sulfuric acid at 181°C (358°F) and 208°C (406°F) are shown in Fig. 4-46. A 2.5% tungsten alloy appears to be about the optimum tungsten content for resistance to sulfuric acid. Fig. 4-47 compares the corrosion in concentrated sulfuric acid of a 2.5% tungsten alloy ("63" metal) with electron-beam-melted tantalum ("69" metal). This figure indicates that in the 175° to 210°C (347° to 410°F) temperature range, the 2.5% tungsten alloy can be used at a temperature about 15 deg to 20 deg C (27 deg to 36 deg F) higher than can tantalum and have equivalent corrosion rates.

Corrosion rates in concentrated hydrochloric acid at 100°C (212°F) are 41 μm/yr (1.6 mpy) for tantalum and 23 μm/yr (0.9 mpy) for the 2.5% tungsten alloy.

In concentrated nitric acid at 198°C (388°F), neither the 2.5% tungsten alloy nor tantalum show measurable corrosion.

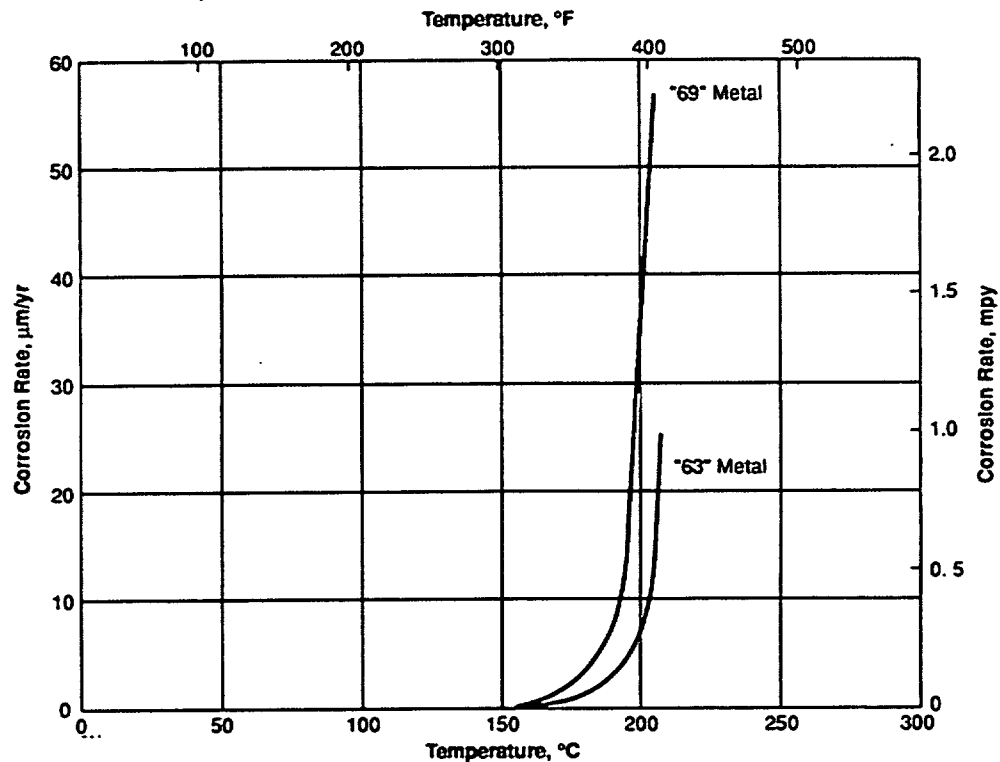
In 20% hydrofluoric acid, alloys containing more than 18% tungsten show a negligible corrosion rate.

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**Figure 4-46. Corrosion Rates for Tantalum-Tungsten Alloys Exposed to Concentrated Sulfuric Acid at 181° and 208° C (358° and 406° F) as a Function of Tungsten Content (Ref. 174)**



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**Figure 4-47. Corrosion Rates of Tantalum "69" Metal (Electron-Beam-Melted Tantalum) and "63" Metal (Tantalum—2.5% Tungsten—0.15% Columbium) Exposed to Concentrated Sulfuric Acid (Ref. 174)**

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In hot and cold concentrated hydrochloric and sulfuric acids, the corrosion rate of tantalum-columbium alloys increases in proportion to the columbium content. In general, tantalum-columbium alloys containing more than about 5% to 10% columbium are much less resistant to corrosion than tantalum.

The entire tantalum-titanium alloy system has excellent resistance to corrosion in boiling and 190°C (374°F) nitric acid of varying concentrations.

Titanium is not resistant to hydrochloric acid, whereas tantalum is resistant. Therefore, alloys rich in titanium corrode at high rates, but tantalum-rich alloys approach the corrosion resistance of pure tantalum.

In boiling and 190°C (374°F) sulfuric acid, the corrosion rate of tantalum-titanium alloys increases with increasing sulfuric acid concentration and increasing titanium content.

The entire tantalum-molybdenum alloy system is extremely corrosion resistant. When the alloy contains more than about 50% tantalum, the corrosion-resistant characteristics of tantalum are exhibited.

### 4-13.2.2.3 Corrosion in Alkaline Solutions

Sodium and potassium hydroxide solutions tend to destroy the metal by forming successive layers of scale on its surface. The rate of destruction increases with concentration and temperature. Tantalum is attacked at room temperature by concentrated alkaline solutions and is dissolved by molten alkalis. However, tantalum is fairly resistant to dilute alkaline solutions.

In alkaline solutions the corrosion rate of tantalum-tungsten alloys is minimized at about 60 atom % tantalum.

### 4-13.2.2.4 Corrosion by Salts and Salt Solutions

Tantalum is not attacked by dry salts or by salt solutions at any concentration or temperature unless hydrofluoric acid is liberated when the salt dissolves or a strong alkali is present. Hypochlorites do not affect tantalum unless they are strongly alkaline, and the same is true of all chlorides, bromides, and iodides. Fluorides, however, will attack tantalum.

### 4-13.2.2.5 Corrosion by Organic Compounds

Tantalum is completely resistant to most organic compounds including solutions of acetic, lactic, and oxalic acids and of phenol. Most organic salts, gases, alcohols, ketones, aldehydes, and esters have no effect on tantalum. Specific exceptions are compounds that may hydrolyze to hydrofluoric acid or contain free sulfur trioxide or strong alkalis. Mixtures of anhydrous methanol with chlorine, bromine, or iodine cause pitting of tantalum at 65°C (149°F).

Tantalum is completely inert to human body fluids.

### 4-13.2.3 High-Temperature Corrosion

Tantalum is stable in air at 250°C (482°F) and below. At 300°C (572°F) tantalum shows a tarnish after a 24-h exposure. The rate of corrosion increases rapidly at higher temperatures. At 500°C (932°F) the white oxide Ta<sub>2</sub>O<sub>5</sub> begins to form; Fig. 4-48 is a plot of corrosion rate as a function of temperature. After a certain period of time, which ranges from over 6 h at 500°C (932°F) to less than 2 min at 900°C (1652°F), the reaction becomes linear. Varying the relative humidity from 0 to 100% does not affect the oxidation behavior in air at 600° to 800°C (1112° to 1472°F).

The reaction of oxygen with tantalum is initially parabolic but transforms to a linear rate after a period of time. Increasing the temperature not only increases the rate of oxidation but also decreases the time required for the reaction to change from parabolic to linear. Under a pressure of 10<sup>5</sup> Pa (1 bar or 1 atm) of oxygen, tantalum oxidizes catastrophically at 1300°C (2372°F).

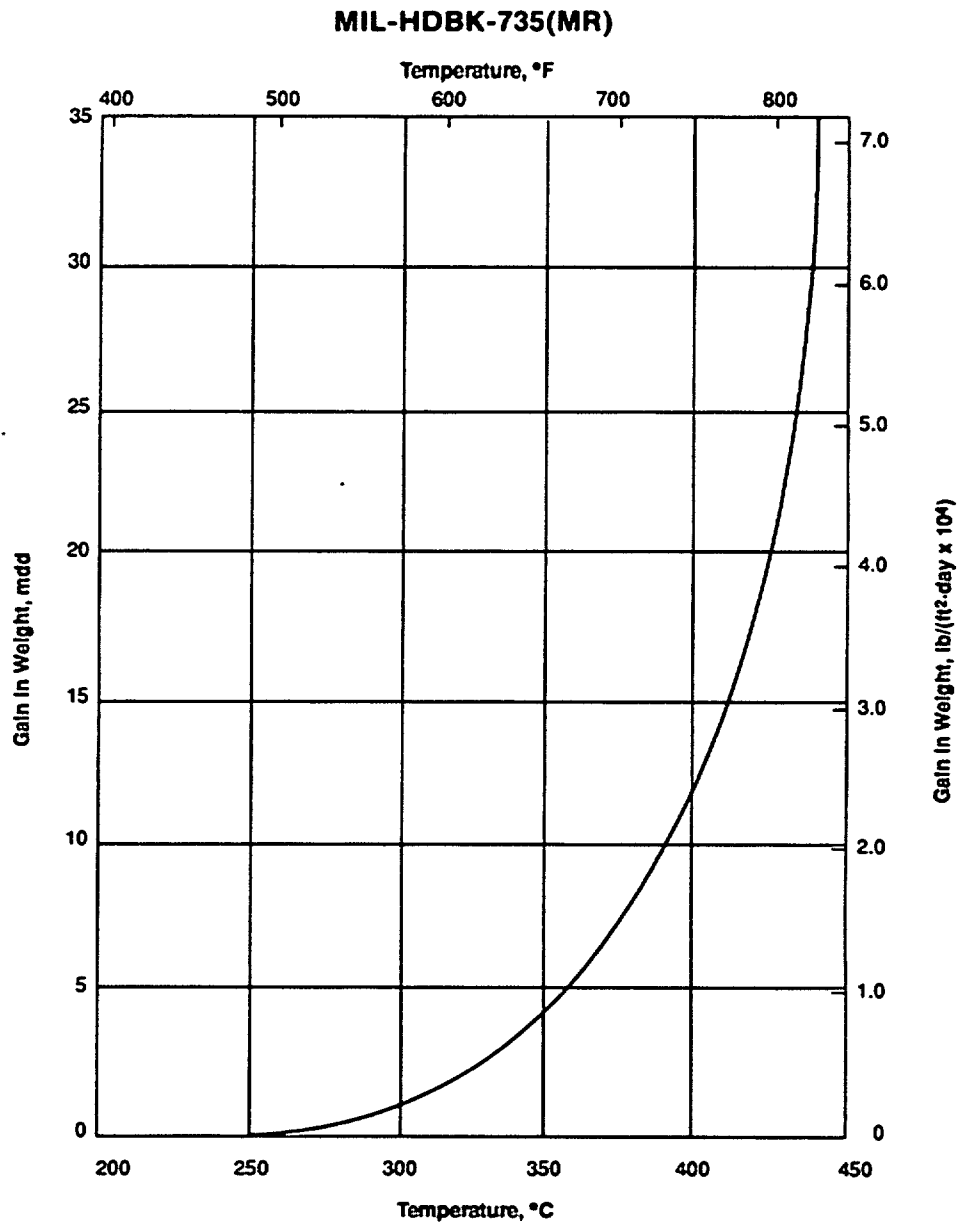
Tantalum is not adversely affected when heated with steam at 198°C (388°F). At temperatures above 1127°C (2240°F) water is decomposed by tantalum with absorption of oxygen by the metal and evolution of hydrogen, but at temperatures lower than 927°C (1700°F), this reaction is very slow.

Fluorine attacks tantalum at room temperature. Tantalum is totally inert to wet or dry chlorine, bromine, and iodine up to 150°C (302°F). Chlorine begins to attack tantalum at about 250°C (482°F). The reaction is violent after 35 min at 450°C (842°F), and at 500°C (932°F) the reaction is instantaneous. The presence of water vapor decreases the attack by chlorine. Bromine attacks tantalum at 300°C (572°F), and iodine attack begins at about the same temperature.

At elevated temperatures tantalum reacts directly with carbon, boron, and silicon. Tantalum phosphides are formed by heating tantalum filings in phosphorous vapor at 750° to 950°C (1382° to 1742°F). Tantalum reacts with sulfur or hydrogen sulfide at red heat and is severely attacked by selenium and tellurium vapors at temperatures of 800°C (1472°F) and higher.

Generally, tantalum shows good resistance to most of the low-melting liquid metals, as indicated in Table 4-117. Pure tantalum has excellent corrosion resistance to pure alkali metals; however, this resistance is adversely affected by the presence of oxygen. The presence of oxygen as an impurity in either the tantalum metal or the molten alkali metal can result in catastrophic corrosion of the tantalum.

Molten sodium and potassium hydroxides, and pyrosulfates dissolve tantalum. Table 4-118 lists some temperatures at which various chemical environments attack tantalum.



This paper was originally presented at the Chicago Section of The Electrochemical Society on 4 May 1954 but was not published.

**Figure 4-48. Corrosion Rate of Tantalum in Air as a Function of Temperature (Ref. 174)**

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TABLE 4-117. EFFECTS OF MOLTEN METALS ON TANTALUM (Ref. 174)

| MEDIA                      | TEMPERATURE,<br>°C (°F) | CODE* |
|----------------------------|-------------------------|-------|
| Aluminum                   | Molten                  | NR    |
| Antimony                   | To 1000 (1832)          | NR    |
| Bismuth                    | To 900 (1652)           | E     |
| Cadmium                    | Molten                  | E     |
| Gallium                    | To 450 (842)            | E     |
| Lead                       | To 1000 (1832)          | E     |
| Lithium                    | To 1000 (1832)          | E     |
| Magnesium                  | To 1150 (2102)          | E     |
| Mercury                    | To 600 (1112)           | E     |
| Potassium                  | To 900 (1652)           | E     |
| Sodium                     | To 900 (1652)           | E     |
| Sodium-Potassium<br>Alloys | To 900 (1652)           | E     |
| Zinc                       | To 500 (932)            | E/V   |
| Tin                        | —                       | V     |
| Uranium                    | —                       | V     |

\*E = no attack, V = variable depending on temperature and concentration, NR = not resistant

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In spite of extensive research to improve the high-temperature oxidation resistance of the refractory metals—such as tantalum, columbium, tungsten, and molybdenum—by alloying, no satisfactory oxidation-resistant alloy has been developed. Due to the high-temperature performance of the individual refractory alloys, e.g., their propensity to develop relatively low-melting or volatile oxides or nonprotective, porous oxide films, the probability of developing such an alloy is not high.

A 10% tungsten-tantalum alloy is somewhat more resistant to oxidation in air at high temperatures than tantalum is, but without some type of protective coating, the oxidation resistance of the material is not adequate to consider the alloy a candidate material for the hot section of gas turbine engines.

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TABLE 4-118. TEMPERATURES AT WHICH VARIOUS MEDIA ATTACK TANTALUM (Ref. 175)

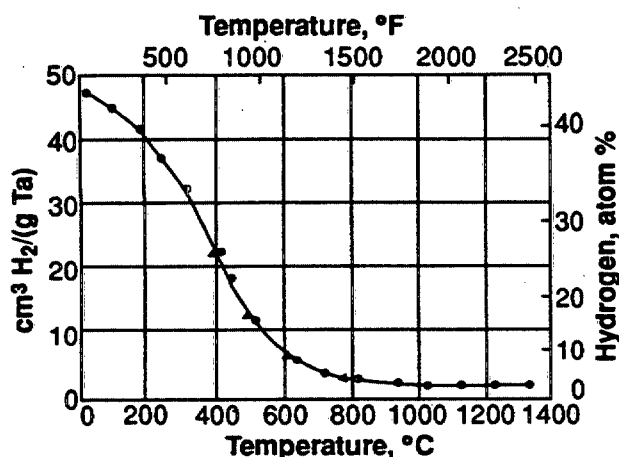
| MEDIUM  | STATE   | REMARKS   |
|---|---------|---|
| Air   | Gas     | At temperatures over 300°C (572°F)  |
| Alkaline solutions  | Aqueous | At pH >9, moderate temperature, some corrosion  |
| Ammonia   | Gas     | Pits at high temperatures and pressures   |
| Bromine   | Gas     | At temperatures over 300°C (572°F)  |
| Chlorine, wet   | Gas     | At temperatures over 250°C (482°F)  |
| Fluorides, acid media   | Aqueous | All temperatures and concentrations   |
| Fluorine  | Gas     | At all temperatures   |
| HBr, 25%  | Aqueous | Begins to corrode at temperatures over 190°C (374°F)  |
| Hydrocarbons  | Gas     | React at temperatures around 1500°C (2732°F)  |
| HCl 25%   | Aqueous | Begins to corrode at temperatures over 190°C (374°F)  |
| HF  | Aqueous | Corrodes at all temperatures and pressures  |
| Hydrogen  | Gas     | Causes embrittlement, especially at temperatures over 400°C (752°F)   |
| HBr   | Gas     | At temperatures over 400°C (752°F)  |
| HCl   | Gas     | At temperatures over 350°C (662°F)  |
| HF  | Gas     | At all temperatures   |
| Iodine  | Gas     | At temperatures over 300°C (572°F)  |
| Nitrogen  | Gas     | At temperatures over 300°C (572°F)  |
| Oxalic acid, saturated solution   | Aqueous | At temperatures of about 100°C (212°F)  |
| Oxygen  | Gas     | At temperatures over 350°C (662°F)  |
| H <sub>3</sub> PO <sub>4</sub> , 85%  | Aqueous | Corrodes at temperatures over 180°C (356°F) (at higher temperatures for lower concentrations)                       |
| Potassium carbonate   | Aqueous | Corrodes at moderate temperatures depending on concentration  |
| Sodium carbonate  | Aqueous | Corrodes at moderate temperatures depending on concentration  |
| NaOH, 10%   | Aqueous | Corrodes at about 100°C (212°F)   |
| NaOH  | Molten  | Dissolves metal rapidly at temperatures over 320°C (608°F)  |
| Sodium pyrosulfate  | Molten  | Dissolves metal rapidly at temperatures over 400°C (752°F)  |
| H <sub>2</sub> SO <sub>4</sub> , 98%  | Aqueous | Begins to corrode at temperatures over 175°C (347°F); lower concentrations begin to corrode at higher temperatures. |
| H <sub>2</sub> SO <sub>4</sub> (oleum) (over 98% H <sub>2</sub> SO <sub>4</sub> ) | Fuming  | Corrodes at all temperatures  |
| Sulfuric trioxide   | Gas     | At all temperatures   |
| Water   | Aqueous | Corrodes at pH >9; reacts at high temperatures  |

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## 4-13.2.4 Hydrogen Embrittlement

Tantalum dissolves a considerable amount of hydrogen at comparatively low-temperatures. The maximum limit of solubility is 50 atom %. The solubility of hydrogen in tantalum as a function of temperature is shown in Fig. 4-49. Atomic hydrogen can be absorbed by tantalum, even at room temperature. The presence of hydrogen



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Figure 4-49. Hydrogen-Tantalum Solubility Isobar ( $1.01 \times 10^5$  Pa) (1 atm) (Ref. 174)

decreases the ductility, strength, and density of tantalum, and it increases hardness and electrical resistivity. If permanent damage to the metal has not occurred, annealing or degassing at  $800^\circ\text{C}$  ( $1472^\circ\text{F}$ ) or a higher temperature restores the metal to its original condition.

Tantalum does not react appreciably with hydrogen below  $350^\circ\text{C}$  ( $662^\circ\text{F}$ ), and above this temperature the rate of reaction increases with increasing temperature to approximately  $450^\circ\text{C}$  ( $842^\circ\text{F}$ ). Between  $450^\circ$  and  $539^\circ\text{C}$  ( $842^\circ$  and  $1002^\circ\text{F}$ ), the reaction rate decreases with increasing temperature because the low-temperature hydride decomposes. Above  $540^\circ\text{C}$  ( $1004^\circ\text{F}$ ) the reaction rate again increases with increasing temperature.

Atomic hydrogen can be generated on a tantalum surface when

1. Tantalum metal is dissolved in hydrofluoric acid
2. Some other metal coupled to tantalum is being dissolved. In other words, tantalum is the cathode in a galvanic couple.
3. Tantalum becomes a cathode because of stray voltage.

## 4-13.2.5 Corrosion Fatigue

Fig. 4-50 compares the corrosion fatigue response of tantalum with that of 2.5% tungsten alloy. The higher strength alloy ("63" metal) shows a fatigue response above that of the commercially pure metal. The material tested was softer than standard material. After final

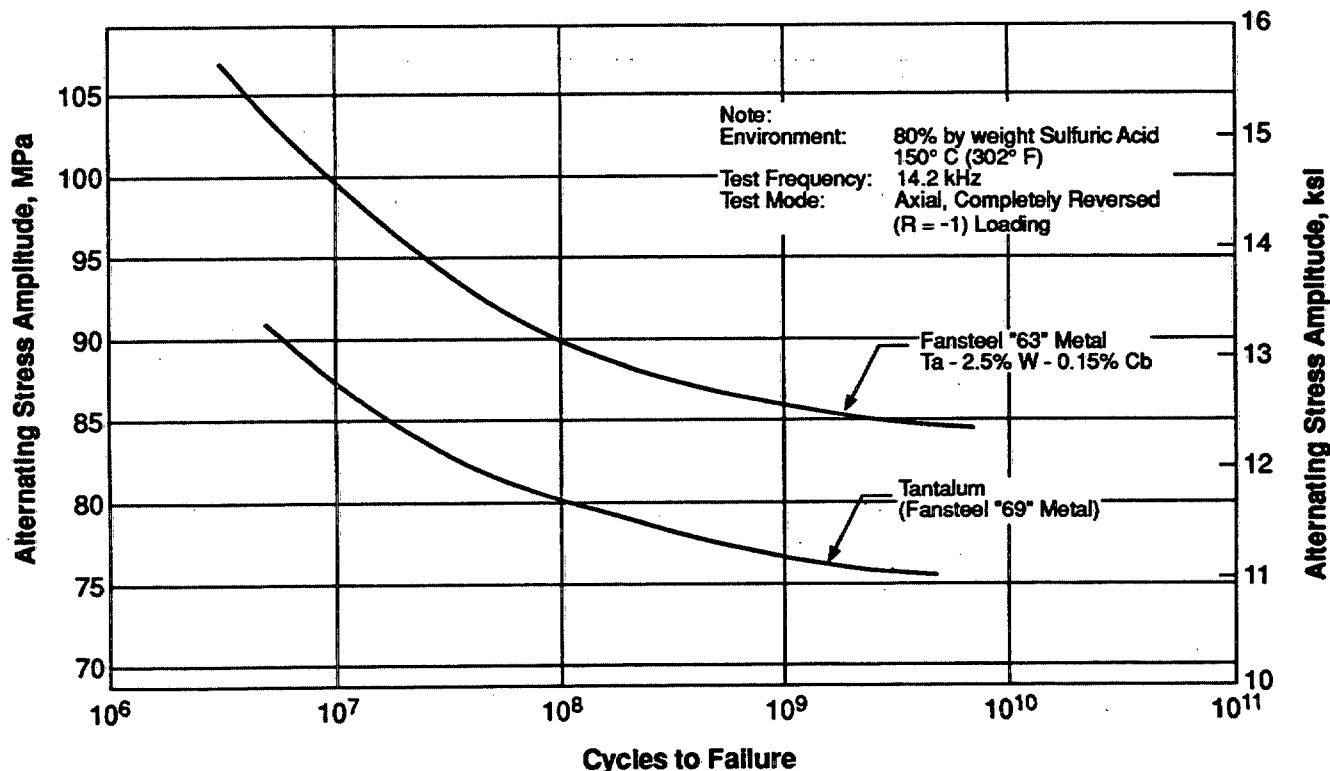


Figure 4-50. Comparison of Fatigue Response of Tantalum ("69" Metal) and "63" Metal in 80%  $\text{H}_2\text{SO}_4$  at  $150^\circ\text{C}$  ( $302^\circ\text{F}$ ) (Adapted from Ref. 176)

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annealing, a soft, large-grained material was used to simulate the material in or near weldments.

### 4-13.3 INTERFACE PROBLEMS

Temperature gradient mass transfer of zirconium, nitrogen, oxygen, and carbon has been observed in liquid alkali metal-tantalum systems at temperatures above 1371°C (2500°F). Also the transfer of elements, such as carbon and nitrogen, from dissimilar metals, such as stainless steel, to tantalum has been observed in a common alkali metal system.

When welding tantalum, it is necessary to reduce not only the temperature at which the metal may be exposed to moisture, carbon, oxygen, and nitrogen but also the amount of time. Exposure of the metal to any atmosphere (except the inert gases) under the required conditions of time and temperature will probably cause embrittlement. Of the embrittling species only hydrogen can be removed by heating the metal in a vacuum.

### 4-13.4 METHODS FOR PREVENTION OF CORROSION

Even though the corrosion resistance of tantalum to hydrochloric acid is good, it can be improved by adding nitric acid and ferric or cupric chloride to the hydrochloric acid.

The effects of oxygen on the corrosion resistance of tantalum can be modified by alloying tantalum with additions such as zirconium and hafnium. These alloying additions remove oxygen from solid solution by the precipitation of ZrO<sub>2</sub> and HfO<sub>2</sub>; heat treatment is necessary to enhance precipitation of the oxide phase.

Hydrogen embrittlement of tantalum can be prevented by several measures. If it is necessary to expose tantalum to hydrofluoric acid, nitric acid added to the hydrofluoric acid helps to prevent hydrogen embrittlement. In dilute hydrofluoric acid the rate of hydrogen absorption is greatly reduced if the tantalum is made electrically positive by impressing 2 to 20 V on the material in an electrolytic cell.

In media in which hydrogen can embrittle tantalum, prevention of embrittlement can be achieved by contacting the tantalum with a material that has a low hydrogen overvoltage and is electrochemically cathodic to tantalum in the same environment. Only the noble metals meet these requirements. Of these, platinum appears to be preferred because it has a particularly low hydrogen overvoltage and has generally excellent corrosion resistance. Very small amounts of the noble metal are needed. For example, exposure at 190°C (374°F) in concentrated hydrochloric acid for over 1000 h did not result in damage to the tantalum when the surface ratio of platinum to tantalum was only 1 to 9500.

A tantalum oxide film can be created by anodizing tantalum to 20 V. If the film is maintained on the

tantalum at all times, this method prevents hydrogen embrittlement and provides improved corrosion resistance to severe environments. Another method for preventing hydrogen embrittlement of tantalum is to electrically insulate tantalum completely from all other metals in an assembly.

The application of refractory metal alloys such as tantalum in environments requiring hot oxidation resistance is of major interest. The tantalum-10% tungsten alloy is a candidate material for gas turbine engine blades, discs, and vanes, as well as for combustor lines and ducts. The turbines must operate at inlet temperatures between 1260° and 1649°C (2300° and 3000°F). Because the high-temperature oxidation resistance is inadequate, efforts have been directed toward developing coating systems for the tantalum-10% tungsten alloy; silicide coatings are considered promising. In the intermediate temperature range of 760° to 871°C (1400° to 1600°F), however, the coatings fail due to a phenomenon called pesting, which causes disintegration of the coating material. Levy and Falco have shown that a complex disilicide coating gives good oxidation resistance to the tantalum-10% tungsten alloy if a preoxidation treatment of the coating is performed at 1149°C (2100°F) (Refs. 177 and 79). The coating contains tungsten, molybdenum, vanadium, and titanium. The preoxidation treatment alleviates the pesting problem that can occur with this coating when heating rates rise less than 10 deg C/min (18 deg F/min) as the temperature is raised from ambient to 1538°C (2800°F).

### 4-13.5 EXAMPLES OF CORROSION PROBLEMS

#### 4-13.5.1 Gun-Tube Erosion

The bore surfaces of gun tubes undergo erosion as a result of firing. This erosion ultimately causes loss of muzzle velocity, range, and accuracy. Tantalum has been tested as a gun-tube coating in a program to develop a solution to the gun-tube problem (Ref. 69). Partial 20-mm (0.79-in.) liners of Stellite 21 and gun steel were electroplated with 127- $\mu$ m (5-mil) thick coatings of tantalum.

The tantalum coatings swaged off the hard Stellite surface after test firing. The Stellite surface then eroded in the conventional manner. After firing 1100 rounds, however, the tantalum coating on the steel liner looked polished. The steel substrate under the coating had annealed and lost most of its strength as a result of the 799°C (1471°F) electrodisposition of tantalum from fused salts. It mechanically deformed along with the coating under firing. At some point this deformation stabilized, and there was no further erosion. These results indicate that tantalum shows promise as a gun-tube coating. The properties of the coating and substrate need to be optimized to result in acceptable performance.



**MIL-HDBK-735(MR)****4-13.5.2 Sulfuric Acid Handling in Ammunition Plants**

There are a number of Army ammunition plants in the United States. Several of these plants are involved in processing sulfuric acid and nitric acid for the production of nitroguanidine (NG) and TNT.

The selection of construction materials for equipment—storage tanks, receiver tanks, heat exchangers, lines, condensers, and pumps—that will handle acid solutions such as those used in the manufacture of NG and TNT should not be based solely on published corrosion data unless it is known that the conditions involved are adequately and specifically covered by the reference data. Seemingly minor differences in impurities or environmental conditions may make a major difference in the actual service corrosion rates. For example, impurities such as halides generally cause increased corrosion. Aeration or the presence of oxidizing agents generally accelerates corrosion of nonferrous materials and reduces corrosion of stainless steels, but the extent of these effects depends on specific conditions. Increasing temperature and velocity generally increase corrosion rates. It is mandatory, therefore, to consider all general corrosion data as only an indicator of relative resistance and a guide to which materials should be studied further with respect to limiting conditions.

Corrosion studies were carried out to provide data for selecting construction materials. Short-term electrochemical tests and long-term surveillance tests of candi-

date materials were conducted under conditions that simulated the actual service environment (Ref. 178). Tantalum is a candidate metal for sulfuric acid concentrators (bayonet heater), and 304L stainless steel has been proposed for use as the low-, middle-, and high-stage distillate tank material. The conclusions of the study are listed in Table 4-119.

**4-14 TITANIUM AND TITANIUM ALLOYS**

Titanium is a highly corrosion-resistant structural metal that has a high strength-to-weight ratio. Its density of 4501 kg/m<sup>3</sup> (281 lbm/ft<sup>3</sup>) is midway between aluminum, 2691 kg/m<sup>3</sup> (168 lbm/ft<sup>3</sup>), and iron, 7897 kg/m<sup>3</sup> (493 lbm/ft<sup>3</sup>).

Chemically pure titanium is a soft metal that is impractical to use in mechanical structures. Commercially pure titanium, however, is strengthened by adding relatively small amounts of oxygen (0.1% to 0.4%) and nitrogen (0.01% to 0.025%), as well as small amounts of iron, carbon, and hydrogen. The composition and mechanical properties of commercially pure grades of titanium are given in Table 4-120.

Almost all metallic elements are soluble in titanium, and alloys have been made that contain aluminum, iron, chromium, manganese, vanadium, tin, zirconium, and molybdenum. The chemical composition and mechanical properties of some common titanium alloys are given in Table 4-121.

**TABLE 4-119. CANDIDATE METALS FOR THE SAC SYSTEM (Ref. 178)****TANTALUM**

1. Is easily passivated in 50% to 94% H<sub>2</sub>SO<sub>4</sub> at temperatures up to but not exceeding 195°C (383°F)
2. Exhibits an extensive passive region
3. Secondary dissolution occurs at very noble potentials that are unlikely to be seen in service.
4. No pitting in evidence
5. No deleterious effect of fluoride ion up to 50 ppm
6. Ammonium sulfate is beneficial and extends the passive range.
7. Long-term immersion tests show no significant weight change in 2000 h of exposure at 85°C (185°F).
8. There was good correlation between electrochemical and long-term immersion results.
9. Is satisfactory for the various stages of the vacuum evaporator heaters provided that temperatures do not reach or exceed 195°C (383°F)

**304L STAINLESS STEEL**

1. Exhibits active-passive transition in concentrations of H<sub>2</sub>SO<sub>4</sub> to 30%
2. The critical current for passivity and the current in the passive range increase with the concentration and temperature of H<sub>2</sub>SO<sub>4</sub>.
3. The material passivates more easily in H<sub>2</sub>SO<sub>4</sub> concentrations below 20%.
4. Passivity is unstable between 40% and 80% H<sub>2</sub>SO<sub>4</sub>.
5. Passivity is stable in 94% H<sub>2</sub>SO<sub>4</sub>.
6. Addition of HNO<sub>3</sub> to H<sub>2</sub>SO<sub>4</sub> facilitates passivation and enhances stability.
7. Electrochemical and long-term immersion data correlate well.
8. May be considered a construction material for the low-, middle-, and high-stage distillate storage tanks. This material may also be considered a candidate for the product acid storage tank.

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TABLE 4-120. PROPERTIES OF COMMERCIAL PURE GRADES OF TITANIUM (Ref. 179)

| GRADE                          | Ti35A      | Ti50A    | Ti65A    | Ti75A    |
|--------------------------------|------------|----------|----------|----------|
| % C max                        | 0.08       | 0.08     | 0.08     | 0.08     |
| % N max                        | 0.05       | 0.05     | 0.05     | 0.05     |
| % H max, sheet                 | 0.015      | 0.015    | 0.015    | 0.015    |
| bar                            | 0.0125     | 0.0125   | 0.0125   | 0.0125   |
| billet                         | 0.0100     | 0.0100   | 0.0100   | 0.0100   |
| % Fe max                       | 0.12       | 0.20     | 0.25     | 0.30     |
| UTS, MPa (ksi), sheet          | 245 (35.5) | 345 (50) | 448 (65) | 552 (80) |
| bar                            |            |          |          | 483 (70) |
| 0.2% YS, MPa (ksi), sheet      | 172 (25)   | 276 (40) | 379 (55) | 483 (70) |
| bar                            |            |          |          | 414 (60) |
| Elongation in 51 mm (2 in.), % | 25         | 22       | 20       | 15       |
| Brinell hardness               | 120        | 200      | 225      | 265      |

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TABLE 4-121. SOME PROPERTIES OF COMMON TITANIUM ALLOYS (Ref. 179)

| ALLOY                          | Ti-0.20Pd  | Ti-5Al-2.5Sn | Ti-6Al-4V |
|--------------------------------|------------|--------------|-----------|
| % C max                        | 0.08       | 0.08         | 0.08      |
| % N max                        | 0.05       | 0.05         | 0.05      |
| % H max, sheet                 | 0.015      | 0.0175       | 0.015     |
| bar                            | 0.0125     | 0.0125       | 0.0125    |
| billet                         | 0.0100     | 0.0100       | 0.0100    |
| % Fe max                       | 0.25       | 0.50         | 0.25      |
| % Pd nom                       | 0.15       | —            | —         |
| % Al nom                       | —          | 4.0-6.0      | 5.75-6.75 |
| % Sn nom                       | —          | 2.0-3.0      | —         |
| % V nom                        | —          | —            | 3.5-4.5   |
| UTS, MPa (ksi)                 | 345 (50)   | 827 (120)    | 896 (130) |
| 0.2% YS, MPa (ksi)             | 276 (40)   | 793 (115)    | 827 (120) |
| Elongation in 51 mm (2 in.), % | 22 (sheet) | 10           | 10        |
| Brinell hardness               | 200        | Rc36         | Rc36      |

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Titanium solidifies from the molten state as the beta phase; this occurs at 1673°C (3043°F) for pure titanium. As it continues to cool, the material undergoes an allotropic phase transformation to the alpha phase, which occurs at 833°C (1531°F) for pure titanium. An alpha-beta alloy, such as Ti-6Al-6V-2Sn, contains alloying additions that stabilize each of the two allotropic forms. Alloys with high fracture toughness contain alpha particles having a high aspect ratio.

Titanium is relatively easy to fabricate, but it tends to seize and gall in machining operations. Welding should be done under an argon or helium inert gas blanket. Stress relieving results in no metallurgical change if temperatures are kept below 649°C (1200°F), but heating above this

temperature may cause grain growth and some loss of ductility and fracture toughness. Welding and stress relief heat treatments do not affect corrosion characteristics.

Although the melting point of titanium is 1660°C (3020°F), the metal may begin to form a scale in air at temperatures as low as 316°C (600°F). Therefore, all casting must be done under a high vacuum.

Titanium is a relatively expensive material. It is more costly than stainless steel but less costly than nickel-base alloys.

Multiphase alloys such as the workhorse, Ti-6Al-4V, and the newer Corona 5, Ti-4.5Al-5Mo-1.5Cr, are heat treatable, and their mechanical properties are strongly influenced by microstructural changes.

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### 4-14.1 TYPES OF CORROSION

The corrosion resistance of titanium is the result of a stable, protective, self-healing, strongly adherent oxide film on the metal surface that is formed under oxidizing, neutral, or naturally occurring conditions. The film, however, does not form under strong reducing conditions, so rapid attack results. In slightly reducing environments or in environments that form complex ions with titanium, tendencies to corrode depend upon the presence of metal ion inhibitors, alloying elements, temperature, and other variables.

The alloys of titanium do not form distinctive classes that can be related to a characteristic corrosion response in specific environments. The corrosion characteristics of the alloys are essentially those of commercially pure titanium; incremental deviations result from the alloying elements. Pure titanium is somewhat less corrosion resistant than some titanium alloys. Commercially pure titanium has an alpha structure, whereas some alloys have a beta structure and some have a mixed alpha-beta structure. The crystal structure can influence passivity parameters and create surface galvanic effects (Refs. 180 and 181), e.g., a homogeneous single-phase alloy will passivate more readily than a multiphase alloy.

Titanium alloys that are formed by powder metallurgy techniques generally have corrosion characteristics similar to equivalent wrought alloy compositions. However, magnesium chloride inclusions in powder metallurgy alloys serve as sites that initiate pitting. A powder metallurgy alloy containing low levels of magnesium chloride will give better service than one containing a few parts per million of magnesium chloride (Ref. 182).

#### 4-14.1.1 Galvanic Corrosion

In the passive state titanium is the cathode in a galvanic couple. In reducing environments in which the oxide film

breaks down, titanium becomes the anode in a galvanic couple. In seawater there is no appreciable galvanic corrosion when titanium is coupled to austenitic 18/8 stainless steel, Hastelloy, or Monel. Titanium is cathodic to aluminum, carbon steel, zinc, and magnesium in seawater. The rate of corrosion of these less noble metals depends upon the ratio of the surface areas of the two metals in the galvanic couple, and this relationship is illustrated in Fig. 4-51.

#### 4-14.1.2 Uniform Corrosion

##### 4-14.1.2.1 Weathering Corrosion

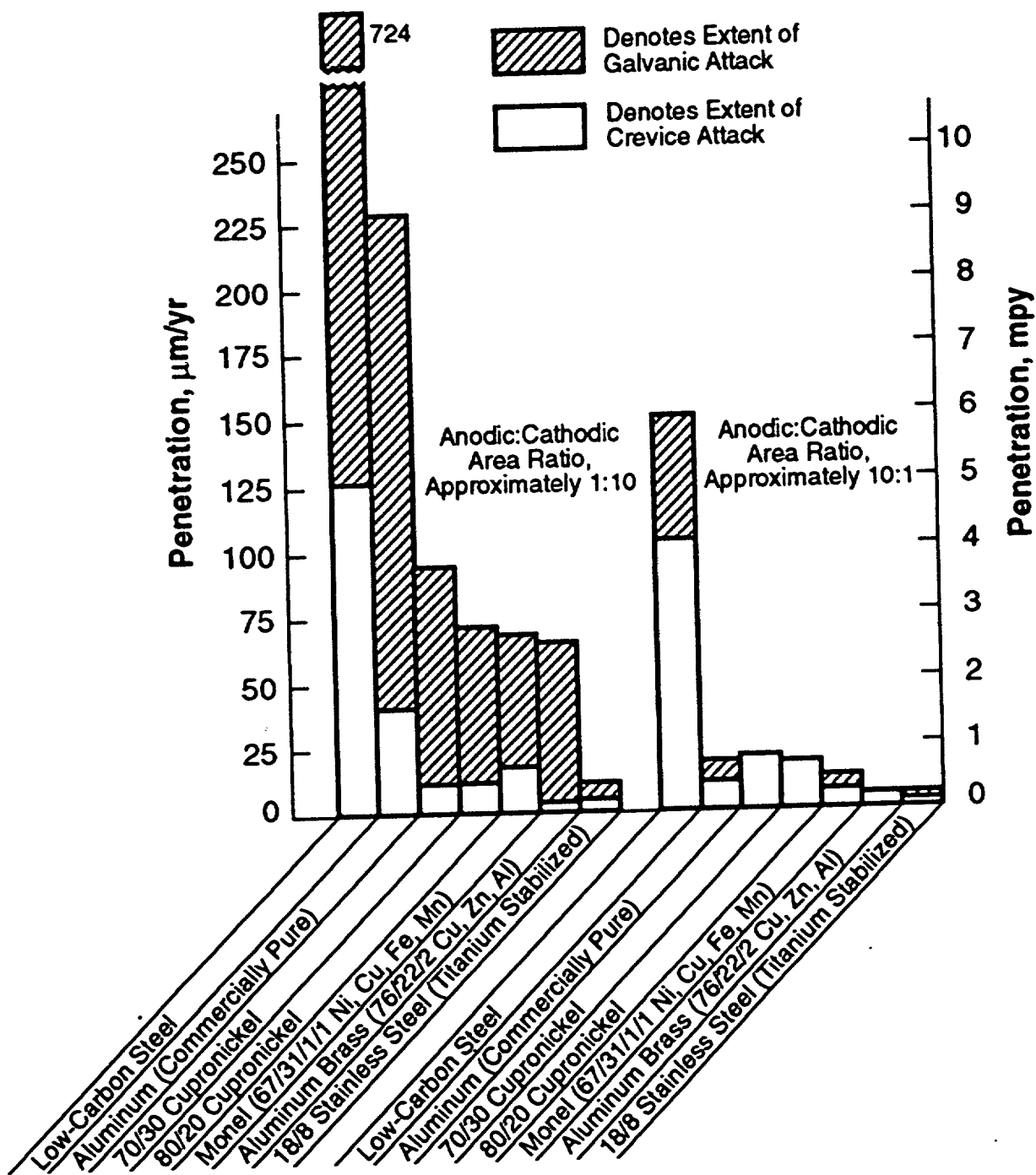
Titanium alloys, regardless of type, have excellent resistance to atmospheric corrosion, as was indicated in 7-yr exposure tests of eight titanium alloys at four test sites—Kure Beach, NC (East Coast marine), Newark, NJ (industrial), Point Reyes, CA (West Coast marine), and State College, PA (rural). Although slight staining and isolated pinpoint discoloration occurred, these conditions are not associated with significant metal loss through either general or pitting corrosion. In addition, the mechanical properties remained essentially unchanged (Ref. 184). The alloys exposed were 6Al-4V, 8 Mn, 2.5Al-16V, 8Al-2Cb-1Ta, commercially pure titanium, 2Fe-2Cr-2Mo, 5Al-2.5Sn, and 4Al-3Mo-1V.

##### 4-14.1.2.2 Corrosion in Natural Waters

Titanium is immune to corrosion in all natural waters at temperatures up to the boiling point.

Exposure of titanium at various depths in the ocean showed no attack on the metal, and titanium is immune to attack in highly polluted seawater. Biological organisms, such as barnacles, adhere to titanium surfaces but do not promote attack. Above 316°C (600°F) the protective film begins to lose its passivating characteristics, and corrosion occurs.

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Figure 4-51. Behavior of Metal-to-Titanium Galvanic Couples Exposed to 2500 h in Aerated Seawater (Ref. 183)

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## 4-14.1.2.3 Corrosion in Acid Solutions

Titanium has an acceptably low corrosion rate in nitric acid in many concentrations, at many temperatures, and under many conditions. At elevated temperatures attack can occur for short periods of time followed by subsequent passivation. Table 4-122 and Fig. 4-52 present corrosion rate data at various nitric acid concentrations and temperatures. Passivity is greatly increased at elevated temperatures by the addition of a small amount of a silicon-containing substance, such as powdered silicon, iron silicide, sodium silicate, kaolin, silicone oil, or asbestos powder (Ref. 186).

The reaction between titanium alloys and fuming nitric acid can become pyrophoric. Fuming nitric acid with less than 1.34% water or more than 6%  $\text{NO}_2$  is capable of sensitizing titanium-base alloys to the point that violent pyrophoric reactions may develop.

Titanium is resistant to dilute solutions of sulfuric acid at low temperatures. However, minor amounts of many metal ions in a higher valence state, e.g.,  $\text{Fe}^{+3}$  or  $\text{Cu}^{+2}$ , greatly reduce the corrosive attack on titanium. Because of this fact, titanium is frequently found to be resistant to a sulfuric acid environment. Table 4-123 illustrates the resistance of titanium to sulfuric acid.

Titanium corrodes in hydrochloric acid as indicated in Table 4-124. It is not resistant to concentrations above 10% by weight at room temperature. The presence of ferric or cupric ions, chromic acid, and nitric acid in hydrochloric acid has a beneficial effect in passivating titanium. The data in Table 4-125 indicate this.

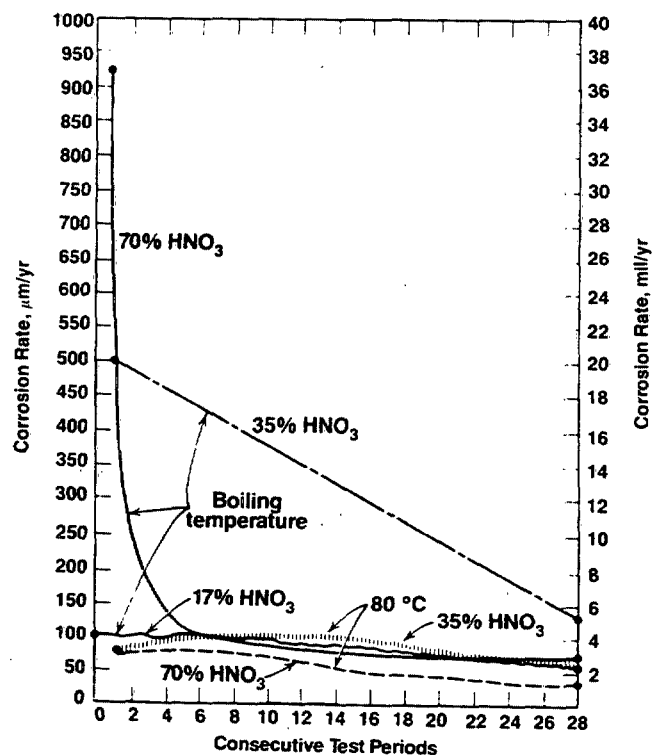
Titanium corrodes very rapidly in hydrofluoric acid. Concentrations as low as 0.05% will attack the metal. When hydrofluoric acid is used to pickle titanium, five

**TABLE 4-122. RESISTANCE OF TITANIUM TO AERATED NITRIC ACID (Ref. 185)**

| CONCENTRATION,<br>% | CORROSION RATE, $\mu\text{m}/\text{yr}$ (mpy) |                |                  |
|---------------------|---|----------------|------------------|
|                     | 24°C<br>(75°F)                                | 35°C<br>(95°F) | 100°C<br>(212°F) |
| 5                   | —   | 2.5 (0.1)      | 15.2 (0.6)       |
| 10                  | —   | 5.1 (0.2)      | 33.0 (1.3)       |
| 20                  | —   | 5.1 (0.2)      | —                |
| 50                  | —   | 5.1 (0.2)      | 5.1 (0.2)        |
| 65                  | —   | Nil            | 99.1 (3.9)       |
| 70                  | —   | 10.2 (0.40)    | —                |
| 98*                 | 2.5 (0.1)                                     | —              | —                |
| Red fuming*         | 2.5 (0.1)                                     | —              | —                |
| White fuming*       | 2.5 (0.1)                                     | —              | —                |

\*Not aerated

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**Figure 4-52. Median Corrosion Rates of Ti75A in Different Concentrations of Nitric Acid at Different Temperatures at Various States of Exposure to Consecutive 24-h Tests (Ref. 185)**

parts of nitric acid should be used for every part of hydrofluoric acid. Titanium also corrodes in solutions of aluminum fluoride.

Titanium corrodes in hot phosphoric acid. Unalloyed titanium shows a corrosion rate of 0.25 mm/yr (10 mpy) in 30% by weight phosphoric acid at room temperature and in 1% by weight boiling phosphoric acid. Ti-Pd alloy shows a corrosion rate of 0.13 mm/yr (5 mpy) in 10% by weight boiling phosphoric acid. Heavy metal ions and oxidizing agents passivate titanium in phosphoric acid.

Titanium resists a number of mixed acids, for example, aqua regia, which is a mixture of hydrochloric and nitric acids. Table 4-126 lists the corrosion rates for various sulfuric-nitric acid mixtures.

## 4-14.1.2.4 Corrosion in Alkaline Solutions

Titanium exhibits excellent resistance to bases over a wide range of concentrations. Attack can occur in certain hot, strong caustics, as shown in Table 4-127. The hydroxides of calcium, magnesium, and barium have relatively little effect on titanium at boiling temperatures and in concentrated solutions.

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TABLE 4-123. RESISTANCE OF TITANIUM TO SULFURIC ACID (Ref. 185)

| REAGENT   | CONCENTRATION, %                  | TEMPERATURE, °C (°F) | CORROSION RATE, mm/yr (mpy) |
|---|-----------------------------------|----------------------|-----------------------------|
| Sulfuric acid   | 1                                 | 38 (100)             | 0.366 (14.4)                |
|   | 5                                 | 38 (100)             | 0.610 (24.0)                |
|   | 10                                | 38 (100)             | 1.036 (40.8)                |
|   | 20                                | 38 (100)             | 1.793 (70.6)                |
|   | 30                                | 38 (100)             | 2.073 (81.6)                |
|   | 1                                 | 100 (212)            | 0.914 (36.0)                |
| Sulfuric acid + 0.25 CuSO <sub>4</sub><br>+ 0.50 CrO <sub>3</sub><br>+ 0.5 MnO <sub>2</sub> | 5                                 | 100 (212)            | 2.438 (96.0)                |
|   | 30                                | 100 (212)            | 0.089 (3.5)                 |
|   | 30                                | 100 (212)            | Nil                         |
| Sulfuric + nitric acid  | 40                                | 38 (100)             | Nil                         |
|   | 52:48<br>14:83 + H <sub>2</sub> O | 38 (100)             | 0.025 (1.0)                 |
|   |                                   | 38 (100)             | 0.089 (3.5)                 |

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TABLE 4-124. RESISTANCE OF Ti75A TO HYDROCHLORIC ACID (Adapted From Ref. 185)

| ACID CONCENTRATION, wt % | TEMPERATURE, °C (°F) | CORROSION RATES, mm/yr (mpy)* |
|--------------------------|----------------------|-------------------------------|
| 5                        | 38 (100)             | 0.053 (2.09)                  |
| 10                       | 38 (100)             | 0.396 (15.6)                  |
| 5                        | 66.0 (150)           | 1.524 (60)                    |
| 10                       | 66.0 (150)           | 3.10 (122)                    |
| 37                       | 38 (100)             | 11.13 (438)                   |

\*Average of two heats

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TABLE 4-125. INHIBITION OF CORROSION OF TITANIUM IN HYDROCHLORIC ACID (Ref. 185)

| INHIBITOR      | CONCENTRATION, % | CORROSION RATE, mm/yr (mpy) |
|----------------|------------------|-----------------------------|
| None           | 0                | 7.01 (276)                  |
| Copper sulfate | 1                | 0.051 (2)                   |
| Chromic acid   | 1                | 0.025 (1)                   |
| Nitric acid    | 1                | 0.102 (4)                   |

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TABLE 4-126. RESISTANCE OF TITANIUM TO MIXTURES OF SULFURIC AND NITRIC ACIDS AT 60° C (140° F) (Ref. 187)

| ACID CONCENTRATION, % |             | CORROSION RATE, mm/yr (mpy) |
|-----------------------|-------------|-----------------------------|
| SULFURIC ACID         | NITRIC ACID |                             |
| 0                     | 100         | 0.0076 (0.3)                |
| 1                     | 99          | 0.0025 (0.1)                |
| 5                     | 95          | 0.0051 (0.2)                |
| 10                    | 90          | 0.0102 (0.4)                |
| 50                    | 50          | 0.381 (15)                  |
| 80                    | 20          | 1.57 (62)                   |
| 90                    | 10          | 0.229 (9)                   |
| 95                    | 5           | 1.88 (74)                   |
| 99                    | 1           | 1.91 (75)                   |
| 100 (35° C (95° F))   | 0           | 5.49 (216)*                 |

\*Nitrogen saturated, 100 cm<sup>3</sup>/min

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TABLE 4-127. RESISTANCE OF TITANIUM TO ALKALINE SOLUTIONS (Ref. 185)

| MEDIUM              | CONCENTRATION,<br>% | TEMPERATURE,<br>°C (°F) | CORROSION RATE,<br>mm/yr (mpy) |        |
|---------------------|---------------------|-------------------------|--------------------------------|--------|
| Sodium hydroxide    | 10                  | Boil                    | Nil                            |        |
|                     | 50                  | 38 (100)                | 0.00025                        | (0.01) |
|                     | 50                  | Boil                    | 0.051                          | (2)    |
|                     | 73                  | Boil                    | 0.127                          | (5)    |
|                     | 7                   | 191 (375)               | 18.5                           | (730)  |
| Potassium hydroxide | 13                  | 29 (85)                 | Nil                            |        |
|                     | 25                  | Boil                    | 0.305                          | (12)   |
|                     | 50                  | 29 (85)                 | Nil                            |        |
|                     | 50                  | Boil                    | 2.74                           | (108)  |
| Ammonium hydroxide  | 28                  | 27 (80)                 | Nil                            |        |
| Sodium carbonate    | 25                  | Boil                    | Nil                            |        |

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#### 4-14.1.2.5 Corrosion in Chlorine Environment

Titanium has excellent resistance to wet chlorine gas; however, it is rapidly attacked by dry chlorine gas. About 1% water is sufficient for passivation under static conditions at room temperature, but about 1.5% water is required at 200°C (392°F).

Chlorine in solution tends to passivate titanium. Therefore, titanium is highly resistant to attack by chlorinated brine, chlorine dioxide, chlorates, hypochlorites, and boiling solutions of sodium chlorate. Increasing the temperature and chloride concentration do not affect uniform corrosion. Seawater and brine fluid at a speed of 9.1 m/s (30 ft/s) have no effect on uniform corrosion (Ref. 188).

#### 4-14.1.2.6 Corrosion in Organic Compounds

Titanium generally shows good corrosion resistance in organic compounds, as shown in Table 4-128. In organic acids, as in mineral acids, the behavior of titanium depends on whether the environment is oxidizing or reducing. Titanium resists attack by acetic acid over a wide range of concentrations and at temperatures well above the boiling point. Titanium is used extensively in terephthalic acid and adipic acid up to 204°C (400°F) at 67% concentration. It shows resistance in citric, tartaric, stearic, lactic, and tannic acids and in phenol. Borderline corrosion rates are encountered in formic acid, and relatively rapid attack can occur in oxalic acid. Table 4-129 lists the corrosion rates of titanium by organic acids.

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TABLE 4-128. RESISTANCE OF TITANIUM TO ORGANIC COMPOUNDS (Ref. 185)

| MEDIUM                                    | CONCENTRATION, % | TEMPERATURE, °C (°F)  | CORROSION RATE, mm/yr (mpy) |        |
|---|------------------|-----------------------|-----------------------------|--------|
| Acetic anhydride                          | 99 to 99.5       | 20 (68) to boiling    | 0.127                       | (5)    |
| Adipic acid + 15-20% glutaric + 2% acetic | 25               | 3 to 200 (38 to 392)  | 0.0                         |        |
| Adiponitrile solution                     | Vapor            | 371 (700)             | 0.0076                      | (0.3)  |
| Adipyl chloride + chlorobenzene           | —                | —                     | 0.0025                      | (0.1)  |
| Aniline hydrochloride                     | 5 to 20          | 35 to 100 (95 to 212) | 0.00076                     | (0.03) |
| Aniline + 2% aluminum chloride            | 98               | 316 (600)             | 20.4                        | (803)  |
| Benzene + HCl, NaCl                       | Vapor and liquid | 80 (176)              | 0.0051                      | (0.2)  |
| Carbon tetrachloride                      | 99               | Boiling               | 0.127                       | (5)    |
| Chloroform                                | 100              | Boiling               | 0.00025                     | (0.01) |
| Chloroform + water                        | —                | Boiling               | 0.127                       | (5)    |
| Cyclohexane + traces formic acid          | —                | 150 (302)             | 0.0025                      | (0.1)  |
| Ethyl alcohol                             | 95               | Boiling               | 0.0127                      | (0.5)  |
| Ethylene dichloride                       | 100              | Boiling               | 0.127                       | (5)    |
| Formaldehyde                              | 37               | Boiling               | 0.127                       | (5)    |
| Tetrachloroethylene                       | 100              | Boiling               | 0.127                       | (5)    |
| Tetrachloroethane                         | 100              | Boiling               | 0.127                       | (5)    |
| Trichloroethylene                         | 99               | Boiling               | 0.0025                      | (0.1)  |

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TABLE 4-129. CORROSION OF TITANIUM BY ORGANIC ACIDS (Ref. 189)

| ACID              | CONCENTRATION, % | CORROSION RATE, mm/yr (mpy)* |               |
|-------------------|------------------|------------------------------|---------------|
|                   |                  | 60°C (140°F)                 | 100°C (212°F) |
| Acetic            | All              | Nil                          | Nil           |
| Chloroacetic      | 30-100           | —                            | 0.127 (5)     |
| Citric            | All              | —                            | 0.013 (0.5)   |
| Dichloroacetic    | 100              | —                            | 0.127 (5)     |
| Formic            | All              | 0.0025 (0.1)                 | 0.0051 (0.2)  |
| Formic*           | 10               | —                            | Nil           |
|                   | 25               | —                            | 2.44 (96)     |
|                   | 50               | —                            | 7.62 (300)    |
|                   | 90               | —                            | 3.00 (118)    |
| Lactic            | 10               | 0.0025 (0.1)                 | 0.048 (1.9)   |
|                   | 25               | 0.0025 (0.1)                 | 0.053 (2.1)   |
|                   | 50               | 0.0025 (0.1)                 | 0.056 (2.2)   |
|                   | 85               | 0.0051 (0.2)                 | 0.0076 (0.3)  |
| Lactic**          | 10               | —                            | 0.015 (0.6)   |
|                   | 50               | —                            | 0.020 (0.8)   |
|                   | 25               | 12.7 (500)                   | 49.3 (1940)   |
| Oxalic            | —                | —                            | Dissolved†    |
| Propionic         | Vapor            | —                            | 0.127 (5)††   |
| Stearic           | 100              | —                            | 0.013 (0.5)   |
| Tartaric          | All              | —                            | 1778 (70,000) |
| Trichloroacetic** | 100              | —                            | 14.5 (571)    |
| Tichloroacetic    | 100              | —                            |               |

\*Based on a 6-day test at static conditions

\*\*Boiling, aerated

†190°C (374°F)

††182°C (360°F)

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## 4-14.1.3 Crevice Corrosion

Titanium undergoes pitting and crevice corrosion attack in chloride solutions under certain conditions. Crevice corrosion of titanium can occur in gasketed joints, between overlaps, in the roller-expanded tube-sheet joints of heat exchangers, and under heavy scale deposit. Severity of the attack increases with temperature, halide ion concentration, and decreasing pH. For example, crevice attack is seldom seen in saline solutions below 121°C (250°F).

Fig. 4-53 shows the relationship between the temperature and pH of saturated NaCl solutions, i.e., the values at which corrosion attack occurs on commercially pure, or unalloyed, titanium. The crevice corrosion resistance of titanium alloys, such as Ti-Pd and Ti-0.8Ni-0.3Mo (ASTM Grade 12), is greatly improved over the range  $0.5 \leq \text{pH} \leq 9$  compared to unalloyed titanium.

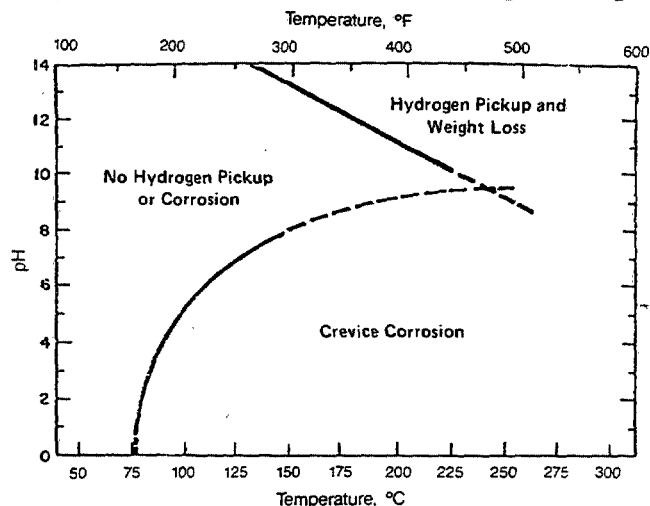
Teflon and fluorocarbon materials accelerate the corrosion of titanium when coupled in a crevice; apparently these materials furnish halide ions to the crevice. Attack is common at temperatures in the 204°C (400°F) range.

Crevice corrosion has not been observed at  $\text{pH} > 9$ . Failures that have occurred in chloride solutions at elevated temperatures and at pH values  $\geq 10$  have resulted from hydrogen embrittlement.

## 4-14.1.4 Erosion Corrosion

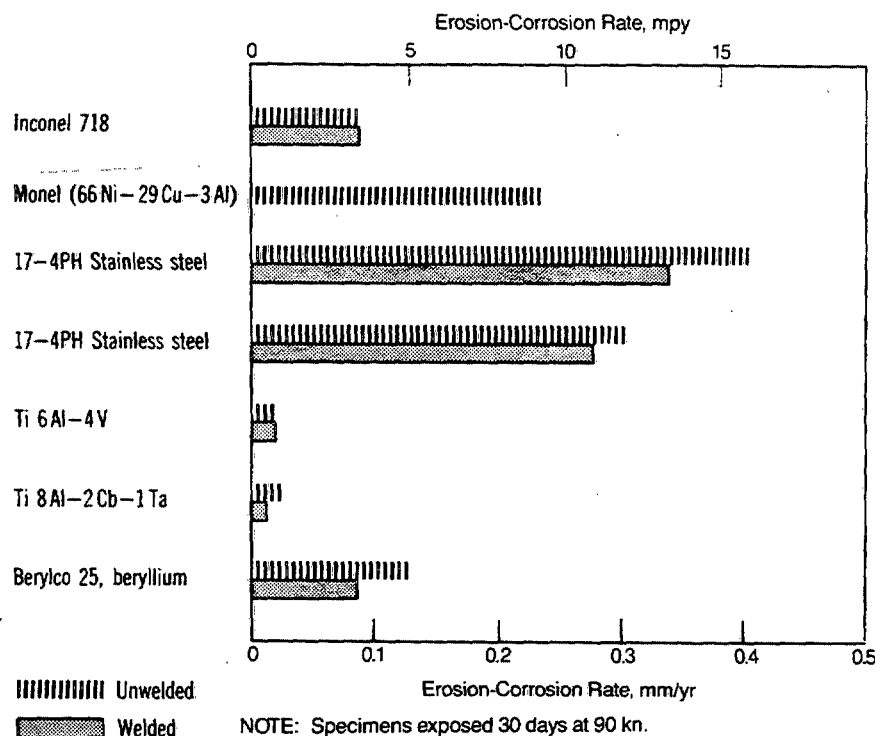
Titanium is used for propellers, shafting, valves, and

pipings for applications in which the velocity effects would damage other commonly used structural materials. For example, Ti-6Al-4V alloy has been used for ship propellers and ship hydrofoils because of its excellent resistance to high-velocity seawater. Jet erosion-corrosion rates in seawater for several metals, including two titanium alloys, are shown in Fig. 4-54. The harder, higher strength



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**Figure 4-53. Effect of Temperature and pH on Crevice Corrosion of Unalloyed Titanium (Grade 2) in Saturated Brine (Ref. 190)**



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**Figure 4-54. Jet Erosion-Corrosion Rates in Seawater (Ref. 185)**

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alloys are more resistant to cavitation than is commercially pure titanium.

**4-14.1.5 High-Temperature Corrosion****4-14.1.5.1 Oxidation****4-14.1.5.1.1 Oxidation in Air**

Oxidation studies of titanium alloys in air and oxygen at temperatures of 550° and 600°C (1022° and 1112°F) show that the metallurgical microstructure does not have significant influence (Ref. 191). Based upon comparison of the oxidation kinetics of the different alloys, the effects of the different alloying elements on the oxidation resistance of titanium are

1. Aluminum is positive.
2. Molybdenum and silicon appear to have a positive effect.
3. Tin does not seem to have a significant effect.
4. Vanadium has a negative effect, especially with increasing temperatures.

Oxidation studies of binary titanium alloys in the temperature range of 550° to 700°C (1022° to 1292°F) indicate that vanadium over 2% by weight has a very negative effect. However, for low concentrations of silicon (0.5% by weight), the oxidation resistance of titanium improves considerably.

**4-14.1.5.1.2 Titanium Combustion**

Titanium is widely used in gas turbine engines; it is used extensively in the fan/compressor units. As compressor operating conditions have become more severe, temperatures and pressures have increased and there has been a corresponding increase in the number of incidents of rapid oxidation of titanium components, which result in extensive damage.

Titanium is a combustion hazard because it ignites before it melts. Therefore, it does not have the latent heat of fusion as a potential heat sink. Its heat of combustion is relatively high, and its specific heat and thermal diffusivity are relatively low.

Instances of titanium blade and vane ignition and combustion have occurred in gas turbine compressors over a wide range of ambient pressures and temperatures. Initiating conditions may include blade-tip rubbing on the adjacent casing or blade/structure rubbing that results from compressor stalls during which blades deflect into the casing, from rotor imbalance, from entrapment of broken airfoil elements, or from aircraft maneuvers. Aerodynamic heating of compressor components during a stall also contributes to ignition of titanium gas turbine components. Although improved compressor seals reduce the blade-tip rubbing problem, the high-velocity airstream in axial-flow compressors enhances the continued combustion of any titanium blade or vane that does ignite. This continued combustion causes burning particles and molten metal to slough off. These particles can be entrained in the airstream and impinge on downstream components; thus the combustion spreads. The extent of damage depends on the conditions prevalent at the time of ignition, i.e., it can vary from burning the tips of a few compressor blades to catastrophic destruction of an entire engine.

The factors involved in titanium combustion are listed in Table 4-130, and the relative combustion hazards of several titanium alloys are shown in Table 4-131.

**4-14.1.5.2 Oxidation in Steam**

The following conclusions are drawn from a study on the oxidation of titanium in steam at temperatures from 400° to 550°C (752° to 1022°F) (Ref. 192):

1. Oxidation in steam is more rapid than in air.
2. Prior thermal and mechanical treatments have little effect.
3. Impurity concentrations of iron and oxygen have little effect.
4. A cubic rate law is applied during the protective stage. However, rapid oxidation of titanium occurs after a time at temperatures above 500°C (932°F).
5. Approximately half of the hydrogen generated is absorbed into the metal.

**TABLE 4-130. FACTORS INVOLVED IN TITANIUM COMBUSTION (Ref. 193)**

| IGNITION SOURCES          | COMBUSTION FACTORS                     | RESULTS   |
|---------------------------|--|---|
| High-energy rub           | Temperature<br>Pressure                | Minor damage<br>Component replacement<br>Component repair |
| High heating rates—stall  | Aerodynamics<br>Velocity<br>Turbulence | Major damage<br>Engine replacement<br>Loss of aircraft    |
| Tip recirculation         | Geometry<br>Thickness                  |   |
| Fracture<br>Melt droplets | Melt dispersal                         |   |

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TABLE 4-131. SUSCEPTIBILITY OF TITANIUM ALLOYS TO COMBUSTION (Ref. 193)

| ALLOYS             | REMARKS   |
|--------------------|---|
| Common Alloys      |   |
| 6Al-4V             | Burn relatively easily                              |
| 8Al-1V-1Mo         | Burn equally well                                   |
| 6Al-2Sn-4Zr-2Mo    |   |
| 6Al-2Sn-4Zr-6Mo    | Commonly used in turbine engines                    |
| Beta Alloys        |   |
| 3Al-8V-6Cr-4Mo-4Zr | Less combustible than common alloys                 |
| 3Al-8V-7Cr-4Sn-1Zr | Possible vane or case application                   |
| 3Al-15V-3Cr-3Sn    |   |
| Aluminides         | Combustible up to 24% by weight                     |
|                    | High Al content, noncombustible, and poor ductility |
| Low melting        |   |
| 13Cu-1.5Al         | Developmental castable alloys                       |
| 13Cu-5Mo           | Less combustible than common alloys                 |
| 9Fe                |   |
| 11Co               |   |

## 4-14.1.5.3 Corrosion in High-Temperature Water

Titanium is completely resistant to distilled water at all oxygen levels. No attack occurs in high-purity water at high temperatures, i.e., 499° to 572°C (930° to 1061°F).

## 4-14.1.5.4 Liquid Metal Corrosion

At temperatures above 316°C (600°F) titanium has relatively poor resistance in many liquid metals. Its

resistance to some liquid metals is indicated in Table 4-132.

Titanium has been used successfully in molten aluminum. A contaminated surface layer forms on the titanium, and this layer provides protection (Ref. 185). Zinc is quite corrosive toward titanium. Specimens of titanium disappear completely in less than 50 h at 446°C (835°F).

TABLE 4-132. CORROSION OF TITANIUM BY LIQUID METALS (Refs. 185 and 189)

| LIQUID METAL        | TEMPERATURE, °C (°F)     | CORROSION            |
|---------------------|--------------------------|----------------------|
| Bismuth-lead        | 482 (900)                | Poor resistance*     |
| Bismuth-lead-tin    | 649 (1200)               | Poor resistance*     |
| Bismuth-lead-indium | 649 (1200)               | Poor resistance**    |
| Cadmium             | 499 (930)                | Severely attacked    |
| Gallium             | <399 (<750)              | Resists attacks      |
|                     | 449 (840)                | Rapid attack         |
|                     | >538 (>1000)             | Severely attacked    |
| Lead                | 299 (570)                | Good resistance      |
|                     | 816 (1500)               | Attacked             |
| Lithium             | >799 (>1470)             | Limited service life |
| Mercury             | <149 (<300)              | Can be used          |
|                     | 149 to 316 (300 to 600)  | Limited resistance   |
| Sodium              | <599 (<1110)             | Can be used          |
|                     | 599 (1110) to 899 (1650) | Limited resistance   |
| Sodium-potassium    | <499 (<930)              | Resistant            |
|                     | 899 (1650)               | Limited resistance   |
| Tin                 | <499 (<930)              | Resistant            |
| Zinc                | 446 (835)                | Specimens dissolve   |

\*Addition of 4% chromium to titanium results in good resistance.

\*\*Addition of 4% chromium to titanium results in limited resistance.

**MIL-HDBK-735(MR)****4-14.1.6 Stress-Corrosion Cracking**

Titanium and its alloys have a relatively good record of freedom from stress-corrosion cracking in service. They are, however, susceptible to stress-corrosion cracking in several environments.

Unalloyed, i.e., commercially pure, titanium having an oxygen content less than 0.2% is susceptible to stress-corrosion cracking in the following environments:

1. Methanol and some higher alcohols in both the liquid and vapor states. Adding 1% to 5% water to methanol inhibits crack initiation on a smooth surface if the solution is not contaminated with about 10 ppm chloride. Water does not inhibit growth of a preexisting crack, even in the absence of chloride. As a practical rule, titanium structures should not be exposed to methanol in any form. Methanol is a constituent of many industrial substances, e.g., marking fluids, deicing fluids, and paint removers.

2. Cadmium and possibly mercury liquid metals

3. Red fuming nitric acid. The presence of water inhibits attack. A specification for an inhibited acid calls for up to 14% NO<sub>2</sub> and 2.5% H<sub>2</sub>O with the balance HNO<sub>3</sub>.

The titanium alloys, including the workhorse alloy Ti-6Al-4V, are more susceptible to stress-corrosion cracking than unalloyed titanium. They are susceptible to stress-corrosion cracking in the following environments:

1. Methanol with a small amount of hydrogen chloride is a most aggressive environment. The resistance to stress-corrosion cracking of some alloys in this environment can be improved by the addition of sodium nitrate (Refs. 194 and 195).

2. Mercury, gallium, and molten cadmium cause rapid cracking of stressed titanium alloys. Solid silver causes titanium alloys to crack at temperatures above 343°C (650°F). Solid cadmium in intimate contact with various titanium alloys causes cracking at temperatures as low as 38°C (100°F).

3. Red fuming nitric acid can cause stress-corrosion cracking.

4. Nitrogen tetroxide will cause stress-corrosion cracking in titanium alloys unless it is inhibited with 0.6% to 1% NO.

5. In addition to methanol, the following organic compounds have been reported to cause stress-corrosion cracking in titanium alloys: ethanol, ethylene glycol, carbon tetrachloride, chlorinated diphenyl at 316°C (600°F), monomethyl hydrazine, trichlorofluoromethane, and trichloroethane. However, none of these materials is as potentially dangerous as methanol.

6. Moist chlorine gas at temperatures greater than 288°C (550°F) and hydrogen chloride can cause stress-corrosion cracking of titanium alloys.

7. Hot salt stress-corrosion cracking occurs with titanium alloys, but not unalloyed titanium, under the following conditions: sodium chloride deposited on the

surface, temperature exceeding 274°C (525°F), and the presence of water vapor and oxygen. MIL-STD-1568 (Ref. 94) states that "All applications of titanium above 316°C (600°F) should include consideration of the hot salt cracking phenomenon." Only minute quantities of sodium chloride, such as that resulting from fingerprints, are necessary to cause stress-corrosion cracking.

8. Aqueous solutions containing chloride, bromide, and iodide ions are effective stress-corrosion cracking environments for many alloys. Fluoride, hydroxide, sulfide, sulfate, nitrate, perchlorate, cyanide, and thiocyanate ions have no effect. Alkali and alkaline earth cations have little effect on cracking (Ref. 196). The resistance to cracking in aqueous sodium chloride solutions is significantly influenced by alloy composition and microstructure. Additions of molybdenum, columbium, or vanadium reduce or eliminate susceptibility to chloride-enhanced propagation of cracks in precracked specimens (Ref. 186). High aluminum, high oxygen, and high tin in aluminum-bearing titanium alloys increase susceptibility to stress-corrosion cracking. The workhorse alloy, Ti-6Al-4V, is reasonably resistant if its oxygen content is less than 1300 ppm. The sensitivity of several titanium alloys to crack propagation in sodium chloride solutions is given in Table 4-133. Ti 50A and low oxygen Ti-6Al-4V have sufficient resistance to aqueous chloride stress-corrosion cracking to be used safely in many applications.

**4-14.1.7 Hydrogen Cracking**

Sustained-load cracking in inert environments (including air) is a type of slow crack growth that is important in highly stressed critical components. It is similar to stress-corrosion cracking except that it is much slower and it occurs in the total absence of a reactive environment. Sustained-load cracking is associated with hydrogen dissolved in the titanium during processing. Vacuum annealing can reduce the hydrogen levels to less than 10 ppm, and at this concentration the potential for sustained-load cracking is low. Low strain rate embrittlement is most frequently associated with alpha-beta titanium alloys, although it also occurs in alpha titanium.

Hydrogen embrittlement occurs under conditions that allow hydrogen to enter titanium and that exceed the concentration, about 100 to 150 ppm, needed to form a hydride phase. Titanium hydride needles form and cause crack initiation and brittle fracture of titanium under conditions of impact loading. The conditions for generating the hydride phase include

1. Alkaline solutions above the boiling point

2. Acidic conditions that cause the oxide film to become unstable

3. Cathodic generation of hydrogen on the metal surface as a result of coupling titanium to a galvanically active metal

4. Sufficiently high temperature, greater than 77°C

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TABLE 4-133. SENSITIVITY OF TITANIUM ALLOYS TO CRACK PROPAGATION BY CHLORIDE IONS (Ref. 197)

| Titanium Alloys That Undergo Accelerated Crack Propagation in Ambient 3% by weight Sodium Chloride | Titanium Alloys That Do Not Undergo Accelerated Crack Propagation in Ambient 3% by weight Sodium Chloride |
|--|---|
| Unalloyed Ti (with high oxygen content, i.e., 0.317%)  |   |
| Ti-8Mn   | Ti-2Al-4Mo-4Zr  |
| Ti-2.25Al-1Mo-11Sn-5Zr-0.2Si (IMI-679)   | Ti-4Al-3Mo-1V   |
| Ti-3Al-11Cr-13V  | Ti-5Al-2Sn-2Mo-2V   |
| Ti-4Al-4Mn   | Ti-6Al-2Mo  |
| Ti-5Al-2.5Sn   | Ti-6Al-2Sn-1Mo-1V   |
| Ti-6Al-2.5Sn   | Ti-6Al-2Sn-1Mo-3V   |
| Ti-6Al-4V  | Ti-6Al-2Cb-1Ta-0.8Mo  |
| Ti-6Al-3Cb-2Sn   | Ti-6.5Al-5Zr-1V   |
| Ti-6Al-4V-1Sn  | Ti-6Al-2.5Mo (as received and beta annealed + water quench + 593°C (1100°F) aged for 2 h)                 |
| Ti-6Al-4V-2Co  |   |
| Ti-6Al-6V-2.5Sn  |   |
| Ti-7Al-2Cb-1Ta   |   |
| Ti-6Al-3Cb (as received and beta annealed)   |   |
| Ti-6Al-3Mo   |   |
| Ti-7Al-3Cb-2Sn   |   |
| Ti-8Al-1Mo-1V  |   |
| Ti-8Al-3Cb-2Sn   |   |

(170°F), to allow hydrogen to diffuse into titanium, but 2% moisture is enough to prevent absorption of molecular hydrogen at temperatures below 316°C (600°F).

#### 4-14.1.8 Fretting

Titanium alloys are highly susceptible to the reduction of fatigue life by fretting at interfaces between titanium alloys or titanium and other metals.

#### 4-14.2 INTERFACE PROBLEMS

Contaminated surface layers of titanium mill products can result in subsequent corrosion and failure. For example, iron smears on titanium surfaces destroy the protective oxide film and allow hydrogen to access the underlying metal. Trace amounts of iron embedded in the surface of welds that have been steel-wire brushed can be points of initiation for local attack. Joints heavily contaminated as a result of improper shielding during welding and surfaces scratched during fabrication can also suffer localized attack.

The combustion of titanium at elevated temperatures in air has been discussed in par. 4-14.1.5.1. Titanium is normally passive to gaseous oxygen. At moderate to high pressure, however, violent burning can occur when freshly formed surfaces are exposed. Missile pressure vessels made of titanium alloys have been known to react violently when fresh metal surfaces are exposed to liquid

oxygen. The reactivity of titanium ruptured in gaseous oxygen is shown in Fig. 4-55.

#### 4-14.3 METHODS FOR PREVENTION OF CORROSION

The surfaces of titanium mill products—sheet, plate, bar, forging, and extrusion—should be 100% machined, chemically milled, or pickled to remove all contaminated zones and layers formed while the material was at elevated temperature. The purpose is to remove contamination resulting from mill processing, heat treating, and elevated temperature forming operations (Ref. 18).

The excellent corrosion resistance of titanium is due to a protective oxide film. Therefore, the object of corrosion prevention measures is to create and maintain those conditions in a service environment that favor formation of a passive film. Moisture in chlorine gas; tetravalent titanium ions in hot nitric acid; silicon-containing substances in hot nitric acid; Fe<sup>+3</sup> or Cu<sup>+2</sup> ions in sulfuric acid; and ferric or cupric ions, chromic acid, and nitric acid in hydrochloric acid are all measures that improve the passivity of titanium. It is when the protective film is destroyed that discoloration often occurs. The color change appears at a few points and then radiates out in rainbow-like patterns showing rings of yellow, bronze, blue, and gray. Once the film becomes powdery and porous, localized attack proceeds.

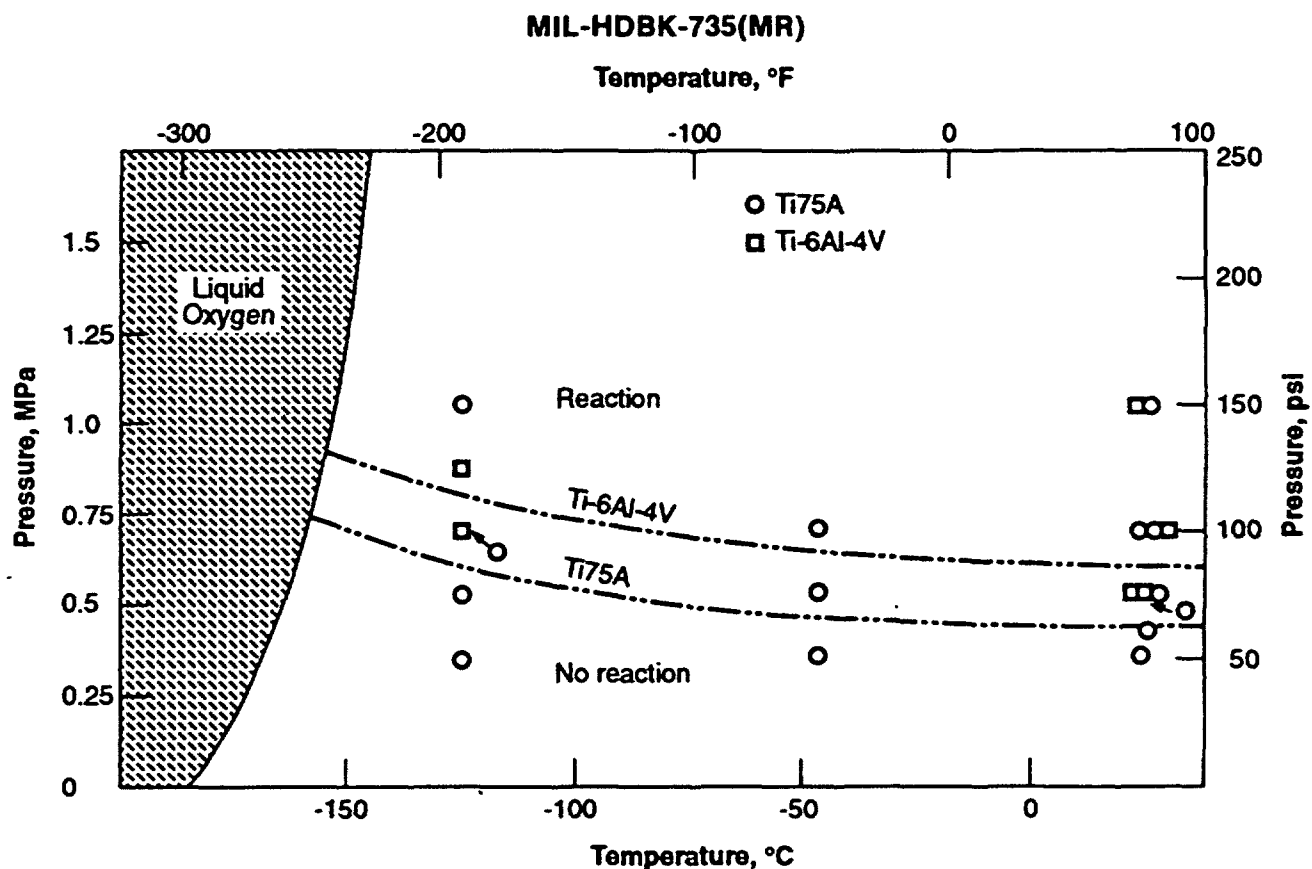


Figure 4-55. Reactivity of Titanium Ruptured in Gaseous Oxygen (Ref. 198)

Care must be taken to insure that cleaning fluids and other chemicals are not used on titanium assemblies where entrapment can occur. Known contaminants that can produce stress-corrosion cracking at various temperatures include hydrochloric acid, trichlorethylene, carbon tetrachloride, all chlorides, chlorinated cutting oils, freons, and methyl alcohol (Ref. 18).

Titanium parts should not be cadmium plated, and silver brazing of titanium parts should be avoided for elevated temperature applications. Cadmium-plated clamps, fixtures, and jigs should not be used for fabrication or assembly of titanium components or structures (Ref. 18).

The practical stress-corrosion cracking hazards to titanium involve a wide range of environments. For some groups of environments, such as natural waters and nearly neutral aqueous solutions, the cracking occurs only in the presence of a preexisting crack-like flaw. Unalloyed titanium and the widely used Ti-6Al-4V alloy are reasonably resistant to stress-corrosion cracking in these environments. Other alloys should be avoided unless specific stress-corrosion cracking tests using pre-cracked specimens demonstrate compatibility with the service environment. Fracture mechanics tests readily characterize the stress-corrosion cracking behavior of alloys.

For two chemical oxidizers,  $N_2O_4$  and red fuming nitric

acid, practical control of the problem is available through controlling the composition of the oxidizers. Standardized specifications are available for "safe" compositions, which are mentioned in par. 4-14.1.6.

For some environments, such as methanol, mercury, cadmium, or silver, the necessary strategy is simply to exclude them from titanium surfaces. Tests on Ti-3Al-8V-6Cr-4Mo-4Zr alloy in methanolic solutions indicate that the stress-corrosion cracking susceptibility can be significantly improved by the addition of sodium nitrate  $NaNO_3$  (Ref. 195).

Several measures have been tested for preventing crevice corrosion of titanium. These include

1. Oxidation of the titanium surface in air at temperatures greater than  $400^\circ C$  ( $752^\circ F$ ) prevents corrosion (Ref. 199).

2. Cuprous ions produced by galvanic action between titanium and copper in a crevice passivate titanium. Molybdate ions also passivate titanium. Creation of a surface film by anodizing titanium in a molybdate solution prevents crevice corrosion (Ref. 200).

3. A  $PdO-TiO_2$  coating prepared at  $500^\circ C$  ( $932^\circ F$ ) can prevent crevice corrosion in hot chloride solution (Ref. 201).

4. Nickel and palladium are effective alloying elements for improving the crevice corrosion resistance of titanium (Ref. 199).

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Potential coating systems have been evaluated for protection of titanium alloys from hot salt stress-corrosion cracking up to temperatures of 482°C (900°F) and from oxidation embrittlement up to 649°C (1200°F) (Ref. 202). Diffusion-type coatings containing Si, Al, Cr, Ni, or Fe as single-coating elements or in various combinations were evaluated. All of the coatings investigated demonstrated excellent oxidation resistance, but none of the coatings provided protection from hot salt stress corrosion.

Anodically formed oxide coatings have been tested for their ability to counteract the severe galling that occurs in bearings when titanium is subjected to medium- to high-intensity rubbing or sliding forces (Ref. 203). The coatings are said to have value in preventing hot salt stress-corrosion cracking and galvanic attack of dissimilar metals.

Ion implantation of palladium into titanium has potential application in providing resistance to hot salt stress-corrosion cracking and to crevice corrosion (Ref. 204).

Coatings have been tested for application in controlling titanium combustion in gas turbine engines (Ref. 205). The result of screening several coatings is shown in Table 4-134. There were six specimens that did not burn and one that burned only minimally at the milder test conditions. These seven coating systems were combustion tested at more severe burn conditions; the results are shown in Table 4-135. High-cycle fatigue tests were also conducted on these specimens, and based on these tests, ion-vapor-deposited aluminum and Pt/Cu/Ni were selected as the "best" coating systems. These two coatings are compared in Table 4-136.

#### 4-14.4 EXAMPLES OF CORROSION PROBLEMS

The combustion of titanium in gas turbine engines is discussed in par. 4-14.1.5.1.

The Army is very concerned with reducing the weight of components of weapons and aircraft systems. Titanium

**TABLE 4-134. SCREENING TEST RESULTS (Ref. 205)**

| COATING TESTED      | BURN SEVERITY, %   |  |
|---------------------|--|--|
|                     | 371°C (700°F),<br>0.758 MPa<br>(110 psia*),<br>244 m/s<br>(800 ft/s) | 454°C (850°F),<br>0.758 MPa<br>(110 psia*),<br>244 m/s<br>(800 ft/s) |
| Chromium            | 67   |  |
| Cr - 1% Mo          | 0  | 37   |
| Sputtered Cr -5% Mo | 0  | 18   |
| IVD aluminum        | 0  | ~1   |
| Aluminum-manganese  | 0  | 55   |
| 1 μ platinum        | 100  |  |
| Cr-TiC cermet       | 0  | ~1   |
| Cr-Mo + IVD Al      | 13   |  |
| Cr-Mo + Al-Mn       | 0  | 0  |
| Cr-Mo + Cu + Ni     | 0  | 0  |
| Cr-Mo + Ni          | 0  | 0  |
| Pt + IVD Al         | 0  | 38   |
| Pt + Al + Mn        | 56   |  |
| Pt + Cu + Ni        | 0  | 0  |
| Nickel-phosphorus   | No test  | 25   |

\*psia = pounds per square inch absolute, i.e., gage plus atmospheric pressure

alloys can provide, on a strength-to-weight basis, a material equivalent to a very high-strength steel. For example, the beta-titanium alloy Ti-3Al-8V-6Cr-4Mo-4Zr was considered a candidate alloy for the SCOUT vehicle torsion bar. Testing determined that the alloy was immune to stress-corrosion cracking in aqueous sodium chloride solutions such as those experienced in a marine environment. The alloy, however, was very susceptible to stress-corrosion cracking in methanolic solutions (Ref. 214). Fortunately, this susceptibility could be mitigated by the addition of sodium nitrate as an inhibitor.

**TABLE 4-135. COMBUSTION RESULTS (Ref. 205)**

| COATING SYSTEM           | PRESSURE,<br>MPa (psia*) | TEMPERATURE,<br>°C (°F) | AIR VELOCITY,<br>m/s (ft/s) | BURN<br>SEVERITY, % |
|--------------------------|--------------------------|-------------------------|-----------------------------|---------------------|
| IVD aluminum             | 0.758 (110)              | 482 (900)               | 244 (800)                   | 47.5                |
| Pt/Cu/Ni                 | 0.965 (140)              | 454 (850)               | 244 (800)                   | 47.0                |
| Chrome-moly/Cu/Ni        | 0.965 (140)              | 454 (850)               | 244 (800)                   | 44.6                |
| Chrome-moly/Ni           | 0.965 (140)              | 454 (850)               | 244 (800)                   | 58.8                |
| Chrome-moly/IVD aluminum | 0.965 (140)              | 454 (850)               | 244 (800)                   | 60.0                |
| Chrome-moly/Al-Mn        | 0.965 (140)              | 454 (850)               | 244 (800)                   | 64.7                |
| Chromium-moly/cermet     | 0.965 (140)              | 454 (850)               | 244 (800)                   | 100.0               |

\*psia = pounds per square inch absolute, i.e., gage plus atmospheric pressure

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TABLE 4-136. SUMMARY OF TEST RESULTS (Ref. 205)

|                    | Pt/Cu/Ni* | IVD Al* |
|--------------------|-----------|---------|
| Combustion         | +         | ++      |
| High cycle fatigue | 0         | 0       |
| Tensile            | 0         | 0       |
| Creep rupture      | 0         | 0       |
| Stress rupture     | +         | 0       |
| Erosion            | +         | +       |
| Adhesion           | Good      | Good    |
| Static oxidation   | —         | —       |
| Diffusion          | 0         | 0       |
| Thermal shock      | 0         | 0       |
| Stress analysis    | 0         | 0       |

\*0 = No significant influence due to coating

— = Coating had degrading effect on baseline.

+ = Coating appeared to provide improvement over baseline.

## 4-15 TUNGSTEN AND TUNGSTEN ALLOYS

Tungsten has a very high density, 19297 kg/m<sup>3</sup> (1204.7 lbm/ft<sup>3</sup>), and the highest melting point, 3410°C (6170°F), among metals.

Tungsten is used as an alloying element in stainless steels, tool steels, refractory alloys, and heat-resisting and corrosion-resisting superalloys. In general, it adds strength and restricts grain growth, especially at elevated temperatures.

Tungsten wire is used for incandescent lamp filaments and in developmental tungsten fiber-superalloy metal matrix composites. These composites are intended for application in high-temperature gas turbine components. Tungsten rods are used for lamp filament supports, glass-to-metal seals, electrical contacts, electrodes for arc lamps, and in welding and electrical discharge machining.

Other forms of tungsten are used in various parts in vacuum tubes and in X-ray and transmitter tubes. Tungsten and molybdenum are used in thermal radiation shields for high-temperature furnaces. Tungsten, tungsten alloys, and composites are used as counterweight materials for aircraft control surfaces, nozzle inserts in rockets, instrumentation components, gyroscope rotors, semiconductor supports, nuclear shielding materials, and ammunition components.

## 4-15.1 TYPES OF TUNGSTEN ALLOYS

The addition of molybdenum, niobium, and tantalum to tungsten produces grain refining in the as-cast condition and higher strength at elevated temperatures. Addition of rhenium improves the ductility of molybdenum and tungsten. Tungsten-thoria (ThO<sub>2</sub>) alloys have high tensile and creep strength above 2000°C (3632°F). Tungsten-2% ThO<sub>2</sub> has superior high-temperature properties over tungsten-1% ThO<sub>2</sub>, which is the composition of lamp wire. Adding 0.35 mol % of hafnium carbide to tungsten greatly improves its strength in the temperature range 1650° to 2200°C (3002° to 3992°F). If 4 atom % of rhenium is added to the tungsten-hafnium carbide alloy, the low-temperature ductility is improved without affecting the high-temperature strength.

Tungsten composites have been developed that are essentially three-component pseudoalloys consisting of large amounts of tungsten combined with either a nickel-copper or a nickel-iron matrix. Other elements, such as manganese, cobalt, and molybdenum, are added for strengthening. These alloys are produced by powder metallurgy techniques.

## 4-15.2 TYPES OF CORROSION

## 4-15.2.1 Uniform Corrosion

## 4-15.2.1.1 Corrosion in Aqueous Solution

The reaction of tungsten with various reagents is shown in Table 4-137.

TABLE 4-137. REACTION OF TUNGSTEN WITH VARIOUS REAGENTS (Ref. 207)

| TEMPERATURE<br>°C (°F)     | F <sub>2</sub>   | HF +<br>HNO <sub>3</sub> | HCl +<br>HNO <sub>3</sub> | HNO <sub>3</sub> | H <sub>2</sub> SO <sub>4</sub> |                                | KOH    | H <sub>2</sub> O <sub>2</sub> | KOH + NaNO <sub>3</sub> +<br>H <sub>2</sub> O <sub>2</sub> NaNO <sub>2</sub><br>(or O) (or O) |     | Cl <sub>2</sub>   |
|----------------------------|------------------|--------------------------|---------------------------|------------------|--------------------------------|--------------------------------|--------|-------------------------------|---|-----|-------------------|
|                            |                  |                          |                           |                  | HCl                            | H <sub>3</sub> PO <sub>4</sub> |        |                               |   |     |                   |
| 20 (68)                    | —WF <sub>6</sub> | dis                      | ox.                       | sl at.           | —                              | —                              | —      | —                             | sl at.  | —   | —                 |
| 100 to 110<br>(212 to 230) | —                | —                        | dis                       | ox.              | sl at.                         | sl at.                         | sl at. | dis                           | dis   | —   | —                 |
| 250 to 300<br>(482 to 572) | —                | —                        | —                         | —                | —                              | dis                            | dis    | —                             | —   | dis | —WCl <sub>6</sub> |

WF<sub>6</sub>, WCl<sub>6</sub> = reacts to form the indicated compound

dis = dissolution

ox. = oxidation

sl at. = slight attack



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Tungsten has good resistance to attack by most acids. It is attacked only slightly by hot or cold hydrofluoric acid, by hot dilute or concentrated hydrochloric or sulfuric acids, and by cold nitric acid. Warm nitric acid and a cold mixture of hydrofluoric and nitric acids react with tungsten to form the oxide  $WO_3$ . Hot aqua regia, a mixture of hydrochloric and nitric acids, rapidly attacks tungsten, but the reaction is much slower in cold aqua regia. Aqueous solutions of ammonia and alkalis do not corrode tungsten in the absence of oxygen or an oxidizer such as  $H_2O_2$ .

## 4-15.2.1.2 Corrosion in Halogen Gases

Bromine and iodine attack tungsten at red heat, chlorine attacks at temperatures above  $250^\circ C$  ( $482^\circ F$ ), and fluorine attacks tungsten vigorously at any temperature.

## 4-15.2.2 Corrosion at Elevated Temperatures

Tungsten resists attack by molten sodium hydroxide or potassium hydroxide. Vigorous reaction occurs, however, when the molten alkali salts contain an oxidizing agent, such as a nitrate, nitrite, or chlorate.

Tungsten forms nitrides with ammonia and carbides with carbon monoxide. It is attacked by  $CO_2$  at  $1200^\circ C$  ( $2192^\circ F$ ) and by oxides of nitrogen at high temperatures. Hydrogen does not dissolve in tungsten nor does it form hydrides.

Chemicals that attack tungsten at elevated temperatures are shown in Table 4-138, and the corrosion of tungsten in some liquid metals is shown in Table 4-139.

## 4-15.2.3 Oxidation of Tungsten

Tungsten oxidizes according to a parabolic rate law below  $399^\circ C$  ( $750^\circ F$ ) in air or oxygen. At temperatures above  $1100^\circ C$  ( $2012^\circ F$ ) tungsten oxidizes at a linear rate with time. In the  $400^\circ$  to  $1100^\circ C$  ( $752^\circ$  to  $2012^\circ F$ ) range, the reaction rate tends toward a linear rate as exposure time increases. The amount of cold-working of the

TABLE 4-138. TEMPERATURE SCALE OF ATTACK OF TUNGSTEN BY VARIOUS MATERIALS (Ref. 207)

| TEMPERATURE,<br>$^\circ C$ ( $^\circ F$ ) | COMPOUND                   |
|---|----------------------------|
| 500 (932)                                 | HCl, $O_2$                 |
| 800 (1472)                                | $NH_3$                     |
| 900 (1652)                                | CO, Br, I, $CS_2$ , $H_2O$ |
| 1000 (1832)                               | $C_xH_r(N_2 + H_2)$        |
| 1100 (2012)                               | C                          |
| 1200 (2192)                               | $CO_2$                     |
| 1500 (2732)                               | $N_2$                      |
| 1750 (3182)                               | $ZrO_2$                    |
| 2000 (3632)                               | MgO, BeO                   |
| 2100 (3812)                               | $ThO_2$                    |
| 2500 (4532)                               | $Al_2O_3$                  |

tungsten also increases the tendency toward a linear rate. Above  $500^\circ C$  ( $932^\circ F$ ) cracks appear in the adherent blue oxide film. Evaporation of the volatile oxide  $WO_3$  becomes substantial above  $800^\circ C$  ( $1472^\circ F$ ), and above  $1100^\circ C$  ( $2012^\circ F$ ) the oxide sublimates as rapidly as it is formed (Ref. 208).

The behavior of tungsten as a heating element toward various furnace atmospheres is compared with that of molybdenum and tantalum in Table 4-140.

## 4-15.3 INTERFACE PROBLEMS

## 4-15.3.1 Metal-to-Metal

Typical interface problems with tungsten occur between a metallic coating and the tungsten substrate or between tungsten filaments and the matrix metal in composites.

The following reactions can occur at service temperatures or at the elevated temperatures necessary to form a protective coating or a tungsten fiber-metal matrix composite:

TABLE 4-139. CORROSION OF TUNGSTEN IN LIQUID METALS (Ref. 57)

| LIQUID METAL          | TEMPERATURE,<br>$^\circ C$ ( $^\circ F$ ) | CORROSION RATE,<br>mm/yr (mpy) | EXPOSURE TIME,<br>h |
|-----------------------|---|--------------------------------|---------------------|
| Bismuth-lead eutectic | 1093 (2000)                               | 14.0 (551)                     | 24                  |
| Sodium                | 999 (1830)                                | None                           | 167                 |
| Zinc                  | 446 (835)                                 | 7.6 (299)                      | 50                  |
|                       | 699 (1290)                                | 63.5 (2500)                    | 50                  |
| Potassium             | 299 (570)                                 | Resistant                      | —                   |
| Sodium-potassium      | 593 (1100)                                | Resistant                      | —                   |
| Gallium               | 799 (1470)                                | Resistant                      | —                   |
| Magnesium             | 599 (1110)                                | Resistant                      | —                   |

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TABLE 4-140. BEHAVIOR OF HIGH-TEMPERATURE HEATING ELEMENT MATERIALS TOWARD FURNACE ATMOSPHERES (Ref. 209)

| ATMOSPHERE   | MOLYBDENUM  | TUNGSTEN  | TANTALUM  |
|--|---|---|---|
| Air or gases containing oxygen   | Incipient oxidation beyond 400° to 500°C (752° to 932°F); strong evaporation above 800°C (1472°F)   | Incipient oxidation beyond 500°C (932°F); strong evaporation above 1200°C (2192°F)                  | Oxidation and nitride formation above 500°C (932°F)   |
| Hydrogen   |   |   |   |
| Dry (<0.5 g water/m <sup>3</sup> (3.1 × 10 <sup>-5</sup> lb/ft <sup>3</sup> )) | Stable up to melting point  | Stable up to melting point  | Hydride formation at 400° to 800°C (752° to 1472°F); beyond that, stable up to melting point, surface oxidation |
| Wet (<20 g water/m <sup>3</sup> (1.2 × 10 <sup>-3</sup> lb/ft <sup>3</sup> ))  | Stable up to 1400°C (2552°F); beyond that, growth of metal needles on surface with material wastage | Stable up to 1400°C (2552°F); beyond that, growth of metal needles at surface with material wastage | Hydride formation and strong oxidation beyond 450°C (842°F)   |
| Cracked ammonia (dry)  | Stable up to melting point  | Stable up to melting point  | Nitride and hydride formation above 400°C (752°F); at higher temperatures, thorough nitrification               |
| Partially burnt ammonia (dry)  | Stable up to melting point  | Stable up to melting point  | Nitride and hydride formation above 400°C (752°F); at higher temperatures, thorough nitrification               |
| Partially burnt illuminating gas, generator gas, etc.                          | Stable up to 1300°C (2372°F); surface carbonization above 1200°C (2192°F)                           | Stable up to 1400°C (2552°F); surface carbonization above 1300°C (2372°F)                           | Nitride, carbide, and hydride formation; becomes brittle  |
| Inert gas (argon, helium)  | Stable up to melting point  | Stable up to melting point  | Stable up to melting point  |
| Vacuum   |   |   |   |
| <1.33 Pa (<10 <sup>-2</sup> torr)  | Stable up to 1700°C (3092°F)  | Stable up to 2000°C (3632°F)  | Becomes brittle through getter action on gas residues   |
| <0.0133 Pa (<10 <sup>-4</sup> torr)  | Strong evaporation above 1800°C (3272°F)  | Strong evaporation above 2400°C (4352°F)  | Strong evaporation above 2200°C (3992°F)  |

From "Metallic Heating Element Materials for High-Temperature Furnaces" by R. Kieffer and F. Benesovsky, *Metallurgia*, September 1958.

1. Diffusion-penetration accompanied by recrystallization of the grain at the tungsten surface
2. Formation of a two-phase zone
3. Solid solution reaction without subsequent recrystallization.

The most damaging of these reactions for a tungsten fiber-metal matrix composite is diffusion-penetration accompanied by recrystallization (Ref. 210).

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## 4-15.3.2 Metal-to-Nonmetal

Reactions can also occur between a metal oxide protective film and the tungsten substrate. The high temperatures required for sintering during the formation of a protective oxide film can recrystallize the tungsten substrate. Also tungsten silicide coatings are limited by the continuous diffusion that occurs during use and results in a gradual increase in the outer silica layer as well as in the formation of a lower silicide below the silica layer (Ref. 211).

## 4-15.4 METHODS FOR PREVENTION OF CORROSION

Although tungsten possesses desirable properties at high temperatures, such as high melting point, high modulus of elasticity, high strength, and low vapor pressure, it has low resistance to oxidation in air above 1121°C (2050°F). Therefore, protective coatings are required for tungsten and its alloys at high temperatures.

Metal coatings are ductile and adherent to tungsten. Nickel-chromium coatings are generally used at 1000° to 1400°C (1832° to 2552°F). Noble metal coatings of the

platinum group resist oxidation for a relatively long time at temperatures up to 1650°C (3002°F). The interdiffusion of tungsten with platinum and rhodium produces zones that are brittle and have low heat resistance. Barrier layers of rhenium, ruthenium, and iridium restrict this interdiffusion. Hafnium-tantalum coatings are used for higher service temperatures. Metal coatings for tungsten are listed in Table 4-141.

Refractory oxides are very stable in an oxidizing medium. To provide protection as a coating for tungsten, they should have a high melting point, high thermal conductivity, and low vapor pressure at the service temperature. Some refractory oxide coatings used for tungsten are shown in Table 4-142. In this list only zirconium dioxide  $ZrO_2$  has a thermal expansion close to that of tungsten. Spalling of the coating can result from a large difference in thermal expansion. The maximum service temperature of these simple oxides is about 2000°C (3632°F). Some complex oxides, such as  $SrZrO_3$  and  $Nd_2Zr_2O_7$ , may form suitable protective coatings for tungsten. Multiple layers of different metal oxide coatings may provide adequate protection. Coatings combining metals and metal oxides are used in specific applications.

TABLE 4-141. METAL COATINGS FOR TUNGSTEN (Adapted from Ref. 212)

| COATING ALLOY      | APPLICATION METHOD                             | LIFE AT MAXIMUM SERVICE TEMPERATURE |          |
|--------------------|--|-------------------------------------|----------|
|                    |  | TEMPERATURE, °C (°F)                | LIFE, h  |
| Ni-22Cr            | Electroplating                                 | 900 to 1200 (1652 to 2192)          | —        |
| Au + (Ni-Cr)       | Electroplating                                 | 1095 to 1375 (2003 to 2507)         | 500      |
| Ni-Si-B-Cr         | Electroplating                                 | 1095 to 1375 (2003 to 2507)         | 1 to 200 |
| Ni-Si-B-Cr         | Electroplating                                 | 1095 to 1375 (2003 to 2507)         | 1 to 200 |
| Ni-Si-Cr-B-W       | Electroplating                                 | 1095 to 1375 (2003 to 2507)         | 1 to 200 |
| Ni-Cr-P            | Electroplating                                 | 1095 to 1375 (2003 to 2507)         | 1 to 200 |
| Ni-Si-B            | Electroplating                                 | 1095 to 1375 (2003 to 2507)         | 1 to 200 |
| Al-Si              | Immersion of W into melts at 1300°C (2372°F)   | 1450 (2642)                         | —        |
| Pt (127 μm thick)  | Electroplating from cyanides                   | 1650 (3002)                         | 5        |
| Pt-30 Rh           | Electroplating from cyanides                   | 1650 (3002)                         | 5 to 10  |
| Rh-Cr-Si-Cr layers | Electroplating (Rh), vapor deposition (Cr, Si) | 1640 (2984)                         | 1        |
| Hf-27 Ta           | Electroplating, plasma spraying, etc.          | 2095 (3803)                         | —        |
| Hf-20 Ta           | Electroplating, plasma spraying, etc.          | 2095 (3803)                         | —        |
| Hf-20 Ta-2 Mo      | Electroplating, plasma spraying, etc.          | 2095 (3803)                         | —        |
| Sn-25 Al, Sn-50 Al | Electroplating, dipping                        | 1895 (3443)                         | 1        |

From *Tungsten: Sources, Metallurgy, Properties, and Applications* by Stephen W.H. Yih and Chun Wang. Copyright © by Plenum Press, 1979.

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TABLE 4-142. REFRACTORY OXIDE COATINGS FOR TUNGSTEN\* (Ref. 213)

| OXIDE                            | MELTING POINT,<br>°C (°F) | THERMAL CONDUCTIVITY  | VAPOR PRESSURE<br>AT 1730°C,<br>(3146°F), Pa (atm) | MAXIMUM TEMPERATURE<br>(0 to 100 h),<br>°C (°F) | THERMAL EXPANSION,<br>25 to 1500°C<br>(77 to 2732°F), % |
|----------------------------------|---------------------------|---|--|---|---|
|                                  |                           | AT 1205°C (2201°F),<br>J/(cm·s·°C)<br>(Btu·in./(s·in <sup>2</sup> ·°F)) |  |   |   |
| Al <sub>2</sub> O <sub>3</sub>   | 2049 (3720)               | 0.054 (7.2 × 10 <sup>-5</sup> )   | 0.58 (5.7 × 10 <sup>-6</sup> )                     | 1982 (3600)                                     | 1.37  |
| BeO                              | 2571 (4660)               | 0.172 (2.3 × 10 <sup>-4</sup> )   | ≈ 0.012 (1.2 × 10 <sup>-7</sup> )                  | 2093 (3800)                                     | 1.52  |
| CeO <sub>3</sub>                 | 2649 (4800)               | — —   | —  | —   | —   |
| Cr <sub>2</sub> O <sub>3</sub>   | 2343 (4250)               | ≈ 0.126 (≈ 1.7 × 10 <sup>-4</sup> )                                     | 1.22 (1.2 × 10 <sup>-5</sup> )                     | 1800 (3272)                                     | —   |
| HfO <sub>2</sub>                 | 2810 (5090)               | — —   | —  | 2093 (3800)                                     | 0.93  |
| MgO                              | 2799 (5070)               | 0.054 (7.2 × 10 <sup>-5</sup> )   | ≈ 0.51 (5 × 10 <sup>-6</sup> )                     | 1982 (3600)                                     | 2.23  |
| SiO <sub>2</sub>                 | 1727 (3140)               | — —   | —  | 1593 (2900)                                     | —   |
| ThO <sub>2</sub>                 | 3204 (5800)               | 0.021 (2.8 × 10 <sup>-5</sup> )   | 1.32 × 10 <sup>-5</sup> (1.3 × 10 <sup>-10</sup> ) | 2288 (4150)                                     | 1.50  |
| Y <sub>2</sub> O <sub>3</sub>    | 2410 (4370)               | — —   | —  | 1982 (3600)                                     | —   |
| ZrO <sub>2</sub>                 | 2688 (4870)               | 0.021 (2.8 × 10 <sup>-5</sup> )   | ≈ 0.10 (1 × 10 <sup>-6</sup> )                     | 1899 (3450)                                     | 0.79  |
| TiO <sub>2</sub>                 | 1838 (3340)               | 0.033 (4.4 × 10 <sup>-5</sup> )   | —  | 1816 (3300)                                     | —   |
| MgAl <sub>2</sub> O <sub>4</sub> | — —                       | —   | —  | 1982 (3600)                                     | —   |
| W                                | — —                       | —   | —  | —   | 0.75  |

\*The method of slurry application with subsequent sintering or fusion usually is used.

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As a group, the carbides, borides, nitrides, and silicides oxidize more slowly than tungsten. They do not, however, afford sufficient protection. Nevertheless, some silicides form a protective coating of silicon dioxide upon oxidation. Tungsten disilicide is generally used as a protective coating in the temperature range of 1300° to 1800°C (2372° to 3272°F).

#### 4-15.5 EXAMPLES OF CORROSION PROBLEMS

A tungsten alloy component of Army ammunition readily corrodes in air saturated with water vapor (Ref. 214). The composition of the alloy, which is prepared using powder metallurgy techniques, is 90% W, 7.5% Ni, and 2.5% Co. This process produces an alloy consisting of rounded tungsten particles surrounded by a layer of matrix solid solution. In general, the tungsten particles are in contact and the matrix phase is confined to discontinuous interparticle interstices.

Corrosion tests were conducted for comparison on a series of similar alloy specimens including pure tungsten. The corrosion behavior was examined by electrochemical potentiostatic polarization methods and by weight loss measurements in full immersion tests (Ref. 215). The tests were conducted in aqueous solutions buffered to pH 4, 9, and 12 with and without 0.1M NaCl. The conclusions of

the electrochemical measurements are as follows:

1. All the alloys studied undergo an active-passive transition.
2. As the pH increases, the corrosion-related parameters also increase.
3. The corrosion rates of tungsten and most of its alloys are increased slightly in solutions containing chloride ion. However, at pH 12 the chloride ion has minimal effect.
4. In the absence of chloride ion, the alloys appear to be more resistant in solutions of pH 4.
5. Alloys containing copper are the least corrosion resistant in the 0.1M NaCl solution.

The data from the total immersion tests in 5% NaCl solution showed that pure tungsten has the lowest corrosion rate and that the alloys containing copper have the highest.

All of the materials studied showed good corrosion resistance in aqueous solutions. Corrosion penetration was less than 305 μm/yr (12 mpy). Examination of one alloy, however, showed that the matrix phase is attacked more readily than the tungsten phase. Therefore, calculated penetration rates based on weight loss underestimate penetration in the matrix areas. Furthermore, attack on the matrix can result in loss of strength and ductility.

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## 4-16 URANIUM AND URANIUM ALLOYS

Uranium is a dense metal. It is 80% heavier than the same volume of lead, but it is slightly less dense than tungsten. The density of elemental uranium is 18,948 kg/m<sup>3</sup> (1182.9 lbm/ft<sup>3</sup>), the melting point is 1132°C (2070°F), and the boiling point is 3818°C (6904°F).

Natural uranium contains only 0.7% of the fissionable isotope, U-235. Depleted uranium contains 0.2% U-235. Therefore, production of metal enriched in U-235 yields large amounts of depleted uranium as a by-product. Because it is a by-product, depleted uranium is less expensive than other high-density materials. For example, tungsten has a higher raw material cost and is more expensive to fabricate.

High-density materials have many important uses such as counterweights for aircraft control surfaces, vibration damping in high-inertia rotational devices, shielding for penetrating ionizing radiation, and for armor-piercing projectiles. Many of these applications involve high tolerances that do not permit the formation of thick corrosion surface scales.

### 4-16.1 TYPES OF ALLOYS

The low-temperature form of uranium, alpha uranium, is stable below 662°C (1224°F), beta uranium is stable from 662° to 769°C (1224° to 1416°F), and gamma uranium is stable from 769°C (1416°F) to the melting point, which is 1132°C (2070°F). Because of its anisotropic structure and its tendency to exhibit a preferred orientation, the alpha phase is often unstable during thermal cycling. Therefore, the objective of alloying uranium is to retain the isotropic gamma phase at low temperature and improve dimensional stability.

Several elements are miscible in gamma uranium. Molybdenum, columbium, zirconium, and titanium have been used to stabilize the gamma phase. These elements are essentially insoluble in alpha uranium and have been alloyed with uranium alone to produce binary alloys or in combination to produce higher order alloys. These alloys are quenched to retain the gamma phase or to form a metastable variant of the alpha phase. They are then aged to improve mechanical properties.

In terms of environmental degradation, pure uranium and alloys with up to a few percent alloying additions behave in one manner and alloys with higher alloying additions behave in a different manner. The primary application of depleted uranium is as a high-density material; therefore, the principal interest is in those alloys containing only a few percent of alloying additions, which are referred to as "lean" uranium alloys.

The addition of gamma-stabilizing, alloying elements

to uranium results in a more corrosion-resistant material. The alloy additions, however, also increase susceptibility to stress-corrosion cracking. Therefore, "lean" alloys behave like uranium in that they are reactive in the environment, but they are not highly susceptible to embrittlement or cracking. "Rich" alloys are more susceptible to stress-corrosion cracking but are more corrosion resistant.

### 4-16.2 TYPES OF CORROSION

#### 4-16.2.1 Uniform Corrosion

##### 4-16.2.1.1 Corrosion in Acid Solutions

Uranium is resistant to attack by 27% sulfuric acid, dilute perchloric acid, and organic acids.

Uranium is slowly attacked by dilute hydrochloric acid, hydrobromic acid, hydroiodic acid, nitric acid, cold 85% phosphoric acid, and concentrated hot sulfuric acid.

Uranium has a high corrosion rate in solutions of concentrated hydrochloric acid, boiling phosphoric acid, and boiling perchloric acid.

The corrosion rates of U-0.75 Ti and U-2 Mo in hydrochloric acid and sulfuric acid are shown in Table 4-143. These results are based upon potentiodynamic polarization measurements.

##### 4-16.2.1.2 Corrosion in Alkaline Solutions

Uranium is resistant to attack by alkali metal hydroxides, such as sodium hydroxide and potassium hydroxide, and is slowly attacked by hot ammonium hydroxide.

The corrosion rates of U-0.75 Ti and U-2 Mo in sodium hydroxide are shown in Table 4-143. These results are based upon potentiodynamic polarization measurements.

Uranium is dissolved by sodium hydroxide solutions containing hydrogen peroxide- or sodium peroxide-water mixtures.

**TABLE 4-143. CORROSION OF URANIUM ALLOYS IN VARIOUS SOLUTIONS (Ref. 216)**

| SOLUTION                             | CORROSION RATE,* $\mu\text{m}/\text{yr}$ (mpy) |                             |
|--------------------------------------|--|-----------------------------|
|                                      | U-0.75Ti                                       | U-2Mo                       |
| 1.0 N HCl                            | 205.74 (8.10)                                  | $8.628 \times 10^3$ (339.7) |
| 2.0 N HCl                            | 876.3 (34.5)                                   |                             |
| 2.5 N HCl                            | $1.04 \times 10^4$ (410)                       |                             |
| 3.0 N HCl                            | $1.356 \times 10^4$ (534)                      |                             |
| 5.0 N HCl                            | $5.037 \times 10^4$ (1983)                     |                             |
| 1.0 N H <sub>2</sub> SO <sub>4</sub> | 3.6 (0.14)                                     | 1.5 (0.06)                  |
| 1.0 M NaOH                           | 29.5 (1.16)                                    | 155 (6.10)                  |
| 50 ppm NaCl                          | 1.0 (0.04)                                     | 1.8 (0.07)                  |
| 3.5% NaCl                            | 6.6 (0.26)                                     | 0.8 (0.03)                  |

\*Determined from potentiodynamic polarization measurements

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## 4-16.2.1.3 Corrosion in Salt Solutions

Metallic uranium reacts vigorously with aqueous solutions of potassium persulfate, but its reaction is less rapid with ammonium persulfate.

Although uranium is only slightly attacked by cupric sulfate, it dissolves rapidly in solutions of copper-ammonium chloride.

Metallic uranium is a sufficiently powerful reducing agent to displace many metals from solutions of their salts. For example, solutions of  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{AgNO}_3$ ,  $\text{SnCl}_2$ ,  $\text{PtCl}_4$ , and  $\text{AuCl}_3$  yield precipitates of the corresponding metals when treated with uranium.

The corrosion rates of U-0.75 Ti and U-2 Mo in sodium chloride solutions are shown in Table 4-143. These results are based upon potentiodynamic polarization measurements.

## 4-16.2.1.4 Corrosion in Organic Compounds

At temperatures from 66° to 93°C (150° to 200° F), the vapors of carbon tetrachloride, chloroform, and trichloroethylene react slowly with metallic uranium. At temperatures above 1000°C (1832° F), the reaction with carbon tetrachloride is rapid. Uranium is subject to corrosion by a mixture of chlorinated biphenyls. The rate of attack increases rapidly with increasing temperature.

## 4-16.2.1.5 Corrosion in Water

The corrosion of uranium in distilled, aerated water is very low at room temperature. If the concentration of dissolved oxygen is allowed to diminish, however, hydrogen is produced and eventually the protective oxide film breaks down. The corrosion rate then increases dramatically. The effect of temperature on corrosion rate is illustrated in Fig. 4-56. At temperatures of 80°C (176° F) and above, the corrosion rate is relatively high and no low-corrosion-rate induction period is evident.

In stagnant areas in which the concentration of hydrogen can build up as the oxygen is depleted, corrosion accelerates. Uranium undergoes a form of crevice corrosion related to this phenomenon. The actual rates are influenced by uranium heat treatment, residual impurities in the uranium, and electrolytes present in the water.

Addition of the gamma-phase stabilizers, i.e., titanium, zirconium, columbium, and molybdenum, to uranium results in alloys that are more corrosion-resistant. Lean uranium alloys containing gamma-phase stabilizers show an initial weight gain when immersed in distilled water. After an incubation period during which an oxide film builds up and provides protection, continual spalling of the oxide film leads to a constant rate of weight loss (Ref. 218).

The incubation period for immersion in distilled water at 70°C (158° F) increases from about 200 h for U-0.75 Ti specimens to 1300 h for U-2.0 Ti specimens. The postin-

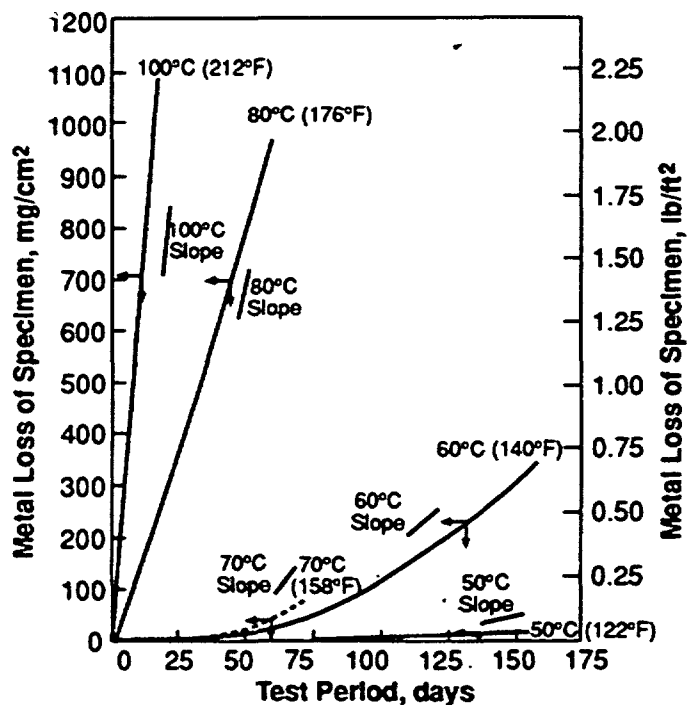


Figure 4-56. Corrosion of Standard Uranium in Aerated, Distilled Water (Ref. 217)

cupation period weight loss rate at 70°C (158° F) is about  $6.6 \times 10^{-3} \text{ mg/cm}^2 \cdot \text{h}$  ( $9.4 \times 10^{-8} \text{ lb/in.}^2 \cdot \text{h}$ ) for the U-0.75 Ti and  $2.4 \times 10^{-3} \text{ mg/cm}^2 \cdot \text{h}$  ( $3.4 \times 10^{-8} \text{ lb/in.}^2 \cdot \text{h}$ ) for U-2.0 Ti. At 50°C (122° F), however, the incubation times are shorter. The U-0.75 Ti period is 100 h and the U-2.0 Ti period is 800 h. The corrosion rate for the U-1.0 Ti alloy is  $1.54 \times 10^{-3} \text{ mg/cm}^2 \cdot \text{h}$  ( $2.2 \times 10^{-8} \text{ lb/in.}^2 \cdot \text{h}$ ) and  $3.2 \times 10^{-3} \text{ mg/cm}^2 \cdot \text{h}$  ( $4.6 \times 10^{-8} \text{ lb/in.}^2 \cdot \text{h}$ ) for the U-2.0 Ti alloy at 50°C (122° F).

## 4-16.2.2 Corrosion in Gases

## 4-16.2.2.1 Corrosion in Air and Oxygen

Freshly polished uranium metal is bright silver in color. Uranium metal oxidizes slowly in air at room temperature, and first it takes on a golden yellow tarnish. As oxidation proceeds, the surface film becomes darker and after a few days the metal appears black. As long as this surface film is not disturbed, attack will cease.

In a relatively dry atmosphere an adherent, nonporous oxide film forms and grows at the rate of only a few microns per year. High humidity or a temperature above 75°C (167° F) causes the formed oxide film to be non-adherent. The effect of temperature on the corrosion rate of uranium in air is shown in Table 4-144. In the temperature range of 120° to 150°C (248° to 302° F), the corrosion-versus-time curves are parabolic. At higher temperatures, from 166° to 221°C (330° to 430° F), the oxidation rate becomes linear with time.

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TABLE 4-144. EFFECT OF TEMPERATURE ON CORROSION OF URANIUM IN AIR (Ref. 219)

| TEMPERATURE |       | WEIGHT<br>g (lb)                    | OXIDIZED<br>% | PENETRATION,* |         |
|-------------|-------|-------------------------------------|---------------|---------------|---------|
| °C          | (°F)  |                                     |               | cm/yr         | (ipy)   |
| 20**        | ( 68) | Nil                                 | Nil           | Nil           | Nil     |
| 100         | (212) | 0.0416 (9.17 × 10 <sup>-5</sup> )   | 0.05          | 0.25          | (0.10)  |
| 134         | (273) | 0.0791 (17.44 × 10 <sup>-5</sup> )  | 0.09          | 0.51          | (0.20)  |
| 200         | (392) | 0.8010 (17.66 × 10 <sup>-4</sup> )  | 0.89          | 5.03          | (1.98)  |
| 300         | (572) | 1.6000 (35.27 × 10 <sup>-4</sup> )  | 1.77          | 10.06         | (3.96)  |
| 400         | (752) | 8.6300 (19.03 × 10 <sup>-3</sup> )  | 9.53          | 54.31         | (21.38) |
| 500         | (932) | 11.5300 (25.41 × 10 <sup>-3</sup> ) | 12.75         | 72.49         | (28.54) |

\*Based on original mass of 90.4744 g (19.95 × 10<sup>-2</sup> lbm), density of 18900 kg/m<sup>3</sup> (1179.9 lbm/ft<sup>3</sup>), and original surface area of 18.4 cm<sup>2</sup> (2.9 in.<sup>2</sup>). Because there was some loss on each 4-h test, the results were corrected to refer to the original values.

\*\*After 11 days the increase in mass was 0.0002 g (4.4 × 10<sup>-7</sup> lbm), which equals 0.0002%.

Massive uranium shapes, i.e., not powdered uranium, oxidize without burning in the temperature range of 500° to 700°C (932° to 1292°F). However, the metal will ignite when it is heated in the range of 700° to 1000°C (1292° to 1832°F).

The ignition temperature in air is within 20 deg C (36 deg F) of that in oxygen. The ignition temperature of uranium powder in the size range of -20 + 25 mesh, which is equivalent to a diameter of 711 μm (28 mils), is 285°C (545°F) in air and 305°C (581°F) in oxygen. Uranium powder in the size range of -270 + 325 mesh, which is equivalent to a diameter of 43 μm (1.7 mils), ignites at 240°C (464°F) in air and 234°C (453°F) in oxygen. Uranium chips, such as those produced by machining, may ignite in air if overheated, and uranium powder may ignite spontaneously if it is poured through air.

At room temperature, moisture in air can oxidize uranium slowly to UO<sub>2</sub>. In closed systems the formation of some uranium hydride accompanies oxidation; in an open system hydrogen evolves.

The corrosion of U-0.75 Ti and U-2 Mo in moist air is slow (Ref. 220). Zabielski *et al.* noted corrosion rates of 0.51 and 1.19 μm per yr (0.020 and 0.047 mpy) for U-0.75 Ti and U-2 Mo exposed to a 95% relative humidity environment at 45°C (113°F) (Ref. 216). However, a 5% salt fog environment accelerated corrosion by a factor of more than 3000. Pitting occurred over the cross sections, and appreciable corrosion occurred at the edges of the disc-shaped test specimens. The results of the humid air-salt fog tests are shown in Table 4-145. These results are based upon weight loss measurements. Based upon salt fog and moist nitrogen exposures, coating systems to protect U-0.75 Ti penetrators used in the US Air Force rapid-fire gun, GAV-81A, are not believed to be necessary for long-term storage (Ref. 221). Nevertheless, U-0.75 Ti lost 7% of its weight in 30 days of exposure to salt fog (Ref. 220).

TABLE 4-145. CORROSION OF URANIUM ALLOYS IN HUMID AIR AND SALT FOG (Ref. 216)

| ENVIRONMENT                       | CORROSION RATE,* |              |
|-----------------------------------|------------------|--------------|
|                                   | μm/yr (mpy)      |              |
|                                   | U-0.75 Ti        | U-2 Mo       |
| 5% Salt fog<br>(23-day exposure)  | 4790 (188.6)     | 4775 (188)   |
| 95% Humidity<br>(40-day exposure) | 0.51 (0.02)      | 1.19 (0.047) |

The effect of moisture in the atmosphere can be isolated by exposing specimens of the metal to humidified nitrogen. Uranium does not react with nitrogen at ordinary temperatures.

Lean uranium-titanium alloys exposed to 95% relative humidity nitrogen at 70°C (158°F) show a rapid initial corrosion period of less than 60 h. This initial period is followed by a period during which little weight change occurs. Conditions were such that water did not condense on the test specimens. Increasing the titanium content of the alloys reduces the corrosion rate. For example, increasing from U-0.8 Ti to U-2.0 Ti results in a hundred-fold decrease in the extent of corrosion (Ref. 218). Exposure of the specimen to condensing conditions approximates conditions of immersion in water.

## 4-16-2.2.2 Corrosion in Hydrogen

Powdered uranium reacts rapidly with hydrogen gas at 0°C (32°F) to form the hydride UH<sub>3</sub>. At room temperature the reaction generates much heat. A clean uranium surface reacts immediately with pure hydrogen, but a surface that has been exposed to air will not begin to react until about 30 min after exposure to hydrogen. The

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decomposition temperature of the hydride is 432°C (810°F). Therefore, the reaction of hydrogen with uranium, which is most rapid at temperatures near 215°C (419°F), declines to zero when the dissociation pressure of uranium hydride equals the imposed hydrogen pressure.

Hydrogen embrittles uranium; however, there is not a consensus on the amount of hydrogen required, the magnitude of the effect, or the mechanism. The embrittling effect of hydrogen in uranium can result from hydrogen in solid solution or as a hydride phase. Because of the low solubility of hydrogen in uranium, the most likely mechanism is formation of a hydride phase.

Uranium reacts with water vapor to form  $UO_2$  and liberate hydrogen. This hydrogen is probably responsible for the embrittlement observed in water environments. The lean alloys require more hydrogen to produce embrittlement than does pure uranium.

#### 4-16.2.2.3 Corrosion in Nitrogen

Although uranium does not react with nitrogen at room temperature, fine uranium powder reacts rapidly with nitrogen above 300°C (572°F). Massive uranium shapes start reacting with moist nitrogen at 330°C (626°F) and with dry nitrogen at 370°C (698°F). The rate of reaction is appreciable at 450°C (842°F) and increases rapidly at higher temperatures.

#### 4-16.2.2.4 Corrosion in Sulfur and Selenium Vapors and Halide Gases

Uranium burns at 500°C (932°F) in sulfur vapor; selenium reacts similarly with uranium. Fluorine reacts vigorously with metallic uranium at room temperature to form uranium hexafluoride. Chlorine reacts with massive uranium metal shapes at a moderate rate at temperatures of 500° to 600°C (932° to 1112°F), but at 150° to 180°C (302° to 356°F) powdered metal burns in chlorine. Uranium turnings react with bromine at 650°C (1202°F), and uranium metal is attacked by iodine vapor at 350°C (662°F).

#### 4-16.2.2.5 Corrosion by Liquid Metals

Pure, finely divided uranium metal prepared in an oxide-free state by decomposition of uranium hydride readily amalgamates with mercury. Massive forms of uranium metal are not appreciably attacked by liquid sodium or by sodium-potassium alloys. Apparent attack by these liquid metals results from oxygen present in the liquid metal. For example, little corrosion occurs in liquid sodium under 457°C (855°F), but between 457° and 599°C (855° and 1110°F) an oxide film forms. Calcium added to liquid sodium inhibits corrosion of uranium.

Uranium that had been heated for six days in lithium at 600°C (1112°F) showed a slight reaction layer (Ref. 222). Molten lead (Refs. 223 and 224), bismuth (Ref. 225),

lead-bismuth (Ref. 39), and gallium (Ref. 226) all react readily with uranium.

#### 4-16.2.2.6 Corrosion by Steam

The corrosion of uranium metal by steam is compared to its corrosion in air as a function of temperature in Fig. 4-57. Attack by steam is much more vigorous than attack by air, and hydrogen evolved in the steam-uranium oxidation reacts with the uranium if the temperature is not too high. At temperatures above 450°C (842°F)  $UO_2$  is the principal reaction product.

#### 4-16.2.3 Hydrogen Embrittlement and Stress-Corrosion Cracking

Uranium and all its alloys are susceptible to embrittlement and/or stress-corrosion cracking. Therefore, almost all uranium alloys are quenched to retain the gamma phase or to form a metastable variant of the alpha phase. The alloys are then aged to improve the mechanical properties. High-temperature aging of quenched uranium alloys results in a balanced two-phase alloy, i.e., alpha plus gamma. The susceptibility of the quenched material to stress-corrosion cracking increases with aging until the balanced two-phase structure begins to form. The balanced two-phase microstructure is the most resistant to stress-corrosion cracking; thus susceptibility to cracking decreases with continued aging. The lean alloys crack in water; however, oxygen inhibits this cracking. The rich alloys, i.e., those with higher solute contents, do not crack in water but will crack in oxygen, and they are very sensitive to the presence of chloride ions in aqueous solution. The lean alloys, however, are much less sensitive to chloride ions.

Stress-corrosion cracking occurs at stress intensity levels above a threshold designated  $K_{Isc}$ . (See par. 2-2.9 for a discussion of stress-corrosion cracking.)

Threshold stress intensity values for several uranium alloys in salt-laden, moist air are listed in Table 4-146.

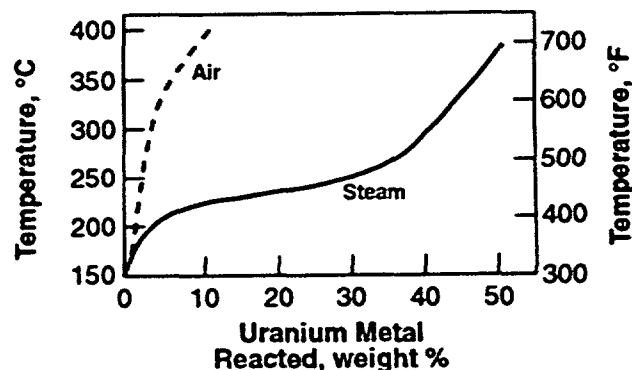


Figure 4-57. Comparison of Corrosion Rates for Uranium in Air and in Steam in Temperature Range of 150° to 400°C (302° to 752°F) (Ref. 227)



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**TABLE 4-146. COMPARISON OF FRACTURE TOUGHNESS AND THRESHOLD STRESS INTENSITY FOR DEPLETED URANIUM ALLOYS IN 98% RELATIVE HUMIDITY SALT-LADEN AIR (Ref. 228)**

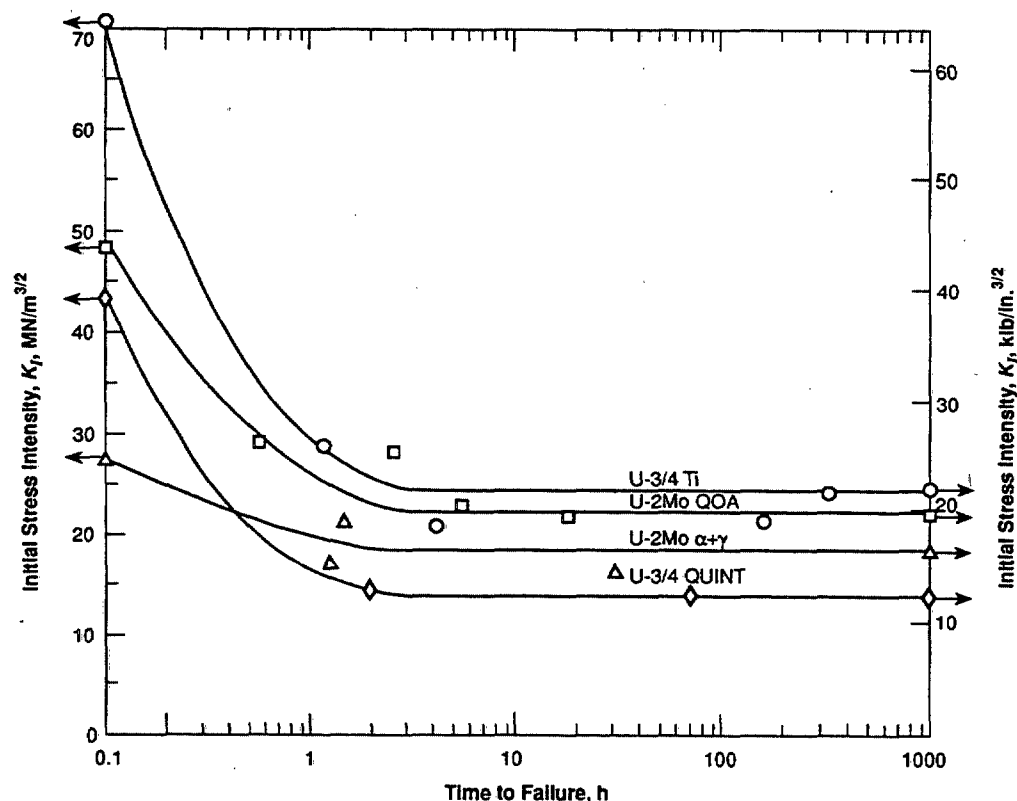
| ALLOY                       | $K_{IC}$ ,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) | $K_{Iscs}$ ,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) | $\Delta K_{IC} - K_{Iscs}$ ,<br>MN/m <sup>3/2</sup> (klb/in. <sup>3/2</sup> ) |
|-----------------------------|---|---|---|
| U-2Mo QOA                   | 48.6 (44.2)   | 20.8 (18.9)   | 27.8 (25.3)   |
| U-2Mo ( $\alpha + \gamma$ ) | 27.9 (25.4)   | 21.5 (19.6)   | 6.4 ( 5.8)  |
| U-3/4 Quint                 | 43.3 (39.4)   | 15.6 (14.2)   | 27.7 (25.2)   |
| U-3/4 Ti                    | 69.0 (62.8)   | 24.2 (22.0)   | 44.8 (40.8)   |

Also listed are the stress intensity factors  $K_{IC}$  that cause fast fracture solely because of overload. Initial stress intensity  $K_I$  as a function of time to failure is shown in Fig. 4-58. For stress-corrosion cracking resistance in salt-laden, moist air, the alloys rank in this order: U-3/4Ti, U-2Mo QOA, U-2Mo( $\alpha + \gamma$ ), and U-3/4Quint.  $K_{Iscs}$  values for the U-2Mo alloys are not significantly lower than the value for U-3/4Ti. The decrease in fracture toughness ( $\Delta K_{IC} - K_{Iscs}$ ) because of exposure to the environment, however, is much more significant for the U-3/4Ti and U-3/4Quint alloys than for the U-2Mo.

The chemical compositions of these alloys are listed in Table 4-147. The mechanical properties in dry and salt-

laden, moist air are recorded in Table 4-148, and the thermochemical processing of these alloys is given in Table 4-149.

Another study determined the critical threshold stress intensity factor for stress-corrosion cracking  $K_{Iscs}$  of several uranium alloys that are candidates for penetrator and nuclear shell applications (Ref. 229). The alloys were in the as-extruded condition, and the environments were distilled water (contained <1 ppm Cl<sup>-</sup>) and a 3.5% sodium chloride solution (>21,000 ppm Cl<sup>-</sup>). A limited number of stress-corrosion cracking tests were performed in solutions containing 50 ppm chloride ion (Cl<sup>-</sup>) to determine the effect of this chloride ion concentration.



**Figure 4-58. Initial Stress Intensity as a Function of Time to Failure (Ref. 228)**

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**TABLE 4-147. CHEMICAL ANALYSES IN WEIGHT PERCENT FOR DEPLETED URANIUM ALLOYS (Ref. 228)**

|    | ALLOY                |                      |                      |
|----|----------------------|----------------------|----------------------|
|    | U-2Mo                | U-3/4Ti              | U-Quint              |
| Mo | 2.00                 | $96 \times 10^{-4}$  | 0.84                 |
| Nb | —                    | $<10 \times 10^{-4}$ | 0.70                 |
| Zr | —                    | —                    | 0.86                 |
| Ti | $<1 \times 10^{-4}$  | 0.71                 | 0.44                 |
| V  | $<1 \times 10^{-4}$  | $<1 \times 10^{-4}$  | 0.16                 |
| Al | $25 \times 10^{-4}$  | $35 \times 10^{-4}$  | $75 \times 10^{-4}$  |
| Si | $5.5 \times 10^{-4}$ | $127 \times 10^{-4}$ | $97 \times 10^{-4}$  |
| Fe | $60 \times 10^{-4}$  | $45 \times 10^{-4}$  | $140 \times 10^{-4}$ |
| Cu | $10 \times 10^{-4}$  | $10 \times 10^{-4}$  | $15 \times 10^{-4}$  |
| C  | $100 \times 10^{-4}$ | $10 \times 10^{-4}$  | $40 \times 10^{-4}$  |
| U  | Balance              | Balance              | Balance              |

The chemical compositions of these alloys are shown in Table 4-150, the mechanical properties are given in Table 4-151, and the stress-corrosion cracking results are shown in Table 4-152.

The threshold stress intensity factor  $K_{Isc}$  for stress-corrosion cracking in air and aqueous environments is plotted as a function of yield strength for the various alloys in Fig. 4-59. Also plotted are the critical flaw depths for propagation of a stress-corrosion crack. A long, thin crack is assumed. For a given flaw depth an alloy with a  $K_{Isc}$  value above the critical flaw-depth line should be selected if stress-corrosion cracking is to be avoided.

**TABLE 4-148. MECHANICAL PROPERTIES OF DEPLETED URANIUM ALLOYS IN DRY AIR AND SALT-LADEN, MOIST AIR (Ref. 228)**

| MATERIAL               | % RH | 0.2% YIELD STRENGTH |     | ULTIMATE TENSILE STRENGTH |     | % ELONGATION IN IN 4 DIAMETERS | HARDNESS Rc | YOUNG'S MODULUS† |                    |
|------------------------|------|---------------------|-----|---------------------------|-----|--------------------------------|-------------|------------------|--------------------|
|                        |      | MPa                 | ksi | MPa                       | ksi |                                |             | GPa              | ksi                |
| U-2Mo QOA              | 0    | 796                 | 115 | 1243                      | 180 | 6.7                            | 37.0        | 159              | $23.0 \times 10^3$ |
|                        | 98   | 735                 | 107 | 1043*                     | 151 | —**                            |             |                  |                    |
| U-2Mo ( $\alpha + T$ ) | 0    | 642                 | 93  | 952                       | 138 | 3.0                            | 37.0        | 164              | $23.8 \times 10^3$ |
|                        | 98   | 735                 | 107 | 1126*                     | 163 | —**                            |             |                  |                    |
| U-3/4Quint             | 0    | 721                 | 105 | 1305                      | 189 | 11.9                           | 37.0        | 160              | $23.2 \times 10^3$ |
|                        | 66   | 728                 | 106 | 1016*                     | 147 | 1.5                            |             |                  |                    |
|                        | 98   | 742                 | 108 | 1058*                     | 153 | 1.6                            |             |                  |                    |
| U-3/4Ti                | 0    | 824                 | 120 | 1339                      | 194 | 7.1                            | 37.0        | 172              | $24.9 \times 10^3$ |
|                        | 66   | 823                 | 119 | 1036*                     | 150 | 1.4                            |             |                  |                    |
|                        | 98   | 762                 | 111 | 920*                      | 133 | 1.5                            |             |                  |                    |

\*Maximum stress at fracture

\*\*Specimen failed at artificial notch

†Average of five readings

**TABLE 4-149. THERMOMECHANICAL PROCESSING OF DEPLETED URANIUM ALLOYS (Ref. 228)**

| ALLOY                  | PROCESSING   |
|------------------------|--|
| U-2Mo QOA              | T extruded into rectangular plate at 100°C (212°F); solution treated for 2 h and helium quenched; aged at 500°C (932°F) for 5 h and air cooled.  |
| U-2Mo ( $\alpha + T$ ) | As per U-2 Mo QOA above plus: solution treated at 800°C (1472°F) for 2 h and water quenched; heated to 615°C (1139°F) for 5 h and water quenched; aged at 400°C (752°F) for 5 h and slow cooled. |
| U-3/4Quint             | As extruded at 1000°C (1832°F)   |
| U-3/4Ti                | As $\alpha$ extruded at 630°C (1166°F)   |

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TABLE 4-150. CHEMICAL ANALYSIS OF URANIUM ALLOYS (Ref. 229)

| ALLOY     | WEIGHT, ppm |     |    |    | WEIGHT, % |      |      |      |      |
|-----------|-------------|-----|----|----|-----------|------|------|------|------|
|           | C           | H   | O  | N  | Mo        | Nb   | Zr   | Ti   | V    |
| 3/4% Ti   | <10         | 2.4 | 20 | 7  | —         | —    | —    | 0.70 | —    |
| 3/4% Quad | 50          | 1.6 | 40 | 54 | 0.73      | 0.74 | 0.70 | 0.49 | —    |
| 1% Quad   | 22          | 4.4 | 74 | —  | 1.03      | 1.04 | 0.98 | 0.62 | —    |
| 1% Quint  | 59          | —   | —  | 23 | 1.00      | 1.00 | 0.94 | 0.47 | 0.57 |

TABLE 4-151. MECHANICAL PROPERTIES OF URANIUM ALLOYS (Ref. 229)

| ALLOY     | ULTIMATE TENSILE STRENGTH |       | 0.2% YIELD STRENGTH |       | ELONGATION, % | REDUCTION IN AREA, % | HARDNESS, Rc |
|-----------|---------------------------|-------|---------------------|-------|---------------|----------------------|--------------|
|           | MPa                       | ksi   | MPa                 | ksi   |               |                      |              |
| 3/4% Ti   | 1114                      | 161.6 | 607                 | 88    | 4.5           | 4.6                  | 32           |
| 3/4% Quad | 1379                      | 200   | 769                 | 111.5 | 16.5          | 25.4                 | 41           |
| 1% Quad   | 1613                      | 234   | 1172                | 170   | 8.0           | 20.5                 | 47           |
| 1% Quint  | 1940                      | 281.4 | 1627                | 236   | 3.5           | 4.6                  | 52           |

TABLE 4-152. SUMMARY OF URANIUM STRESS-CORROSION CRACKING RESULTS (Ref. 229)

| ENVIRONMENT  | 3/4% Ti             |                        |                   |       | 3/4% Quad           |                        |                   |       |
|--|---------------------|------------------------|-------------------|-------|---------------------|------------------------|-------------------|-------|
|  | STRESS INTENSITY, K |                        | MINIMUM THICKNESS |       | STRESS INTENSITY, K |                        | MINIMUM THICKNESS |       |
|  | MN/m <sup>3/2</sup> | klb/in. <sup>3/2</sup> | mm                | in.   | MN/m <sup>3/2</sup> | klb/in. <sup>3/2</sup> | mm                | in.   |
| Air  | 26                  | 24                     | 0.38              | 0.015 | 52                  | 47                     | 11.0              | 0.44  |
| Water  | 23                  | 21                     | 0.28              | 0.011 | 44                  | 40                     | 8.1               | 0.32  |
| 3.5% NaCl  | 16                  | 15                     | 0.15              | 0.006 | 13                  | 12                     | 0.74              | 0.029 |
| 50 ppm Cl <sup>-</sup>                             | —                   | —                      | —                 | —     | —                   | —                      | —                 | —     |
| 50 ppm Cl <sup>-</sup><br>+ 0.1M NaNO <sub>3</sub> | —                   | —                      | —                 | —     | —                   | —                      | —                 | —     |
| ENVIRONMENT  | 1% Quad             |                        |                   |       | 1% Quint            |                        |                   |       |
|  | STRESS INTENSITY, K |                        | MINIMUM THICKNESS |       | STRESS INTENSITY, K |                        | MINIMUM THICKNESS |       |
|  | MN/m <sup>3/2</sup> | klb/in. <sup>3/2</sup> | mm                | in.   | MN/m <sup>3/2</sup> | klb/in. <sup>3/2</sup> | mm                | in.   |
| Air  | 35                  | 32                     | 2.3               | 0.089 | 22                  | 20                     | 0.46              | 0.018 |
| Water  | 31                  | 28                     | 1.7               | 0.068 | 10                  | 9                      | 0.10              | 0.004 |
| 3.5% NaCl  | 8                   | 7                      | 0.10              | 0.004 | 5                   | 5                      | 0.025             | 0.001 |
| 50 ppm Cl <sup>-</sup>                             | 10                  | 9                      | 0.18              | 0.007 | 5                   | 5                      | 0.025             | 0.001 |
| 50 ppm Cl <sup>-</sup><br>+ 0.1M NaNO <sub>3</sub> | —                   | —                      | —                 | —     | 18                  | 16                     | 0.28              | 0.011 |

Note: ASTM minimum thickness =  $2.5 (K/\sigma_y)^2$  where  $K$  is the stress intensity given in the table and  $\sigma_y$  is the yield strength given in Table 4-151, both are given in consistent units.

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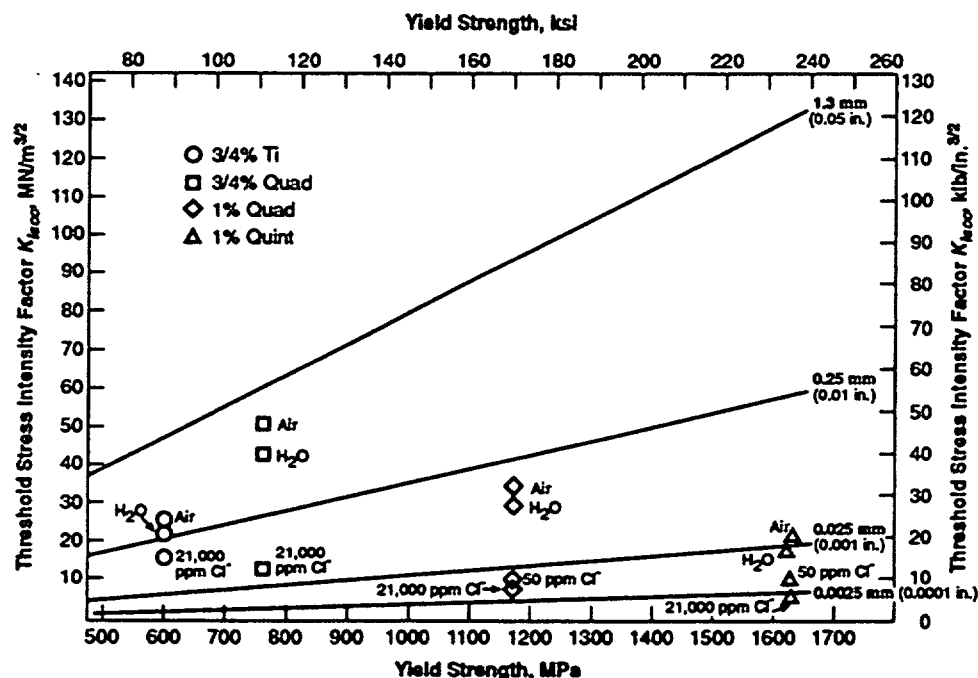


Figure 4-59.  $K_{Isc}$  for Uranium Alloys in Air, Distilled Water, and a 3.5% Sodium Chloride Solution, Shown as a Function of Yield Strength and Four Values of Crack Size (Ref. 229)

The critical flaw sizes for the various alloys follow:

1. U- $\frac{3}{4}$ Ti Alloy:

- In both water and air: 0.25 mm (0.01 in.)
- In 3.5% salt solution: 0.025 mm (0.001 in.)

2. U- $\frac{3}{4}$ Quad Alloy:

- In both water and air: 0.25 mm (0.01 in.)
- In 3.5% salt solution: 0.025 mm (0.001 in.)

3. U-1Quad Alloy:

- In both water and air: 0.025 mm (0.001 in.)
- In 3.5% salt solution: 0.0025 mm (0.0001 in.)

4. U-1Quint Alloy. This alloy is the most susceptible

to stress-corrosion cracking of the alloys tested. In most environments a flaw depth of only 0.0025 mm (0.0001 in.) can be tolerated. Based upon these crack depth tolerances, the alloys can be listed in the following order of increasing stress-corrosion cracking susceptibility: U- $\frac{3}{4}$ Quad, U- $\frac{3}{4}$ Ti, U-1Quad, and U-1Quint. Note, however, that the order of increasing yield strength is the same.

A series of uranium-columbium alloys were tested for stress-corrosion cracking in air and aqueous chloride environments (Ref. 230). The chloride-anion environment is more aggressive than the air environment. Water vapor is the primary stress corrodent for the most susceptible alloy, U-2.25Cb, and oxygen is primarily responsible for the stress-corrosion cracking of the more resistant alloys, U-6Cb and U-8Cb. The U-4.25Cb alloy is susceptible in both water vapor and air environments.

#### 4-16.2.4 Galvanic Corrosion

Uranium is anodic to nickel (Ref. 231), and it is generally anodic to stainless steel (Ref. 232). Uranium is cathodic to aluminum (Ref. 233), cadmium, and zinc (Ref. 231).

#### 4-16.3 INTERFACE PROBLEMS

A major problem in creating a metal coating on uranium is achieving a good metallic bond. Uranium has a high affinity for oxygen, and an oxide film on uranium prevents the formation of an adequate bond.

Oxidation of uranium by moisture in a gas occurs slowly at room temperature. In a closed system some uranium hydride is formed. If the moisture is a contaminant in an inert gas, the amount of hydride formed may be appreciable and the product may ignite spontaneously when subsequently exposed to air. If a large excess of oxygen is present, the hydride will become oxidized with the evolution of hydrogen. This may constitute an explosion hazard.

#### 4-16.4 METHODS FOR PREVENTION OF CORROSION

##### 4-16.4.1 Inhibitors

Some inhibitors have been found that protect uranium alloys from corrosion or stress-corrosion cracking. The dissolution of U-3Mo, U-1.75Ti, and U- $\frac{3}{4}$ Ti can be

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inhibited by  $\text{NO}_3^-$ ,  $\text{CrO}_4^{2-}$ , and  $\text{SO}_4^{2-}$  (Ref. 234). The  $\text{CrO}_4^{2-}$  ion is the most effective of these. The intergranular cracking in U-7.5Nb-2.5Zr can be stopped by  $\text{ClO}_4^-$  (Ref. 235).  $\text{NO}_3^-$  and  $\text{CN}^-$  provide an inhibiting effect on stress-corrosion cracking (Ref. 236). Passivation has been observed in 1N  $\text{KNO}_3$ -0.001 N KCl.

### 4-16.4.2 Coatings

Protective oxide films on uranium can provide long-term protection in oxygen and water at room temperature; they deteriorate, however, at elevated temperatures. These oxide films are not used on uranium alloys to inhibit stress-corrosion cracking.

Depending on their formulation, organic coatings may be corrosive, may be ineffective, or may provide protection as long as the surface is free of defects or scratches. Therefore, organic coatings do not reliably protect uranium and uranium-titanium alloys from atmospheric attack (Ref. 237). One approach to protecting uranium in oxygen and water environments is to oxidize the surface and then expose it to organic vapors near  $400^\circ\text{C}$  ( $752^\circ\text{F}$ ). Polymer coatings can also be prepared by using a radio frequency discharge with various plasma gases (Ref. 238).

Electroplated nickel is the most extensively used protective film for uranium. However, care must be exercised to insure the plating process used does not generate hydrogen. Nickel coatings are cathodic to U-0.75Ti and U-10Mo; therefore, the nickel coating can accelerate the stress-corrosion cracking of these alloys.

Cadmium and zinc are anodic to U-Ti. Even if they are flawed, they provide protection. They do not, however, adhere to the alloy. A successful process for forming a metallic coating is to plate first with nickel. The nickel plate is then covered with zinc, which is followed by a chromate finish.

A coating of zinc-10 nickel provides good protection for U-0.75Ti in salt-fog and open-moist-nitrogen atmospheres (Ref. 239), but in closed-moist-nitrogen atmospheres the coatings deteriorate rapidly.

Penetrators and aircraft counterweights can be protected by zinc and zinc-tin coatings at a reasonable cost (Ref. 237). Electroplated nickel is also effective but the cost is high.

The finish required for depleted uranium used in Army aircraft is nickel plating to the requirements of MIL-P-27418 plus one coat of MIL-P-23377 Type 1 primer that is 0.015 to 0.023 mm (0.6 to 0.9 mil) thick.

Ion-plated aluminum films can protect uranium and uranium alloys at temperatures as high as  $100^\circ\text{C}$  ( $212^\circ\text{F}$ ) for a limited time (Ref. 240). The coating is cathodic to a U-0.75Ti alloy, so flaws in the coating accelerate stress-corrosion cracking. Aluminum films have been applied to U-4.5Cb alloy in several ways (Ref. 235). Coatings produced by plasma spraying, chemical-vapor deposition, and physical-vapor deposition inhibited stress-corrosion cracking of the alloy. Electrodeposited aluminum was not effective, but electroplated cadmium was effective.

Zabielski *et al.* found that corrosion rates of U-0.75Ti and U-2Mo specimens coated with ion-vapor-deposited aluminum were very slow compared to the rates of uncoated specimens after 28 days of exposure to 5% salt fog at  $35^\circ\text{C}$  ( $95^\circ\text{F}$ ) (Ref. 216). Corrosion of the underlying alloys occurred due to pinhole defects in the coating.

### 4-16.5 EXAMPLE OF CORROSION PROBLEMS

The depleted uranium alloys used as penetrators in tank main armament rounds are susceptible to stress-corrosion cracking during storage in moist air environments. Studies have linked stress-corrosion cracking to the presence of both residual stresses and oxycarbonitride inclusions in the as-fabricated penetrators (Refs. 241 and 242). These inclusions are regions of stress concentration and localized corrosion, as well as sites for the initiation of cracks. Typical stress-corrosion cracks in uranium penetrators are illustrated in Fig. 4-60. Tensile stresses necessary for stress-corrosion cracking result from corrosion product formation within the alloy and from residual stresses developed during manufacturing. Residual stresses result from plastic deformation, thermal strains, and phase transformation during fabrication of uranium alloy parts.

Penetrators have been produced by grinding hot-rolled alloy, by forging, and by casting techniques. Each of these techniques produces different stress distributions in the product. The ground, hot-rolled material has large, tangential, tensile stresses on the surface that are on the order of 379 MPa (55 ksi). The forged and cast penetrators are either in a compressive surface-stress state or exhibit considerably lower tensile surface stress—maximum 97 MPa (14 ksi).

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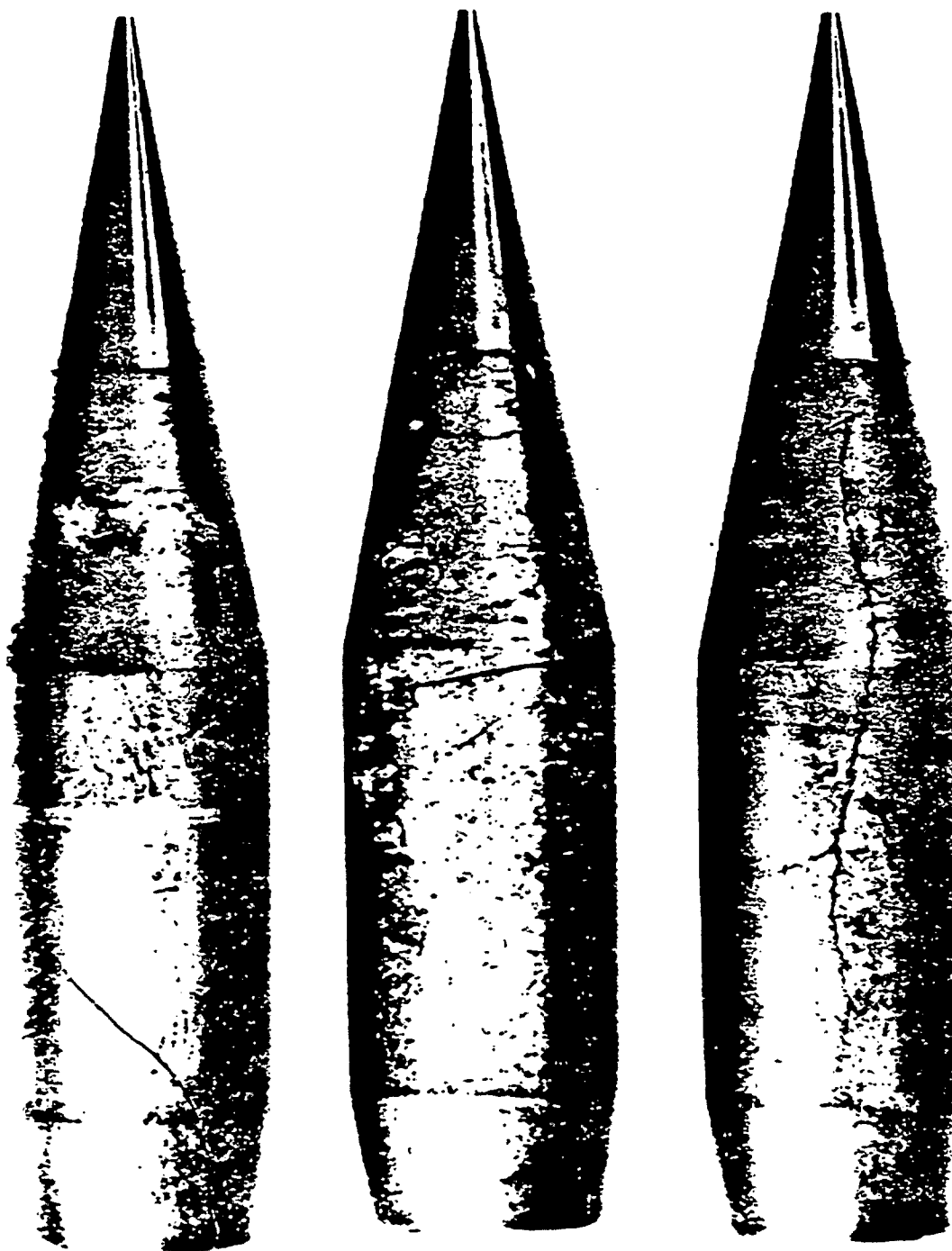


Figure 4-60. Typical Stress-Corrosion Cracks in Uranium Penetrators (Ref. 228)

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Surface tensile stresses are necessary for stress-corrosion cracking. A corrosion product film can be a continuation in the reaction layer of the crystal structure of gamma uranium. Such a corrosion film is adherent and can be protective in an oxidizing environment. However, the corrosion film is under compression while the metal in contact with the film is under tension. An oxide film about 1  $\mu\text{m}$  (0.04 mil) thick can stress the metal surface to its elastic limit. A brittle metal can form discontinuous cracks originating at the surface. This stress phenomenon has been observed in alloys of uranium and 10% by weight of columbium. Adding 1.5 to 2.0% by weight of zirconium improves the resistance of the alloy to stress-corrosion cracking, but greater additions decrease its resistance.

Alloying elements and heat treatments that resist the type of failure associated with cracking include

1. Those that form and stabilize the gamma phase
2. Those that form and stabilize at least one type of martensitic alpha-phase uranium
3. Those that refine the grain structure.

The concepts of linear elastic fracture mechanics are used to characterize the level of stress below which stress-corrosion cracking will not occur with a given surface flaw. This approach assumes that the propagation of cracks is predictable in terms of the magnitude of tensile stresses at the crack tip. It relates the opening of the crack to a stress.

As a consequence of several in-bore failures of a projectile during low-temperature firing, an intensive fracture toughness study of the core material, U-0.75Ti, was done (Ref. 243). Based upon this study, Zabielski and Levy developed a minimum fracture toughness requirement of 33  $\text{MN}/\text{m}^{3/2}$  (30  $\text{klb}/\text{in.}^{3/2}$ ) at  $-46^\circ\text{C}$  ( $-50^\circ\text{F}$ ) that should be incorporated into the U-0.75Ti penetrator specification to insure launch integrity.

### 4-17 ZINC AND ZINC ALLOYS

Elemental zinc has a density of 7130  $\text{kg}/\text{m}^3$  (445.1  $\text{lb}/\text{ft}^3$ ), a melting point of  $419.6^\circ\text{C}$  ( $787.3^\circ\text{F}$ ), and a boiling point of  $907^\circ\text{C}$  ( $1665^\circ\text{F}$ ).

Table 4-153 lists the chemical compositions of different grades of zinc. These compositions are used as the basis for producing various grades of rolled zinc, die castings, and zinc coatings. The mechanical property requirements of the end product or the workability of the alloy determines which composition should be used. The purer grades, i.e., those low in cadmium content, are used where maximum deep-drawing properties are required and where stiffness or rigidity is not of primary importance. (Greater stiffness is obtained with the copper-hardened alloys.) For maximum creep resistance the zinc-copper-titanium alloy is used.

Although zinc is available in many forms, e.g., sheet,

plate, strip, and pressure die castings, the primary use of zinc for corrosion control is as a coating for steel. Zinc can protect steel galvanically. Zinc-coated steel is commonly used in various kinds of structures and in many fabricated parts such as automobile bodies and appliance cabinets; pole, line, and marine hardware; pails, cans, and boxes; and nails, hooks, bolts, and nuts.

Four methods of applying metallic zinc coatings are in general use—hot-dip galvanizing, electrodeposition, thermal spraying, and sheradizing. Metallic zinc dust is also applied as a pigment in paint. Each of these methods is discussed briefly:

1. *Hot-Dip Galvanizing*. This method involves dipping the prepared steel in a bath of molten zinc to form the coating. Because the steel reacts with the molten zinc and the zinc and steel interdiffuse, the coating consists of layers of zinc-iron alloys that are progressively richer in zinc nearer the outer surface.

2. *Electrodeposition*. This method produces a deposit of pure zinc. The deposits are very ductile, and coated articles can be fabricated without damage. Also the thickness of the deposit can be accurately controlled.

3. *Thermal Spraying*. This process applies a spray of molten zinc particles to a surface. Upon impact they flatten and to some degree interlock with the surface irregularities. The sprayed coating is somewhat rough and porous.

4. *Sheradizing*. This method is a cementation process. Zinc dust is heated to a temperature near its melting point ( $371^\circ\text{C}$  ( $700^\circ\text{F}$ )) and is brought into intimate contact with the steel. An iron-zinc coating forms on the steel by diffusion.

### 4-17.1 TYPES OF CORROSION

#### 4-17.1.1 Galvanic Corrosion

In aqueous solutions zinc is anodic to metals such as iron, nickel, lead, tin, and copper. Zinc is cathodic to magnesium, and it can be either anodic or cathodic to aluminum. In neutral and acid environments zinc is usually the anode, but in high-pH solutions aluminum is the anode.

The galvanic effect of zinc-steel couples in various salt solutions is illustrated in Table 4-154.

Hot-dipped zinc coatings are not pure zinc; they consist of a series of zinc-iron alloys progressively richer in iron closer to the steel surface. Each layer is anodic to that below it. As the coating is attacked, the tendency is toward uniformly spreading corrosion rather than toward pitting or local attack.

Temperature affects the potential of zinc in various solutions. Therefore, steel-zinc couples can undergo a transition from zinc being anodic to zinc being cathodic to steel under some conditions.

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TABLE 4-153. COMPOSITIONS OF ZINC MATERIALS (Ref. 244)

| SPECIFICATION FOR SLAB ZINC<br>ASTM designation B6-77 part 9 |               |               |                  |                             |
|--|---------------|---------------|------------------|-----------------------------|
| GRADE  | IMPURITIES, % |               |                  |                             |
|  | Lead<br>(max) | Iron<br>(max) | Cadmium<br>(max) | Zinc (min by<br>difference) |
| Special high grade   | 0.003         | 0.003         | 0.003            | 99.990                      |
| High grade   | 0.07          | 0.02          | 0.03             | 99.90                       |
| Intermediate   | 0.20          | 0.03          | 0.40             | 99.5                        |
| Brass special  | 0.6           | 0.03          | 0.50             | 99.0                        |
| Prime Western  | 1.6           | 0.05          | 0.50             | 98.0                        |

| TYPICAL COMPOSITIONS OF ROLLED ZINC<br>COMPOSITIONS (BALANCE ZINC), % |               |           |           |            |           |
|---|---------------|-----------|-----------|------------|-----------|
| Lead  | Iron<br>(max) | Cadmium   | Copper    | Magnesium  | Titanium  |
| 0.05 max  | 0.010         | 0.005 max | 0.001 max | —          | —         |
| 0.05-0.12   | 0.012         | 0.005 max | 0.001 max | —          | —         |
| 0.30-0.65   | 0.020         | 0.20-0.35 | 0.005 max | —          | —         |
| 0.05-0.12   | 0.012         | 0.005 max | 0.65-1.25 | —          | —         |
| 0.05-0.12   | 0.015         | 0.005 max | 0.75-1.25 | 0.007-0.02 | —         |
| 0.20 max  | 0.015         | 0.01 max  | 0.5-0.8   | —          | 0.08-0.16 |

STANDARD SPECIFICATION FOR ZINC-BASE ALLOY DIE CASTINGS  
ASTM designation B86-76 part 7

| ELEMENT      | COMPOSITIONS, %      |                    |
|--------------|----------------------|--------------------|
|              | Alloy AG 40A (XXIII) | Alloy AC 41A (XXV) |
| Copper       | 0.25 max*            | 0.75-1.25          |
| Aluminum     | 3.5-4.3              | 3.5-4.3            |
| Magnesium    | 0.020-0.05           | 0.03-0.08          |
| Iron, max    | 0.100                | 0.100              |
| Lead, max    | 0.005                | 0.005              |
| Cadmium, max | 0.004                | 0.004              |
| Tin, max     | 0.003                | 0.003              |
| Zinc         | Remainder            | Remainder          |

\*For the majority of commercial applications, a copper content in the range of 0.25% to 0.75% will not adversely affect the serviceability of die castings.

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TABLE 4-154. EQUAL AREA ZINC-STEEL COUPLES VS VARIOUS SOLUTIONS (Ref. 245)

| SOLUTION               | CORROSION RATE, mm/yr (mpy)* |             |             |       |
|------------------------|------------------------------|-------------|-------------|-------|
|                        | UNCOUPLED                    |             | COUPLED     |       |
|                        | Zinc                         | Steel       | Zinc        | Steel |
| M/20 Magnesium sulfate | +                            | 0.066 (2.6) | 0.086 (3.4) | +     |
| M/20 Sodium sulfate    | 0.284 (11.2)                 | 0.254 (10)  | 0.838 (33)  | +     |
| M/20 Sodium chloride   | 0.254 (10)                   | 0.254 (10)  | 0.762 (30)  | +     |
| M/200 Sodium chloride  | 0.112 (4.4)                  | 0.178 (7)   | 0.218 (8.6) | +     |
| Carbonic acid          | 0.010 (0.4)                  | 0.074 (2.9) | 0.038 (1.5) | +     |
| Calcium bicarbonate    | +                            | 0.150 (5.9) | +           | +     |
| Tap water (hard)       | +                            | 0.071 (2.8) | +           | +     |

\*Specimens of equal area partially immersed for 39 days

+Specimens gain weight

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## 4-17.1.2 Uniform Corrosion

## 4-17.1.2.1 Weathering Corrosion

Corrosion in the atmosphere is usually not influenced by the small amounts of other elements that may be present in zinc or in a zinc coating.

Zinc is a very active metal in the galvanic series; however, it owes its high degree of atmospheric corrosion resistance to the formation of basic carbonate films. Therefore, environmental conditions that interfere with the formation of such films or that lead to the formation of soluble films can result in the rapid attack of zinc.

The corrosion rate for zinc is much higher in industrial atmospheres than in rural or marine atmospheres. The relative corrosivity of four types of atmospheres is shown in Table 4-155. This corrosivity is calculated from the average 20-yr corrosion rates for all of the zinc compositions exposed.

The most important controlling factors in the weathering corrosion of zinc are humidity and sulfur dioxide. The poor performance of zinc in environments containing sulfur pollution can be explained by the fact that zinc is amphoteric and is most resistant in the range of about  $6 \leq \text{pH} \leq 12$ . During periods of high pollution the strong acidity developed by the moisture film as a result of the sulfur dioxide  $\text{SO}_2$  picked up from the air causes the

protective patina to be redissolved, and some of the zinc also may be corroded. In an industrial region that experiences high rainfall, the corrosion rate may be reduced on a fully exposed exterior surface because the rain washes away acidic contaminants. A sheltered surface exposed to the same polluted atmosphere will corrode at high rates during rainy, i.e., high humidity, periods because the acidic film is not washed away.

In marine atmospheres high humidity and airborne seasalts create environments corrosive to zinc. Industrial atmospheres, however, are usually more corrosive to zinc than typical marine environments because in a marine environment the rate of attack tends to decrease over time for a number of years before finally stabilizing at a fairly constant rate.

The corrosion caused by condensed moisture on some tropical islands is aggravated by chlorides from coral dust. Desert sand and dust containing appreciable amounts of water-soluble salts—such as chlorides and sulfates of sodium, calcium, and magnesium—increase the corrosion of zinc caused by condensed moisture.

Mechanical properties of zinc die castings have an important effect on their applications; therefore, changes in these properties are often a more meaningful measure of corrosion damage than loss in weight. The average

TABLE 4-155. CORROSION OF ZINC IN VARIOUS ATMOSPHERES (Ref. 246)

| TYPE OF ATMOSPHERE | AVERAGE PENETRATION     |       | RATIO OF PENETRATION RATE TO THAT AT PHOENIX |
|--------------------|-------------------------|-------|--|
|                    | $\mu\text{m}/\text{yr}$ | mpy   |  |
| Industrial         | 6.4                     | 0.252 | 36.0   |
| Seacoast           | 1.5                     | 0.058 | 8.3  |
| Rural              | 1.1                     | 0.042 | 6.0  |
| Arid (Phoenix)     | 0.2                     | 0.007 | 1.0  |

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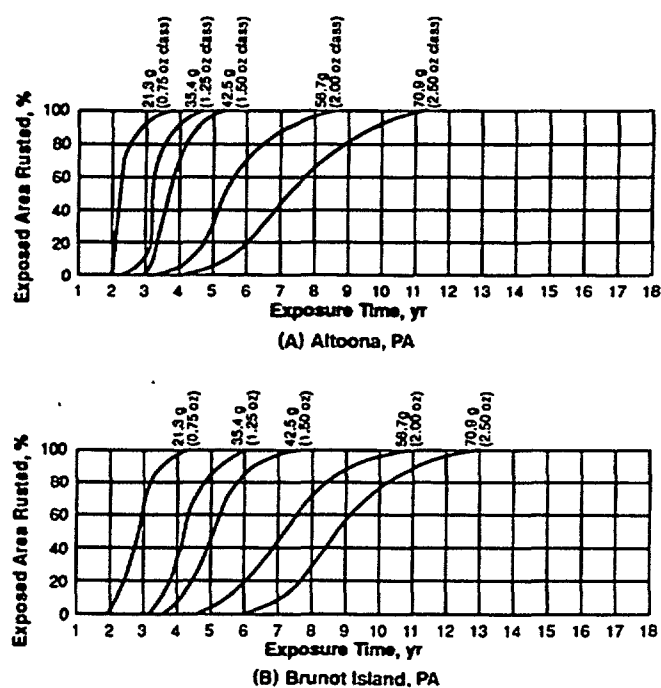
properties of two alloys after 20 yr of exposure at two industrial, one rural, and two indoor locations are summarized in Table 4-156. The percentage changes from the original values are also included. The industrial atmosphere appears to be the most harmful. A large decrease in impact strength of both alloys occurred in the interval between the 10- and 20-yr exposure periods in the industrial atmospheres. A similar decrease occurred for the alloy AC41A exposed to the indoor atmosphere.

Arbitrary values, such as time to initial rusting or to some percentage of the total surface showing rust, have been used to measure the life of zinc-coated articles. The life of a zinc coating—as measured by time to first rust—is proportional to its weight or thickness. The progressive development of rust on panels exposed to industrial atmospheres is shown in Fig. 4-61. The method of applying zinc coatings does not have a significant effect on their longevity. Typical corrosion rates for galvanized steel, according to the type of atmosphere, are given in Table 4-157.

#### 4-17.1.2.2 Corrosion in Neutral Aqueous Solutions

Zinc corrodes at a peak rate in distilled water at 65°C (149°F), but this rate is much slower at lower and at higher temperatures. A correlation exists among the temperature, the nature of the corrosion film, and the corrosion rate. This correlation is shown in Table 4-158 for distilled water.

Zinc is not significantly corroded in distilled water that is free of oxygen and CO<sub>2</sub>, and attack is slow in distilled water containing oxygen. In stagnant water, however, pitting corrosion increases in proportion to the oxygen concentration.



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Figure 4-61. Life of Zinc Coatings in Industrial Atmospheres, Indicating the Progressive Development of Rust (Ref. 248)

TABLE 4-156. CHANGE IN MECHANICAL PROPERTIES OF ZINC DIE-CAST ALLOYS UPON EXPOSURE TO SEVERAL NATURAL ATMOSPHERIC ENVIRONMENTS\* (Ref. 247)

|   | AFTER 20 yr OF EXPOSURE |                      |                   |                   |
|---|-------------------------|----------------------|-------------------|-------------------|
|   | ORIGINAL VALUE          | OUTDOOR** INDUSTRIAL | OUTDOOR RURAL     | INDOOR (-)        |
| Alloy AC41A tensile strength, MPa (ksi)     | 305 (44.3)              | 211 C (30.6)         | 259 (37.6) (-15%) | 254 (36.9) (-17%) |
| Alloy AC41A elongation in 5.1 cm (2 in.), % | 7                       | 3.7 (-50%)           | 9 (+28%)          | 12 (+71%)         |
| Alloy AC41A hardness, Rockwell E            | 91                      | 78 (-14%)            | 80 (-10%)         | 83 (-8%)          |
| Alloy AC41A Charpy impact, J (ft·lb)        | 55.6 (41)               | 12.2 (9) (-78%)†     | 44.7 (33) (-20%)  | 27.1 (20) (-52%)† |
| Alloy AG40A tensile strength, MPa (ksi)     | 254 (36.9)              | 206 (29.9) (-19%)    | 225 (32.6) (-12%) | 228 (33.1) (-10%) |
| Alloy AG40A elongation in 5.1 cm (2 in.), % | 15                      | 7 (-47%)             | 18 (+20%)         | 21 (+40%)         |
| Alloy AG40A hardness, Rockwell E            | 83                      | 72 (-13%)            | 67 (-19%)         | 74 (-11%)         |
| Alloy AG40A Charpy impact, J (ft·lb)        | 52.9 (39)               | 16.3 (12) (-69%)     | 51.5 (38) (-3%)   | 54.2 (40) (+3%)   |

\*20 yr of exposure at New York, NY, at Altoona, PA (outdoor industrial), and at State College, PA (outdoor rural)

\*\*Figures in parentheses are the percentage changes from the original values caused by exposure.

†Large change between 10 and 20 yr of exposure

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TABLE 4-157. EXAMPLES OF CORROSION RATES ON GALVANIZED STEEL EXTERNALLY EXPOSED

| ATMOSPHERE | APPROXIMATE RATE |              | THEORETICAL<br>LIFE OF 305-g/m <sup>2</sup><br>(1-oz/ft <sup>2</sup> ) SURFACE, yr |
|------------|------------------|--------------|--|
|            | $\mu\text{m/yr}$ | mpy          |  |
| Industrial | 5.33 to 7.62     | 0.21 to 0.30 | 6 to 8   |
| Seacoast   | 1.52 to 2.54     | 0.06 to 0.10 | 17 to 28   |
| Suburban   | 1.27 to 1.78     | 0.05 to 0.07 | 24 to 34   |
| Rural      | 1.02 to 1.27     | 0.04 to 0.05 | 34 to 43   |

TABLE 4-158. EFFECT OF TEMPERATURE ON THE CORROSION OF ZINC IN DISTILLED WATER\* (Ref. 250)

| TEMPERATURE,       |                    | CORROSION RATE          |                           |       |       | APPEARANCE<br>OF CORROSION FILM |
|--------------------|--------------------|-------------------------|---------------------------|-------|-------|---------------------------------|
| $^{\circ}\text{C}$ | $^{\circ}\text{F}$ | mg/dm <sup>2</sup> ·day | (lb/ft <sup>2</sup> ·day) | mm/yr | mpy   |                                 |
| 20                 | 68                 | 3.9                     | ( $8 \times 10^{-5}$ )    | 0.020 | 0.78  | Gelatinous, very adherent       |
| 50                 | 122                | 13.7                    | ( $28 \times 10^{-5}$ )   | 0.070 | 2.74  | Less gelatinous, adherent       |
| 55                 | 131                | 76.2                    | ( $156 \times 10^{-5}$ )  | 0.386 | 15.2  | Mostly granular, nonadherent    |
| 65                 | 149                | 576.6                   | ( $1181 \times 10^{-5}$ ) | 2.931 | 115.4 | Granular to flaky, nonadherent  |
| 75                 | 167                | 459.9                   | ( $942 \times 10^{-5}$ )  | 2.337 | 92.0  | Granular, flaky, nonadherent    |
| 95                 | 203                | 58.6                    | ( $120 \times 10^{-5}$ )  | 0.297 | 11.7  | Compact, dense, nonadherent     |
| 100                | 212                | 23.4                    | ( $48 \times 10^{-5}$ )   | 0.119 | 4.7   | Very dense and adherent         |

\*Rolled, high-grade zinc immersed for 15 days in water aerated by air bubbles; specimen rotated at 56 rpm

Reprinted from "Effect of Temperature on the Corrosion of Zinc" by G. L. Cox, *Industrial & Engineering Chemistry*. Published 1931 by the American Chemical Society.

The presence of CO<sub>2</sub> increases the corrosion rate of zinc because CO<sub>2</sub> reacts with oxide or hydroxide corrosion products to form basic carbonates, and these carbonate films are less protective than the hydroxide films.

Soft or distilled waters are more corrosive to zinc than hard waters containing dissolved salts, such as carbonates and bicarbonates, which form protective films. Nitrates, sulfates, and chlorides in natural waters tend to increase corrosion. Their effect, however, is overcome in hard waters by the protective films formed by carbonates.

Temperature has an effect on the corrosion of zinc in natural, hot waters that is similar to its effect in distilled water. The temperature for maximum corrosion is determined by the nature of the water. In one study maximum attack occurred at 40°C (104°F) in industrial water, at 60°C (140°F) in drinking water, and at 90°C (194°F) in seawater (Ref. 251). Dissolved salts affect the corrosion of zinc in seawater. The high chloride content of seawater tends to increase corrosion, but the presence of magnesium and calcium inhibits attack.

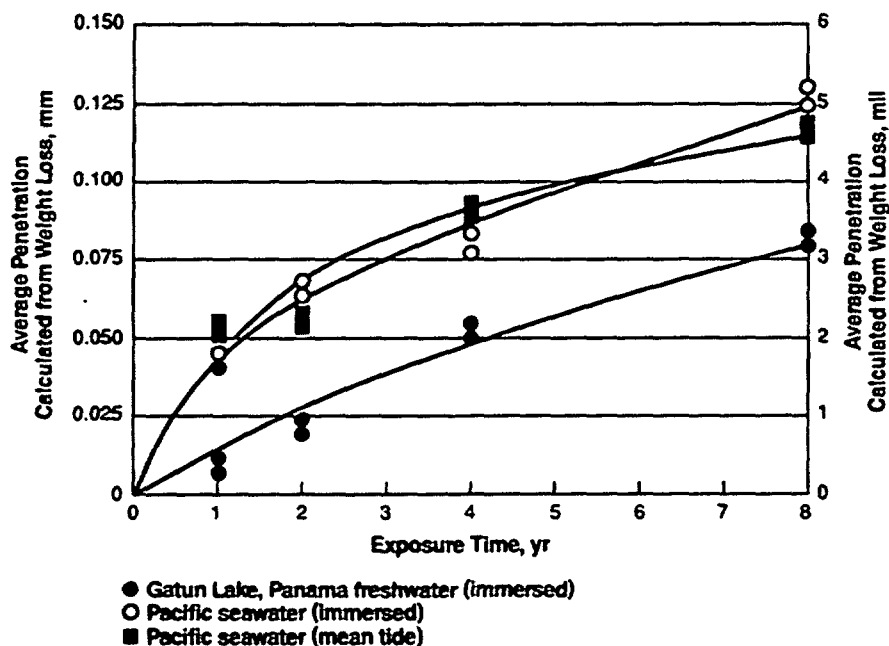
An example of the effect of duration of exposure on the corrosion rate of zinc in natural waters is given in Fig. 4-62. Initially, the corrosion rate in seawater is greater than it is in freshwater. After about 2 yr, however, the rate in seawater decreases to approximately that in freshwater.

#### 4-17.1.2.3 Corrosion in Acid and Alkaline Solutions

Zinc is amphoteric, i.e., it is subject to attack by both acidic and alkaline solutions. This property is illustrated in Fig. 4-63, which shows the effect of pH on the corrosion of zinc. As indicated, zinc is rapidly attacked at acidic pH values below ~3.5 and alkaline pH values greater than 12.

Table 4-159 shows typical corrosion rates in acid solutions, and Table 4-160 shows typical corrosion rates in alkaline solutions. Both of these tables are based upon relatively dilute solutions. The corrosion rates are much higher at higher concentrations.

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Figure 4-62. Corrosion-Time Curves for Zinc Exposed to Tropical Waters in the Panama Canal Zone (Adapted from Ref. 252)

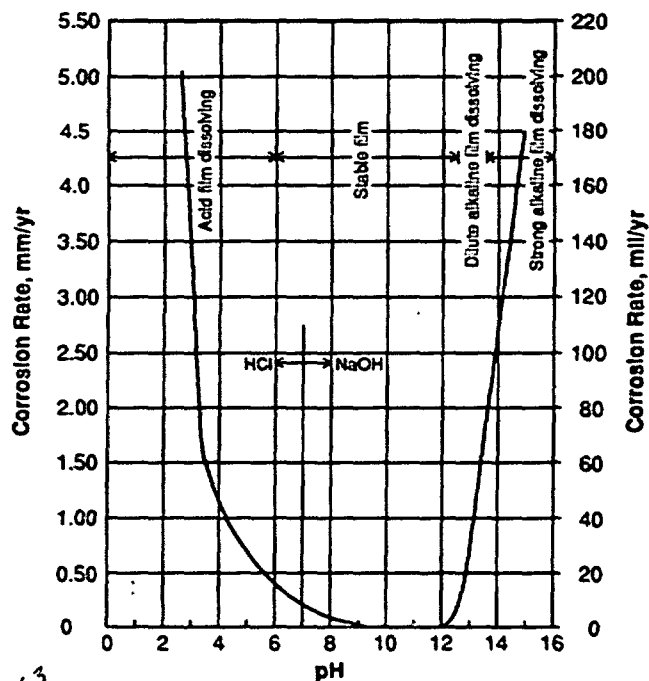


Figure 4-63. Effect of pH Values on Corrosion of Zinc (Ref. 253)

#### 4-17.1.2.4 Corrosion in Organic Compounds

Zinc may be used in contact with many organic liquids provided they are substantially free from water and have a nearly neutral pH value. At room temperature these liquids include the following: acetone, ethanol, methanol, gasoline, glycerin, lubricating oils, phenol, and trichloroethylene. There is no system for generalizing the resistance of zinc to organic compounds. Therefore, if data cannot be found concerning a particular compound, a test should be conducted. Ref. 254 contains an extensive list of the corrosion susceptibilities of zinc to various organic and inorganic materials.

#### 4-17.1.3 High-Temperature Corrosion

Generally, zinc is not used above the boiling point of water, 100°C (212°F). It has low structural strength at high temperatures. Zinc coatings are corroded by dry steam (superheated), oxidizing gases, and sulfidizing gases. Also, zinc forms a partially protective coating in dry oxygen at 399°C (750°F) (Ref. 255).

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TABLE 4-159. CORROSION OF ZINC IN ACID SOLUTIONS (Ref. 254)

| TEST CONDITION       | CORROSION RATE, mm/yr (mpy)* |                 |
|----------------------|------------------------------|-----------------|
|                      | 3.6% HYDROCHLORIC ACID**     | 6% ACETIC ACID† |
| Total immersion:     |                              |                 |
| Quiet                | 38.1 (1500)                  | 16.5 (650)      |
| Air-agitated         | 33.0 (1300)                  | 18.8 (740)      |
| Alternate immersion: |                              |                 |
| Continuous           | 116.8 (4600)                 | 22.9 (900)      |
| Intermittent         | 114.3 (4500)                 | 4.32 (170)      |
| Spray (30 days)      | 1.42 (56)                    | 2.41 (95)       |

\*Based on 48-h exposure at room temperature with specimens previously exposed for 48 h

\*\*pH about 1

†pH about 3

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TABLE 4-160. CORROSION OF ZINC IN ALKALINE SOLUTIONS (Ref. 254)

| TEST CONDITION       | CORROSION RATE, mm/yr (mpy)* |                         |
|----------------------|------------------------------|-------------------------|
|                      | 3.9% SODIUM HYDROXIDE        | 3.4% AMMONIUM HYDROXIDE |
| Total immersion:     |                              |                         |
| Quiet                | 0.46 (18)                    | 0.30 (12)               |
| Air-agitated         | 0.89 (35)                    | 0.71 (28)               |
| Alternate immersion: |                              |                         |
| Continuous           | 9.40 (370)                   | 2.79 (110)              |
| Intermittent         | 2.29 (90)                    | 0.30 (12)               |
| Spray (30 days)      | 0.015 (0.6)                  | <0.005 (<0.2)           |

\*Based on 48-h exposure at room temperature with specimens previously exposed for 48 h

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## 4-17.2 INTERFACE PROBLEMS

### 4-17.2.1 Metal-to-Metal

A principal use of zinc is as a coating for steel. The metal-to-metal interface is used to provide anodic protection to the base metal in most atmospheres and in natural waters. Thus the zinc provides a sacrificial corrosion effect that protects exposed areas of the steel. The width of the exposed steel that can be protected increases with the electrical conductivity of the contacting moisture. It may be as much as 6.4 mm (0.25 in.) in atmospheric exposures. Zinc, however, is not always anodic to steel. The galvanic potential can reverse in oxygenated water at temperatures greater than 70°C (158°F).

In the tropics, where nightly condensation can occur, the corrosion of zinc is rapid, and a heavy film of white corrosion product forms on the surface. This film absorbs moisture and therefore maintains a reactive environment. Corrosion is rapid if this film is protected from the washing action of heavy rains. If the film is washed off frequently, however, the time that the reactive environment exists on the surface is reduced; thus the corrosion correspondingly decreases.

Galvanized items that are stacked or stored in humid environments undergo wet-storage stain. A voluminous white corrosion product forms, which is caused by retention of condensation or rainwater between contacting surfaces. The appearance of the corrosion is objectionable even if the actual damage is not. Quenching the galvanized product in sodium chromate solutions of from 0.05 to 0.15% by weight at solution temperatures between 27° and 93°C (80° and 200°F) provides several months of protection from storage staining.

Failure sometimes occurs in a brittle manner after hot-dip galvanizing. This failure results from "galvanizing embrittlement". The amount of cold working is the most significant factor in this type of failure. If the steel is susceptible to strain aging and undergoes sufficiently severe cold working, the 454°C (850°F) temperature of the galvanizing bath accelerates the aging process. This of course reduces the interval until failure. Generally, susceptible material fails almost immediately upon removal from the galvanizing bath. A minimum bending radius of three times the section thickness usually will preclude the extent of cold working necessary to result in

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"galvanizing embrittlement". The aluminum content of the galvanizing bath affects chromate performance; therefore, the aluminum level should be maintained below 0.005%.

### 4-17.2.2 Metal-to-Nonmetal

Neither zinc nor galvanized zinc should be used in handling food products. Acidic foods, such as citrus fruit and tomatoes, can accumulate a potentially serious toxic concentration of zinc.

The likelihood of drinking waters developing harmful levels of dissolved zinc when transported in galvanized pipe is remote. Transported water is low in oxygen and will not attack the pipe walls. Galvanized pipe has been used in domestic water supplies for many years.

Organic acids leached from shingles of redwood, red cedar, and oak, built-up tar roofs, and the action of rainwater drained from copper roofs and flashings may result in relatively high rates of corrosion of zinc or galvanized steel flashings and gutters.

Zinc in contact with certain organic chemicals may cause polymerization or may catalyze some other undesirable change that would alter the original composition or properties of a product. For example, zinc catalyzes the decomposition of uninhibited trichloroethylene in contact with water.

A test program on the interaction of galvanized steel with soils conducted by the National Institute of Standards and Technology came to the following conclusions (Ref. 256):

1. The life of galvanized steel buried in soil is greatly dependent on the nature of the soil.
2. A nominal  $610\text{-g/m}^2$  (2-oz/ft<sup>2</sup>) coating would provide protection for at least 10 yr in inorganic, oxidizing soils.
3. A  $915\text{-g/m}^2$  (3-oz/ft<sup>2</sup>) coating is adequate for 10 to 13 yr in most inorganic, reducing soils. However, this coating would not provide adequate protection in highly reducing organic or inorganic soil or in cinders.
4. In some of the more corrosive soils, corrosion of the steel after the zinc has been completely destroyed is considerably less than that of uncoated steel specimens.

### 4-17.3 METHODS FOR PREVENTION OF CORROSION

As indicated previously, zinc surfaces are severely attacked in industrial atmospheres. Zinc coatings in particular have a short life span. The resistance of a zinc coating, however, is greatly improved by applying a topcoat of a suitable paint system. Paint coatings, however, cannot be applied directly to a zinc surface. The metal surface must first be cleaned and pretreated to provide a surface that will receive and hold paint. The most common chemical pretreatment uses phosphate coatings that may be applied by dipping, spraying, or

brushing. Proprietary chromate films are best suited to coatings that employ baking rather than air-drying. Wash primers, originally developed for use on steel, are also used on zinc.

Sometimes a fine grit is used to roughen a zinc surface. A common method of preparing externally exposed zinc surfaces for paint is to allow them to weather for at least 6 mo. A more convenient alternative to natural weathering is to select a paint system directly compatible with fresh zinc surfaces, and several paint systems have been developed for this application.

Corrosion of zinc by water and many aqueous salts can be reduced with inhibitors, e.g., sodium dichromate, borax, sodium silicate, and sodium hexametaphosphate. Dichromates are widely used if the water pH is adjusted to be slightly alkaline. A basic dichromate film on zinc surfaces inhibits corrosion of the part by supplying hexavalent chromium to water (Ref. 257). This method, or a modification, is used to protect die-cast zinc carburetors from corrosion by water in the fuel.

## 4-18 METAL MATRIX COMPOSITES

A composite material is the physical combination of two or more discrete substances. Each component substance interacts with its neighbors such that important properties of the composite are changed from those of the individual components. Most composites of interest consist of fibers or filaments of one material embedded in another, which is called the matrix. The functions of the matrix are to provide a compatible and protective embedment for the load-carrying filaments, to assist in equalizing loads between adjacent fibers, and to allow the exploitation of the very high strength of the fibers.

A wide variety of polymer matrix and carbon matrix composites are available. Metal matrices, however, are desirable in composites for many structural applications because of their high-temperature properties and because their ductility allows the efficient distribution of stresses among the fibers in a composite.

Metal matrix composites have several advantages over conventional metallic systems. These include the ability to

1. Take advantage of the anisotropic character of the composite for the efficient design and fabrication of structures
2. Tailor-make a material to meet a specific set of engineering strength or stiffness requirements
3. Increase the stiffness, strength, and stability of such common engineering alloys as aluminum, titanium, and nickel.

The lightweight metals, e.g., aluminum, magnesium, and titanium, are used as the matrix to achieve very high-strength composites that can function in ambient environments or at temperatures up to 600°C (1112°F). The superalloy metal matrix composites are likely to

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experience the high-temperature (1200°C (2192°F)) oxidation and hot corrosion environments of gas turbine engines.

Advanced gas turbine engines are being designed for gas inlet temperatures as high as 1371°C (2500°F), but the best available superalloys are suitable up to only 1038°C (1900°F). Accordingly, air cooling of critical components, such as blades and vanes, is necessary to achieve improved performance and high fuel efficiency. Superalloys have apparently reached their performance limits in these applications. An approach being used to improve these materials is reinforcement with high-temperature, high-strength filaments.

Fiber-reinforced superalloys can increase component life, decrease maintenance, and improve performance. Typical reinforcements include tungsten alloy wires and silicon carbide filaments. Typical matrix materials are FeCrAlY alloys, cobalt-base alloys, and stainless steels (for moderate temperature applications).

The properties required of matrices related to corrosion are

1. Oxidation and hot corrosion resistance at temperatures up to 1147°C (2097°F). The fibers lack oxidation resistance and must be protected by the matrix.

2. Compatibility with the fibers at fabrication and operating temperatures so that fiber strength is not excessively degraded by interdiffusion

3. A thermal expansion match with the fibers so that component distortion and delamination do not occur.

#### 4-18.1 TYPES OF CORROSION

##### 4-18.1.1 Matrix-Fiber Compatibility

A useful metal matrix composite does not exhibit gross chemical reaction between the matrix and the reinforcement during consolidation, secondary processing steps, and in-service use. Some degree of reaction, however, is

required to achieve bonding of the matrix with the filament. An example of gross chemical reaction between carbon filament and metal matrix is the formation of metal carbides.

Aluminum, molybdenum, tantalum, and tungsten have been shown to form carbides readily at temperatures near their melting points (Ref. 258). The thermodynamic tendency to react, as indicated by large, negative, free energies of formation, would also include iron, nickel, magnesium, and cobalt as carbide formers. The rates of reaction, however, may be low.

Burte and Lynch have found that there are few metal candidate materials for matrices that do not react with graphite at elevated temperatures (Ref. 259). When graphite fibers were coated with various metals, such as aluminum, nickel, cobalt, copper, platinum, and nickel-chromium, the following chemical reactions and structural recrystallization phenomena occurred (Ref. 258):

1. The unstable carbide  $Al_4C_3$  was found after heat treatment of aluminum-coated graphite fibers at 600°C (1112°F). A sharp strength drop-off occurred at 600°C (1112°F) for aluminum graphite composite.

2. Extensive structural recrystallization was observed with nickel-graphite at 1000°C (1832°F), and a loss in strength of the graphite occurred at 900°C (1652°F).

3. Chromium readily formed the carbide  $Cr_3C_2$  at 1000°C (1832°F) and weakened the structure. The fiber strength was reduced at 600°C (1112°F).

4. Graphite fiber strength decreased in the 600°C (1112°F) range for cobalt, copper, and platinum.

The interdiffusion of the fiber and matrix can greatly reduce the strength of the fibers. The interdiffusion of W-1ThO<sub>2</sub> with FeCrAlY has been studied (Ref. 260), and Table 4-161 lists the measured interdiffusion reaction zone depth in the fiber at the corresponding exposure

TABLE 4-161. THERMAL STABILITY OF FeCrAlY COMPOSITE\* (Ref. 260)

| EXPOSURE           |      | TIME,<br>h | REDUCTION IN<br>FIBER AREA,<br>% | REACTION ZONE WIDTH,  |                       |
|--------------------|------|------------|----------------------------------|-----------------------|-----------------------|
| TEMPERATURE,<br>°C | °F   |            |                                  | mm                    | in.                   |
| 1038               | 1900 | 10         | < 0.5                            | $0.36 \times 10^{-2}$ | $0.14 \times 10^{-3}$ |
|                    |      | 100        | < 0.5                            | $0.38 \times 10^{-2}$ | $0.15 \times 10^{-3}$ |
|                    |      | 1000       | < 0.5                            | $0.89 \times 10^{-2}$ | $0.35 \times 10^{-3}$ |
| 1093               | 2000 | 10         | < 0.5                            | $0.30 \times 10^{-2}$ | $0.12 \times 10^{-3}$ |
|                    |      | 100        | < 0.5                            | $0.66 \times 10^{-2}$ | $0.26 \times 10^{-3}$ |
|                    |      | 1000       | 9.5                              | $1.78 \times 10^{-2}$ | $0.70 \times 10^{-3}$ |
| 1149               | 2100 | 10         | < 0.5                            | $0.41 \times 10^{-2}$ | $0.16 \times 10^{-3}$ |
|                    |      | 100        | 0.88                             | $1.17 \times 10^{-2}$ | $0.46 \times 10^{-3}$ |
|                    |      | 1000       | 16.10                            | $3.20 \times 10^{-2}$ | $1.26 \times 10^{-3}$ |

\*0.038 cm (0.015 in.) diameter W-1% ThO<sub>2</sub> fiber

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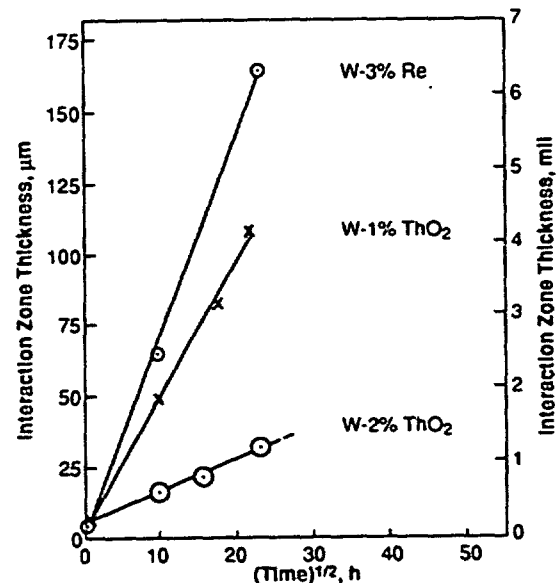
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times. At 1038°C (1900°F) the reaction depth is almost insignificant; at 1093°C (2000°F) only 10% of the fiber area reacted after 1000 h.

Ahmad *et al.* have investigated the reinforcement of FeCrAlY with silicon carbide filament (Ref. 261). Silicon carbide has good physical and mechanical properties, but it reacts with most metals at elevated temperatures; therefore, it must be protected with a suitable barrier. A 12.7- $\mu\text{m}$  (0.5-mil) thick tungsten layer was applied to the filament by a chemical vapor deposition process. The tungsten gave adequate protection to the filament up to 982°C (1800°F), but in some cases the interaction between the tungsten and the matrix was excessive. At 1038° to 1093°C (1900° to 2000°F), filament-coating interaction, in addition to tungsten-matrix interaction, became serious. Above 900°C (1652°F) significant tungsten interaction occurred and degraded the filament.

Ahmad and Barranco have investigated reinforcing cobalt-base alloy MAR M322 with tungsten wires (Ref. 262). Compatibility investigations showed that the interaction of the matrix and fiber is greatly reduced by increasing the tungsten content of the matrix alloy. Also, compatibility is improved by using thoriated tungsten wires as the reinforcing fiber. The results are illustrated in Fig. 4-64, and the compositions of matrix alloys are shown in Table 4-162. The fabrication process used was investment casting. Minimum pour temperature, 1400° to 1450°C (2552° to 2642°F), and high mold temperature, 1370°C (2498°F), gave the best infiltration. Following pouring, the mold was cooled as quickly as possible to reduce filament-matrix interaction.

Helmink and Piwonka investigated the investment casting techniques used to produce nickel- and cobalt-base superalloys reinforced with continuous tungsten fibers (Ref. 263). The problem with liquid metal fabrication processes is the inability to control fiber-matrix interactions. The results indicate that this is indeed the case for uncoated tungsten fibers and for conventionally cast nickel-base superalloy matrices. However, tungsten fibers in an MAR M322E matrix is a compatible com-



NOTE: For W-1% ThO<sub>2</sub>/Mar M 322 (25%W), W-3% Re/Mar M 322 (25%W), and W-2% ThO<sub>2</sub>/Mar M 322 (25%W-E alloy) composites

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Figure 4-64. Rate of Growth of Filament-Matrix Interaction Zone at 1093°C (2000°F) vs Time (Ref. 262)

posite. Fiber-matrix interactions are minimal, 0.009 to 0.018 mm (0.00035 to 0.0007 in.), even for solidification rates that are much slower than those used for investment casting. Nevertheless, these interactions may be unacceptable for very small tungsten filaments.

The continuous casting technique was investigated as an approach to reducing the time that reinforcing filaments are exposed to the liquid matrix metal at high temperatures. The results, shown in Table 4-163, indicate

TABLE 4-162. COMPOSITION (WEIGHT PERCENT) AND DESIGNATION OF MATRIX ALLOYS (Ref. 262)

| ALLOY            | C    | Cr   | W    | Ni   | Ti   | Ta  | Zr  |
|------------------|------|------|------|------|------|-----|-----|
| MAR M322 (Std) A | 1.0  | 21.5 | 9.0  | —    | 0.75 | 4.5 | 1.5 |
| MAR M322 (B)     | 1.0  | 21.5 | 20.0 | —    | 0.75 | 4.5 | —   |
| MAR M322 (C)     | 1.0  | 21.5 | 25.0 | —    | 0.75 | 4.5 | —   |
| MAR M322 (D)     | 0.75 | 21.5 | 25.0 | 10.0 | 0.75 | 4.5 | —   |
| MAR M322 (E)     | 0.30 | 21.5 | 25.0 | 10.0 | 0.75 | 3.5 | —   |
| MAR M302         | 0.85 | 21.5 | 10.0 | —    | —    | 9.0 | 0.2 |

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TABLE 4-163. FIBER DIPPING RESULTS FOR MAR M200-Hf MATRIX—TUNGSTEN FIBERS (Ref. 263)

| METAL TEMPERATURE, |      | EXPOSURE TIME, | LOSS IN FIBER AREA, %        |                              |                              |
|--------------------|------|----------------|------------------------------|------------------------------|------------------------------|
|                    |      |                | 0.76 mm (0.030 in.) DIAMETER | 0.38 mm (0.015 in.) DIAMETER | 0.20 mm (0.008 in.) DIAMETER |
| °C                 | °F   | s              |                              |                              |                              |
| 1343               | 2450 | 15             | 1.2                          | —                            | —                            |
| 1343               | 2450 | 30             | 2.1                          | 3.1                          | —                            |
| 1399               | 2550 | 5              | 1.8                          | 5.5                          | 6.6                          |
| 1399               | 2550 | 15             | 4.8                          | 4.4                          | 7.6                          |
| 1399               | 2550 | 30             | 9.9                          | 8.1                          | 8.0                          |
| 1399               | 2550 | 60             | 13.6                         | 21.0                         | 17.3                         |
| 1399               | 2550 | 120            | 19.9                         | 25.6                         | 63.5                         |

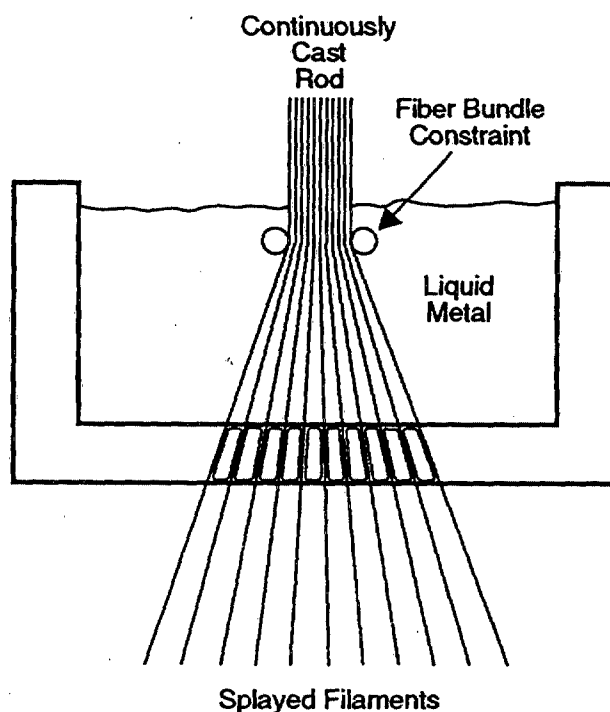
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increasing fiber dissolution with increasing metal temperature and exposure time and decreasing fiber diameter. Nevertheless, the relatively small fiber dissolution indicates that this process may have potential for industrial application. The way in which it might be applied is to manufacture continuously cast fiber-filled rods as indicated in Fig. 4-65. Subsequently, metal would be cast around these rods to form the blade shape. The matrix-alloy compositions are shown in Table 4-164.

#### 4-18.1.2 Corrosion With and Without Exposure of the Fibers

Metal matrix material experiences the corrosion conditions of the application and exhibits the types and extent of damage characteristic of that metal. However, if the fiber reinforcement is exposed to the corrosive medium, the fiber material will become involved in the corrosion process in the following ways:

1. Preferential corrosion of the exposed fiber
2. Selective corrosion attack at the fiber-matrix interface
3. Establishment of a galvanic cell between the fiber and matrix materials. A graphite fiber will almost always be cathodic to the matrix materials.



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Figure 4-65. Representation of a Bottom-Fed, Vertical Continuous Casting Operation for Fiber Reinforcement (Ref. 263)

TABLE 4-164. NOMINAL MATRIX COMPOSITIONS (WEIGHT PERCENT) (Ref. 263)

| ALLOY DESIGNATION | C    | Cr   | W    | Co   | Ni  | Ta  | Ti   | Al | Cb | B     | Hf |
|-------------------|------|------|------|------|-----|-----|------|----|----|-------|----|
| MAR M322E         | 0.30 | 21.5 | 25   | Bal* | 10  | 3.5 | 0.75 | —  | —  | —     | —  |
| MAR M200 + Hf     | 0.11 | 9    | 12.5 | 10   | Bal | —   | 2    | 5  | 1  | 0.015 | 2  |

\*Bal = Balance

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Dull *et al.* exposed 6061 aluminum alloy matrix-Thornel 50 graphite fiber composites in distilled water and 3.5% salt solutions (Ref. 264). Exposure temperatures were 25°C (77°F), 50°C (122°F), and 75°C (167°F), and the results were monitored for up to 1000 h. As indicated in Fig. 4-66, maximum corrosion rates occurred immediately after exposure and decreased with increasing time of exposure. At temperatures above 50°C (122°F) the corrosion rate of the composite in the salt solution increased greatly, as illustrated in Fig. 4-67. The results indicate that the galvanic effect was a significant factor in the corrosion of the composite.

Sedricks *et al.* studied the effects of galvanic coupling on the corrosion behavior of an aluminum matrix-boron fiber composite in a salt solution (Ref. 265). The results of this study indicate that galvanic coupling was not a factor because of the low electrical conductivity of boron, but localized corrosion at the matrix-fiber interface was observed.

Vassilaros *et al.* exposed a composite produced from pitch-base VSB-32 carbon fibers and a matrix of 6061 aluminum to naturally flowing seawater, tidal immersion, and a marine atmosphere (Ref. 266). Fig. 4-68 illustrates

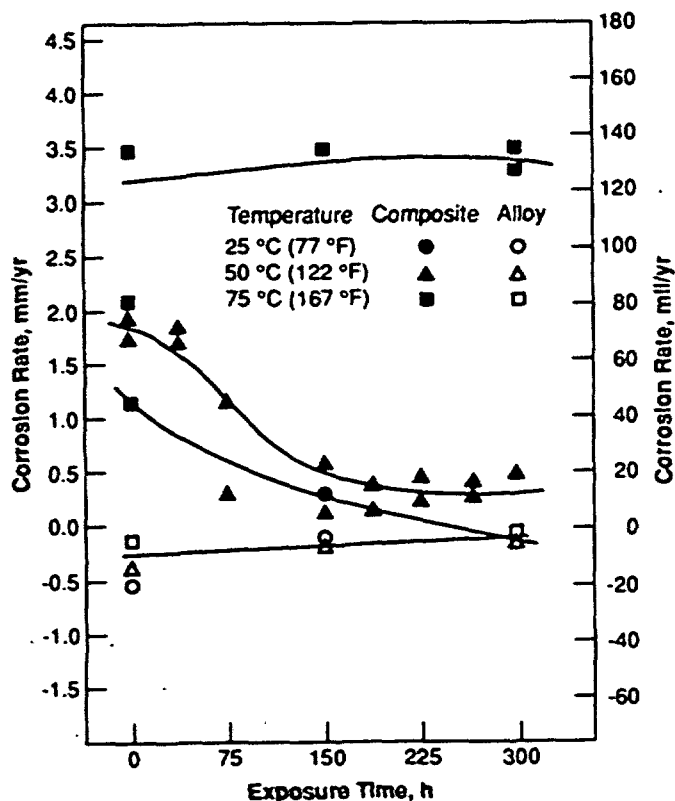


Figure 4-66. Effect of Exposure Time on Corrosion Rate of 6061 Aluminum Alloy-Thornel 50 Graphite Composite in 3.5% NaCl Solution Between 25° and 75° C (77° and 167° F) (Ref. 264)

the types of corrosion attack observed. Two types of composites were exposed. In one type additional aluminum 6061 foils were wrapped around the wires. These composites are referred to as "encapsulated". The other composite did not have this added encapsulation material. The graphite-aluminum composites were exposed with and without edge protection. The edge protection was a continuous bead of room temperature vulcanizing compound applied to selected panels, which isolated the exposed graphite fibers from the environment. Corrosion measurements, and fatigue testing were carried out, and residual mechanical properties were measured. The conclusions were

1. The overall corrosion performance of the composite reflected the performances of the graphite-aluminum substrate and the surface foils. The dominant factor in the corrosion of VSB-32/Al 6061 composite was the galvanic potential between the carbon fibers and the aluminum. As long as the surface foils of the composite prevented invasion of the matrix by the corrodent, the corrosion performance was that of the surface foil. After matrix invasion occurred, the galvanic cell was activated and accelerated corrosion occurred.

2. If no evidence of corrosion attack was observed, there was no significant degradation in mechanical properties in any of the marine environments. If corrosion attack had occurred—as evidenced by severe pitting, blistering, and foil delamination—the composite displayed substantial reduction in tensile strength.

3. The fatigue strength of VSB-32/Al 6061 composite increased with fiber strengthening in direct response to the increase in tensile strength.

4. Reduction in fatigue strength of VSB-32/Al 6061 due to the effect of seawater exposure was less than that experienced with 6061-T6 plate.

Kerr *et al.* exposed several high-temperature composite materials to thermal aging, ambient aging, fatigue creep, fracture, tensile stress, and real-time flight simulation (supersonic) exposure (Ref. 267). One of the materials was a boron-aluminum composite. The results indicate that boron-aluminum is subject to pitting and subsequent intergranular corrosion cracking when exposed for long periods in an industrial seacoast environment. These corrosion cracks can seriously degrade the matrix-controlled properties by acting as crack initiators. In addition, severe degradation of the aluminum matrix on both unidirectional and cross-plyed boron-aluminum composite was observed during fatigue tests in which the cyclic stress ratio was 0.1 and the temperature was 288°C (550°F). Testing in an inert, i.e., oxygen-free, atmosphere or lowering the temperature to 232°C (450°F) significantly decreases the matrix degradation. Based on these results, a maximum use temperature of 232°C (450°F) was set for boron-aluminum composites subjected to fatigue loading in air.

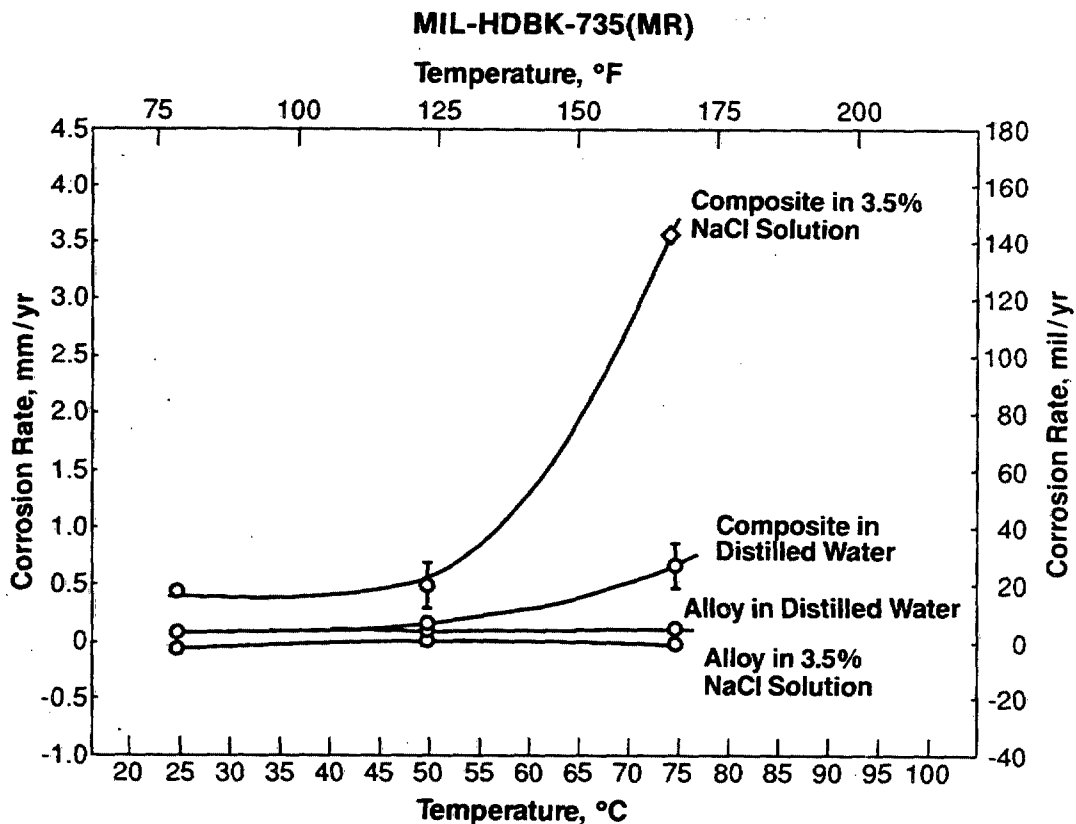


Figure 4-67. Corrosion Rates After 150 h of Exposure for 6061 Aluminum Alloy-Thornel 50 Graphite Composite and 6061 Aluminum Alloy in 3.5% NaCl Solution and Distilled Water at Various Temperatures (Ref. 264)

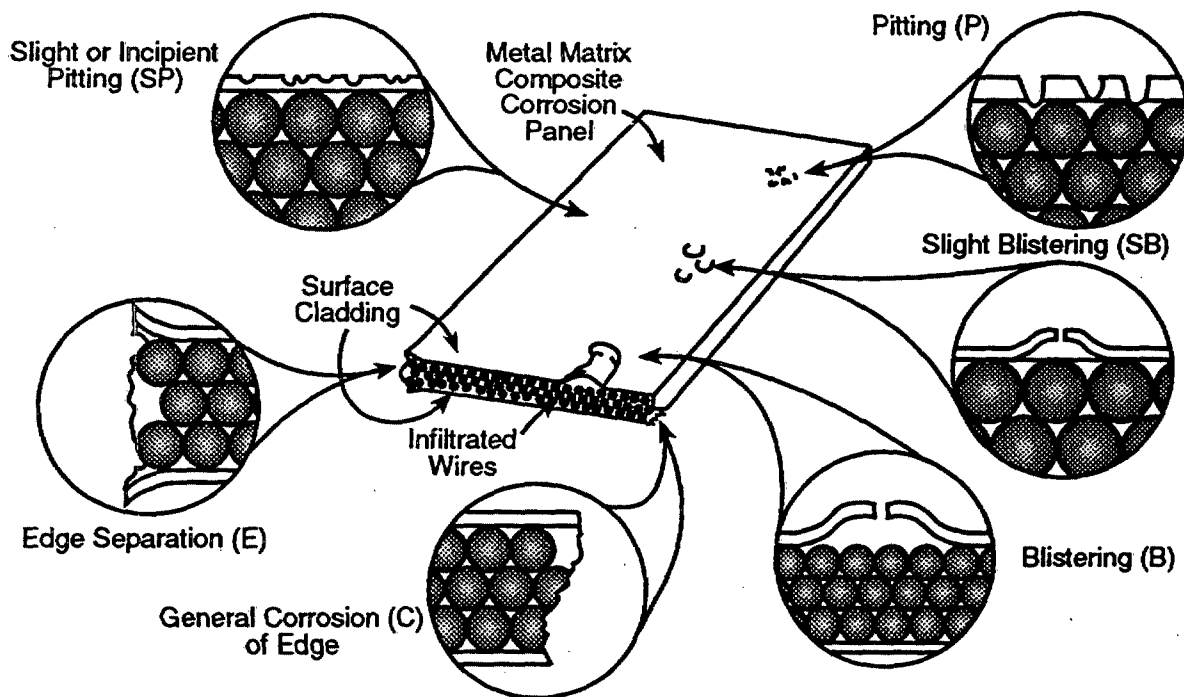


Figure 4-68. Illustration of Types of Corrosion Attack (Ref. 266)

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The high-temperature oxidation and corrosion resistance of W-1ThO<sub>2</sub> fibers + FeCrAlY matrix composites with completely encased fibers is dependent on the FeCrAlY matrix. Alloys based on the ternary Fe-Cr-Al with yttrium additions are among the most oxidation-resistant alloys known. Therefore, the composite based on this matrix should have adequate oxidation and corrosion resistance. However, if the fibers were exposed to engine gases, accelerated fiber oxidation would occur.

Fig. 4-69 illustrates the principal paths for the oxidation and corrosion of exposed fibers. Oxidation proceeding perpendicularly to the fibers would destroy the exposed fibers, but the intervening matrix would prevent oxidation of subsequent layers. Oxidation parallel to the fibers is potentially more severe. All of the exposed fibers in the cross section could be oxidized along their entire length. Studies conducted to evaluate oxidation along fibers, however, showed only limited oxidation penetration of the fibers (Ref. 260).

#### 4-18.2 METHODS FOR PREVENTION OF CORROSION

Approaches used to improve filament-matrix compatibility include

1. Developing new reinforcements that are thermodynamically stable with respect to the matrix
2. Developing diffusion barrier coatings that reduce the filament-matrix interaction
3. Developing alloy additions that reduce the activity of the diffusing species
4. Developing composite fabrication techniques that minimize the time the filament and matrix are at high temperatures.

Examples of diffusion barrier coatings that have been used to reduce the reaction between graphite fibers and aluminum are silicon carbide, silicon dioxide-silicon carbide mixtures, titanium boride, and titanium boride-titanium carbide mixtures. The most severe conditions

for graphite-aluminum composites occur during the fabrication process when the graphite fibers are infiltrated with molten aluminum.

It is important to design and fabricate assemblies that incorporate composite materials so that the fiber reinforcement is not exposed to a corrosive environment. Exposure of fibers in a transverse direction should result in corrosion of only the surface layers, whereas exposure in a longitudinal direction can provide a continuous path for corrosion of the fibers.

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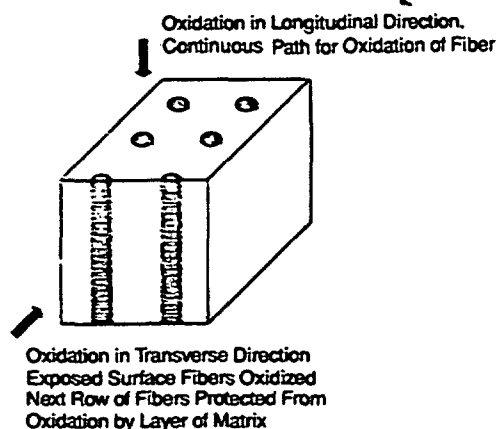


Figure 4-69. Principal Paths for Exposed Fiber Oxidation (Ref. 264)

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## CHAPTER 5

# CORROSION TESTING

*Corrosion testing as a source of information from which reasonably accurate predictions of metal performance in a particular environment or service may be made is discussed. The details of conducting laboratory corrosion tests are discussed and field corrosion testing is described. The common types of accelerated corrosion testing and the approaches used to accelerate corrosion processes are discussed. Stress-corrosion cracking tests are discussed. The content of the test report is described. Standard test methods related to corrosion are listed.*

### 5-1 INTRODUCTION

Most corrosion occurs on complex materials in a complex and changing environment. A design engineer must specify materials that are adequate for the intended service. Information included in a specification can be based upon previous experience with similar materials in similar environments or upon theory that describes the underlying processes. If either experience or theory is inadequate, it will be necessary to obtain the information from corrosion testing. A corrosion testing program must be based upon an understanding of the objectives, a realization of the importance of the material specification decision, and a realistic view of the time and resources required.

### 5-2 TYPES OF CORROSION TESTING

Corrosion tests may be conducted under closely controlled conditions in the laboratory on relatively small metal specimens or on materiel components. Field tests may be conducted under actual service conditions and may involve relatively small specimens or full-scale articles. Accelerated tests, which may be conducted in the laboratory or the field, are described in par. 5-3.

#### 5-2.1 LABORATORY TESTING

Attention should be given to the test specimen, the corrodent, exposure conditions, and assessment of results.

##### 5-2.1.1 Test Specimen

Corrosion tests of commercial alloys should use mill products that are representative of the production material to be used. Experimental or nonstandard alloys may not be representative of commercial products, and tests should be repeated when the production scale increases. If possible, a fabrication history should be obtained; such a history would list the major fabricating steps together with a precise analysis of alloy composition. Table 5-1 is an example of a form used to record the fabrication history of an aluminum extrusion.

The test specimen should represent the metallurgical condition of the application. Cast, wrought, and powder metallurgy metals cannot be interchanged. The various methods of casting, heat treating, and working affect grain structure and homogeneity, and these characteristics affect corrosion susceptibility. In tests of compatibility with chemicals or evaluation of protective coatings, the grain structure of the test specimen may not be critical. Cast bar or rolled sheet is commonly used. Important test specimen considerations are surface finish, cleaning, and residual stresses. If the application of a mill product is intended, the test specimen should have a surface finish equivalent to the mill product. If the application of a machined component is intended, the test specimen should be machined similarly. Edges should be filed, machined, or ground smooth. Sheared or blanked edges must be machined, ground, or filed deeply enough to remove the layer of severely cold-worked metal.

After machining, test specimens should be degreased just prior to measurement of weight and dimensions. A solvent vapor degreaser is usually used. If handling contaminates the specimens, they should be degreased again just prior to exposure in the corrodent. Because of the toxic nature of solvents, they should be avoided. Wearing gloves will prevent contamination of the specimens.

A specimen should be of a size and shape to facilitate reliable examination of the corrosion effects of interest. The size should be large enough so that nonuniform corrosion is evident. Specimens evaluated by depth of attack should be thick enough so that they are not perforated. Specimens having a large surface-to-volume ratio improve the sensitivity of weight change measurements. Corrosion of exposed edges may require large edge-to-surface ratios if edge effects are of concern or the opposite if surface effects are of concern. Standardized size and shape for all specimens in a series result in exposure of the same surface area and hence the same degree of accuracy. If corrosion evaluation is to be based upon weight change, the size of the specimen should be such that it can be weighed on available balances having

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TABLE 5-1. FABRICATION HISTORY FOR STANDARD EVALUATIONS OF ALUMINUM ALLOY EXTRUSIONS\*

## A. MELTING AND CASTING OPERATIONS

1. Charge Components:

2. Alloying Procedure:

3. Fluxing Procedure:

4. Casting Data:

| Casting Method | Ingot Diameter | Pouring Temperature | Metal Head | Lowering Rate | Water Volume | Skimmer |
|----------------|----------------|---------------------|------------|---------------|--------------|---------|
|----------------|----------------|---------------------|------------|---------------|--------------|---------|

5. Cast Analysis: (percent of alloying elements, remainder = aluminum)

| Cast No. | Cu | Fe | Si | Mn | Mg | Zn | Zi | Cr | Ti | Be | Pb |
|----------|----|----|----|----|----|----|----|----|----|----|----|
|----------|----|----|----|----|----|----|----|----|----|----|----|

6. Gas Determinations:

7. Etch Results:

## B. PREHEATING AND EXTRUSION OPERATIONS

|               |                     |                       |
|---------------|---------------------|-----------------------|
| 1. Preheat:   | Soaking temperature | Time at temperature   |
|               | Total cycle time    |                       |
| 2. Reheat:    | Furnace setting     | Cycle time            |
|               | Exit time           |                       |
| 3. Extrusion: | Type of die         | Ingot size            |
|               | Maximum effort      | Maximum exit speed    |
|               | Runout length       | End scrap, Front Rear |

## C. FINISHING OPERATIONS

|   |                |
|---|----------------|
| 1. Solution Heat Treatment:                             | Furnace type   |
| Soak temperature, Maximum                               | Minimum        |
| Time at temperature                                     | Cycle time     |
| Type of quench  | Rate of quench |
| 2. Stretcher Straightening Operation:                   |                |
| No. of mm/m (in./ft)                                    | mm/m (in./ft)  |
| 3. Additional straightening operations (give sequence): |                |
| 4. Precipitation Heat Treatment (aging) Furnace Type    |                |
| Soak temperature, maximum                               | Minimum        |
| Time at temperature                                     | Cycle time     |
| 5. Etch Results:  |                |

## D. MECHANICAL TENSILE PROPERTIES

Test direction:

| Test location | Tensile strength Pa (psi) | Yield strength Pa (psi) | Elongation (% in 4D) |
|---------------|---------------------------|-------------------------|----------------------|
| FRONT         |                           |                         |                      |
| MIDDLE        |                           |                         |                      |
| REAR          |                           |                         |                      |

\*This table shows an example of one method used to report the fabrication history. A standard form is prepared and the pertinent data are merely filled in. The data required will, of course, vary with the type of metal and product being made. The more important data, such as ingot size, composition, times and temperatures of heat treatments and tensile properties, are required for all metal systems and products.

the requisite capacity, sensitivity, and accuracy. A balance having an accuracy of less than 10% of the smallest expected weight loss (gain) is probably adequate. Many commercial analytical balances have capacities of 200 g and sensitivities of 0.01 mg. Standard ASTM tensile specimens are convenient to use if loss in tensile properties is to be evaluated. Flat tensile specimens machined before exposure are subject to notch effects resulting from

corrosion on the edges. It may, therefore, be more meaningful to cut flat tensile specimens from a corroded test panel.

Relatively thick specimens are required if the corrodent is aggressive. If the specimen is dissolved or perforated, the information obtained is limited. Alternatively, the exposure time may be shortened. The size of the specimen relative to the volume of corrodent should be such that



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the corrosion reaction and dissolved corrosion products do not significantly affect the composition of the corrodent. If galvanic characteristics are to be determined, the cathode-to-anode size ratios and geometry must be known and controlled.

Exposing a single specimen may give valid results provided that more than one independent measurement is made on the specimen. However, exposing a single specimen may be a poor procedure if it provides only a single value of a variable. The number of specimens used in a test depends upon

1. The statistical accuracy needed
2. The cost of a test
3. The known reproducibility of a test
4. The number of variables to be investigated.

In some testing programs periodic evaluation of a specimen relates exposure period to corrosion. If the evaluation can be conducted without changing the corrosion characteristics of the specimen, the same specimens can be used throughout the testing period. An example of such an evaluation is an in situ electrochemical measurement of the corrosion rate. If, however, the examination results in the destruction of the specimen or modification of its corrosion characteristics, multiple sets of specimens must be exposed initially. An example of such an examination is chemical removal of the corrosion scale to determine specimen weight loss. Build-up of corrosion scale can be expected to influence corrosion rate, and its removal changes the corrosion characteristics. Therefore, if three specimens are required to give reasonable accuracy to each corrosion determination, 36 specimens would be required to measure the corrosion each week for 12 weeks.

The use of suitable controls is vital in corrosion tests. Specimens used as controls should be from the same stock and should be prepared in the same manner as those used for corrosion tests. The same method of measurement and degree of accuracy should be used for both sets of specimens. Also any treatment to induce stresses or remove residual stresses in the test specimens should be applied to the control specimens.

When the corrosion tests are of short duration or when the metal is such that the characteristic being evaluated does not change during long-term storage, the original control data need to be obtained just once. In some cases, however, certain characteristics change with time, even in the absence of corrosion. In these cases a set of control specimens must be provided for each period of corrosion testing. Control specimens should be protected from corrosion and stored at the same temperature at which the corrosion tests are conducted.

Each specimen, whether test or control, should be identified uniquely and permanently, and the method of marking should not affect the corrosion process. For example, the so-called "lead" pencil markings are anodic

to most metals. The graphite in pencil lead can initiate sites of corrosion on most metals.

### 5-2.1.2 Corrosion Test Environment

Standard and readily reproducible test environments are useful in screening tests of metals and corrosion prevention materials. Tests with different environments, which include a given environment at different temperatures or concentrations, define the range of utility of an alloy or corrosion prevention materials such as coatings or inhibitors. Laboratory tests in which the test medium simulates some characteristics of a service environment can determine at minimum cost that a material is probably suitable. It is often difficult to emulate complex and variable service environments in the laboratory; therefore, obtaining a detailed characterization of the service environment is a necessary prerequisite.

Small variations in the corrosion test environment can often cause large variations in the outcome. Therefore, controls based on corrosion characteristics are necessary to determine whether the corrosive medium possesses and maintains the intended degree of corrosivity. The usual procedure is to expose a well-established, previously tested alloy as a control to determine the degree of consistency of the results throughout the test period. In another control method specimens are exposed for at least three periods of increasing duration. Changes in the corrosion rates of metals can be caused either by a change in the condition of the metal or by a change in the corrosive environment. Through the use of proper control specimens, as described in par. 5-2.1.1, and the proper experimental design, the significance of each of these factors can be determined and accounted for.

### 5-2.1.3 Conditions of Exposure

Specimens are exposed to a liquid phase electrolyte that is present either in bulk or as a condensed surface film in most corrosion tests. The liquid phase may be either highly viscous, such as a grease or gel, or a suspension, such as an emulsion or paste. The most common types of corrosion test exposure include total immersion, partial immersion, alternate immersion in a regular cycle in the liquid and out of it into a vapor space, spraying the liquid on the specimen, and exposing the specimen in a vapor that is in equilibrium with a liquid so that the vapor condenses on the surface of the specimen.

Test conditions include temperature, pressure if a vapor phase is involved, the velocity of the test medium relative to the specimen, the degree of aeration, the characteristics of any impressed electrical currents, the duration of exposure, and the frequency if the test is cyclical.

The simplest laboratory test is exposure of a single specimen in a beaker of corrodent. Multiple specimens of the same lot of metal may be exposed in the same

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container provided that the volume of the corrosive medium is sufficient to maintain its original properties throughout the test. Important considerations in tests involving multiple specimens are

1. All specimens must be isolated from one another and from direct contact with supporting racks. Inert, nonabsorptive racks or spacers of plastic or porcelain usually are used for this purpose.

2. Specimens should be arranged so that corrosion products from one specimen do not contaminate other specimens.

3. The corrosive environment should be equally accessible to all specimens.

4. In liquid immersion tests, specimens of different metals should not be exposed in the same container. For example, aluminum alloys containing copper are separated from copper-free aluminum alloys.

5. If metal containers are used, special precautions are required to prevent metal-to-metal contact.

### 5-2.1.4 Assessment of Results

The outcome of a corrosion test is described in terms of the effects on the test specimen. Every test should consider effects that can be observed visually, both naturally and with magnifying or imaging devices. These effects include changes in reflectivity, tarnish, discoloration, pits, blisters, exfoliation, and intergranular corrosion.

Corrosion results in weight changes. High-temperature oxidation results in weight gain because scale forms. Aqueous corrosion can also create surface films, but these are removed before weighing in order to measure the loss of metal to corrosion. If the corrosion products dissolve, aqueous corrosion results in weight loss. Typically, the weight loss is converted into uniform loss per unit area per unit time or penetration per unit time.

Mechanical properties can change as a result of corrosion. If the corrosion is simple, uniform wasting, the change in mechanical properties is directly related to the amount of penetration. Localized corrosion, such as pitting, and dealloying, however, can diminish mechanical properties out of proportion to the measured weight loss.

The chemical composition of very small areas of a corroded specimen can be examined with an electron probe microanalyzer to determine the composition of corrosion films or of microstructural components such as grain boundaries or individual grains.

Electrochemical characteristics can change as a result of polarization and formation of surface films. Corrosion current measurements represent corrosion rates, whereas corrosion potential measurements indicate the oxidizing power of the environment to which a specimen is exposed and the ability of the specimen to passivate. Impedance measurements conducted by impressing an alternating current on a specimen can yield information on the state

of the specimen surface, and the results of the measurement can be correlated with the corrosion behavior of the specimen. Reaction of the specimen with the environment often yields products that can be measured. Gas can evolve, and the concentration of corroding ions or the pH of the solution can change.

Because of the widespread availability of computer and statistical programs, concepts of statistical experiment design and statistical data analysis can be applied readily to corrosion testing. As a practical matter, however, statistical concepts do not dominate the design of corrosion testing programs. The number of specimens exposed or the number of measurements taken is a compromise between cost and accuracy, and this number is usually fewer than the number desired for statistical evaluation. Statistically designed experiments might fall into the following categories:

1. Comparison of different heats of an alloy

2. The effects of one variable at several levels (The most common variable in corrosion testing is time.)

3. Experiments in which there are several variables but no interactions among them, using orthogonal squares

4. Experiments in which there are several interacting variables, using factorials.

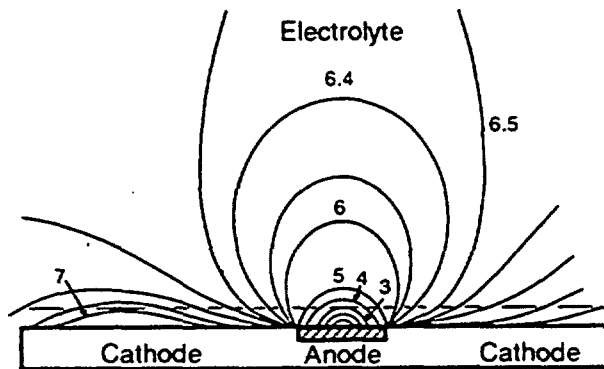
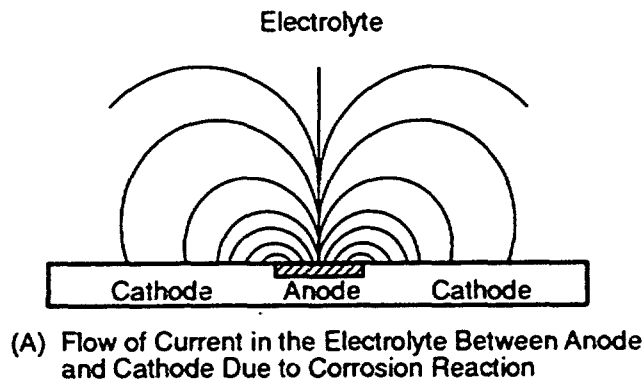
### 5-2.1.5 The Scanning Reference Electrode Technique for Local Corrosion

The scanning reference electrode technique (SRET) measures potential variation in the electrolyte just above a flat surface (Ref. 1). Therefore, it is used to study localized forms of corrosion in which there is a flow of current between anode and cathode. SRET does not directly measure the potential variations of the metal surface; it responds to current variations in the electrolyte solution. The flow of current and potential pattern for localized corrosion are shown schematically in Fig. 5-1.

The SRET consists of a "passive" reference probe with a fine capillary tip, a system to drive the probe across a path close to the flat surface, and a system to measure and analyze the potential pattern generated by the corrosion reaction. SRET studies the electrochemical process without changing the local environment over the corroding site or influencing the rate of corrosion. A quasi-three dimensional map of the surface is generated and shows anodic sites as "hills" and cathodic sites as "valleys".

Kackley and Levy have adapted the SRET to study the corrosion of aluminum weldments in a sodium fluoride NaF electrolyte (Ref. 2). Their system is computerized to direct the path of the reference electrode and to analyze the data. A schematic of the system is shown in Fig. 5-2. The objective of the investigation was to evaluate welding parameters in terms of the corrosion of the weldment and heat-affected areas. The test specimen was scanned repeatedly until the entire area of interest had been

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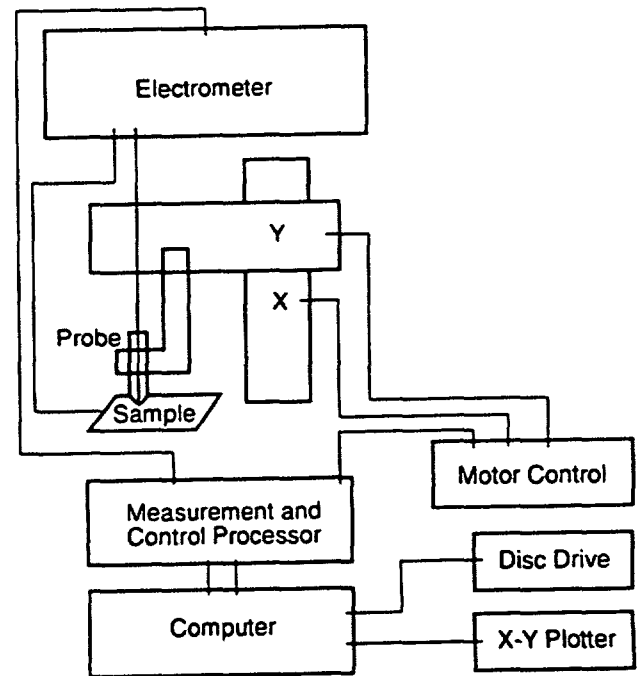


This figure is Figure 2 from a paper entitled "Computer-Aided Electrochemical Corrosion Study of Aluminum Weldments in NaF" coauthored by N. Kackley and M. Levy, *Computer-Aided Acquisition and Analysis of Corrosion Data*, PV 85-3, (1984). This paper was originally presented at the Fall 1984 Meeting held in New Orleans, LA.

### Figure 5-1. Flow of Current and Potential Pattern for Localized Corrosion (Ref. 2)

covered. This generated a three-dimensional potential surface, typically showing a ridge over the weldment area. The scans were repeated at regular intervals of time. Because of the variability inherent in the electrolyte potential over time, the data can be examined only for general trends or rankings rather than absolute corrosion rates or corrosion initiation times. In general, better corrosion resistance is related to smaller potential differences between the weld and base metal and to longer time to develop a maximum potential difference.

The SRET can generate large volumes of data. Therefore, it is important not to overgeneralize based on a few data points or to place excessive importance on the precision of inherently variable data. The scan of corrosion potential, however, can be related to specimen microstructure and constituent microanalysis to yield a deeper understanding of the corrosion process.



This figure is Figure 1 from a paper entitled "Computer-Aided Electrochemical Corrosion Study of Aluminum Weldments in NaF" coauthored by N. Kackley and M. Levy, *Computer-Aided Acquisition and Analysis of Corrosion Data*, PV 85-3 (1984). This paper was originally presented at the Fall 1984 Meeting held in New Orleans, LA.

### Figure 5-2. Schematic of Electrochemical Scanning System (Ref. 2)

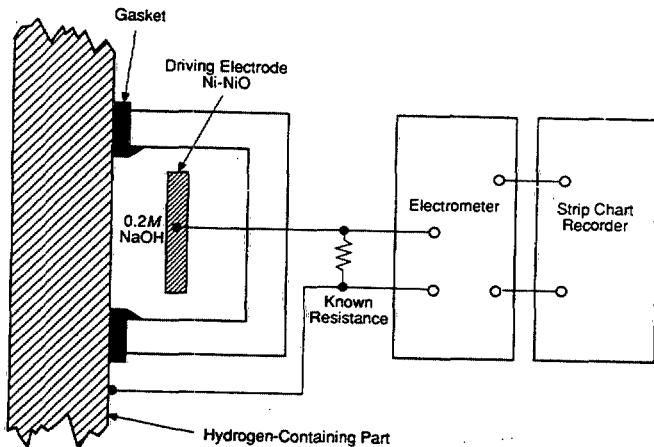
#### 5-2.1.6 The Barnacle Electrode Procedure for Hydrogen Embrittlement

The barnacle electrode is a small device that can be fixed to a steel structural part or test specimen to define an exact area. The specimen is the anode and the electrode incorporates a nickel-nickel oxide cathode. The cell is filled with a 0.2-molar solution of sodium hydroxide. The barnacle electrode is illustrated schematically in Fig. 5-3.

The barnacle electrode anodically oxidizes hydrogen to water. When it is affixed to a piece of metal containing hydrogen, hydrogen, which diffuses from the metal, is oxidized to water. The hydrogen level in the chamber is maintained at zero, and thus provides a diffusion sink. The current required to oxidize the hydrogen is a direct measure of the rate of permeation of the hydrogen.

The device has been employed in indexing embrittlement of high-strength AISI 4340 steel as a function of hydrogen content, measuring the loss of hydrogen from an HY-130 steel weldment, and relating the hydrogen content of cadmium-electroplated steel to bakeout conditions (Ref. 3).

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**Figure 5-3. Schematic of Barnacle Electrode Measuring Apparatus (Ref. 3)**

### 5-2.2 FIELD CORROSION TESTING

Laboratory corrosion tests can be related to anticipated service performance by theory, by simulation, and by experience. Because of the variability and complexity of typical service environments, inferences based on theory and simulation are risky. The utility and validity of basing performance expectations on laboratory corrosion tests must be confirmed by field corrosion testing, which should be an integral part of the materiel development process.

As part of the materiel design process, field testing has inherent limitations, e.g.

1. Usually only a limited number of prototype or preproduction items can be made available for testing, and they may not represent production processes and materials.

2. A large number of potential operating environments exist.

3. There is a short time period during which tests can be conducted.

Because of these limitations, field corrosion tests, per se, do not receive adequate attention during the materiel development process. Most field testing is coincidental with performance testing. Because of this fact, the testing is relatively short, and test conditions are not selected to yield corrosion information.

Much field test data are available from standard metal panels that have been exposed to specific atmospheric environments, and these tests have many of the controls of laboratory tests. The uncontrolled variable is the environment, which is fixed by the geographic location and the microclimate of the exposure facility. However, in the time period required to accumulate long-term experience, the environment of a location may change, new alloys may replace some of those exposed, and production methods may change, and each of these

changes would modify the composition and condition of an alloy.

Some of the specific problems that may arise in atmospheric corrosion tests are (Ref. 4)

1. Sites change in corrosivity over substantial periods of time.

2. Short-term tests (those of less than 2-yr duration) may show relative differences in material performance, but do not necessarily reflect the true corrosive nature of a site.

3. There are substantial differences in the performance of materials boldly exposed versus materials exposed in shelters. For example, galvanized panels have higher metal loss rates on the underside than on the sky-facing side. Corrosion in tropical rain forests is relatively low for steel and zinc. There is no pollution, the test panels are washed regularly by pure rainwater, there is screening from the sun by the forest canopy, and diurnal temperature variations are small.

4. The elevation, angle of exposure, degree of shading, and direction of exposure all influence results.

5. Static exposures do not usually give results comparable to dynamic exposures, such as vehicle tests. Three approaches have been taken to measure the corrosivity of atmospheric exposure sites:

1. One approach measures the weight loss of standard reference materials and compares this measurement with published data from other sites. Even if the response of the standard material correlates with that of the test material, the standard material does not provide direct information about which environmental factors contributed to the corrosion process.

2. The weather station data can characterize an atmospheric corrosion exposure site because weather and pollution factors are measured on a regular basis. However, there has been little success analyzing this mass of data and relating it to the corrosion process.

3. A third approach is to measure the variables that are considered to relate directly to the corrosion process. The factors most commonly measured are temperature, time of wetness, sulfur, and chloride. This method is most successful if one factor, such as chloride concentration, is predominant over the others affecting the corrosion process. Problems arise, however, if there are interactions among the factors.

Test coupons often are exposed to working environments. For example, test coupons attached to vehicle underbodies are exposed to roadway environments and test sections in piping systems are exposed to the flowing fluids of processing units.

Corrosion testing that is intermediate between the laboratory and the field is conducted in test facilities that simulate many characteristics of the service environment. An example is environmental chambers that simulate arctic or tropical conditions.

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Operational experience can provide a great deal of information concerning corrosion in the field environment. Unfortunately, it is usually poorly documented and available too late to influence the production design. If operational experience does indicate serious shortcomings, the only alternative may be a costly remedial program. Nevertheless, operational experience can add to the store of knowledge. For this information to be useful, it must be properly documented, correctly assessed, and organized for ready retrieval.

Early operational experience can provide information concerning expected future failures if the proper distribution of failures with time is applied to the data. The failure distribution with time of electromechanical and mechanical components that show only random failures (inconsistent failure rate) can be described by a Weibull function (Ref. 5), which can be reduced to a straight line by taking logarithms twice. If the failure data plot as a straight line on Weibull paper, the Weibull expression is that describing the line. If the failure data plot as a curve, however, the proper values of the Weibull parameters are determined by trials until a straight line is achieved. Extreme value, or Gumbel's distribution (Ref. 6), has been applied to local corrosion. The maximum pit depth of a large area of material can be estimated by examination of the maximum pit depths from small portions of the area (Ref. 7).

### 5-3 ACCELERATED CORROSION TESTING

Tests are needed that intensify the corrosion process by simulating the effects of a long-term environmental exposure in a short period of time.

Most forms of corrosion increase as a function of time in a given environment. Corrosion damage is cumulative and irreversible. The rate of corrosion in many corroding systems may increase, level off, or decrease as a result of the cumulative effects of the corrosion process. Corrosion-assisted processes such as corrosion cracking appear to have an incubation period, but this represents the time required for sufficient damage to accumulate to lead to catastrophic failure.

If an accelerated corrosion test is to have utility, one of the following conditions must apply:

1. A critical corrosion factor, such as corrodent concentration, is intensified with time in the corrosion process. Therefore, if it is artificially intensified, the effect of time is simulated.

2. A relationship exists between the time of an exposure and a controlling corrosion factor such that short-term corrosion with a high exposure factor intensity is equivalent to long-term corrosion with a low exposure factor intensity. For example, exposure for 1000 h at 50°C (122°F) may result in corrosion equivalent to 1 h at 82°C (180°F).

3. Critical exposure factors are independent of the period over which they occur. For example, 10,000 stress cycles accumulated in 10 h result in the same damage as 10,000 stress cycles accumulated in 1000 h.

Accelerated corrosion tests are inherently laboratory tests because of the need to intensify artificially an exposure factor over that experienced in the field. An argument can be made, however, that some natural environments accumulate corrosion damage more rapidly than others. Therefore, exposure in a tropical climate may be considered an accelerated test that indicates what might occur in a more temperate climate over a longer period of time.

Some of the techniques employed to accelerate corrosion include

1. Increasing temperature
2. Increasing humidity
3. Increasing chloride ion concentration
4. Adding oxidizers or aeration
5. Controlling pH, usually at a strong acid or alkaline level
6. Increasing flow velocity or agitation
7. Galvanic coupling
8. Stimulation by applied electrical currents.

The useful techniques can be specific to certain metals and alloys. Four common types of accelerated corrosion tests are exposure to

1. Dispersed fog spray
2. High humidity
3. Simulated atmosphere
4. Liquid by immersion.

Several types of dispersed fog spray tests are called for in materiel procurement specifications, and all operate on the same general principle. Specimens are exposed to a continuous or an intermittent spray. Other principal variations are the composition of the liquid sprayed and the test temperature.

Common test solutions are

1. Pure water
2. 3.5%, 5%, and 20% solutions of sodium chloride
3. Sodium chloride solutions acidified to a specified pH or with metal ions added to the solution which will plate out on certain areas of the metal and accelerate localized corrosion.

Spray tests are used principally to obtain a rapid evaluation of the protection afforded by coatings such as paint, anodic films, and surface conversion coatings. A common practice is to cut through the coating—but not the metal—by intentionally placing a controlled score mark on the specimen before exposure.

High relative humidity is another accelerated exposure environment. Commercial test equipment is available that can be set for any combination of relative humidity and temperature; different results will be obtained depending on whether or not the moisture condenses on the specimen.

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The accelerating corrosion effects of atmospheric pollutants are examined in controlled environment chambers in which a variety of gases, vapors, and particulate matter is introduced and allowed to contact and condense on the test specimen.

Probably the most common accelerated corrosion test method is immersion in a liquid. Obvious differences in test procedures are the solutions used, agitation rates, and temperature.

Another variable is the method of immersion, e.g.,

1. Total immersion (specimen completely immersed in the solution)

2. Alternate immersion (specimen immersed in the solution for a period, removed from the solution, and allowed to dry; the cycle is repeated)

3. Partial immersion (the lower portion of the specimen is immersed in the solution and the upper half in air or in vapor in the case of a closed system).

The last method actually evaluates three conditions of exposure: the immersion zone, the liquid-air interface line, and the vapor or air zone.

Much of the information concerning corrosion testing also applies to metal surfaces protected by coatings. In addition to the variations in formulation that may occur, small variations in applying these coatings can have a significant influence on their effectiveness.

Paint evaluation can incorporate one or more of the following, which are listed in order of increasing relevance to performance under service conditions:

1. Manufacturers' claims and literature
2. Reports of performance from associates or other users
3. Laboratory tests of panels under controlled conditions
4. Field exposure results from test fences or established testing facilities

5. Field exposure panels in the service environment
6. Limited scale field tests
7. Larger scale field tests that incorporate judging of application characteristics

8. Service tests or usage in which area covered and amount of paint used constitute a major application.

Laboratory tests are relied upon despite their relatively low ability to predict performance in service environments. Representative laboratory tests are listed in Table 5-2. The salt spray (fog) test is one of the most widely used accelerated tests for coatings. In the salt spray test there are three failure types generally evaluated: blistering, rusting, and undercutting from a scribe mark. A scale for evaluating blistering is shown in Fig. 5-4. This scale has been modified from ASTM guidelines given in ASTM D714 (Ref. 9) by adding trace, very few, few, etc. to assist in interpretation of results. ASTM guidelines for rust resistance given in ASTM D610 (Ref. 10) are illustrated in Fig. 5-5. Both of these guidelines involve subjective interpretation.

A salt fog test of 500 h is typical in the coatings industry and can indicate relative differences in the performance of coatings. However, correlations between exposure times in the salt fog test can only predict exposure in field conditions when a specific correlation has been verified experimentally (Ref. 11).

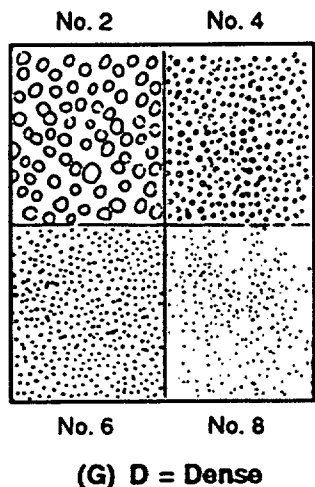
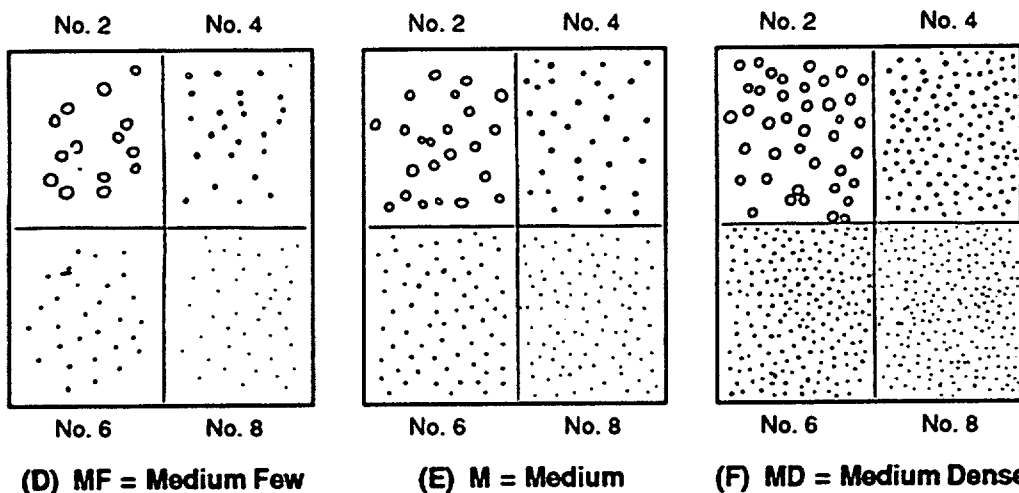
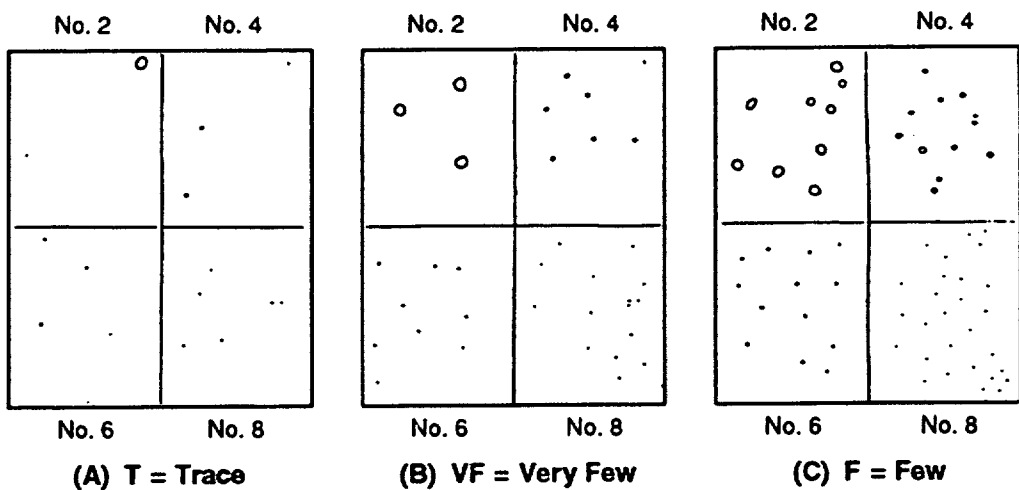
A cyclic salt spray test has been standardized in West Germany by the Association of German Manufacturers of Automobiles (VDA Standard Test Method 621-412). Experiments indicate that 6 weeks of testing are as severe as 18 weeks by natural weathering with salt spray in West Germany and as severe as 36 weeks by natural weathering in West Germany without salt spray. Whether this correlation has wider validity has not been determined (Ref. 12).

**TABLE 5-2. REPRESENTATIVE LABORATORY PAINT TESTS (Ref. 8)**

|                                    |                                 |
|------------------------------------|---------------------------------|
| 1. Freshwater immersion            | b. Ethanol                      |
| 2. Synthetic seawater immersion    | c. Ammonia                      |
| 3. 5% hydrochloric acid immersion  | d. Tincture iodine              |
| 4. 5% salt spray (fog)             | e. Tincture Merthiolate         |
| 5. Condensing humidity test        | g. Phenol                       |
| 6. Weatherometer tests—two types   | h. Concentrated acids           |
| 7. Physical tests                  | (1) acetic                      |
| a. Forward and reverse impact      | (2) nitric                      |
| b. Adhesion                        | (3) phosphoric                  |
| c. Heat resistance                 | (4) sulfuric                    |
| d. Gloss and color                 | 9. Electrochemical measurements |
| 8. Stain chemical resistance tests |                                 |
| a. Acetone                         |                                 |

Table from "Testing Corrosion Resistance of Coatings" by F. P. Helms, *Handbook on Corrosion Testing and Evaluation*, Ed., W. H. Ailor, p. 652 (1971). Published by J. Wiley and Sons, Inc., and sponsored by The Electrochemical Society, Inc.

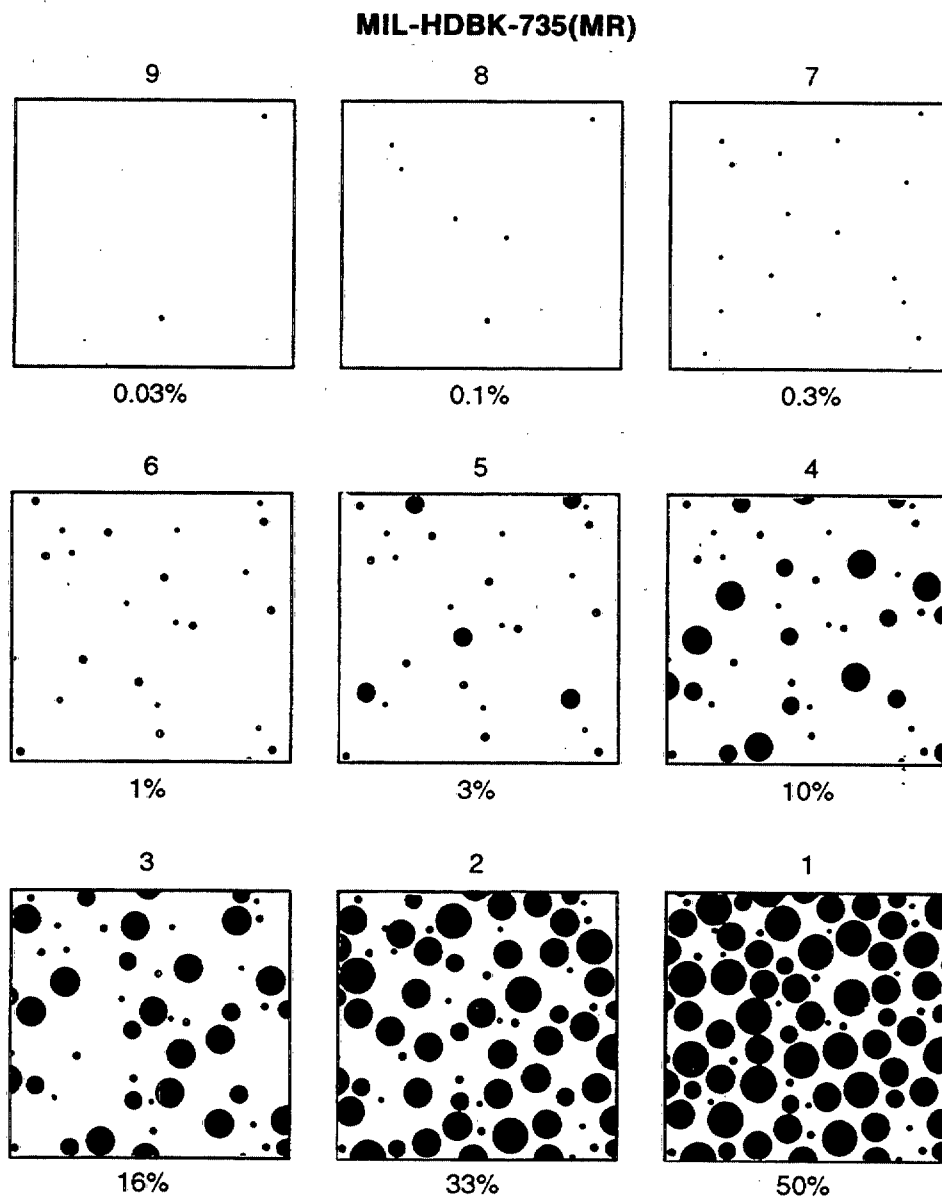
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| ACTUAL SIZE OF BLISTERS |  |                           |
|-------------------------|--|---------------------------|
| No. 2                   |  | 6.35 mm<br>(1/4 in.) dia  |
| No. 4                   |  | 3.18 mm<br>(1/8 in.) dia  |
| No. 6                   |  | 1.59 mm<br>(1/16 in.) dia |
| No. 8                   |  | 0.79 mm<br>(1/32 in.) dia |

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**Figure 5-4. Scale for Evaluating Degree of Paint Blistering (Ref. 11)**



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**Figure 5-5. Rating of Painted Steel Surfaces as a Function of Area Percent Rusted (Ref. 11)**

Many attempts have been made to correlate short-term electrochemical measurements with long-term performance of coatings in service. In general, poor coatings can be identified, but ranking of good coatings is less reliable. General trends are found, e.g., increased electrical resistance corresponds to improved corrosion resistance. Electrochemical methods are most successful when they are applied to

1. Characterize changes in organic coatings during exposure
2. Investigate mechanisms of corrosion protection and breakdown of protection
3. Provide an accelerated test for a generic system of coatings in a specific environment (Ref. 13).

#### 5-4 STRESS-CORROSION TESTING

A metal is susceptible to stress-corrosion cracking when it exhibits greater deterioration in its mechanical properties through the combined action of a sustained tensile stress and corrosion than would occur from the separate actions taken together. Stress-corrosion cracking resistance can be established only by exposing both unstressed and stressed specimens to the test environment. In that way failures resulting from stress-corrosion cracking can be distinguished from those resulting from a reduction in load-supporting area by corrosion.

Tests are performed on materials of known susceptibility to stress-corrosion cracking to evaluate protective coatings or specific structural assemblies and as



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quality control tests. There is no need to expose accompanying unstressed specimens in these cases.

Testing to determine the stress-corrosion susceptibility of an alloy in a particular environment may serve a diversity of objectives. Some of these objectives are listed in Table 5-3.

The objectives of a stress-corrosion cracking test determine the most pertinent of many elements that must be considered in specifying a test procedure. The range of considerations is listed in Table 5-4.

Most stress-corrosion cracking tests are conducted on relatively small specimens under laboratory or service

**TABLE 5-3. TYPICAL OBJECTIVES OF STRESS-CORROSION CRACKING TESTS (Ref. 14)**

- 
1. Screening tests
    - a. Compare experimental alloy compositions and tempers
    - b. Compare variations in environment
    - c. Develop a quality-control test
  2. Predicting stress-corrosion performance in service
    - a. Determine the resistance to stress-corrosion cracking of an actual or simulated structure in anticipated service environment
    - b. Determine the best material to fill a need through accelerated tests
    - c. Determine the effectiveness of protective treatments
    - d. Duplicate the response of a material that failed in service
  3. Determining whether the product meets specifications
  4. Investigating the mechanisms of stress corrosion
- 

Table from "Stress-Corrosion Cracking" by H. L. Craig, Jr., D. O. Sprowls, and D. E. Piper, *Handbook on Corrosion Testing and Evaluation*, Ed., W. H. Ailor (1971). Published by J. Wiley and Sons, Inc., and sponsored by The Electrochemical Society, Inc.

**TABLE 5-4. NECESSARY CONSIDERATIONS IN PLANNING A STRESS-CORROSION TEST PROGRAM (Ref. 14)**

- 
1. Available information concerning alloy, environment, and application
  2. Test material
    - a. Influence of composition and temper
    - b. Type of manufactured product; thickness
    - c. Commercially fabricated or laboratory sample
    - d. Influence of location and orientation of test specimens
  3. Design of test specimen and method of stressing
    - a. Smooth
    - b. Mechanically precracked
    - c. External loading (constant load, deformation)
    - d. Residual stresses
  4. Influence of environment
    - a. Anticipated service
    - b. Natural environments
    - c. Accelerated test media
  5. Influence of time and number of tests
    - a. Number of stress levels
    - b. Number of replicate specimens
    - c. Duration of test
    - d. Criterion of failure
  6. Evaluation and reporting
    - a. Type of data to satisfy purpose of the test
    - b. Limitations of test procedure
    - c. Statistical analyses
- 

Table from "Stress-Corrosion Cracking" by H. L. Craig, Jr., D. O. Sprowls, and D. E. Piper, *Handbook on Corrosion Testing and Evaluation*, Ed., W. H. Ailor (1971). Published by J. Wiley and Sons, Inc., and sponsored by The Electrochemical Society, Inc.

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exposure conditions. These conditions are listed in Item 2 of Table 5-4. It is important that the test specimens adequately represent the manufactured product.

It is also important that the method of loading and the influence of stress raisers reflect the service environment. These considerations are listed in Item 3 of Table 5-4.

#### 5-4.1 SUSTAINED LOAD AND CONSTANT DEFORMATION TESTING

Most stress-corrosion cracking service failures occur under tensile stresses of unknown magnitude that usually result from residual rather than applied stresses. Table 5-5 lists many of the sources of sustained tension that gives rise to service failures. The wedging action of corrosion products may exert very high forces in crevices and cracks. These forces contribute another source of unknown stresses in addition to the applied known stresses. Therefore, testing at nominal or design stresses may be misleading. Accordingly, a test should be conducted at stresses approaching the yield strength.

The configuration of the test specimen and the means of applying the load strongly influence the outcome of a stress-corrosion cracking test. Included in the category of externally loaded smooth specimens are

1. Direct-Tension Specimens Under Sustained Load or Sustained Deformation (constant strain). Crack growth rate is higher under constant load. The average tensile stress on the uncracked section increases rapidly as the crack propagates. When the notch fracture strength is reached, the specimen breaks. Because of plastic deformation, however, a specimen under constant deformation may not break.

2. Bent Beam Specimens of Alloy Sheets, Plates, and Bars. The stress of principal interest is the longitudinal tension stress on the convex surface. A stress gradient exists through the thickness ranging from maximum tension on the outer surface to maximum compression on the inner surface. The stresses vary from mid-length to the ends of the specimen and can also vary across the width.

3. U-bend specimens of approximately 180 deg around a predetermined radius contain large amounts of elastic strain in addition to plastic strain. For this reason, the U-bend specimen provides one of the most severe tests available for smooth stress-corrosion test specimens. The circumferential stress is of principal interest and is not uniform.

4. The C-ring is a constant-strain specimen with tensile stress produced on the exterior of the ring by tightening a bolt centered on the diameter of the ring. C-ring specimen stress of principal interest is circumferential. The stress varies around the circumference of the C-ring from 0 at each bolt hole to a maximum at the middle of the arc opposing the stressing bolt. Tensile stress on the inside surface can be imposed by spreading the ring. An almost constant load can be developed by using a calibrated spring placed on the loading bolt.

5. O-ring specimens are used in tests in which hoop stresses are desired. A plug inserted in the specimen generates the stresses.

6. For many purposes flexural loading imposed on tuning-fork-type specimens are adequate and require less bulky and expensive stressing apparatus than dead weight tensile loading.

**TABLE 5-5. METHODS OF STRESSING MOST APPLICABLE TO VARIOUS SOURCES OF SUSTAINED TENSION IN SERVICE (Ref. 14)**

| SOURCE OF SUSTAINED TENSION IN SERVICE | CONSTANT DEFLECTION | CONSTANT LOAD |
|--|---------------------|---------------|
| Residual Stress                        |                     |               |
| Quenching                              | X                   | —             |
| Forming                                | X                   | —             |
| Welding                                | X                   | —             |
| Misalignment                           | X                   | —             |
| Interference Fasteners                 | X                   | —             |
| Interference Bushings                  |                     |               |
| Rigid                                  | X                   | —             |
| Flexible                               | —                   | X             |
| Flareless Fittings                     | X                   | —             |
| Clamps                                 | X                   | —             |
| Hydraulic Pressure                     | X                   | X             |
| Dead Weight                            | —                   | X             |
| Faying Surface Corrosion               | X                   | X             |

Table from "Stress-Corrosion Cracking" by H. L. Craig, Jr., D. O. Sprowls, and D. E. Piper, *Handbook on Corrosion Testing and Evaluation*, Ed., W. H. Ailor (1971). Published by J. Wiley and Sons, Inc., and sponsored by The Electrochemical Society, Inc.

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Such processes as forming, straightening, swaging, and welding generate residual stresses. Test specimens can be devised that incorporate residual stresses.

Precracked specimens for external loading have several important features for stress-corrosion cracking testing:

1. They can be used with linear elastic fracture mechanics to develop stress-corrosion cracking thresholds in terms of resistance to catastrophic crack growth. See par. 2-2.9.1 for a discussion of linear elastic fracture mechanics.
2. The rate of growth of stress-corrosion cracks and other environmentally induced cracks can be characterized.
3. Variable and prolonged periods of incubation of stress-corrosion cracks in testing some alloys can be avoided.

A given alloy is sensitive to stress-corrosion cracking in specific chemical species in the environment. Therefore, exposure conditions must include all of the factors for which susceptibility is being tested. Tests in the laboratory allow close control of environmental factors; however, tests should expose an alloy to all of the environmental factors to which it may be sensitive in service.

Typically field testing can include seawater immersion, atmospheric exposure to marine and industrial environments, and exposure to process streams in chemical plants. Because stress-corrosion cracking results in catastrophic failure, the most important result of field testing is determination of the susceptibility of an alloy to the environment.

Most laboratory stress-corrosion testing is accelerated testing. To predict the stress-corrosion cracking performance of an alloy over a long period in the intended service, the test procedure should produce the same type and path of cracking that occurs in service. The corrodent should contain the specific chemical species believed responsible for stress-corrosion cracking of the type of alloy under study. Furthermore, the corrodent should result in a minimum of general corrosion. The validity of accelerated stress-corrosion testing requires correlation with service experience or with appropriate field tests.

Standardized environments developed as test media for specific classes of alloys include

1. Boiling magnesium chloride solutions for stainless steels
2. Polythionic acids for stainless steels and related alloys
3. Mercurous nitrate for copper and copper alloys
4. Mattsson's solution for copper-zinc alloys (brasses)
5. Alternate immersion testing in 3.5% sodium chloride for aluminum, ferrous, and other alloys
6. Hot salt environment for titanium and other alloys.

The stress cracking process consists of an incubation period, a crack propagation period, and mechanical

fracturing or yielding. During the incubation period there is no cracking, but there may be a reaction at the oxide film and metal surface. The incubation period is often used as the criterion of failure of smooth specimens; however, the time to failure may be only slightly longer than the incubation period and much easier to determine. The criterion of failure of precracked specimens is fracture with sustained load stressing or crack arrest when loaded by constant crack opening displacement.

### 5-4.2 SLOW STRAIN-RATE TESTING

Unlike constant load or constant strain methods of stress-corrosion cracking testing, the slow strain-rate test method usually results in failure of the specimen in not more than a few days (Ref. 15). The failure will be either ductile fracture or stress-corrosion cracking. It is vital that the mode of failure be ascertained by metallography or fractography. In addition to being an accelerated test, the slow strain-rate test is also a conservative test. If there is no stress-corrosion cracking in the test, there will be no stress-corrosion cracking in service under the conditions tested. However, if stress-corrosion cracking is observed in the test, the alloy may still be acceptable if the stresses can be controlled to avoid stress-corrosion cracking. This determination may require further testing and sound engineering judgment. The strain rates imposed in constant strain-rate methods are similar to the creep rates of the metal.

Although stress-corrosion cracking is experienced by many different types of alloys in a wide variety of environments, the common feature is that under conditions causing stress-corrosion cracking, the alloys are covered by corrosion films. Stress-corrosion cracking is related to rupture of this passivating film and electrochemical surface reactions of the exposed metal. Crack formation and propagation depend upon a critical balance between activity and passivity at the crack tip (Ref. 16). This concept of an anodic film rupture and stress-corrosion cracking mechanism is implicit in any consideration of the slow strain-rate testing technique.

The purpose of constant strain is to promote repetitive film rupture, which must produce sufficient metal dissolution to advance the crack, yet the sides of the crack must remain relatively passive. Strain rate is an important experimental parameter in the slow strain-rate test. If the test is performed at too high a strain rate, the specimen fails by ductile fracture. If the test is conducted at too low a strain rate, the active condition at the crack tip cannot be maintained. The slow strain-rate test will produce stress-corrosion cracking in a critical range of strain rates that are characteristic of each material. For example, experience has shown that steels undergo severe stress-corrosion cracking at a strain rate of about  $10^{-6} \text{ s}^{-1}$  regardless of the test environment (Ref. 17).

Data from slow strain-rate tests include load versus

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time curves, time to failure, and the results of postfailure specimen examination. A set of data is obtained for each strain rate, and the specimen examination data include mechanical and metallographic results. Measures of stress-corrosion cracking severity are based upon metallography, ductility, time to failure, load versus elongation behavior, and various combinations of these measures. Data are usually normalized to a specimen of the same metal tested at the same temperature and strain rate in a solution that does not promote stress-corrosion cracking. Data may be used to rank similar alloys as to stress-corrosion resistance. However, for dissimilar alloys, rough ranking only is advisable (Ref. 18).

Kackley, Czyrkliis, and Levy conducted slow strain-rate testing of Al-Mg and Al-Mg-Zn alloys for stress-corrosion cracking resistance (Ref. 19). Aluminum alloys 5083-H131, 7039-T64, Al-7Mg-H117, and Al-8Mg-131 were tested in dry air and in a 3.5% NaCl solution. The ductility ratios, i.e., ductility in a cracking environment divided by that in a noncracking environment, were determined at three strain rates. The alloys were ranked based on their ductility ratios at the most susceptible strain rate, viz., the lowest ductility ratio. The fracture mode at each strain rate was confirmed by scanning electron microscopic examination of the fracture surface. Resistance to stress-corrosion cracking of these alloys was also measured using precracked double cantilever beam (DCB) specimens. Values of stress intensity for stress-corrosion cracking  $K_{Isc}$  determined in a 3.5% NaCl solution were used to rank the four alloys. The rankings determined by slow strain-rate testing and by DCB specimen testing were compared.

The stress-corrosion cracking susceptibility of 7039-T64 is the only difference between these two rankings. The slow strain-rate results place this alloy just behind alloy 5083 in stress-corrosion cracking, but the DCB testing ranks alloy 7039 as the most susceptible in the as-received condition. The reason suggested for this discrepancy is that the most susceptible strain rate for alloy 7039-T64 is below that used in this investigation.

## 5-5 REPORTING OF TEST DATA

### 5-5.1 THE TEST REPORT

Although any organization involved in corrosion testing may have a standardized reporting format, all reports should contain the following elements:

1. *Synopsis or Abstract.* A brief statement of the most significant test results and conclusions. It is intended to communicate the essence of the work without requiring a time-consuming study of the entire report.

2. *Introduction.* Gives an explanation of the background that justifies the need for the work.

3. *Objective.* Describes the goals of the test. (The purposes of laboratory corrosion testing are described in par. 5-2.1.)

4. *Materials.* Describes the test objects, their sources, metal analyses, sizes, number of samples, and identifying numbers. The considerations used to define the test specimen in laboratory corrosion tests are described in par. 5-2.1.1.

5. *Procedure.* Answers questions such as how were the samples prepared, how were tests conducted, how can test environments be identified (specifically referring to established techniques and standardized tests where applicable). The corrosion test environment in laboratory testing is discussed in par. 5-2.1.2, and the conditions of exposure are discussed in par. 5-2.1.3.

6. *Results.* Describes the findings of the study. It is usually helpful to itemize each result by listing the most important findings first. Considerations used to assess the results of laboratory testing are outlined in par. 5-2.1.4.

7. *Conclusions.* Discusses the meaning of the results. The test results should not be repeated. The meaning relates the purpose of the test to the outcome. For example, the results may resolve a question of suitability of a particular metal or alloy in a functioning article of material.

8. *Status or Recommendations.* Indicates whether the work is complete and describes what additional work should be done or action taken as a consequence of the information gained

9. *Appendix.* Contains tabulations, charts, photographs, references, and other information that will be useful for future review or continuation of the work.

### 5-5.2 CORROSION EFFECTS

Corrosion effects occur at the surface or within the microstructure of the metal. Surface effects are general or localized. The effect occurring within the microstructure of the metal can be characterized as intergranular attack, selective leaching, or cracking. How the effects of corrosion resulting from a test are characterized depends upon how the effects are determined. The types of evaluation commonly applied include

1. Visual examination with the unaided eye
2. Augmented visual examination or instrumental imaging
3. Weight changes
4. Measurement of physical properties
5. Measurement of mechanical or strength properties
6. Electrochemical measurements
7. Chemical composition.

The corrosion effect is usually expressed as a change in some property as a result of test exposure. This change may be gaged on a before-and-after comparison or a comparison with a standard. A graduated scale may describe some effects, whereas others may be simply described as occurring or not. Detailed relationships with test conditions may characterize corrosion effects.

Results of the various types of corrosion effects are

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characterized in terms of specific measurements, e.g.,

1. General Wasting or Uniform Corrosion
  - a. Decrease in thickness
  - b. Change in tensile strength
  - c. Weight loss or gain per unit area
  - d. Percentage of area affected
  - e. Potential of corroding electrode
  - f. Corrosion current
  - g. Chemical composition of surface corrosion products

products

h. Chemical composition of corrosion products in solution

- i. Growth of surface film by ellipsometry

2. Local Attack

a. Visual examination from 0.3 to 0.6 m (1 to 2 ft) for pits, blisters, flaking, and cracking

b. Size and number of pits by comparison with standard pitting chart. Fig. 5-6 shows standard pitting charts that refer to the number and size of pits. A typical example of pitting assessment might be 5 pits (Chart A) of size 1½ (Chart B) that affect 60% of the area.

c. Spacing and width of surface cracks from

standard cracking charts. An assessment of cracking would be similar in concept to that of pitting.

d. Rating of surface defects. Table 5-6 gives the dimensions of the standard defects shown in standard pitting charts in Fig. 5-6 and in standard cracking charts (Ref. 20). Table 5-7 gives the percentage area of metal corroded for size and number of pitting defects. Table 5-8 gives the percentage area of metal corroded for width and spacing of cracking defects.

e. Maximum pit depth

f. Average of 10 deepest pits

g. Pits per unit area of depths greater than some specified amount

h. Pit depth distribution based upon extreme value statistics

i. Loss in tensile strength

j. Presence or absence of crevice corrosion

3. Intergranular Corrosion

a. Presence or absence

b. Type of effect, e.g., exfoliation, weld decay

c. Decrease in tensile strength

d. Arbitrary appraisal of severity

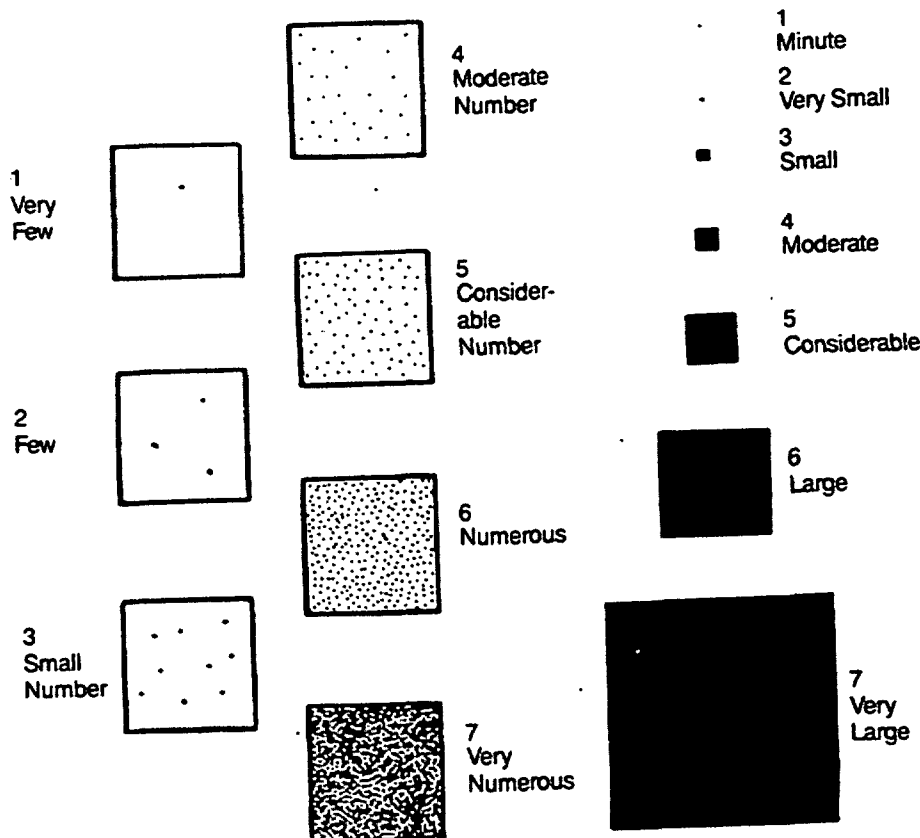


Chart A: Number

Chart B: Size

F. A. Champion, *Corrosion Testing Procedures*, 1965, Chapman & Hall, London, England.

Figure 5-6. Standard Pitting Charts (Ref. 20)

**MIL-HDBK-735(MR)****4. Stress-Corrosion Cracking and Hydrogen Embrittlement**

- a. Incubation period, if determinable
- b. Time to failure at given stress level
- c. Failure mode: intergranular or transgranular

**d. Fracture mechanics parameters**

- e. Hydrogen content of metal by barnacle electrode test (par. 5-2.1.6)

**5. Corrosion Fatigue**

- a. Time to failure at a given mean stress level

**TABLE 5-6. DIMENSIONS OF STANDARD DEFECTS**

| PITTING             |   |        |                     |          | CRACKING (Ref. 20) |       |      |         |       |      |         |
|---------------------|---|--------|---------------------|----------|--------------------|-------|------|---------|-------|------|---------|
| NUMBER *            |   |        | SIZE*               |          | SPACING**          |       |      | WIDTH** |       |      |         |
| (Chart A, Fig. 5-6) |   |        | (Chart B, Fig. 5-6) |          |                    |       |      |         |       |      |         |
| Label               | per cm <sup>2</sup> (per in. <sup>2</sup> ) |        | Label               | Diameter |                    | Label |      |         | Label |      |         |
|                     |   |        |                     | mm       | (in.)              |       | mm   | (in.)   |       | mm   | (in.)   |
| 1                   | 0.3   | (1.94) | ¼                   | 0.05     | (0.002)            | 1     | 12.5 | (0.5)   | ¼     | 0.03 | (0.001) |
| 2                   | 1   | (6.45) | ½                   | 0.1      | (0.004)            | 2     | 6.25 | (0.25)  | ½     | 0.06 | (0.002) |
| 3                   | 3   | (19.4) | 1                   | 0.25     | (0.010)            | 3     | 3.2  | (0.13)  | 1     | 0.13 | (0.005) |
| 4                   | 10  | (64.5) | 1½                  | 0.4      | (0.016)            | 4     | 1.6  | (0.06)  | 1½    | 0.17 | (0.007) |
| 5                   | 30  | (194)  | 2                   | 0.6      | (0.024)            | 5     | 0.8  | (0.03)  | 2     | 0.25 | (0.010) |
| 6                   | 100   | (645)  | 2½                  | 1.0      | (0.04)             |       |      |         | 2½    | 0.38 | (0.015) |
| 7                   | 300   | (1935) | 3                   | 1.4      | (0.06)             |       |      |         | 3     | 0.51 | (0.020) |
|                     |   |        | 3½                  | 2.5      | (0.10)             |       |      |         | 3½    | 0.75 | (0.030) |
|                     |   |        | 4                   | 3.3      | (0.13)             |       |      |         | 4     | 1.0  | (0.039) |

\*The number and size labels and dimensions are from standard pitting charts (Ref. 20). The author of the reference uses additional sizes shown here but not shown in Fig. 5-6.

\*\*The spacing and width labels and dimensions are from supplements to standard cracking charts (Ref. 20) and are used to compare degrees of crack corrosion.

**TABLE 5-7. PERCENTAGE AREA OF METAL CORRODED FOR PITTING DEFECTS OF SIZE AND NUMBER SHOWN IN TABLE 5-6**

| NUMBER*<br>LABELS | SIZE LABELS* |       |      |      |     |      |     |     |     |
|-------------------|--------------|-------|------|------|-----|------|-----|-----|-----|
|                   | ¼            | ½     | 1    | 1½   | 2   | 2½   | 3   | 3½  | 4   |
| 1                 |              | 0.006 | 0.02 | 0.05 | 0.1 | 0.21 | 0.5 | 1.3 | 2.6 |
| 2                 |              | 0.02  | 0.06 | 0.15 | 0.3 | 0.65 | 1.6 | 4   | 8   |
| 3                 | 0.03         | 0.06  | 0.2  | 0.5  | 1   | 2.1  | 5.3 | 13  | 26  |
| 4                 | 0.1          | 0.2   | 0.6  | 1.5  | 3   | 6.5  | 16  | 40  | 80  |
| 5                 | 0.3          | 0.6   | 2    | 5    | 10  | 21   | 53  |     |     |
| 6                 | 1            | 2     | 6    | 15   | 30  | 65   |     |     |     |
| 7                 | 3            | 6     | 20   | 50   | 100 |      |     |     |     |

\*The size and number labels identify the sizes and numbers of pitting defects respectively shown in Fig. 5-6 and listed in Table 5-6.

**TABLE 5-8. PERCENTAGE AREA OF METAL CORRODED FOR CRACKING DEFECTS OF WIDTH AND SPACING SHOWN IN TABLE 5-6**

| SPACING*<br>LABELS | WIDTH LABELS* |     |      |     |      |     |      |     |      |
|--------------------|---------------|-----|------|-----|------|-----|------|-----|------|
|                    | ¼             | ½   | 1    | 1½  | 2    | 2½  | 3    | 3½  | 4    |
| 1                  | 0.2           | 0.4 | 0.8  | 1.2 | 1.6  | 2.4 | 3.2  | 4.8 | 6.4  |
| 2                  | 0.4           | 0.8 | 1.6  | 2.4 | 3.2  | 4.8 | 6.4  | 9.6 | 12.8 |
| 3                  | 0.8           | 1.6 | 3.2  | 4.8 | 6.4  | 9.6 | 12.8 | 19  | 26   |
| 4                  | 1.6           | 3.2 | 6.4  | 9.6 | 12.8 | 19  | 26   | 38  | 51   |
| 5                  | 3.2           | 6.4 | 12.8 | 19  | 26   | 38  | 51   | 77  |      |

\*The width and spacing labels identify the widths of cracks and the spacings between cracks listed in Table 5-6.

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- b. Cyclic stress and frequency
- c. Fracture mechanics parameters
- 6. Impingement
  - a. Weight loss relative to that of standard specimens
  - b. Depth of erosion
  - c. Volume of metal lost in affected area
- 7. Cavitation
  - a. Volume of metal lost
  - b. Relative intensity: size of affected area and depth of penetration
- 8. Dealloying
  - a. Plug type or layer type, geometric dimensions
  - b. Change in physical and mechanical properties
- 9. High-Temperature Corrosion

- a. Weight changes
- b. Type of rate equation, e.g., linear, parabolic, or logarithmic
- c. Chemical composition of corrosion scale
- d. Chemical composition of reaction gasses.

## 5-6 STANDARD TESTS

Tables 5-9 through 5-13 contain test method standards related to corrosion.

The National Association of Corrosion Engineers Standard Test Method TM0169, *Laboratory Corrosion Testing of Metals for the Process Industries*, (Ref. 21) describes the procedures of a simple immersion corrosion test.

TABLE 5-9. FEDERAL TEST METHOD STANDARDS

| Federal Test Method Standard No. 101C, 13 March 1980, <i>Test Procedures for Packaging Materials</i>                                |  | Method No. |
|---|--|------------|
| Method Title  |  |            |
| Contact Corrosivity Test of Solid Materials in Flexible, Rigid, or Granular Forms   |  | 3005       |
| Corrosion-Inhibiting Ability of V.C.I. Vapors   |  | 4031       |
| Federal Test Method Standard No. 151 B, 24 November 1967, <i>Metals, Test Methods</i>   |  | Method No. |
| Method Title  |  |            |
| Synthetic Seawater Spray Test   |  | 812.1      |
| Intergranular Corrosion Test for Aluminum Alloys  |  | 822.1      |
| Stress-Corrosion Test for Aluminum Alloy Plate, Extrusions, and Forgings by Alternate Immersion                                     |  | 823        |
| Federal Test Method Standard No. 791 C, 30 September 1986, <i>Methods of Testing Lubricants, Liquid Fuels, and Related Products</i> |  | Method No. |
| Method Title  |  |            |
| Demerit System for Rating Deposits, Wear, and Corrosion in Internal Combustion Engines  |  | 344.2      |
| Corrosion by Dry, Solid-Film Lubricants in High Humidity (ASTM D2625)   |  | 3814.1     |
| Rust-Preventing Characteristics of Steam-Turbine Oil in the Presence of Water (ASTM D665)   |  | 4011.4     |
| Rust-Preventing Properties of Lubricating Greases (ASTM D1743)  |  | 4012.1     |
| Corrosion of Copper by Petroleum Products, Detection of, by the Copper Strip Tarnish Test (ASTM D130)                               |  | 5325.4     |
| Corrosion of Lead by Lubricating Oils   |  | 5321.2     |
| Corrosion Protection by Coatings: Salt Spray (Fog) Test   |  | 4001.3     |
| Corrosion Protection by Gear Lubricants in the Presence of Moisture   |  | 5326.1     |
| Corrosion Protection (Humidity Cabinet)   |  | 5329.2     |
| Corrosion Protection of Steel Against Sulfurous Acid—Salt Spray by Solid Film Lubricants  |  | 5331.1     |
| Corrosive Sulfur in Electrical Insulating Oils (ASTM D1275)   |  | 5328.4     |
| Corrosiveness of Emulsifiable Cutting Fluids  |  | 5306.5     |
| Corrosiveness of Greases or Semisolid Products at 25°C  |  | 5304.5     |
| Corrosiveness of Greases (Copper Strip 100°C)   |  | 5309.5     |
| Corrosiveness of Lubricants at 232°C (450°F)  |  | 5305.1     |
| Corrosiveness of Oil on a Bimetallic Couple   |  | 5322.2     |
| Corrosiveness and Oxidation Stability of Aircraft Turbine Engine Lubricants   |  | 5307.1     |
| Corrosiveness and Oxidation Stability of Light Oils (Metal Squares)   |  | 5308.7     |

**MIL-HDBK-735(MR)****TABLE 5-10. MILITARY STANDARDS**


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|   |
|---|
| MIL-STD-810, <i>Environmental Test Methods and Engineering Guidelines</i>                                     |
| MIL-STD-202, <i>Test Methods for Electronic and Electrical Component Parts</i>                                |
| MIL-STD-883, <i>Test Methods and Procedures for Microelectronics</i>  |
| MIL-STD-753, <i>Corrosion-Resistant Steel Parts: Sampling, Inspection and Testing for Surface Passivation</i> |

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**TABLE 5-11. ASTM TEST METHODS**


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| METHOD TITLE  | METHOD NO. |
|---|------------|
| Specification for Steel Tie Plates, Low-Carbon and High-Carbon Hot-Worked   | A67        |
| Recommended Practice for Safeguarding Against Embrittlement of Hot-Dip Galvanized Structural Steel Products and Procedure for Detecting Embrittlement                     | A143       |
| Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Stainless Steels   | A262       |
| Practices for Detecting Susceptibility to Intergranular Attack in Ferritic Stainless Steels   | A763       |
| Method for Accelerated Life Test of Nickel-Chromium and Nickel-Chromium-Iron Alloys for Electrical Heating  | B76        |
| Method for Accelerated Life Test of Iron-Chromium-Aluminum Alloys for Electrical Heating  | B78        |
| Method of Salt Spray (Fog) Testing  | B117       |
| Method for Mercurous Nitrate Test for Copper and Copper Alloys  | B154       |
| Method for Copper-Accelerated Acetic Acid-Salt Spray (Fog) Testing (CASS Test)  | B368       |
| Methods for Corrosion Testing of Decorative Chromium Electroplating by the Corrodkote Procedure   | B380       |
| Method for Measurement of Impedance of Anodic Coatings on Aluminum  | B457       |
| Recommended Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure   | B537       |
| Test Method for Hydrogen Embrittlement of Copper  | B577       |
| Method of Electrolytic Corrosion Testing (EC Test)  | B627       |
| Method for Measurement of Corrosion Sites in Nickel Plus Chromium or Copper Plus Nickel Plus Chromium Electroplated Surfaces With the Double-Beam Interference Microscope | B651       |
| Test Method for Seal Quality of Anodic Coatings on Aluminum by Acid Dissolution   | B680       |
| Test Method for Evaluating the Corrosivity of Solder Fluxes for Copper Tubing Systems   | B732       |
| Method of Evaluating the Influence of Wicking-Type Thermal Insulations on the Stress-Corrosion Cracking Tendency of Austenitic Stainless Steel                            | C692       |
| Specification for Cellulosic Fiber (Wood-Base) Loose-Fill Thermal Insulation  | C739       |
| Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete  | C876       |
| Method for Detection of Copper Corrosion From Petroleum Products by the Copper Strip Tarnish Test   | D130       |
| Method for Evaluating Degree of Rusting on Painted Steel Surfaces   | D610       |
| Test Method for Rust-Preventing Characteristics of Inhibited Mineral Oil in the Presence of Water   | D665       |
| Method for Evaluating Degree of Blistering of Paints  | D714       |
| Test Method for Water Resistance of Paper, Paperboard, and Other Sheet Materials by the Dry Indicator Method  | D779       |
| Methods of Sampling and Testing Dipentene   | D801       |
| Method of Assessing the Tendency of Industrial Boiler Waters to Cause Embrittlement (USBM Embrittlement Detector Method)  | D807       |
| Test Method for Copper Corrosion of Industrial Aromatic Hydrocarbons  | D849       |
| Methods of Testing Nonrigid Vinyl Chloride Polymer Tubing Used for Electrical Insulation  | D876       |
| Practice for Sampling Water-Formed Deposits   | D887       |
| Method for Total Immersion Corrosion Test of Water-Soluble Aluminum Cleaners  | D930       |
| Method of Testing Pressure-Sensitive Adhesive-Coated Tapes Used for Electrical Insulation   | D1000      |
| Method for Conducting Exterior Exposure Tests of Paints on Steel  | D1014      |

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TABLE 5-11. (cont'd)

| METHOD TITLE  | METHOD NO. |
|---|------------|
| Test Method for Corrosive Sulfur in Electrical Insulating Oils  | D1275      |
| Method for Total Immersion Corrosion Test for Soak Tank Metal Cleaners  | D1280      |
| Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes   | D1308      |
| Method for Aerated Total Immersion Corrosion Test for Metal Cleaners  | D1374      |
| Method for Corrosion Test for Engine Coolants in Glassware  | D1384      |
| Test Methods for Rubber O-Rings   | D1414      |
| Test Method for Corrosion Produced by Leather in Contact With Metal   | D1611      |
| Test Method for Water Vapor Permeability of Organic Coating Films   | D1653      |
| Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments  | D1654      |
| Test Method for Corrosion-Preventive Properties of Lubricating Greases  | D1743      |
| Test Method for Copper Strip Corrosion by Liquefied Petroleum (LP) Gases  | D1838      |
| Test Method for Resistance of Zippers to Salt Spray (Fog)   | D2059      |
| Practice for Testing Water Resistance of Coatings in 100% Relative Humidity   | D2247      |
| Test Method for Metal Corrosion by Halogenated Organic Solvents and Their Admixtures  | D2251      |
| Method for Simulated Service Corrosion Testing of Engine Coolants   | D2570      |
| Practice for Corrosion Characteristics of Solid Film Lubricants   | D2649      |
| Method of Testing Heat-Shrinkable Tubing for Electrical Use   | D2671      |
| Test Method for Corrosivity of Water in the Absence of Heat Transfer (Weight Loss Methods)  | D2688      |
| Method of Testing Engine Coolants by Engine Dynamometer   | D2758      |
| Test Methods for Corrosivity of Water in the Absence of Heat Transfer (Electrical Methods)  | D2776      |
| Test Method for Filiform Corrosion Resistance of Organic Coatings on Metal  | D2803      |
| Test Method for Cavitation Erosion-Corrosion Characteristics of Aluminum Pumps with Engine Coolants   | D2809      |
| Practice for Testing Engine Coolants in Car and Light Truck Service   | D2847      |
| Test Method for Corrosion Resistance of Coated Steel Specimens (Cyclic Method)  | D2933      |
| Test Methods for Corrosivity of Solvent Systems for Removing Water-Formed Deposits  | D3263      |
| Test Method for Determining Corrosivity of Adhesives Metals   | D3310      |
| Test Method for Stability of Perchloroethylene With Copper  | D3316      |
| Test Method for Determining Electrolytic Corrosion of Copper by Adhesives   | D3482      |
| Test Method for Rust-Preventing Characteristics of Steam Turbine Oil in the Presence of Water (Horizontal Disk Method)  | D3603      |
| Method for Detection of Copper Corrosion From Lubricating Grease by the Copper Strip Tarnish Test   | D4048      |
| Practice for Laboratory Screening of Metallic Containment Materials for Use With Liquids in Solar Heating and Cooling Systems                                 | E712       |
| Practice for Simulated Service Testing for Corrosion of Metallic Containment Materials for Use With Heat Transfer Fluids in Solar Heating and Cooling Systems | E745       |
| Test Method for Corrosion of Steel by Sprayed Fire-Resistive Material Applied to Structural Members   | E937       |
| Method for Electronic Hydrogen Embrittlement Test for Cadmium-Electroplating Processes  | F326       |
| Practice for Static Immersion Testing of Unstressed Materials in Nitrogen Tetraoxide (N <sub>2</sub> O <sub>4</sub> )   | F359       |
| Method for Corrosion Testing of Enveloped Gaskets   | F363       |
| Method for Total Immersion Corrosion Test for Tank-Type Aircraft Maintenance Chemicals  | F482       |
| Method for Total Immersion Corrosion Test for Aircraft Maintenance Chemicals  | F483       |
| Method for Mechanical Hydrogen Embrittlement Testing of Plating Processes and Aircraft Maintenance Chemicals  | F519       |
| Test Method for Adhesion of Gasket Materials to Metal Surfaces  | F607       |
| Test Method for Pitting or Crevice Corrosion of Metallic Surgical Implant Materials   | F746       |
| Recommended Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens   | G1         |
| Practice for Aqueous Corrosion Testing of Samples of Zirconium and Zirconium Alloys   | G2         |

(cont'd on next page)

**MIL-HDBK-735(MR)****TABLE 5-11. (cont'd)**

| METHOD TITLE   | METHOD NO. |
|--|------------|
| Recommended Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing   | G3         |
| Guide for Conducting Corrosion Coupon Tests in Plant Equipment   | G4         |
| Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements  | G5         |
| Definitions of Terms Relating to Corrosion and Corrosion Testing   | G15        |
| Recommended Practice for Applying Statistics to Analysis of Corrosion Data   | G16        |
| Method for Detecting Susceptibility to Intergranular Attack in Wrought Nickel-Rich, Chromium-Bearing Alloys  | G28        |
| Practice for Making and Using U-Bend Stress Corrosion Test Specimens   | G30        |
| Recommended Practice for Laboratory Immersion Corrosion Testing of Metals  | G31        |
| Method for Vibratory Cavitation Erosion Test   | G32        |
| Practice for Recording Data From Atmospheric Corrosion Tests of Metallic-Coated Steel Specimens  | G33        |
| Test Method for Exfoliation Corrosion Susceptibility in 2XXX and 7XXX Series Aluminum Alloys (EXCO Test)   | G34        |
| Practice for Determining the Susceptibility of Stainless Steels and Related Nickel-Chromium-Iron Alloys to Stress-Corrosion Cracking in Polythionic Acids        | G35        |
| Recommended Practice for Performing Stress-Corrosion Cracking Tests in a Boiling Magnesium Chloride Solution   | G36        |
| Test Method for Use of Mattsson's Solution of pH 7.2 to Evaluate the Stress-Corrosion Cracking Susceptibility of Copper-Zinc Alloys                              | G37        |
| Practices for Making and Using C-Ring Stress-Corrosion Cracking Test Specimen  | G38        |
| Practice for Preparation and Use of Bent-Beam Stress-Corrosion Specimens   | G39        |
| Terminology Relating to Erosion and Wear   | G40        |
| Test Method for Determining Cracking Susceptibility of Metals Exposed Under Stress to a Hot Salt Environment   | G41        |
| Practice for Alternate Immersion Stress Corrosion Testing in 3.5% Sodium Chloride Solution   | G44        |
| Recommended Practice for Examination and Evaluation of Pitting Corrosion   | G46        |
| Test Method for Determining Susceptibility to Stress-Corrosion Cracking of High-Strength Aluminum Alloy Products   | G47        |
| Test Method for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by the Use of Ferric Chloride Solution                           | G48        |
| Recommended Practice for Preparation and Use of Direct Tension Stress-Corrosion Test Specimens   | G49        |
| Recommended Practice for Conducting Atmospheric Corrosion Tests on Metals  | G50        |
| Test Method for pH of Soil for Use in Corrosion Testing  | G51        |
| Practice for Exposing and Evaluating Metals and Alloys in Surface Seawater   | G52        |
| Recommended Practice for Simple Static Oxidation Testing   | G54        |
| Method for Field Measurement of Soil Resistivity Using the Wenner Four-Electrode Method  | G57        |
| Practice for Preparation of Stress-Corrosion Test Specimen for Weldments   | G58        |
| Practice for Conducting Potentiodynamic Polarization Resistance Measurements   | G59        |
| Method for Conducting Cyclic Humidity Tests  | G60        |
| Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys     | G61        |
| Classification of Resistance to Stress-Corrosion Cracking of High-Strength Aluminum Alloys   | G64        |
| Method for Visual Assessment of Exfoliation Corrosion Susceptibility of 5XXX Series Aluminum Alloys (Asset Test)   | G66        |
| Test Method for Determining the Susceptibility to Intergranular Corrosion of 5XXX Series Aluminum Alloys by Mass Loss After Exposure to Nitric Acid (NAMLT Test) | G67        |
| Practice for Liquid Sodium Corrosion Testing of Metals and Alloys  | G68        |
| Practice for Measurement of Corrosion Potentials of Aluminum Alloys  | G69        |

(cont'd on next page)

**MIL-HDBK-735(MR)****TABLE 5-11. (cont'd)**

| <b>METHOD TITLE</b>  | <b>METHOD NO.</b> |
|--|-------------------|
| Practice for Conducting and Evaluating Galvanic Corrosion Tests in Electrolytes  | G71               |
| Guide for Crevice Corrosion Testing of Iron-Base and Nickel-Base Stainless Alloys in Seawater and Other Chloride-Containing Aqueous Environments | G78               |
| Practice for Evaluation of Metals Exposed to Carburization Environments  | G79               |
| Guide for Development and Use of a Galvanic Series for Predicting Galvanic Corrosion Performance   | G82               |
| Practice for Measurement of Time of Wetness on Surfaces Exposed to Wetting Conditions as in Atmospheric Corrosion Testing                        | G84               |
| Practice for Modified Salt Spray (Fog) Testing   | G85               |
| Practice for Conducting Moist SO <sub>2</sub> Tests  | G87               |
| Test Method for Monitoring Atmospheric SO <sub>2</sub> Using Sulfation Plate Technique   | G91               |
| Practice for Characteristics of Atmospheric Test Sites   | G92               |

**TABLE 5-12. NATIONAL ASSOCIATION OF CORROSION ENGINEERS  
(NACE) TEST METHOD STANDARDS**

| <b>METHOD TITLE</b>  | <b>METHOD NO.</b> |
|--|-------------------|
| Laboratory Corrosion Testing of Metals for the Process Industries  | TM-01-69          |
| Visual Standard for Surfaces of New Steel Airblast Cleaned With Sand Abrasive  | TM-01-70          |
| Method of Conducting Controlled Velocity Laboratory Corrosion Tests  | TM-02-70          |
| Autoclave Corrosion Testing of Metals in High-Temperature Water  | TM-01-71          |
| Antirust Properties of Cargoes in Petroleum Products Pipeline  | TM-01-72          |
| Methods for Determining Water Quality for Subsurface Injection Using Membrane Filters  | TM-01-73          |
| Laboratory Methods for the Evaluation of Protective Coatings Used as Lining Materials in Immersion Service   | TM-01-74          |
| Dynamic Corrosion Testing of Metals in High-Temperature Water  | TM-02-74          |
| Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate and Calcium Carbonate From Solution (For Oil and Gas Production Systems) | TM-03-74          |
| Visual Standard for Surfaces of New Steel Centrifugally Blast Cleaned With Steel Grit and Shot   | TM-01-75          |
| Performance Testing of Steel and Reinforced Plastic Sucker Rods by the Mixed String, Alternate Rod Method  | TM-02-75          |
| Abrasion Resistance Testing of Thin-Film-Baked Coatings and Linings Using the Falling Sand Method  | TM-03-75          |
| Laboratory Testing of Metals for Resistance to Sulfide Stress Cracking in H <sub>2</sub> S   | TM-01-77          |
| Evaluation of Internal Plastic Coatings for Corrosion Control of Tubular Goods in an Aqueous Flowing Environment   | TM-01-83          |
| Accelerated Test Procedures for Screening Atmospheric Surface Coating Systems for Offshore Platforms and Equipment   | TM-01-84          |
| Evaluation of Pipeline Steels for Resistance to Stepwise Cracking  | TM-02-84          |
| Holiday Detection of Internal Tubular Coatings of Less Than 10 mils (0.25 mm) Dry Film Thickness   | TM-03-84          |
| Evaluation of Internal Plastic Coatings for Corrosion Control of Tubular Goods by Autoclave Testing  | TM-01-85          |
| Holiday Detection of Internal Tubular Coatings of 10 to 30 mils (0.25 to 0.76 mm) Dry Film Thickness   | TM-01-86          |
| Cooling Water Test Units Incorporating Heat Transfer Surfaces  | TM-02-86          |
| Evaluating Elastomeric Materials in Sour Gas Environments  | TM-01-87          |
| Impressed Current Test Method for Laboratory Testing of Aluminum Anodes  | TM-01-90          |

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TABLE 5-13. CORROSION TESTS NOT ISSUED BY ANY STANDARDS ORGANIZATION

GMR Cycle Humidity Test (Opinsky Test) (Ref. 22)

Dip in acid brine and subject to humidity cycling for testing automobile body steels.

Ford Anodized Aluminum Corrosion Test (FACT) (Ref. 23)

Electrochemical test in acid salt solution for evaluating anodizing

SWAAT Test

Standard method for exfoliation testing of aluminum alloys—Reynolds MRD-STP AC 7. Acid seawater spray, 30 min, 100% RH, 90 min

Ferric Sulfate-Sulfuric Acid Test for Ni-Cr-Mo Alloys (Ref. 24)

Quality control and acceptance test for satisfactory heat treatment

Kesternich Test (Ref. 25) (German Standard DIN 50018)

Hot moist SO<sub>2</sub>, followed by ambient conditions for testing metallic protective coatings

Nitric Acid-Hydrofluoric Acid Test (Ref. 26)

For stainless steel weldments

Kape Test (Ref. 27)

Immersion in sodium sulfite for testing the sealing of anodized aluminum

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## CHAPTER 6

# QUALITY ASSURANCE

*Quality assurance is a management function by which conformance of materiel to contract and specification is assured. Standards and specifications are the principal media through which the orderly progression of materiel through the life cycle is managed. Therefore, standardization documents are described in terms of the types that are used, their purpose and content, and their sources and applications.*

*Quality engineering is discussed in terms of logistic support analysis (LSA), the US Army Materiel Command (AMC) corrosion prevention and control program, product sampling inspection, and environmental testing. Logistic support analysis is described in terms of its goals and implementation with respect to materiel systems. The AMC corrosion prevention and control program is described in terms of its purposes, structure, and functioning. Sampling inspection of parts and components is discussed in terms of the risks assumed in various sampling schemes. These risks include accepting some defective products and rejecting some good products. Efficient and effective sampling schemes are required in situations involving costly inspection methods or destructive testing. The purposes of environmental testing and considerations in specifying tests appropriate to corrosion processes are described.*

*Nondestructive tests measure the properties of a material without significantly affecting it. The commonly used nondestructive tests that may have application to corrosion are described. They include magnetic particle, penetrant, radiography, ultrasonic, eddy-current, thermal, and leak testing methods.*

*The true test of a materiel item is performance in the field. Therefore, the importance of capturing failure information, adequately documenting the failure and the operating conditions that are responsible, and reporting the failure experience to the materiel design activity is discussed.*

### 6-1 INTRODUCTION

#### 6-1.1 RELIABILITY, QUALITY ENGINEERING, AND QUALITY ASSURANCE

Reliability is the probability that materiel will perform its mission adequately for the design life under the expected operating conditions (Ref. 1). The materiel designer seeks to provide an article having acceptable reliability, and this goal is accomplished by designing an article with the required quality. Quality is the composite of all the attributes or characteristics, including performance, of an item or product (Ref. 1). If the article, as produced, is to possess the quality designed into it, it must conform to the technical requirements established for it. Specifying and documenting these technical requirements is quality engineering. Quality assurance is defined as a planned and systematic pattern of all actions necessary to provide confidence that an item or product conforms to established technical requirements (Ref. 1). This confidence is obtained by evaluation of production quality controls and by inspections exercised by procedures that are supplemented by direct verification inspection of the product (Ref. 2). Quality assurance is a management function by which conformance of materiel to contract and specification is assured.

#### 6-1.2 MILITARY STANDARDS AND MILITARY SPECIFICATIONS

Quality engineering and quality assurance rely heavily on standards and specifications as a means of communication among parties involved in the design, procurement, production, maintenance, and use of Army materiel. A specification is intended primarily for use in procurement. It clearly and accurately describes the essential and technical requirements for items, materials, or services. Specifications include the procedures to determine that the requirements are met. Specifications for items and materials may also contain preservation, packaging, packing, and marking requirements (Ref. 1).

Standards are documents that establish engineering and technical requirements for procedures, practices, and methods that have been adopted as standard. They may also establish requirements for selection, application, and design criteria for materiel (Ref. 3). Standards represent a consensus among expert practitioners in an engineering and technical specialty. In the procurement of material standards are used to standardize one or more features of an item, such as size, value, or detail of configuration. Standards are referenced in equipment specifications to standardize design requirements that are essential to interchangeability, compatibility, reliability, and maintainability. They provide a designer

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with the descriptions and data normally required for selection and application. Standards disclose or describe the technical features of an item in terms of what it is and what it will do (Ref. 3).

### 6-1.3 TESTING

Testing is a means of determining whether or not a materiel item conforms to established technical requirements. Nondestructive testing (NDT) of production items is an important form of quality assessment, but it is limited to certain characteristics. NDT often gives only an indirect indication of a material property, whereas actual field performance is a true test of materiel performance. An important function of the quality assurance process is to insure that field experience is reported, documented, organized, assessed, and made available to those engaged in the materiel design effort. Failure to perform this function can perpetuate false technical assumptions and the production of inadequate materiel.

### 6-2 STANDARDIZATION

The life cycle of military materiel encompasses the various stages through which it passes from initial concepts to disposal. Standards and specifications are the principal media through which the official and orderly progression through the life cycle phases is managed.

In the concept formulation stage materiel is usually defined and evaluated in terms of performance specifications, which have been established in mission requirements. Requirements are defined in terms of output, function, or operation. In the development stage additional performance and design specifications that further define and control the materiel characteristics are required. These requirements are accomplished through standards that enhance the design, limit costs, and reduce support requirements through interchangeability. Materiel to be produced must be completely defined

through specifications, and these specifications should fully exploit existing standards. Specifications and standards are intended to insure that the produced item has the desired capabilities and that the buyer, user, and seller agree on what they are. The logistic and operational stages of the materiel life cycle—distribution, storage, handling, use, and maintenance—are also controlled through standards and specifications.

Table 6-1 indicates the stages of the materiel life cycle and the key standardization concerns for each stage. This does not exclude other standardization concerns. Different items of materiel address different standardization needs. Nevertheless, Table 6-1 indicates those standardization concerns that must be resolved before a particular life cycle stage is attained.

#### 6-2.1 STANDARDIZATION DOCUMENTS

Standardization documents include specifications, standards, handbooks, qualified products lists, drawings, codes and regulations, and other comparable engineering records. Standardization documents deal with several different aspects of a product. These include

1. *Materials*. Type, compositions, properties, dimensions, and predetermined acceptability
2. *Processes*. Procedures, operations, schedules, and sequences
3. *Methods*. Application, protection, prevention, control, and test measurement
4. *Designs*. Configurations, arrangements, sizes, gages, tolerances, and access for maintenance
5. *Engineering Practices*. Analysis, uncertainty, risk, reliability, assumptions, codes, and regulations
6. *Performance*. Output, consumption rates, limits, wear, deterioration, and service lifetime
7. *Interface*. Coupling, joining, transmitting, transferring, containing, enhancing, and completing.

The important fact is that any one document, such as a specification or standard, deals with a limited set of these considerations. There are several implications of this fact:

**TABLE 6-1. KEY STANDARDIZATION CONCERNS OF THE LIFE CYCLE**

| LIFE CYCLE STAGES    | KEY STANDARDIZATION CONCERN                |
|----------------------|--|
| Mission requirements | Performance                                |
| Concept formulation  | Materials (construction)                   |
| Contract definition  | All relevant to development and production |
| Development          | Design and engineering practices           |
| Production           | Methods and processes                      |
| Logistics            | Materials (preservation and packaging)     |
| Operations           | Methods (maintenance) and interfaces       |
| Disposal             |  |

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1. A great deal of technology is uncodified. It is embodied in expertise, skill, craft, and art that is specific to individuals and organizations.

2. Although standards and specifications are amended as appropriate and periodically updated, they can be misleading, in error, or incomplete.

3. A contractor can often meet the letter of the specification and its referenced standards yet deliver a product having unacceptable performance.

Design and application considerations as well as economic factors govern the selection of materials, processes, and products used in the production of military materiel. These considerations are

1. *General Considerations.* Design, application, and quality considerations, as well as economic factors, shall govern the selection of items and processes used in the design, acquisition, construction, and support of materiel for the Department of Defense (DoD). Whenever acquisition documents do not explicitly specify the items or standards and specifications to be used, selection of a suitable standard or specification for a specific design application shall be the responsibility of the contracting or design activity. In this selection process, the considerations that follow shall govern.

2. *Technical Suitability.* Items and processes shall be selected or tailored from existing standards and specifications that are technically suitable in every respect to the intended application. Factors, such as function, environment, quality, transportability, reliability, strength, safety, and interchangeability shall be considered in the selection to satisfy the design parameters in every respect. The use of a standard, specification, or other document does not in itself insure the suitability of an item or process for any specific application.

3. *Economic Considerations.* When two or more items or processes will satisfy design parameters, selection shall be made according to which is most economical to the Government. Economic factors include, but are not necessarily limited to, consideration of costs (including life cycle costs) related to initial fabrication, production, reliability, operation, maintenance or support, supply, and replacement.

When the design selection has been made, standards and specifications are selected. Selection of a suitable standard or specification for a specific design application is the responsibility of the design activity. The use of a standard, specification, or other document, however, does not in itself insure the suitability of an item for any specific application.

### 6-2.2 ORDER OF PREFERENCE

Standards and specifications are selected in a given order of preference (Ref. 4). Selection of a standard or specification of lower preference is made only when

those above it do not provide an item that is technically or economically suited for the application.

Upon completion of the review of design considerations, standards and specifications shall be considered and selected in the descending group and subgroup order of preference indicated in the following paragraphs unless the acquisition documents specify the specific standards and specifications to be used or a special list.

1. *Group I.* Group I includes those standards and specifications that are mandatory for use by law or regulation pursuant to law. This group includes mandatory standards and specifications issued by the Occupational Safety and Health Administration (OSHA), Department of Transportation (DOT), Environmental Protection Agency (EPA), and Consumer Product Safety Commission (CPSC), as well as mandatory Federal Information Processing Standards (FIPS) and Federal Telecommunication Standards. Group I also includes standards and specifications that implement multinational treaty organization standardization agreements, such as North Atlantic Treaty Organization (NATO) agreements, Standardization Agreements (STANAGs), Allied Quality Assurance Publications (AQAPs), and Quadripartite Standardization Agreements (QSTAGs). The standards and specifications that implement these agreements are mandatory for use in those instances where they apply.

2. *Group II.* Group II includes standards, specifications, handbooks, and related documents promulgated by national and international non-Government standards bodies (NGSB). These documents, often termed voluntary or industry standards and referred to in this book as non-Government standards (NGS), shall be used directly in acquisitions where appropriate, or they may be referenced in other Government or non-Government standards, specifications, or purchase descriptions.

a. Subgroup IIA. Subgroup IIA includes those NGSs formally adopted by the DoD.

b. Subgroup IIB. Subgroup IIB includes those NGSs that have not been formally adopted by the DoD and are not listed in the *Department of Defense Index of Specifications and Standards (DODISS)* (Ref. 5).

3. *Group III.* Group III includes federal series standards and specifications with registered DoD interest.

a. Subgroup IIIA. Subgroup IIIA includes only commercial item descriptions (CIDs).

b. Subgroup IIIB. Subgroup IIIB includes only coordinated federal standards and specifications.

4. *Group IV.* Group IV includes military standards and specifications, and standardized military drawings (SMDs).

a. Subgroup IVA. Subgroup IVA includes co-



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ordinated military standards and specifications (including Joint Army-Navy (JAN)s, Army-Navy (AN)s, and Army-Navy design (AND)s) in accordance with MIL-STD-962 and MIL-STD-961, respectively.

b. Subgroup IVB. Subgroup IVB includes limited coordination military standards and specifications issued by the requiring DoD service, agency, or activity, and SMDs.

### 5. Group V.

a. Subgroup VA. Subgroup VA includes only those interim federal standards and specifications developed by the DoD service, agency, or activity concerned.

b. Subgroup VB. Subgroup VB includes limited coordination or "used-in-lieu-of" military standards and specifications issued by a DoD service, agency, or activity other than the preparing activity of the basic document.

6. Group VI. Group VI includes CIDs and federal standards and specifications for which DoD has not registered interest.

7. Group VII. Group VII includes standards, specifications, and related publications issued by the Government that are outside the military or federal series, and therefore are not listed in the DODISS.

a. Subgroup VIIA. Subgroup VIIA includes those Group VII documents issued by Government agencies other than DoD, e.g., Federal Aviation Administration (FAA) and National Aeronautics and Space Administration (NASA) specifications.

b. Subgroup VIIB. Subgroup VIIB includes those purchase specifications, purchase descriptions, product descriptions, and program-peculiar specifications prepared in accordance with MIL-STD-490 for the non-repetitive acquisition of development items and other items of supply.

8. Group VIII. Group VIII includes all standards and specifications not covered by Groups I through VII.

9. *Special Lists*. When determined necessary by the DoD service, agency, or activity concerned, listing of standards and specifications for special applications may be invoked by contractual provisions. These special lists may also specify documentation that is not in standard or specification form. Such listings are to be developed and organized in consonance with the requirements of MIL-STD-970 (Ref. 4) and, when used, shall take preference over the previously listed groups.

### 6-2.3 INDUSTRY STANDARDS

Department of Defense requires the use of industry standards where those standards are equivalent. The American National Standards Institute (ANSI) is the coordinator of America's voluntary standards system (Ref. 6). The system meets national standards needs by

marshaling the competence and cooperation of commerce and industry, standards developing organizations, and public and consumer interest.

ANSI has several major functions, which are

1. Coordinating the voluntary development of national consensus standards

2. Approving standards as American national standards

3. Managing and coordinating United States participation in the work of nongovernmental international standards organizations

4. Serving as a clearinghouse and information center for American national standards and international standards.

As national coordinator, ANSI assists organizations involved in standardization in the United States to reach agreement on needs for standards, to establish priorities, to plan to meet identified needs, and to avoid duplication of effort. ANSI also offers standards-developing organizations a neutral forum in which to resolve differences and provides procedures and services to help them use their resources effectively.

ANSI approves standards as American national standards when it has verified evidence that consensus exists. The evidence is provided by organizations and committees that voluntarily submit standards to ANSI for approval. These committees and organizations must show that all substantially affected interests have been given an opportunity to participate in the development of a standard or to comment on its provisions and that their views have been carefully considered. Following a period of public review and comment, ANSI conducts independent verification of the adequacy of consensus and then acts on approval. ANSI also coordinates and manages representation of United States voluntary standards interests in nongovernmental international standards organizations. The major ones are the International Organization for Standardization (ISO) and the International Electrochemical Commission (IEC). ANSI is the official member of both.

ANSI is the clearinghouse and information center for all approved American national standards and the international standards issued by ISO and IEC. In addition, it is the US source of standards issued by the national standardizing bodies that cooperate within ISO.

An important source of corrosion-related standards and specifications not issued by ANSI is the National Association of Corrosion Engineers (NACE) (Ref. 7). The interests of the NACE are heavily weighted toward the oil and gas industry, but increasing emphasis is being given to aerospace applications.

Standards and specifications reflect the interests of the preparing organization. Standardization defines a level of acceptability, and different groups will set the acceptability limit in accord with their concerns and their perceptions of how their concerns may be affected.

**MIL-HDBK-735(MR)****6-2.4 PREPARING STANDARDIZATION DOCUMENTS**

The process of preparing, reviewing, coordinating, and issuing a standardization document, such as a specification or standard, is described in Table 6-2. Key to the preparation of a useful document is the technical competence of the preparing activity and the thoroughness of the review and coordination process. It is important to codify as much of the skill and art in the technology as possible. Nevertheless, a standardization document should not discourage positive innovation.

**6-2.5 SPECIFICATIONS IN QUALITY ASSURANCE**

Specifications are an important component of the procurement documentation package. A military specification follows an established format as indicated in Table 6-3. Quality assurance provisions are stated in Section 4 of a federal or military specification.

Several quality assurance issues are often involved in such a specification. These are

1. Is the relationship between process conditions and coating requirements unique? Will the given process conditions always produce an acceptable product? Can an acceptable product result only from a given set of process conditions?

2. Is the acceptable quality level realistic? Is it being consistently met? (Consistently meeting of the level may imply that it should be higher.) Is it difficult to meet? (Consistent difficulty in meeting the acceptable quality level may imply a mismatch between process conditions and product quality.)

3. Will the specified product always give adequate service in the intended use, as spelled out in Section 6.1 of most Government specifications?

4. Is there adequate Government oversight in terms of frequency and competence of Government checks on the process, product, and contractor quality assurance measures?

**6-3 QUALITY ENGINEERING**

Quality engineering encompasses the design, fabrication and construction, and testing process that assures that a quality item is built, that the as-built quality does

**TABLE 6-3. MILITARY SPECIFICATION FORMAT**

| SECTION | HEADING                      |
|---------|------------------------------|
| 1       | Scope                        |
| 2       | Applicable Documents         |
| 3       | Requirements                 |
| 4       | Quality Assurance Provisions |
| 5       | Packaging                    |
| 6       | Notes                        |
| 6.1     | Intended Use(s)              |

not deteriorate during transportation and storage, and that the effects of operational wear and environmental deterioration are restored through maintenance, repair, and refurbishing. Quality engineering is accomplished through rules, procedures, and practices enforced by organizational elements within an institutional structure.

Quality engineering with respect to corrosion prevention and control (CPC) is described in terms of

1. Logistic support analysis (LSA)
2. The Corrosion Prevention and Control Program of the Army
3. Sampling inspection
4. Environmental engineering and testing
5. Inspection in storage.

**6-3.1 LOGISTIC SUPPORT ANALYSIS**

CPC is an important component of LSA in the original equipment design, in manufacturing, in all levels of maintenance, and in the storage process. The objective is to achieve materiel system designs that are as corrosion-free as possible by using design and manufacturing processes that address

1. Selection of materials, coatings, and surface treatments
2. Production processes and process specifications
3. System geometry
4. Material limitations
5. Environmental extremes
6. Storage and ready conditions
7. Preservation and packaging requirements
8. Repair, overhaul, and repair parts requirements
9. Resource availability.

**TABLE 6-2. SEQUENCE OF STEPS IN PREPARING STANDARDIZATION DOCUMENT**

1. Assignee activity assigns project number to preparing activity upon request.
2. Preparing activity prepares draft of document.
3. Document coordinated by preparing activity with review activities (Army, Navy, Air Force, and Defense Supply Agency) and industry. A limited coordination document is coordinated only within the preparing activity's agency and industry.
4. Essential comments are resolved by the preparing activity or, if necessary, at a higher level.
5. Preparing activity arranges for publication of document.

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Implementation of the LSA process must occur as early in the acquisition process as possible. When LSA is implemented, actions are taken to identify, define, quantify, and process logistic support requirements. This analysis process evolves as the acquisition process progresses. The number and type of iterative analyses vary according to the program schedule and complexity.

LSA is the method used to develop a support system for an acquisition program, and it is the system engineering effort that designs the support system as the end-item is being developed. LSA consists of a series of tasks that study the mission, the environment, the support system and the equipment to determine the best way to support the equipment. As a broad set of studies, LSA is performed by the combat developer (normally the US Army Training and Doctrine Command (TRADOC)), the materiel developer (normally the US Army Materiel Command AMC), and the contractor.

MIL-STD-1388/1A divides LSA tasks into five task sections (Ref. 8). The division is made along logical lines. Good management of the LSA program dictates that plans be established and organizational and control techniques be determined. Therefore, the first task section of the military standard, the program surveillance and control section, addresses the management issues. If supportability issues are to influence the choice of an alternative or influence the design, information about such issues must be gathered. The second task section, mission and support systems definition, is primarily designed to gather information to establish parameters, constraints, goals, and assess risk. The third logical step in the process would be determination, examination, and evaluation of different courses of action. Thus the third task section, preparation and evaluation of alternatives, develops and evaluates those courses of action. The fourth step would provide a description of the support system deemed to be the best based upon the results of the third step. The fourth task section, determination of support and manpower, personnel, and training requirements, describes, by way of task analysis, the skills and other resources required to operate and maintain the hardware. Finally, there should be a feedback loop to provide information on the adequacy of support planning. The fifth task section, supportability assessment, provides this feedback loop. The LSA tasks and subtasks are listed in Table 6-4.

**6-3.2 CORROSION PREVENTION AND CONTROL PROGRAM**

US Army Materiel Development and Readiness Command (DARCOM) Regulation No. 702-24 instituted the Army's Corrosion Prevention and Control program (Ref. 9). Commander's Guidance Statement No. 94 established a CPC Center of Excellence (CTX) to carry out the mission. Quality assurance and quality engineering to obviate metal, coating, and polymer degradation are the focus of the program. The goal of CPC is to insure that vehicles, aircraft, and weapons maintain satisfactory performance under the conditions of storage and tactical environments. To achieve this, the CTX incorporates prevention and control in each stage of the life cycle of a system—design, development, production, fielding, maintenance, and depot rebuild.

CPC programs have been established in five areas: design, management, maintenance, training, and awareness. The design program is set up to incorporate state-of-the-art materials, coatings, and configurations into the design of equipment and into contracts. This procedure will be effected by Corrosion Prevention and Advisory Boards (CPABs). CPABs will consist of the project manager, a depot representative, a CPC CTX representative, and major subordinate command (MSC) personnel from engineering, maintenance, quality assurance, and procurement, who will

1. Review contract requirements
2. Provide design guidance
3. Conduct periodic reviews of contractors, MSCs, and technical data packages
4. Disseminate information relative to CPC to major commands (MACOM) and subordinate organizations.

The maintenance program encourages prevention of corrosion and component life extension rather than replacement. Changes in technical manuals will add the best CPC procedures. Maintenance data are collected to monitor corrosion cost.

The management, training, and awareness efforts work together to incorporate CPC into the day-to-day operation of MSCs and maintenance shops. Army depot surveys will identify areas where CPC can be improved and will educate laboratory personnel about field concerns. Training will familiarize personnel with CPC terms and techniques. The awareness program brings industry products and services into the Army, and it keeps defense contractors aware of the desire of the Army to reduce costs.

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TABLE 6-4. LOGISTIC SUPPORT ANALYSIS TASKS AND SUBTASKS (Ref. 8)

| TASK SECTION                                   | PURPOSE OF TASK SECTION  | TASK/SUBTASK   |
|--|--|--|
| 100—Program Planning and Control               | To provide formal program planning and review actions  | 101 — Development of an early logistic support analysis strategy<br>101.2.1 LSA strategy<br>101.2.2 Updates<br>102 — Logistic support analysis plan<br>102.2.1 LSA plan<br>102.2.2 Updates<br>103 — Program and design reviews<br>103.2.1 Establish review procedures<br>103.2.2 Design reviews<br>103.2.3 Program reviews<br>103.2.4 LSA review   |
| 200—Mission and Support Systems Definition     | To establish supportability objectives and supportability-related design goals, thresholds, and constraints through comparison with existing systems and analyses of supportability, cost, and readiness drivers | 201 — Use study<br>201.2.1 Supportability factors<br>201.2.2 Quantitative factors<br>201.2.3 Field visits<br>201.2.4 Use study report and updates<br>202 — Mission hardware, software, and support system standardization<br>202.2.1 Supportability constraints<br>202.2.2 Supportability characteristics<br>202.2.3 Recommended approaches<br>202.2.4 Risks<br>203 — Comparative Analysis<br>203.2.1 Identify comparative systems<br>203.2.2 Baseline comparison system<br>203.2.3 Comparative system characteristics<br>203.2.4 Qualitative supportability problems<br>203.2.5 Supportability, cost, and readiness drivers<br>203.2.6 Unique system drivers<br>203.2.7 Updates<br>203.2.8 Risks and assumptions<br>204 — Technological opportunities<br>204-2.1 Recommended design objectives<br>204-2.2 Updates<br>204-2.3 Risks<br>205 — Supportability and supportability-related design factors<br>205.2.1 Supportability characteristics<br>205.2.2 Supportability objectives and associated risks<br>205.2.3 Specification requirements<br>205.2.4 NATO constraints<br>205.2.5 Supportability goals and thresholds |
| 300—Preparation and Evaluation of Alternatives | To optimize the support system for the new item and to develop a system that achieves the best balance among cost, schedule, performance, and supportability   | 301 — Functional requirements identification<br>301.2.1 Functional requirements<br>301.2.2 Unique functional requirements<br>301.2.3 Risks<br>301.2.4 Operations and maintenance tasks<br>301.2.5 Design alternatives<br>301.2.6 Updates   |

(cont'd on next page)

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TABLE 6-4. (cont'd)

| TASK SECTION  | PURPOSE OF TASK SECTION  | TASK/SUBTASK   |   |   |
|---|--|--|---|---|
| 400—Determination of Logistic Support Resource Requirements | To identify the logistic support resource requirements of the new system in its operational environment(s) and to develop plans for postproduction support | 302 — Support system alternatives<br>302.2.1 Alternative support concepts<br>302.2.2 Support concept updates<br>302.2.3 Alternative support plans<br>302.2.4 Support plan updates<br>302.2.5 Risks<br>303 — Evaluation of alternatives and tradeoff analysis<br>303.2.1 Tradeoff criteria<br>303.2.2 Support system tradeoffs<br>303.2.3 System tradeoffs<br>303.2.4 Readiness sensitivities<br>303.2.5 Manpower and personnel tradeoffs<br>303.2.6 Training tradeoffs<br>303.2.7 Repair level analyses<br>303.2.8 Diagnostic tradeoffs<br>303.2.9 Comparative evaluations<br>303.2.10 Energy tradeoffs<br>303.2.11 Survivability tradeoffs<br>303.2.12 Transportability tradeoffs |   |   |
|   |  | 401 — Task analysis<br>401.2.1 Task analysis<br>401.2.2 Analysis documentation<br>401.2.3 New/critical support resources<br>401.2.4 Training requirements and recommendations<br>401.2.5 Design improvements<br>401.2.6 Management plans<br>401.2.7 Transportability analysis<br>401.2.8 Provisioning requirements<br>401.2.9 Validation<br>401.2.10 ILS output products<br>401.2.11 LSAR updates  |   |   |
|   |  | 402 — Early fielding analysis<br>402.2.1 New system impact<br>402.2.2 Sources of manpower and personnel skills<br>402.2.3 Impact of resource shortfalls<br>402.2.4 Combat resource requirements<br>402.2.5 Plans for problem resolution  |   |   |
|   |  | 403 — Postproduction support analysis<br>403.2 Postproduction support plan   |   |   |
|   |  | 500—Supportability Assessment  | To assure that specified requirements are achieved and deficiencies corrected | 501 — Supportability test, evaluation, and verification<br>501.2.1 Test and evaluation strategy<br>501.2.2 Objectives and criteria<br>501.2.3 Updates and corrective actions<br>501.2.4 Supportability assessment plan (postdeployment)<br>501.2.5 Supportability assessment (postdeployment) |

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### 6-3.3 SAMPLING INSPECTION

The best protection against the acceptance of a defective product is having the product made correctly in the first place. The greatest contribution that statistical quality control makes to better quality lies not in what it contributes to sampling inspection, but in the way it helps to produce a better product.

Inspection is the examination or testing of supplies and services (including where applicable raw materials, documents, data, components, and intermediate assemblies) to determine whether the supplies and services conform to technical and contractual requirements. The inspection criteria used to determine whether the quality requirements have been met are stated in appropriate documents, such as purchase descriptions, project descriptions, inspection instructions, technical orders, drawings, technical bulletins, and military specifications.

Sampling inspection of Army materiel is governed by the following military standards:

1. MIL-STD-105, *Sampling Procedures and Tables for Inspection by Attributes* (Ref. 10)
2. MIL-STD-414, *Sampling Procedures and Tables for Inspection by Variables for Percent Defective* (Ref. 11)
3. MIL-STD-1235, *Single and Multilevel Continuous Sampling Procedures and Tables for Inspection by Attributes, Functional Curves of the Continuous Sampling Plans* (Ref. 12).

Guidance for applying these standards is given in MIL-HDBK-53, *Guide for Sampling Inspection*. This handbook is in three parts that relate specifically to the three military standards that follow:

1. MIL-HDBK-53/1, *Guide for Attribute Lot Sampling Inspection and MIL-STD-105* (Ref. 13)
2. MIL-HDBK-53/2, *Guide for Attribute Continuous Sampling Inspection and MIL-STD-1235* (Ref. 14)
3. MIL-HDBK-53/3, *Guide for Variable Lot Sampling Inspection and MIL-STD-414* (Ref. 15).

Persons with responsibility for specifying acceptance inspection requirements should consult this handbook and the related military standard. The following discussion summarizes MIL-HDBK-53/1.

#### 6-3.3.1 Summary of MIL-HDBK-53/1

Adherence to MIL-STD-105 is frequently required in specifications related to corrosion prevention and control. Inspection by attributes is inspection in which certain characteristics of a product are classified simply as defects or nondefects. If a unit of product contains one or more defects, it is designated as a defective unit. Inspection by variables, as required by MIL-STD-414, is inspection in which a quality characteristic of each unit of product in a sample is measured and the measure is expressed in some cardinal scale, e.g., millimeters of

thickness, hours of duration, and grams of mass. Variables can be converted to attributes by setting some point or range on the scale that separates a defect from a nondefect.

Continuous sampling for inspection by attributes is covered in MIL-STD-1235. In continuous sampling inspection, units are produced and submitted consecutively in the order produced. Lot-by-lot sampling inspection requires that each individual lot be accepted or rejected as a whole, based on inspection results from a sample or samples drawn at random from the lot. As required in MIL-STD-105, each lot or batch should consist of homogeneous units of product. The size of the lot or batch is one of the factors that determines the sample size to be used in sampling inspection.

An attribute lot sampling plan is a statement of the sample size or sizes to be used and the associated acceptance and rejection numbers. The acceptance number is the maximum number of defects or defective units in the sample that will allow acceptance of the lot. The rejection number is the minimum number of defects or defective units in the sample that will cause rejection of the lot.

Attribute lot sampling plans can be grouped into four basic types: single, double, multiple, and sequential. In a single sampling plan the results of a single sample from an inspection lot are conclusive in determining its acceptability. A double sampling plan involves sampling inspection in which the inspection of the first sample leads to a decision to accept, to reject, or to take a second sample. The inspection of the second sample, when required, then leads to a decision to accept or reject the lot. In multiple sampling the decision to accept or reject an inspection lot is reached after one or more samples from the inspection lot have been inspected. The decision will always be reached after not more than a designated number of samples have been inspected. Sequential sampling selects one sample unit at a time, and after each unit is inspected, the decision is made to accept the lot, reject the lot, or inspect another unit. Sampling terminates when the cumulative inspection results determine that an acceptance or rejection decision can be made.

The average amount of inspection for any sampling plan can be computed. On the average, double sampling plans usually require less inspection than single sampling plans, and multiple sampling plans usually require less inspection than double sampling plans.

One hundred percent inspection is the inspection of every unit of product. Sampling inspection is that type of inspection in which a sample consisting of one or more, but not all units of product, is selected at random from the production process output and examined for one or more quality characteristics. When deciding which inspection method to employ, the engineers must

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weigh the lower costs of sampling inspection against the risk of greater cost incurred by permitting defective units of product to be accepted. For quality characteristics deemed to be critical, one hundred percent inspection is required.

According to MIL-STD-105, a critical defect is one that is likely to cause hazardous or unsafe conditions for individuals using, maintaining, or depending on the product. The critical classification is also used for a defect that is likely to prevent performance of a major end-item. Other defect categories are major and minor defects.

Selection of a sampling plan involves consideration of the following:

1. Properties of the sampling plan
2. Ease of administering the sampling plan
3. Protection afforded
4. Amount of inspection required
5. Cost of inspection
6. Size of the lot
7. Continuity of lots (Are the lots being inspected in sequence one after the other from the same producer, or are they a group of isolated lots?)
8. Cost to the consumer resulting from acceptance of a nonconforming item
9. Cost of manufacturing the item
10. Cost of delayed shipments
11. Availability of product from other sources
12. Consumers' past experience with product from the same producer
13. Product packaging
14. Possibility of correcting nonconforming conditions during use.

Several methods have evolved for grouping or indexing sampling plans. MIL-STD-105 makes use of sampling plans based on acceptable quality level (AQL). The worst level of acceptable quality is the AQL. The AQL is defined for lot sampling plans as the maximum percent defective that, for the purpose of sampling inspection, can be considered acceptable as a process average. A typical AQL plan might be based upon a statement by the consumer that he will accept lots of product 97% of the time when the product average is 4% (AQL 4%) or better. The corresponding producer's risk, i.e., the probability of rejecting acceptable product, is  $1 - 0.97 = 0.03$  or 3%.

A large variety of sampling plans can be devised or selected on the basis of the level of protection offered to the producer and/or the consumer at a given quality level. The protection afforded by a sampling plan, i.e., its capability to discriminate between good and bad quality can be accurately calculated. The fact that these risks can be quantified makes it possible to state them statistically (numerically) and predict the quantities rejected on the average over the entire range of possible

product quality. The curve of Fig. 6-1 indicates the relationship between the quality of lots submitted for inspection and the probability of acceptance. Such a curve is called the operating characteristic, or OC curve, of the plan. The risk pattern of each sampling plan is represented by the OC curve of that plan. Thus by studying the OC curve for each plan under consideration, it is possible to compare the relative risks of sampling plans for a given sampling situation. A sampling plan and its associated risks are completely defined by the lot size, sample size, and acceptance number. Except in the case of very small lots, the lot size has relatively little importance in most cases in determining the risks associated with any given sampling plan.

If the risks of a tentative sampling plan are considered unsatisfactory, the effects of sample size and acceptance number on the OC curve can indicate the changes necessary to achieve a satisfactory risk level. An increase in sample size results in a steepening of the OC curve. The steeper the OC curve, the greater the power of the sampling plan to discriminate between "good" and "bad" quality. In general, the effect of increasing the acceptance number is to shift the location of the entire OC curve to the right. Changing the sampling plan in this way generally increases the probability of accepting a lot at a given quality level. Both MIL-STD-105 and MIL-STD-414 contain OC curves for each sampling plan, i.e., sample size and acceptance-rejection criterion, listed.

The severity of inspection is reflected by the total amount of inspection and the accept-reject criterion specified by the quality assurance provisions for the unit of product. Lot sampling inspection provides for two or three degrees of severity of inspection: normal and tightened, or normal, tightened, and reduced. Sam-

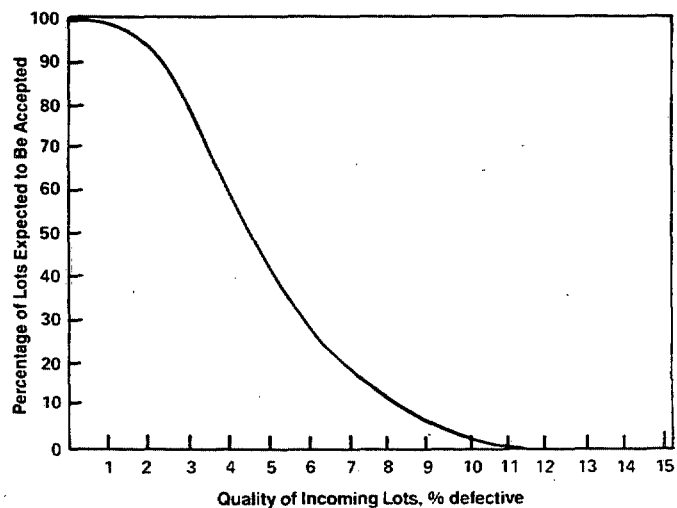


Figure 6-1. Typical Sampling Plan Operating Characteristic (OC) Curve (Ref. 13)

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pling plans with two or three degrees of severity and with the rules of switching from one degree of severity to another are called sampling schemes.

Normal inspection is used when there is no evidence that the quality level of the product being submitted is other than the specified quality level. Normal inspection is usually used at the start of an inspection. Tightened inspection is instituted in accordance with established procedures when it becomes evident that product quality is deteriorating. Reduced inspection may be instituted in accordance with established rules when it is evident that product quality is very good. Tightened inspection is usually met by decreasing the number of defectives or defects per hundred units produced in the sample. Reduced inspection normally requires a smaller sample size than does normal inspection under the same sampling scheme.

Basic to sampling inspection is the selection of a sample that can reasonably be expected to represent the quality of the parent lot. The process of selecting a sample meeting this requirement is called random sampling. Random sampling is any procedure used to draw units from an inspection lot so that each unit in the lot has an equal chance without regard to its quality of being included in the sample. MIL-HDBK-53/1A describes several methods used to achieve random sampling.

When sampling inspection is conducted under a lot sampling plan, the entire lot is rejected if the acceptance criterion is not met. The rejection of many lots introduces many problems for both the producer and the consumer. Sometimes the consumer may agree to buy the rejected lot at a reduced price, especially when the product is in great demand and short supply. The more customary practice, however, requires the rejected lots to be screened, defective units reworked or replaced, and the lot resubmitted by the supplier.

Defective units found by sampling or screening of rejected lots should not be mixed with production lots. At the discretion of the responsible authority, defective units may be

1. Reworked and accumulated over a period of time for subsequent resubmission as a miscellaneous lot that will be inspected for all characteristics
2. Reworked and submitted with the lot from which they were screened
3. Submitted by the supplier with a request for deviation approval
4. Disposed of as scrap by the supplier
5. Disposed of as agreed upon by the supplier and responsible authority.

A resubmitted lot should be given normal or tightened inspection and never reduced inspection. Also sampling plans with an acceptance number of zero may be used.

Should resubmitted lots be inspected for all types or

classes of defects or only for the particular types or classes of defects that caused initial rejection? If only screening was required, inspection can be limited to the class of defects that caused rejection. If the lot was reprocessed, however, a possibility exists that additional defects have been introduced. In such cases, inspection should be performed for all classes of defects.

### 6-3.3.2 Application of MIL-STD-105

MIL-STD-105 is designed for attributes lot-by-lot inspection. The main purpose of every MIL-STD-105 scheme is to accept with a high probability lots whose quality level is equal to or better than the AQL. The AQL is defined as the minimum percent defective that can be considered satisfactory as a process average. The process average is the average percent defective or the average number of defects per hundred units of product submitted by the supplier for original inspection. The estimated process average for a series of lots from sampling inspection data is the ratio of the total number of defectives in the samples from the lots to the total number of units in the sample. (The ratio is multiplied by 100 to give percent.)

The AQL should be considered an index to a sampling plan. The plans are indexed by AQL and by sample size. The sample size is determined from the sample size code letter and from the inspection level. Equivalent single, double, and multiple sampling plans are given. Tables are given for normal, tightened, and reduced inspection together with rules for switching from one type to another.

The sampling plans in MIL-STD-105 are applicable to attribute inspection of the following:

1. *End-Items.* These are completed products that may be inspected before or after packaging and packing for shipment or storage.

2. *Components and Raw Materials.* These are the materials that are shaped, treated, or assembled to form end-items. These materials may be inspected at their source, upon receipt at the point of assembly, or at any convenient place along the assembly process where the end-items are formed.

3. *Operations.* In many cases repetitive work performed by machines and operators can be judged to be acceptable or unacceptable. These work operations may be inspected on a sampling basis to determine whether the process machine, operator, and clerk are performing satisfactorily.

4. *Materials in Process.* Materials may be inspected on a sampling basis to determine their quality after any step along the production line. Inspection may be for quality characteristics that were built into the materials by the production process or for damage or deterioration that occurred while the materials were in temporary storage between production steps.



**MIL-HDBK-735(MR)****5. Supplies in Storage.**

**6. Maintenance Operations.** These operations are usually performed on repairable materials to restore them to serviceable condition. When maintenance or overhaul operations are performed, attribute inspection is made to determine the quality of the product after reconditioning operations have been completed.

**7. Data or Records.** Whenever large volumes of data are processed, e.g., accounting records, cost data, invoices, bills of lading, etc., the attribute sampling inspection procedures of MIL-STD-105 can be used to determine dollar volume, item count, accuracy, or other measures of quality of the data or records.

**8. Administrative Procedures.**

A typical sequence of operations using the sampling procedures and tables for inspection by attributes of MIL-STD-105 is illustrated in Table 6-5.

Inspection levels in general provide the quality engineer a means by which to select one of several sample size code letters for a given lot size. The effect of

offering this choice is to offer several sampling plans, each with approximately the same probability of acceptance when lot quality is worse than the AQL. Table I of MIL-STD-105 gives three general inspection levels numbered I, II, and III and four special inspection levels, numbered S-1, S-2, S-3, and S-4. The general levels are used most often, and it is assumed that Level II is used unless another level is specified. The special inspection levels are designed for situations in which the sample size must be kept small.

When selecting an inspection level, the responsible authority should analyze the following factors in order to optimize the cost-risk relationship:

1. The operating characteristic curves to evaluate the technical properties of the various plans
2. The suppliers' risks and discriminations afforded by the various inspection levels
3. Knowledge of the production process
4. Process capability and quality performance history

**TABLE 6-5. SEQUENCE OF STEPS FOR ATTRIBUTE SAMPLING INSPECTION (Ref. 13)**

| STEPS  | EXPLANATION   |
|--|---|
| 1. Determine lot size                          | 1. Lot size is controlled by the lot formation criteria contained in procurement documents. Otherwise it is established by agreement between the responsible authority and the supplier.  |
| 2. Determine inspection level                  | 2. If the item specification does not give the inspection level, use inspection Level II.   |
| 3. Determine sample size code letter           | 3. The code letter is found in Table 1, MIL-STD-105, and is based on lot size and inspection level.   |
| 4. Determine sampling plans                    | 4. Single sampling is generally selected, although double or multiple sampling may be used.   |
| 5. Establish severity of inspection            | 5. Normal inspection is generally used at the start of a contract or production.  |
| 6. Determine sample size and acceptance number | 6. Assuming normal inspection and given the specified AQL value and sample size code letter, the engineer will find the sample size and acceptance number in Table II-A, MIL-STD-105.   |
| 7. Select sample                               | 7. The sample, consisting of the number of units determined in Step 6, is selected at random from the lot. Additionally, any obvious defectives that have not been selected for the inspection sample are removed from the lot. |
| 8. Inspect sample                              | 8. The defectives (or defects) are counted. If this count does not exceed the acceptance number, the entire lot is accepted. If the count equals or exceeds the rejection number, the lot is rejected.                          |
| 9. Record inspection results                   | 9. Compute the estimated process average if required by operating procedures. Maintain a record of accept-reject decisions so that switching rules may be followed.   |
| 10. Resubmit lot                               | 10. If the lot is not accepted, it may be resubmitted for acceptance only after all units of the lot are reinspected and all defective units are removed or reworked.   |

**MIL-HDBK-735(MR)****5. Item complexity**

**6. Cost and importance of examination or test, particularly when testing is expensive, time-consuming, and/or destructive**

**7. Importance of the quality characteristics being examined, i.e., whether critical, major, or minor**

**8. Analysis of consumers' risks.**

In MIL-STD-105 the sample size is made to depend upon the lot size for the following reasons:

1. A sample of small size that has a high probability of representing the quality of a small lot or batch may be too small to represent with high probability the quality of a large lot or batch.

2. Lots from a good process are more likely to be accepted as the lot size increases, whereas lots from a bad process are more likely to be rejected.

3. A sample size can be afforded with a large lot that would be uneconomical for a small lot.

Six different values of sample size correspond to any given code letter according to whether single, double, or multiple sampling is used and to whether or not reduced inspection is in force. These different values are why code letters rather than purely sample sizes are needed to index tables in MIL-STD-105.

To achieve a balance between consumer and producer protection, the device adopted in MIL-STD-105 is that of normal inspection and tightened inspection. Two sampling plans with rules for switching between them are specified for any given situation. Normal inspection gives the producer the benefit of the doubt, but when sampling results show that an excessive number of lots are being rejected, tightened inspection is instituted to protect the consumer.

In general, a tightened plan has the same sample size as the corresponding normal plan, but it has a smaller acceptance number. If the normal acceptance number is one, however, tightening is achieved by retaining the normal acceptance number and increasing the sample size.

The rule for switching from normal to tightened inspection is that tightened inspection must begin as soon as two of five successive lots have been rejected under original inspection. Once tightened inspection has been instituted, normal inspection is not restored until five successive lots have been accepted under tightened inspection. Acceptance inspection may be continued pending action to improve the quality if 10 (or some other number specified by the responsible authority) consecutive lots remain under tightened inspection. If production quality is consistently good, considerable savings can result by using reduced inspection sampling plans, which have sample sizes only two fifths the size of the normal inspection plans. In addition to the reduction in sample size, the reduced sampling plans have an increased acceptance number.

Reduced inspection is not automatic based on the switching rule alone; it is at the discretion of the responsible authority. A return to normal inspection is required if a lot is not accepted under reduced inspection.

When a defect classification system has been defined for an item, an AQL is assigned to each defect class; thus there would be a separate sampling plan corresponding to each AQL. When defects are classified with separate AQLs for the different classes or group of classes, the switching between normal and tightened inspection is done independently for each class or group of classes for which an AQL is specified. Switching is based upon acceptances or rejections for that particular class or group.

Although the principles of extracting double or multiple plans from the tables of MIL-STD-105 are similar to those for single sampling, the appropriate tables must be used. Successive samples in all plans are equal in size to the first samples. Acceptance and rejection numbers are cumulative. Once an inspection has begun on a sample from a lot under either a single-, double-, or multiple-type sampling plan, inspection is to continue with that type of plan until inspection of the lot is completed. If an appropriate single sampling plan has an acceptance number of zero or a sample size of two, no double or multiple plan is available.

Average sample size curves for double and multiple sampling are given in Table IX MIL-STD-105. These curves are classified by the value of the single sampling acceptance number and may be used to decide whether the reduced amount of sampling from the double or multiple sampling compared to single sampling will be sufficient to be worthwhile. Other factors to be considered in selecting a single, double, or multiple sampling plan are

1. The cost of administering the double or multiple sampling plan compared to the cost of administering a single sampling plan

2. The need for quick and reliable estimates of the process average

3. The availability of inspection personnel and facilities.

The sampling plans in Tables II through V of MIL-STD-105 are designed with consideration only for the risk to the supplier. The sample size, the acceptance number, and the rejection number are chosen to provide a high probability of acceptance when the quality of the lot is at the AQL or better. When the requirement for a low probability of accepting lots with a high percent defective exists, it is usually stated in terms of limiting quality (LQ). LQ is the worst quality the consumer is willing to accept. This low probability of acceptance is called the consumer's risk. Tables VI and VII of MIL-STD-105 give values of LQ for consumers' risks of 10 and 5%, respectively.

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With a few isolated lots there is little or no opportunity for detection of product deterioration and a subsequent shift to a tightened sampling plan. With isolated lots, therefore, it is desirable to begin sampling with a sampling plan that reduces the consumer's risk of accepting a lot with quality worse than LQ. MIL-STD-105 provides sampling procedures for assuring the consumer that lots of quality equal to LQ or worse will be accepted with low probability. The provisions of the standard allow for situations in which either the AQL or the sample code letter are specified along with the LQ.

**6-3.3.3 Example Sampling Plan**

An important corrosion-related specification is MIL-G-45204C, *Gold Plating, Electrodeposited* (Ref. 16). The Section 4, "Quality Assurance Provisions", contents are listed in Table 6-6. The contractor is responsible for all inspections, but the Government reserves the right to perform any of the inspections (4.1). A lot is defined as articles of the same basic metal, type, grade, and class

that are plated under the same conditions and of approximately the same size and shape and are submitted for delivery at one time (4.2). In no instance, however, should the lot exceed the product for one week. One lot sampling criterion is given for visual examinations and another for the other properties to be inspected (4.3). Visual examinations include the determination of removal of plating salts, quality of workmanship, and the existence of identification markings. The other properties to be inspected are plating thickness, adhesion, hardness, heat resistance, embrittlement, and solderability.

The sample for visual examination is inspection Level III with an AQL equal to 1.0% defective in accordance with MIL-STD-105. The sample of the other tests is inspection Level S-3 with an acceptance number of 0 defects in accordance with MIL-STD-105. Inspection is based on attributes because MIL-STD-105 is referenced. The quality requirements that can be specified are listed in Table 6-7. These are taken from par. 6.2, "Ordering data", of MIL-G-45204C. Those attributes that are the

**TABLE 6-6. CONTENTS, PARAGRAPH 4, MIL-G-45204C (Ref. 16)**

|           |  |
|-----------|--|
| 4.        | QUALITY ASSURANCE PROVISIONS   |
| 4.1       | Responsibility for inspection  |
| 4.2       | Lot  |
| 4.3       | Sampling   |
| 4.3.1     | For visual examination   |
| 4.3.2     | For thickness, adhesion, heat resistance, embrittlement, and solderability |
| 4.3.2.1   | Separate specimens   |
| 4.3.2.1.1 | Separate specimens for hardness  |
| 4.3.2.1.2 | Separate specimens for embrittlement relief                                |
| 4.4       | Visual examination   |
| 4.5       | Test procedures  |
| 4.5.1     | Thickness measurements   |
| 4.5.1.1   | Microscopic test   |
| 4.5.1.2   | Beta-backscatter radiation   |
| 4.5.1.3   | X-ray fluorescence   |
| 4.5.2     | Adhesion tests   |
| 4.5.2.1   | Bend test  |
| 4.5.2.2   | Cutting test   |
| 4.5.2.3   | Baking test  |
| 4.5.3     | Hardness   |
| 4.5.4     | Heat resistance  |
| 4.5.5     | Solderability test   |
| 4.5.6     | Embrittlement relief   |
| 4.5.6.1   | Fasteners  |
| 4.5.6.2   | Spring pins, lock rings, etc.  |
| 4.5.6.3   | Other parts  |
| 4.5.7     | Composition  |
| 4.6       | Rejection  |
| 4.6.1     | Examination defects  |
| 4.6.2     | Tests  |
| 4.7       | Reduced testing  |

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subject of inspection are indicated in the table.

In some cases plated articles are not suitable for testing. In other cases sampling of small lots for destructive tests is not desirable. In these situations tests may be conducted on separate specimens plated concurrently with the articles represented. Par. 4.3.2.1 of MIL-G-45204C, "Separate specimens", describes the requirements of these specimens, par. 4.3.2.1.1 describes the requirements for separate specimens for hardness testing, and par. 4.3.2.1.2 describes separate specimens for embrittlement relief testing. Testing for hardness and for embrittlement relief are both destructive in nature.

Compliance with the requirements for removal of plating salts, workmanship, and identification marking

is based upon a visual examination, which is typically carried out at four diameters magnification. Requirement for removal of plating salts, workmanship, and identification marking are described in pars. 3.7.1, 3.8, and 3.9 of MIL-G-45204C, respectively.

Test procedures for compliance with plating thickness, coating purity, heat resistance, solderability, and embrittlement relief are described in par. 4.5 as are the tests required for associated parts, such as fasteners, spring pins, and lock rings.

Rejection criteria are described in par. 4.6, and discretionary reduced testing is described in par. 4.7 of MIL-G-45204C.

An example sample plan based upon a lot or batch size of 500 articles is given in Table 6-8.

**TABLE 6-7. SPECIFICATION REQUIREMENTS FOR ARTICLES CONFORMING TO MIL-G-45204C (Ref. 16)**

"6.2 *Ordering data.* Purchasers should exercise any desired options offered herein and procurement documents should specify the following:

- (a) Title, number, and date of this specification.
- (b) Type, grade and class (or thickness) required (see 1.2).
- (c) Finish required, bright or matte (see 3.1).
- (d) Strikes and underplating required (see 3.4 and 6.3).
- (e) Location of a significant surface (see 3.6.1).
- (f) When heat resistance requirement applies (see 3.6.1).
- (g) Degree of smoothness when required and method of determination (see 3.6.5).
- (h) When embrittlement relief is required and alternate temperature when applicable (see 3.7.2).
- (i) When solderability test is required (see 3.6.6).
- (j) When identification marking is required on the articles (see 3.9).
- (k) Visual examination at 4 diameters magnification, if required (see 4.4).
- (l) Whether baking test for adhesion is required.
- (m) Preparation for delivery (see 5.1).

6.2.1 The manufacturer of the basic metal parts should provide the plating facility with the following data:

- (a) Whether heat treatment has been performed or is required for stress relief (see 3.2.2).
- (b) Hardness of steel parts.
- (c) Ultimate use.
- (d) Tensile loads required for embrittlement relief test (see 4.5.6)."

References are to specification paragraph.

**TABLE 6-8. EXAMPLE SAMPLE PLAN**

|                         | TYPE OF EXAMINATION OR TEST |        |
|-------------------------|-----------------------------|--------|
|                         | VISUAL                      | OTHER  |
| Lot or batch size       | 500                         | 500    |
| Type of sampling        | Single                      | Single |
| Degree of sampling      | Normal                      | Normal |
| Level of inspection     | III                         | S-3    |
| Sample size code letter | J                           | D      |
| Sample size             | 80                          | 8      |
| AQL                     | 1%                          | 0%     |
| Reject acceptable       | 1                           | 0      |
| Rejects unacceptable    | 2                           | 1      |

**MIL-HDBK-735(MR)****6-3.4 ENVIRONMENTAL ENGINEERING AND TESTING**

A key component of the quality assurance process are tests that evaluate the effects of natural and induced environments on military materiel. These tests are intended for appreciation early in the engineering and manufacturing development phase of the materiel acquisition process; however, selected application at other points in the acquisition process may be appropriate.

The test methods of MIL-STD-810 (Ref. 17) are intended to be applied in support of the following objectives:

1. To disclose deficiencies and defects and verify corrective actions
2. To assess equipment suitability for its intended operational environment
3. To verify contractual compliance.

Tailoring is a process of modifying existing benchmark environmental tests to assure that military equipment is designed and tested for resistance to the environmental stresses it will encounter during its life. To assure that proper consideration is given to environments, environmental management plans are formulated. These plans require the following engineering tasks:

1. Determination of life cycle environmental conditions
2. Establishment of environmental design and test requirements, including a test plan
3. Collection and analysis of field data for verification of environmental design and test criteria

Proper attention to each of these tasks insures that

1. The correct environments are identified for testing
2. Engineering development as well as qualification tests are properly phased into the acquisition program of the item
3. Environmental test conditions are traceable to realistic life cycle conditions.
4. Testing is appropriate for the item application.

The overall management of an environmental test program includes consideration of manpower requirements, scheduling, life cycle environmental conditions, test tailoring, test performance, analysis of results, corrective actions, and collection of data about, and analysis of, actual field environments.

A history of events and associated environmental conditions for an item from its release from manufacturing to its retirement from use is determined. This history should include the various stages an item will encounter in its life, such as handling, shipping or storage prior to use, phases between missions such as standby, storage, or transfer to or from repair sites, geographical locations of expected deployment, and

platform requirements. Fig. 6-2 shows generalized environmental profiles that may be used as a baseline to identify the environments most likely to be associated with each stage. The following factors should also be considered:

1. Configuration of the hardware
2. Environment encountered
3. Platform with which the hardware interfaces
4. Interfaces with other equipment
5. Absolute and relative duration of exposure phase
6. Number of times phase will occur and intermittence of phase
7. Probability of occurrence of environmental conditions
8. Geographic location
9. Any other information that will help identify any environmental conditions that may act upon the item.

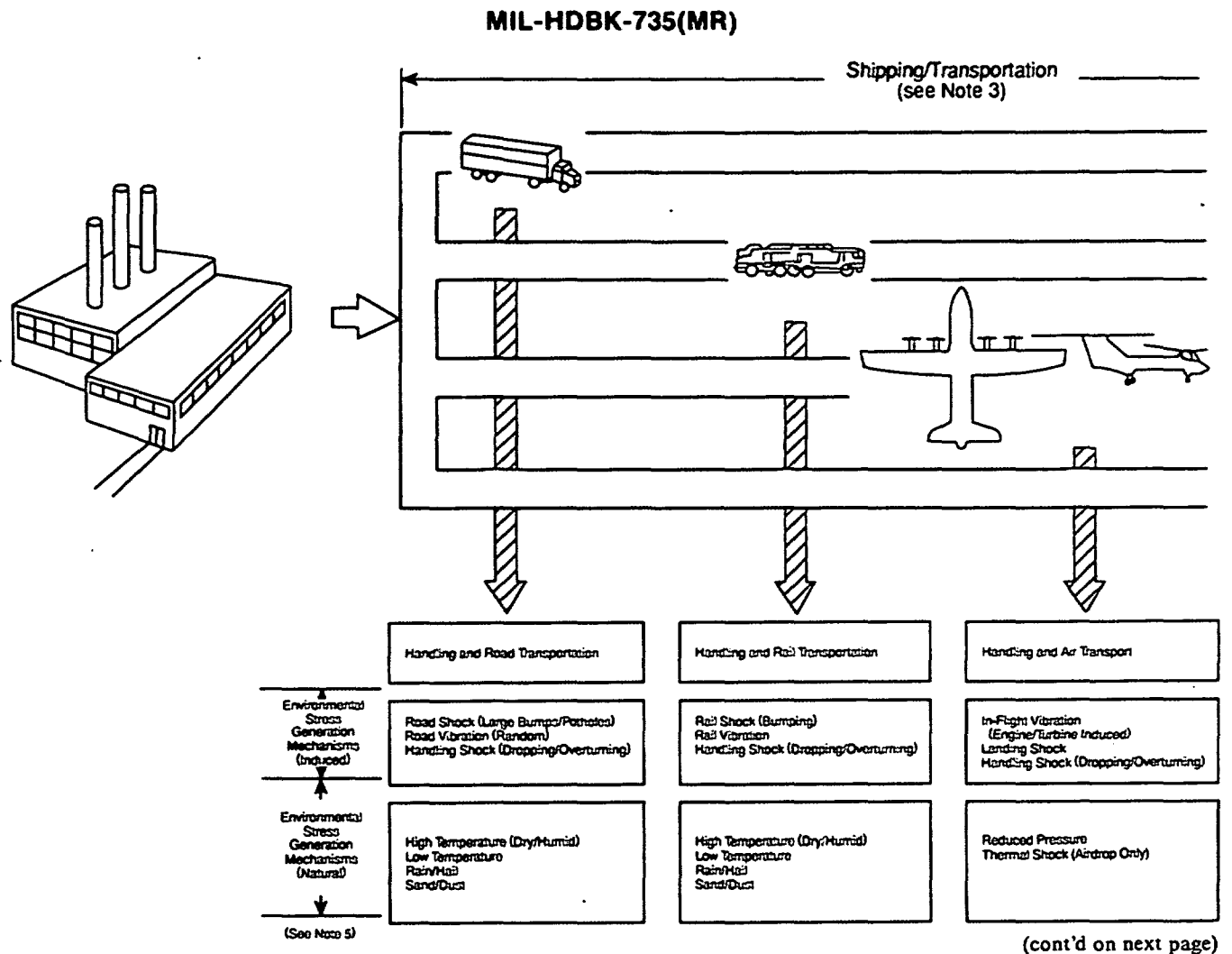
During formulation an environmental test plan, consideration should be given to the following:

1. Probability of environmental occurrence, alone or in combination
2. Expected effects and failure modes
3. Effect on hardware performance and mission success
4. Likelihood of disclosure of problem by the test methods
5. Occurrence of similar environmental stress in more than one stage
6. Experience gained from other equipment similarly deployed.

An operational environmental verification plan should include plans to obtain data on the actual operating or field environments to which the test item will be exposed for comparison with design and test criteria. The plan provides the basis for an analysis of the adequacy of the experimental program.

Field data used in environmental test methods should meet the following requirements:

1. Measurements under controlled environmental conditions should be made on the same test item and/or platform type that will carry the item being tested. It should be noted that equipment may be functionally dissimilar and still be considered similar for environmental stress conditions.
2. Supporting information should include a description of the equipment or supporting platform, the location of the hardware or carrying platform at which the measurements were made, the environmental and operating conditions under which the measurements were made, and the type and calibration status of the data recording and analysis equipment and instrumentation.



**Figure 6-2. Generalized History of Military Hardware (Ref. 17)**

3. Data of quality and quantity to describe the conditions being evaluated should be supplied. Before testing, the test item should be operated at standard ambient conditions to obtain and record data used to determine compliance with the requirements documents and to compare with data obtained before, during, and after the environmental test. The identification and environmental test history of the specific test items should be documented for failure analysis purposes.

The pretest record should include

1. The functional parameters to be monitored during and after the test if they have not been specified in the equipment specification or requirements document. When operation of the test item is required, acceptable functional limits should be included.

2. Additional evaluation criteria.

Unless otherwise specified the test item should be installed in the test facility in a manner that will simulate service usage with connections made and instrumentation attached as necessary:

1. Plugs, covers, and inspection plates not used in operation but used in servicing should remain in place.

2. Mechanical or electrical connections not used but normally protected in service should be adequately protected.

3. For tests during which temperature values are controlled, the test chamber should be at standard ambient conditions when the test item is installed or as specified in the individual methods.

4. The test item should be operated to determine that no malfunction or damage was caused due to faulty installation or handling. The requirement for operation following installation of the test item in the test facility is applicable when operation is required during exposure to the specified test.

5. Test items should be positioned at a sufficient distance from each other or from walls, floors, ceilings, etc., to allow for adequate circulation.

6. If the item to be tested consists of several separate units, these units may be tested separately if the functional aspects are maintained as defined in the

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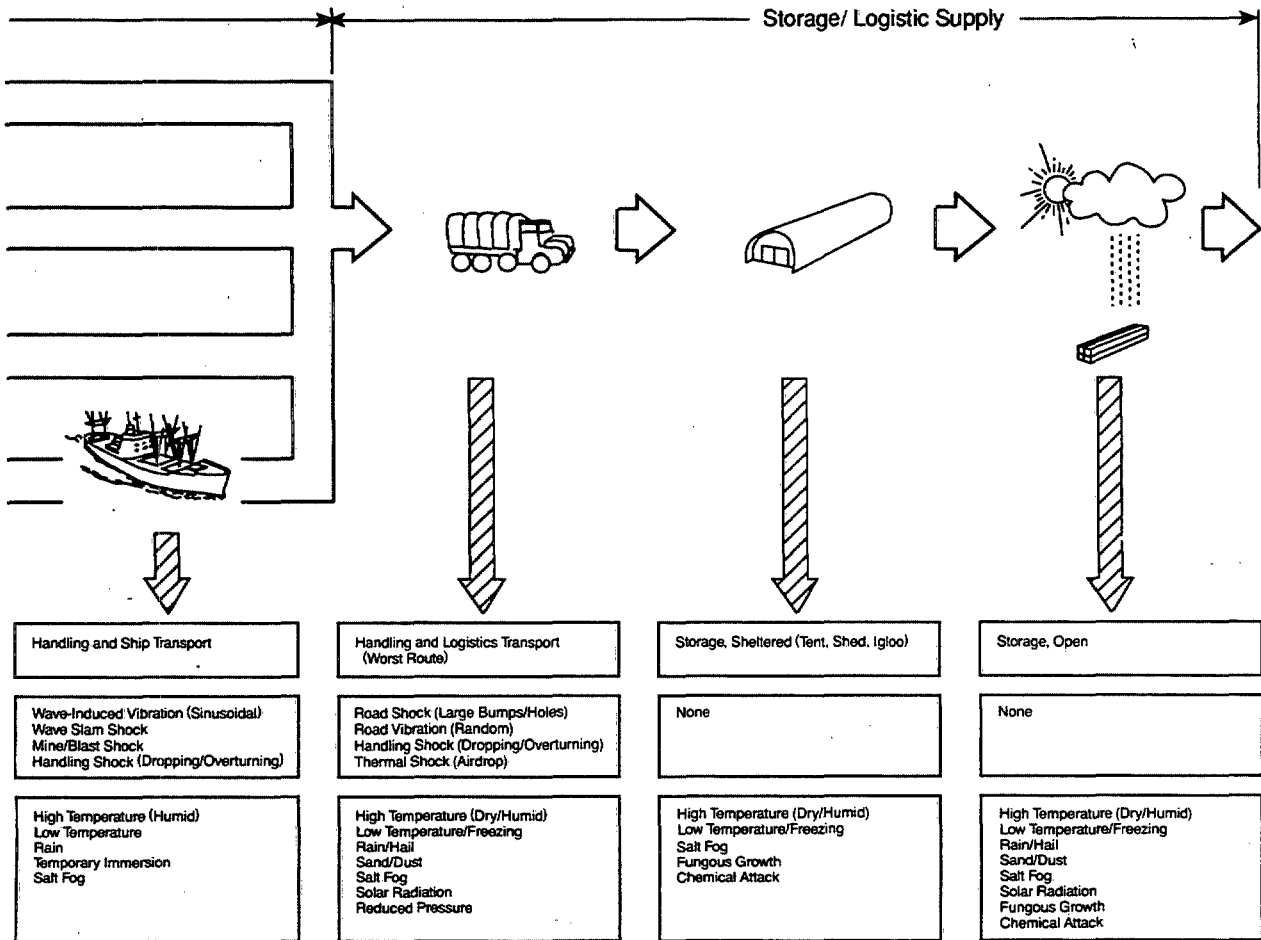


Fig. 6-2 (cont'd)

(cont'd on next page)

requirements document.

When operation of the test item is required during the test exposure, suitable tests should be performed to determine whether the test exposure is producing changes in performance when compared with pretest data.

Unless otherwise specified in the individual test methods, the procedures given in MIL-STD-810 should be followed when a test is interrupted. Guidance is given for intolerance, undertest, and overtest interruptions.

Because combined tests can produce a more realistic representation of the effects of the environment than a series of single-factor tests, combined tests should be used if possible.

At the completion of each environmental test, the test item should be inspected in accordance with the equipment specification, and the results compared with the pretest data. Posttest data should include

1. Complete identification of all test equipment and accessories
2. The actual test sequence (program) used

3. Deviation from the normal test program
4. The room-ambient test conditions recorded periodically during the test period
5. Test item operational data
6. A signature-and-date block for certification of the test data by the test engineer
7. Other data as specified in the individual methods or data requirements documents.

Failure of the test item to meet any one of the conditions that follow constitutes a test item failure:

1. Deviation of monitored functional parameters beyond acceptable limits
2. Nonfulfillment of safety requirements or the development of safety hazards
3. Nonfulfillment of specific test item requirements
4. Changes to the item that could prevent the equipment from meeting its intended service life or maintenance requirements. For example, a corroded oil plug cannot be removed with the specified tools.
5. Deviation from established environmental requirements
6. Additional or different failure criteria, as speci-

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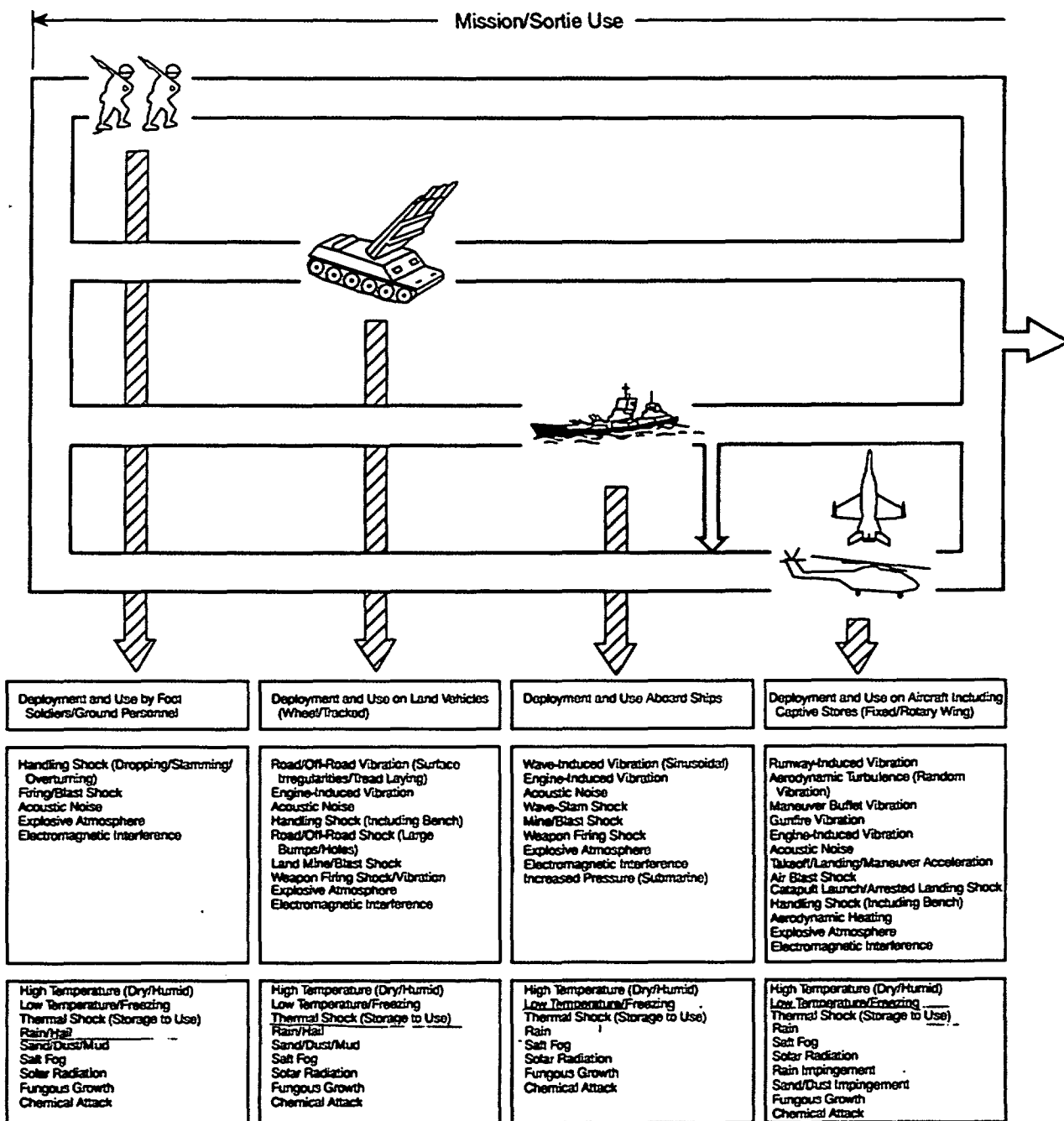


Fig. 6-2 (cont'd)

(cont'd on next page)

fied in the equipment specification.

The climatic regions specified by MIL-STD-810 are designated hot-dry, hot-humid, and cold. Further environmental characterization is given in par. 2.3 of the standard.



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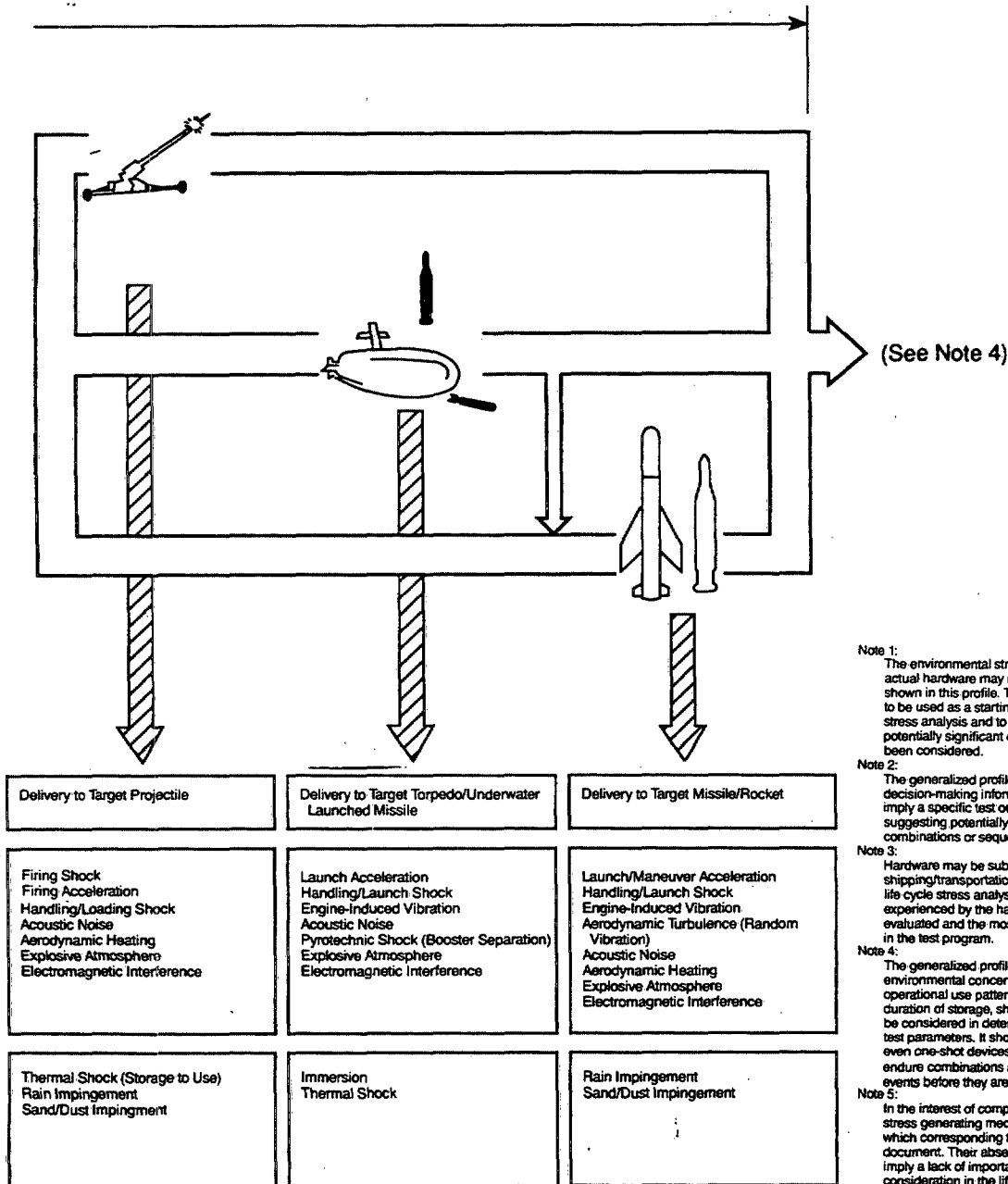


Fig. 6-2 (cont'd)

6-3.5 INSPECTION IN STORAGE

Corrosion prevention and control is usually viewed as producing a durable product that incorporates corrosion prevention measures such as protective coatings. Acceptance sampling inspection determines the quality status of a product as manufactured. If consideration is given during the design of a product to its environmental exposure in transportation, storage, and use, acceptance inspection alone may be adequate to insure a corrosion-resistant product. However, adequate attention is often not given to the exposure conditions of

a product. There may be uncertainty regarding the anticipated environmental exposure or regarding the effects of such environmental exposure on the product.

Environmental testing can reduce uncertainty in the effects of environmental exposure. If some degree of uncertainty remains, however, it is necessary to inspect the product at various times throughout its life. If it has deteriorated through the action of environmental exposure, remedial action can be taken to repair and refurbish the product and to modify, if possible, its environmental exposure. In the field (where the products may be in use) deterioration will be evident to the user,

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but special attention should be given to the product in storage. The Army has unique requirements for long-term storage and stockpiling of materiel in anticipation of contingent future needs.

Storage inspection of materiel items should be integrated with issue policies that define the duration of storage. It is also important that storage inspection be integrated with packaging design. Access to the product is necessary for inspection, but inspection should not compromise packaging effectiveness. The need for inspection of stored items often arises from finding a defective item upon issue or subsequent use. The question then arises as to the relationship between the defective item and the rest of the similar items in storage, i.e., was the item initially defective or did it become defective only as a result of storage? If the item was initially defective, the remaining items in storage are probably not defective except for the few defectives that may have passed acceptance inspection. If, however, the item was not initially defective, perhaps many of the remaining items in storage are defective. It is therefore important to determine whether the defective item was initially defective. Detailed inspections and tests may indicate whether the item was initially defective, but if these further tests are inconclusive, it may be necessary to assume that the item was not initially defective. If the item can influence safety, health, or security, acceptance inspection was performed on all items produced and it is necessary to assume that deterioration of similar items in storage has occurred. All such items must be inspected and reworked or discarded if they are found to be defective. In addition, the packaging and storage of similar items should be improved and a program of periodic inspection should be initiated.

If acceptance inspection was based on sampling, an item found to be defective in storage may or may not have been initially defective. If it was initially defective, the defect could have made it more susceptible to environmental attack, and thus only the initially defective items in the remaining stock are susceptible to similar attack. On the other hand, if the item was not initially defective, all similar items in the remaining stock could be undergoing environmental deterioration. In this case, the condition of the remaining stock could be determined from examination of more samples. If individual production lots in storage can be identified, a storage sampling plan could be devised based on MIL-STD-105 and the assumption that all items in storage are similarly exposed to environmental factors. This is probably not the case, so the production lots may have become fractionated. If the manner in which the fractionation has taken place can be determined, perhaps sample selection can account for the exposure variable. For example, all items on the top row of a stack may be

assumed to have experienced similar environmental exposures.

**6-4 NONDESTRUCTIVE TESTING**

Nondestructive tests measure the properties of a material without significantly affecting it. Although nondestructive tests may create transient effects, they should not create irreversible effects. For example, a liquid used in a test should not be corrosive to the material being tested. The properties measured by nondestructive tests are often indirectly related to the material characteristics of interest. Nondestructive tests related to corrosion can give information concerning the effects of corrosion, ongoing corrosion processes, the presence of conditions conducive to corrosion, and the condition of corrosion prevention and control measures.

Corrosion effects are manifested mainly on the surface of metals. Some forms of corrosion, however, can propagate into the body of a metal section. In many situations, such as corrosion at the interface of faying surfaces, corrosion can be detected only by those nondestructive tests that can penetrate through the metal thickness. Therefore, nondestructive tests of interest in detecting corrosion are those that give indications related to both surface and subsurface deterioration. The various corrosion effects of interest are listed in Table 6-9.

Ongoing aqueous corrosion processes are the result of an electrochemical cell that exhibits a galvanic potential and a corrosion current. A corrosion process also generates reaction products. Nondestructive means

**TABLE 6-9. CORROSION EFFECTS OF INTEREST TO NONDESTRUCTIVE TESTING**

- 
1. Generation of Corrosion Products
    - a. Solid films and scales on a metal surface
    - b. Solid material within the structure of a metal
    - c. Dissolved corrosion products in the environment
    - d. Hydrogen gas
  2. Changes in Metal Properties
    - a. Physical properties
    - b. Mechanical properties
    - c. Dimensions and fit
    - d. Surface texture and appearance
  3. Changes in Structural Continuity
    - a. Pitting
    - b. Perforation
    - c. Opening at a crevice
    - d. Wear
    - e. Crack formation
-

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are available to measure electrochemical characteristics or to indicate the formation of reaction products. Determination that a corrosion environment exists is often sufficient basis for action. In most cases, a test is performed on a relatively small sample of the environment; thus it does not significantly affect the environment itself. A test method that is often used to monitor the corrosiveness of an environment is to expose corrosion coupons in the environment. These coupons may be instrumented to indicate an ongoing process.

The presence of corrosive conditions can be established by instruments that measure the electrical characteristics of corroding specimens. These instruments measure galvanic current, electrical resistance or conductivity, and polarization resistance (Ref. 18), and they provide real-time readout and are therefore an improvement over corrosion coupons that must be periodically removed and evaluated. If the corrosion specimens are constructed of the same materials as the structural members of interest, some indication of corrosion rate can be obtained. However, specimens that are particularly sensitive to some environmental factors may be used as sensitive monitors. Although corrosion meters using test specimens or coupons are not strictly nondestructive, they are nondestructive to the extent that they characterize specific corrosion environments and to the extent that they can be calibrated to the corrosion rate of specific structural members.

The condition of a protective coating indicates that corrosion may have occurred or is possible. The primary concern with coatings is whether they contain defects that can be the site for initiating corrosion and whether they are sufficiently thick and adherent to give adequate long-term protection. Many of the non-destructive test methods that can indicate the surface effects of corrosion are also applicable to coatings.

Inspection by human senses, vision in particular, is the most important form of nondestructive testing for corrosion. Many forms of corrosion have characteristic surface manifestations that can be distinguished by unaided vision; these have been noted in Chapter 2. In many practical situations, however, the corroded surface may be hidden. Flexible borescopes consisting of bundles of fine glass fibers can be used for visual examination of inaccessible surfaces. Devices that provide image magnification may also be applied, but their use is limited by size, portability, and the practicality of using them in a particular setting. Variations of lighting intensity and color may also be useful in some situations. Also photography or other forms of imaging having sensitivity to different parts of the light spectrum may provide visual contrast not available under ambient conditions.

Tactile inspection by touch or instrumentation can give indications of surface roughness changes resulting

from corrosion. Some ongoing corrosion processes, especially those that form hydrogen gas bubbles, generate acoustic emissions that can be detected with very sensitive detectors and high amplification (Ref. 19). The application of heat may be required to increase the corrosion of a suspect area into a detectable range. Corrosion that has resulted in the destruction of the structure of a metal, such as severe exfoliation or dealloying, may be detected by changes in thermal conductivity as measured by surface temperatures. Similar phenomena may result from scale formation or severe changes in metal cross sections. Thermal differences may be detected instrumentally or by the application of temperature-sensitive materials.

The commonly used methods of nondestructive testing that have application to corrosion include

1. Magnetic particle
2. Penetrant
3. Radiography
4. Ultrasonics
5. Eddy current
6. Thermal
7. Leak testing.

Each of these methods is described in the paragraphs that follow.

### 6-4.1 MAGNETIC PARTICLE EXAMINATION

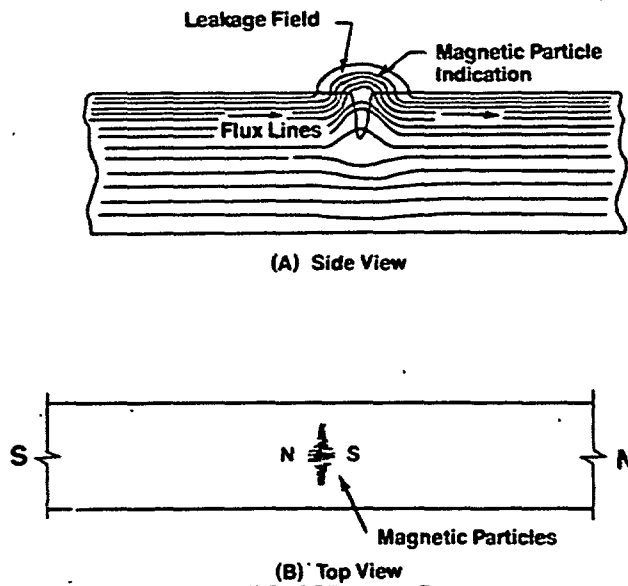
Magnetic particle examination is useful for detecting cracks and other discontinuities at or near the surface of ferromagnetic materials. The magnetic particle method is based on the principle that magnetic lines of force present in a ferromagnetic material are distorted by a change in material continuity, such as a sharp dimensional change or a discontinuity. If such a discontinuity is open or close to the surface of a magnetized material, flux lines will be distorted at the surface, and this distortion produces a flux leakage. When fine magnetic particles are distributed over the area of the flux leakage, they will be held in place and the accumulation of particles will be visible under the proper lighting conditions, as indicated in Fig. 6-3.

Visibility and contrast are important in making the magnetic powder suitable for discontinuity indication. Pigments can color the normally silver-gray iron particles. In some cases, coating the part being tested with a color to improve contrast may be necessary. High visibility and contrast are achieved by coating the magnetic particles with a fluorescent pigment and searching for indications with black light to activate the fluorescent dyes.

Magnetic particle examinations that could be useful in corrosion-related applications are

1. Examine ferromagnetic materials for surface defects that could act as stress raisers for stress-

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**Figure 6-3. Leakage Field at Associated Surface Discontinuity (Ref. 20)**

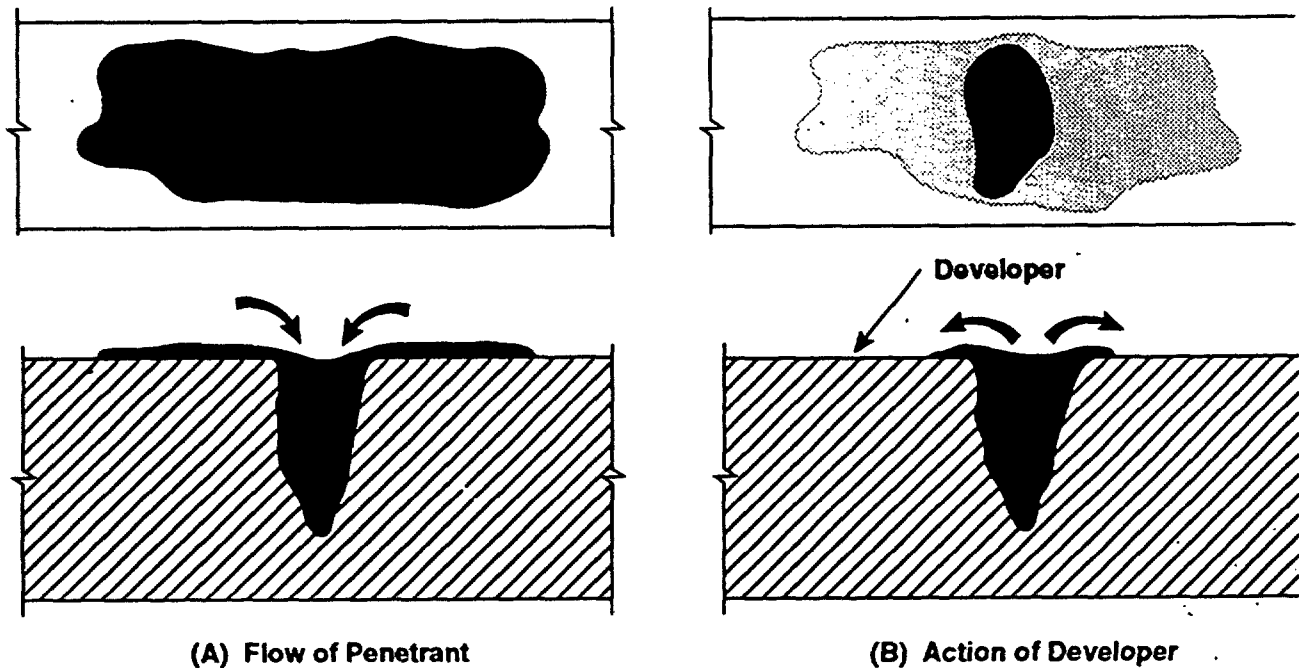
corrosion cracking or as initiation sites for crevice corrosion.

2. Examine ferromagnetic materials for surface damage, such as pitting and intergranular corrosion. Table 6-10 is a listing of military and industrial standards and specifications relating to magnetic particle inspection.

## 6-4.2 LIQUID-PENETRANT INSPECTION

Liquid-penetrant inspection detects discontinuities that are open to the surface. In the process, a liquid penetrant is applied evenly over the surface of the part being tested and allowed to enter discontinuities. After a suitable dwell time, the excess surface penetrant is removed and the part dried. A developer is then applied, which draws the entrapped penetrant out of the discontinuity, staining the developer. The part is then visually inspected to determine the presence or absence of indications. This process is illustrated in Fig. 6-4.

Liquid-penetrant inspection methods can be used effectively in the inspection of nonporous metallic materials, both ferrous and nonferrous, and of nonporous, non-metallic materials, such as ceramics, plastics, and glass. Therefore, the method has application for discontinuities that are potential sites for corrosion and those that result from corrosion. Coatings may be inspected as well as uncoated metals. Caution should be exercised that the materials used in the process—the penetrant, the emulsifier, the solvent remover or water, and the developer—are not corrosive to the materials being examined. Table 6-11 is a list of military and industrial standards and specifications used for penetrant inspection.



**Figure 6-4. Mechanism of Dye Penetrant Testing**

**MIL-HDBK-735(MR)****TABLE 6-10. STANDARDS AND SPECIFICATIONS FOR  
MAGNETIC PARTICLE INSPECTION**

| ISSUED BY                   | DESIGNATION     | TITLE OR EXPLANATION   |
|-----------------------------|-----------------|--|
| Air Force                   | TO 33B-1-1      | Nondestructive Testing Methods, Chapter 2, "Magnetic Particle Method"  |
| Navy                        | NAVAIR 01-1A-16 |  |
| Army                        | TM 43-0103      |  |
| ANSI                        | B31.7           | Code for Pressure Piping, Nuclear Power Piping   |
| ANSI/SAE                    | AMS 2300        | Magnetic Particle Inspection, Premium Aircraft-Quality Steel Cleanliness   |
| ANSI/SAE                    | AMS 2301        | Magnetic Particle Inspection, Aircraft-Quality Steel Cleanliness   |
| ANSI/SAE                    | AMS 2303        | Magnetic Particle Inspection, Aircraft-Quality Steel Cleanliness,<br>Martensitic Corrosion-Resistant Steels  |
| ANSI/SAE                    | AMS 2640        | Magnetic Particle Inspection   |
| ANSI/SAE                    | AMS 2641        | Vehicle, Magnetic Particle Inspection, Petroleum Base  |
| ASM*                        |                 | Metals Handbook, Vol. II, Nondestructive Inspection and Quality Control  |
| ASNT**                      | SNT-TC-1A       | Recommended Practice for Nondestructive Testing Personnel Qualification  |
|                             | Supplement B    | and Certification: Magnetic Particle Testing Method  |
| ASTM                        | A275            | Method for Magnetic Particle Examination of Steel Forgings   |
| ASTM                        | A340            | Definitions of Terms, Symbols, and Conversion Factors Relating to<br>Magnetic Testing  |
| ASTM                        | A456            | Specification for Magnetic Particle Inspection of Large Crankshaft<br>Forgings   |
| ASTM                        | E125            | Reference Photographs for Magnetic Particle Indications on Ferrous<br>Castings   |
| ASTM                        | E709            | Practice for Magnetic Particle Examination   |
| ASTM                        | E1316           | Terminology for Nondestructive Examination   |
| DOD                         | MIL-M-6867      | Magnetic Inspection Units  |
| DOD                         | MIL-I-6870      | Inspection Program Requirements, Nondestructive, for Aircraft and<br>Missile Materials and Parts   |
| DOD                         | MIL-S-23284     | Steel Forgings, Carbon and Alloy, for Shafts, Sleeves, Propeller Nuts,<br>Couplings and Stocks (Rudders and Diving Planes)   |
| DOD                         | MIL-M-47230     | Magnetic Particle Inspection, Soundness Requirements for Materials,<br>Parts, and Weldments  |
| DOD                         | DOD-F-87935     | Fluid, Magnetic Particle Inspection, Suspension Medium, Metric   |
| DOD                         | MIL-STD-271     | Requirements for Nondestructive Testing Methods  |
| DOD                         | MIL-STD-410     | Nondestructive Testing Personnel Qualification and Certification (Eddy<br>Current, Liquid Penetrant, Magnetic Particle, Radiographic, and<br>Ultrasonic)   |
| DOD                         | MIL-STD-798     | Nondestructive Testing, Welding Quality Control, Material Control and<br>Identification and High-Shock Requirements for Piping System<br>Components for Naval Shipboard Use (Radiography, Magnetic Particle,<br>and Penetrant) |
| DOD                         | MIL-STD-1907    | Inspection, Liquid Penetrants and Magnetic Particle Soundness<br>Requirements for Materials, Parts, and Weldments  |
| DOD                         | MIL-STD-1949    | Magnetic Particle Inspection   |
| DOD                         | MIL-STD-2175    | Classification and Inspection of Castings  |
| DOD                         | MIL-HDBK-728/1  | Nondestructive Testing   |
| DOD                         | MIL-HDBK-728/4  | Magnetic Particle Testing  |
| Federal<br>Government       | FED-STD-151     | Test Methods, Metals   |
| General Dynamics<br>Convair | CT-6-3          | Classroom Training Handbook, Nondestructive Testing, Magnetic Particle   |
| NASA                        | SP-3079         | Nondestructive Evaluation Technique Guide  |

\*ASM = American Society for Metals

\*\*ASNT = American Society for Nondestructive Testing

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TABLE 6-11. STANDARDS AND SPECIFICATIONS FOR PENETRANT INSPECTION

| ISSUED BY          | DESIGNATION               | TITLE OR EXPLANATION   |
|--------------------|---------------------------|--|
| Air Force          | TO 33 B-1-1               | Nondestructive Testing Methods, Chapter 6, "Fluorescent and Dye Penetrant Method"  |
| Navy               | NAVAIR 01-1A-16           |  |
| Army               | TM 43-0103                |  |
| ANSI               | B31.7                     | Code for Pressure Piping, Nuclear Power Piping   |
| ANSI/SAE           | AMS 2645                  | Fluorescent Penetrant Inspection   |
| ANSI/SAE           | AMS 2656                  | Contrast Dye Penetrant Inspection  |
| ANSI/SAE           | AMS 3155                  | Oil, Fluorescent Penetrant, Water-Soluble  |
| ANSI/SAE           | AMS 3156                  | Oil, Fluorescent Penetrant, Water-Soluble  |
| ANSI/SAE           | AMS 3157                  | Oil, Fluorescent Penetrant, High Fluorescence, Solvent-Soluble   |
| ANSI/SAE           | AMS 3158                  | Solution, Fluorescent Penetrant, Water-Base  |
| ASNT               | SNT-TC-1A<br>Supplement D | Recommended Practice for Nondestructive Testing Personnel Qualification and Certification: Liquid Penetrant Testing Method   |
| ASTM               | E165                      | Practice for Liquid Penetrant Inspection Method  |
| ASTM               | E270                      | Terminology Relating to Liquid Penetrant Inspection  |
| ASTM               | E433                      | Reference Photographs for Liquid Penetrant Inspection  |
| DOD                | MIL-I-6870                | Inspection Program Requirements, Nondestructive for Aircraft and Missile Materials and Parts   |
| DOD                | MIL-I-25135               | Inspection Materials, Penetrants   |
| DOD                | MIL-F-38762               | Fluorescent Penetrant Inspection Units   |
| DOD                | MIL-STD-271               | Requirements for Nondestructive Testing Methods  |
| DOD                | MIL-STD-410               | Nondestructive Testing Personnel Qualification and Certification (Eddy Current, Liquid Penetrant, Magnetic Particle, Radiographic, and Ultrasonic)   |
| DOD                | MIL-STD-798               | Nondestructive Testing, Welding Quality Control, Material Control and Identification and High-Shock Test Requirements for Piping System Components for Naval Shipboard Use (Radiography, Magnetic Particle, Penetrant) |
| DOD                | MIL-STD-1907              | Inspection, Liquid Penetrant and Magnetic Particle Soundness Requirements for Materials, Parts, and Weldments  |
| DOD                | MIL-STD-6866              | Inspection, Liquid Penetrant   |
| Federal Government | FED-STD-151               | Test Methods, Metal  |
| NASA               | SP-3079                   | Nondestructive Evaluation Technique Guide  |

## 6-4.3 RADIOGRAPHY

## 6-4.3.1 X Rays and Gamma Rays

X rays and gamma rays are high-frequency electromagnetic radiation used in radiography. Gamma or x-radiation is characterized by energy and intensity. Energy determines the thickness of material that can be penetrated and the radiographic contrast, whereas intensity determines the required exposure. Absorption of X rays by materials makes radiography possible. Differential absorption of one material or thickness to another provides the contrast essential to the radiographic process. Gamma and X rays are forms of electromagnetic radiation; therefore, they obey the laws of optics. The geometric aspects of shadow formation apply in radiography.

Fig. 6-5 is an illustration of the geometry considerations in an application of radiography. The source, the

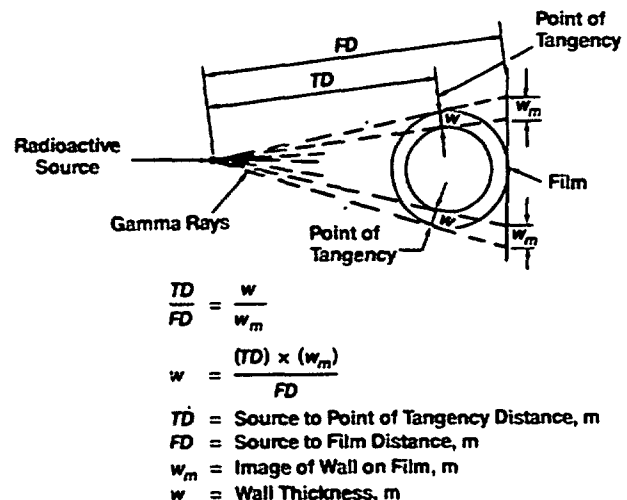


Figure 6-5. Method of Determining Wall Thickness by Radiography

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test object, and the recording film should be geometrically arranged to produce a sharp image.

Unwanted, scattered radiation that reaches the film produces an overall haze or fog that reduces image contrast and contributes to a loss in definition. Because the energy of scattered radiation is degraded, it may be absorbed by lead foils that prevent it from reaching the film. Thus areas external to the area of interest should be masked with lead to minimize the size of the incident radiation beam.

Penetrameters are used to evaluate the sensitivity and resolution of a radiographic image. Contrast sensitivity determines the relative change in material section that is visible. Resolution is a measure of the detail quality in the radiograph.

Radiography is widely used to determine the quality of castings and welds. It detects discontinuities such as voids, cracks, and inclusions of foreign materials. Radiography requires access to both sides of the piece being examined. The source is placed on one side and the film on the other. In some cases, a small radioisotope source may be placed in relatively inaccessible places, such as the interior of pipes. The application of radiography to corrosion is limited to those discontinuities sufficiently great to result in the requisite contrast sensitivity and resolution. Most standard radiography calls for a 2% contrast sensitivity with the capability of resolving a right circular cylinder whose height and diameter are both equal to 2% of the specimen thickness. Table 6-12 is a list of selected standards and specifications for radiographic testing.

### 6-4.3.2 Neutron Radiography

Neutron radiography is a technique identical in most respects to X-ray radiography because for most materials the degree of penetration of the neutron radiation employed is similar to that of X-ray radiation. Neutron radiation, however, is attenuated differently by materials, and the result is that neutron radiography generally supplements X-ray radiography applications.

The most exploited characteristic of neutron radiation is its great sensitivity to the presence of hydrogen atoms. Thus the intrusion of water and organic liquids into assemblies can be readily determined as can the corrosion products such liquids may generate. For example, neutron radiography has been very useful in detecting and mapping the hidden intrusion of water and subsequent corrosion of aircraft structures, particularly those supported internally by aluminum honeycomb materials. The sensitivity of neutron radiation to attenuation by hydrogen is characteristic of its interaction with the hydrogen nucleus.

Except in very special cases, neutrons interact only with the nuclei of atoms in materials; the neutral charge of the neutron allows it to ignore the sea of electrons in

atoms. It is this phenomenon which makes their attenuation by materials so different from that of X rays. It results in neutron radiation attenuation being a characteristic of the nuclear structure of materials and following no easily predicted pattern with increasing atomic mass or material density. To predict the attenuation of neutron radiation in a particular case, each atomic species present must be evaluated individually, and sometimes the isotopic content must also be considered. The uniqueness of this situation results in the ability of neutron radiography to provide high contrast between the light elements, such as boron, lithium, and hydrogen, and the elements of common structural materials, such as iron, aluminum, and copper. Also the relatively high transparency of lead, tin, and uranium for neutron radiation provides similar favorable image contrasts to the common structural materials.

Neutron radiography is performed primarily at sites where a nuclear reactor source of neutrons is available. It is also performed at sites that have a nuclear accelerator in operation. The obvious restriction with such radiography is that the material to be examined must be taken to the site of these relatively large neutron sources. This is often inconvenient or impossible for large assemblies or when large numbers of parts require inspection. In recent years the development of neutron radiography using small accelerator or radioisotopic sources has advanced to a stage where it is now possible to consider neutron radiography being performed at a site convenient to the user, in a manner similar to that of high-energy X-ray radiography. This development is beginning to enable the detection of corrosion in large assemblies such as complete aircraft at their normal maintenance sites, where the early detection of corrosion can considerably reduce repair costs.

### 6-4.3.3 Beta Backscatter

The mass per unit area of a coating can be determined using beta backscatter gages. The thickness can be determined if the coating density is known. Beta particles are high-speed electrons that are emitted from the nuclei of materials undergoing a nuclear transformation. When beta particles impinge upon a material, a certain portion of them is backscattered. The backscatter is essentially a function of the atomic number of the matter.

If a body has a surface coating and if the atomic number of the substrate and of the coating material are sufficiently different, the intensity of the backscatter will be between two limits: the backscatter intensity of the substrate and that of the coating. Thus with proper calibration, the intensity of the backscatter can be used for a measurement of coating mass per unit area.

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TABLE 6-12. STANDARDS AND SPECIFICATIONS FOR RADIOGRAPHIC TESTING

| ISSUED BY | DESIGNATION     | TITLE OR EXPLANATION  |
|-----------|-----------------|---|
| Air Force | TO 33 B-1-1     | Nondestructive Testing Methods, Chapter 5, "Radiographic Inspection Method"   |
| Navy      | NAVAIR 01-1A-16 |   |
| Army      | TM 43-0103      |   |
| ANSI/SAE  | AMS 2635        | Radiographic Inspection   |
| ANSI/SAE  | AMS 2650        | Fluoroscopic X-Ray Inspection   |
| ASME      |                 | ASME Boiler and Pressure Vessel Code-Power Boilers (Section 1)  |
| ASNT      | SNT-TC-1A       | Recommended Practice for Nondestructive Testing Personnel   |
|           | Supplement A    | Qualification and Certification: Radiographic Testing Method  |
| ASTM      | B567            | Standard Method for Measurement of Coating Thickness by the Beta Backscatter Method   |
| ASTM      | E94             | Guide for Radiographic Testing  |
| ASTM      | E142            | Method for Controlling Quality of Radiographic Testing  |
| ASTM      | E155            | Reference Radiographs for Inspection of Aluminum and Magnesium  |
| ASTM      | E186            | Reference Radiographs for Heavy-Walled (2- to 4½-in. (51- to 114-mm)) Steel Castings  |
| ASTM      | E192            | Reference Radiographs of Investment Steel Castings for Aerospace Applications   |
| ASTM      | E242            | Reference Radiographs for Appearances of Radiographic Images As Certain Parameters are Changed  |
| ASTM      | E272            | Reference Radiographs for High-Strength Copper-Base and Nickel-Copper Alloy Castings  |
| ASTM      | E280            | Reference Radiographs for Heavy-Walled (4½- to 12-in. (114- to 305-mm)) Steel Castings  |
| ASTM      | E310            | Reference Radiographs for Tin-Bronze Castings   |
| ASTM      | E390            | Reference Radiographs for Steel Fusion Welds  |
| ASTM      | E446            | Reference Radiographs for Steel Castings Up to 2 in. (51 mm) in Thickness   |
| ASTM      | E505            | Reference Radiographs for Inspection of Aluminum and Magnesium Die Castings   |
| ASTM      | E545            | Method for Determining Image Quality in Thermal Newton Radiographic Testing   |
| ASTM      | E586            | Definition of Terms Relating to Gamma and X Radiography   |
| ASTM      | E592            | Guide to Obtainable ASTM Equivalent Penetrator Sensitivity for Radiography of Steel Plates 0.25 to 2 in. (6 to 51 mm) Thick With X Rays and 1 to 6 in. (25 to 152 mm.) Thick With Cobalt-60 |
| ASTM      | E689            | Reference Radiographs for Ductile Iron Castings   |
| ASTM      | E748            | Practices for Thermal Newton Radiography of Materials   |
| AWS       | A5.10-57 Part 2 | Aluminum X-Ray Standard   |
| AWS       | D3, 4-52        | Rules for Welding Pipe in Marine Construction   |
| AWS       | D3, 4-52 Part 2 | X-Ray Standard for High-Pressure, High-Temperature Steam Piping   |
| DOD       | MIL-I-6870      | Inspection Program Requirements, Nondestructive for Aircraft and Missile Materials and Parts  |
| DOD       | MIL-A-11356     | Steel Armor, Cast, Homogeneous Combat Vehicle Type (0.25 to 12 in. Inclusive)   |
| DOD       | MIL-R-45774     | Radiographic Inspection, Soundness Requirements for Fusion Welds in Aluminum and Magnesium Missile Components   |
| DOD       | MIL-STD-139     | Radiographic Inspection, Soundness Requirements for Aluminum and Magnesium Castings (For Small Arms Parts)  |
| DOD       | MIL-STD-271     | Requirements for Nondestructive Testing Methods   |
| DOD       | MIL-STD-410     | Nondestructive Testing Personnel Qualification and Certification (Eddy Current, Liquid Penetrant, Magnetic Particle, Radiographic and Ultrasonic)   |



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TABLE 6-12. (cont'd)

| ISSUED BY   | DESIGNATION                | TITLE OR EXPLANATION   |
|---|----------------------------|--|
| DOD   | MIL-STD-453                | Inspection, Radiographic   |
| DOD   | MIL-STD-798                | Nondestructive Testing, Welding Quality Control, Material Control and Identification and High-Shock Test Requirements for Piping System Components for Naval Shipboard Use (Radiography, Magnetic Particle, and Penetrant) |
| DOD   | MIL-STD-1257               | Radiographic and Visual Soundness Requirements for Cobalt-Chromium Alloy Liners (For Small Arms Barrels)   |
| DOD   | MIL-STD-1264               | Radiographic Inspection for Soundness of Welds in Steel by Comparison to Graded ASTM E390 Reference Radiographs  |
| DOD   | MIL-STD-1265               | Radiographic Inspection, Classification and Soundness Requirements for Steel Castings  |
| Federal Government<br>National Institute<br>for Standards and<br>Technology (Former<br>National Bureau of<br>Standards) | FED-STD-151<br>Handbook 55 | Test Methods, Metals<br>Protection Against Betatron-Synchrotron Radiation up to 100 Million Electron Volts   |
| National Institute<br>for Standards and<br>Technology (Former<br>National Bureau of<br>Standards)                       | Handbook 66                | Safe Design and Use of Beta-Ray Sources  |
| NASA  | SP-3079                    | Nondestructive Evaluation Technique Guide  |

#### 6-4.4 ULTRASONIC EXAMINATION

The human ear cannot detect sounds with frequencies above about 16,000 Hz; thus any sound above this limit is ultrasonic. For purposes of nondestructive inspection it is better to consider ultrasonic waves as being confined to liquids and solids and as having frequencies in the millions of hertz. Like sound, ultrasonic waves require a transmission coupling medium of some sort. There are several modes by which ultrasonic waves are propagated through materials. These include

1. Longitudinal or compression waves (L waves) are widely used in ultrasonic testing. Ultrasonic energy is propagated by small elastic displacements of particles or elements in a medium. Longitudinal waves are defined as simple compression-rarefaction waves in which the particle displacement is in the direction in which the waves are traveling, as illustrated in Fig. 6-6. Longitudinal waves will propagate through solids, liquids, and gases.

2. Shear or transverse waves (S waves) are next in importance to longitudinal waves in ultrasonic testing. In shear waves, particle displacement occurs at right angles to the direction of propagation, as illustrated in Fig. 6-7. The velocity with which shear waves travel is about one half that of longitudinal waves. Because wavelength is proportional to velocity, the length of shear waves is much shorter than that of longitudinal

waves. In the practical sense, shear waves will not propagate through liquids or gases because there is little or no resistance to shear in these media.

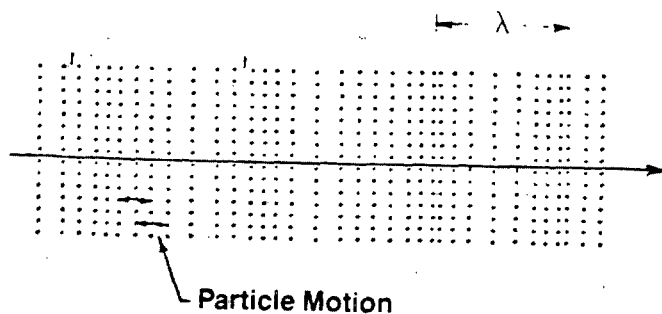


Figure 6-6. Longitudinal Wave

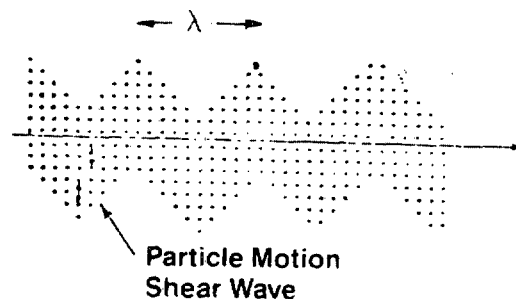
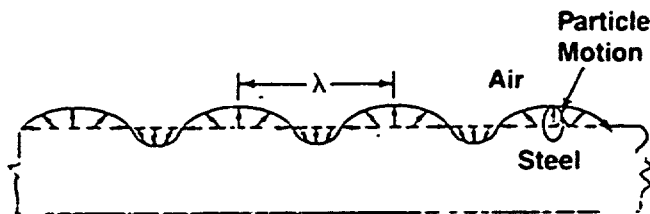


Figure 6-7. Shear Wave

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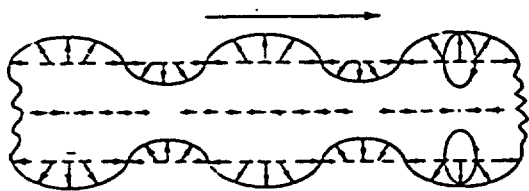
3. Surface or Rayleigh waves travel over the surface of a solid material and penetrate it to a depth of about one wavelength. Particle displacement is elliptical in the vertical plane along the direction of travel, as illustrated in Fig. 6-8. To propagate, the surface wave must travel along a surface that is bounded on one side by the strong shear forces of the solid and on the other by the nearly nonexistent shear forces between gas molecules. The velocity of surface waves is about 90% of that of shear waves in the same material.

4. When ultrasonic vibrations are transmitted into a thin sheet or plate whose thickness is comparable to the wavelength of the ultrasonic energy, plate or Lamb waves are produced. There are two basic types of Lamb waves: symmetrical and asymmetrical. Each is capable of having an unlimited number of modes. Examples of particle displacement for the two types of waves are shown in Fig. 6-9. The pattern of displacement is very complex and resembles the elliptical orbit of particles of surface waves. The velocity of these waves depends not only on the material through which the wave is traveling but also on the frequency, incident angle, and plate thickness. Lamb waves are not used extensively in ultrasonic testing.

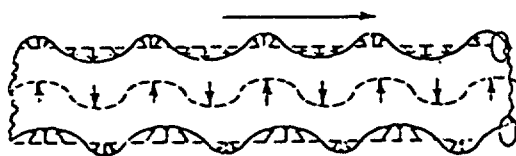


NOTE: Elliptical oscillation path of particle on right.

**Figure 6-8. Surface Wave on Steel**



(A) Symmetrical



(B) Asymmetrical

NOTE: Small arrows indicate primary direction of particle oscillation at a particular instant.

**Figure 6-9. Plate Waves in a Solid**

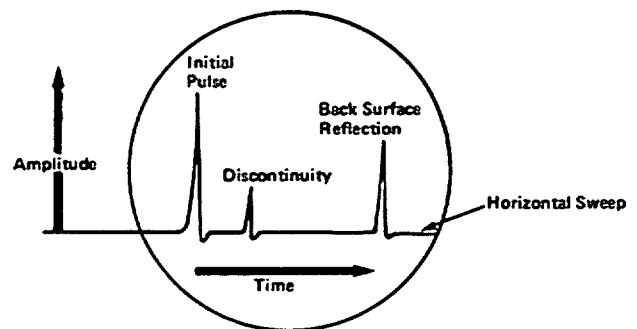
When an ultrasonic wave encounters an abrupt change in acoustical impedance, part of the energy is reflected and part is transferred across the interface.

The principles of reflection and refraction are most important in application of ultrasonics to nondestructive testing. The energy of the incident wave may be partitioned among several modes of reflected and refracted waves. Mode conversion at the interface is used in nondestructive testing, particularly by shear-wave and angle-beam inspections.

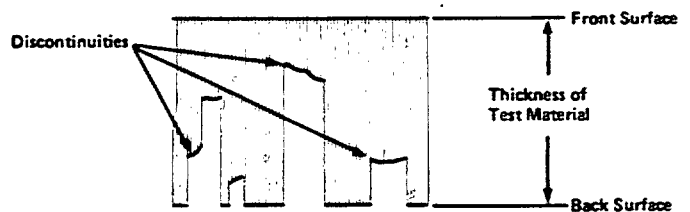
There are three major displays used in ultrasonic testing applications illustrated in Fig. 6-10. These are

1. The A-scan is a time-versus-amplitude display. From the signal located on a cathode-ray-tube screen, the depth of a defect within a material and an estimate of its size can be determined as illustrated in Fig. 6-10(A). If thickness rather than discontinuity location is being measured, the time between the initial pulse and the back-surface reflection is a measure of thickness in a material.

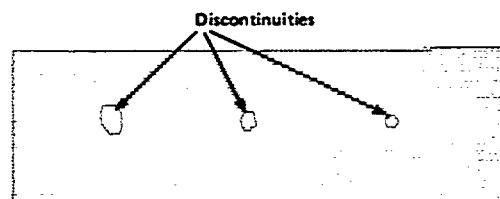
2. The B-scan presentation reveals a cross-sectional view of the material being examined. This type of



(A) A-Scan Presentation



(B) B-Scan Presentation



(C) C-Scan Presentation

**Figure 6-10. A-, B-, and C-Scan Ultrasonic Presentations (Ref. 20)**

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presentation displays the front and back surfaces and relative location of defects within the material as illustrated in Fig. 6-10(B).

3. The C-scan presentation is a plan view similar to a radiograph as shown in Fig. 6-10(C). It outlines the contour of the defect on a plan view of the specimen but does not reveal any information as to the depth of the defect.

Ultrasonic inspection may be divided into the following three classes according to how the probing energy is used:

1. In pulse-echo testing, pulses of ultrasonic sound are generated by the test instrument and introduced into a material. The sound travels through the material and is reflected back to the transducer from the opposite side or from any location in the material where there is an abrupt change in acoustic impedance. Inspection using pulse-echo techniques is particularly useful when only one surface of the test item is accessible. The pulse-echo system is illustrated in Fig. 6-11.

2. Through-transmission testing operates on the principle of transmitting sound waves through a test specimen with one transducer and receiving them with a second transducer. The through-transmission system is illustrated in Fig. 6-12. The transmitted sound can be either continuous or pulsed. The presence of a discontinuity is indicated by a reduction in the magnitude of sound energy reaching the receiving transducer. The through-transmission system provides better near-surface resolution than the pulse-echo approach.

3. Stationary waves are produced when continuous longitudinal waves are introduced into a test specimen. The frequency of these longitudinal waves must be properly related to the thickness and acoustic velocity of the material. When the test frequency is such that the specimen thickness is exactly equal to one half or to multiples of the ultrasonic wavelength, the test specimen will resonate and cause a loading effect on the transducer. In resonance testing, access to only one surface of the specimen is required. Accuracy can be very high

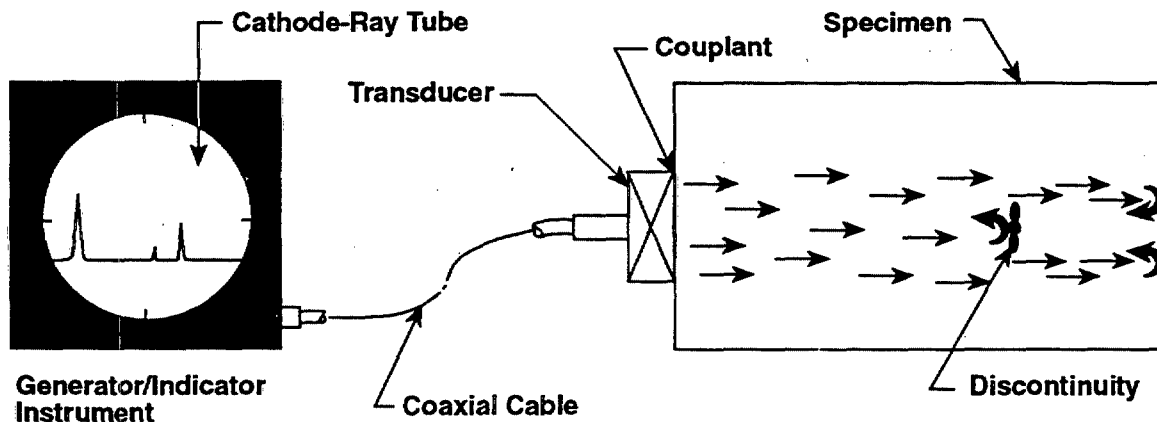


Figure 6-11. Pulse-Echo System

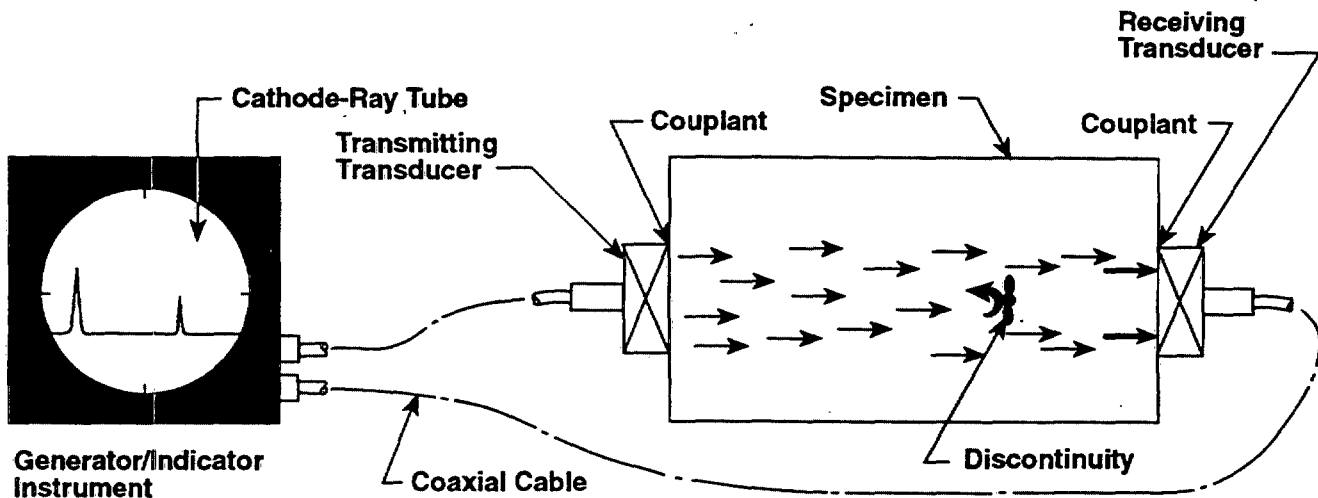


Figure 6-12. Through-Transmission System

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if the test operator uses very exact electrical and mechanical devices. The resonance system is illustrated in Fig. 6-13.

In any method of ultrasonic inspection, the transducer must be coupled to the test-material surface. In contact inspection the surface being inspected is exposed to the environment and the transducer is in contact through a thin couplant film, as illustrated in Fig. 6-14. Small, lightweight, portable equipment is commercially available and a minimum of test instruments and accessories are required. The method is adaptable to a wide variety of field and shop applications because in contact inspection the main functions of the couplant are to exclude air between the transducer and the test specimen and to provide an acoustical path for transmission of the ultrasonic wave from one surface to the other.

The several methods and classes of ultrasonic inspection can be combined in a number of ways to provide a variety of testing techniques. The normal or straight-beam pulse-echo contact test is applicable for thickness measurements and the detection of planar defects and voids. The shear-wave angle beam test is sensitive to discontinuities with reflecting areas nonparallel to the test surface. Surface or Rayleigh-wave pulse-echo contact testing is applicable to the detection of defects that are at or near and nominally perpendicular to the surface. Examples of such defects are fatigue cracks and heat treatment cracks. Pulse-echo, plate-wave, or Lamb-wave angle beam contact testing is useful for inspecting thin materials. This method is applicable to defects nominally perpendicular to the surfaces and located anywhere throughout the thickness. Dual transducer pulse-echo contact testing can detect discontinuities before the transmission of the pulse is complete.

Through-transmission may also be used in the contact

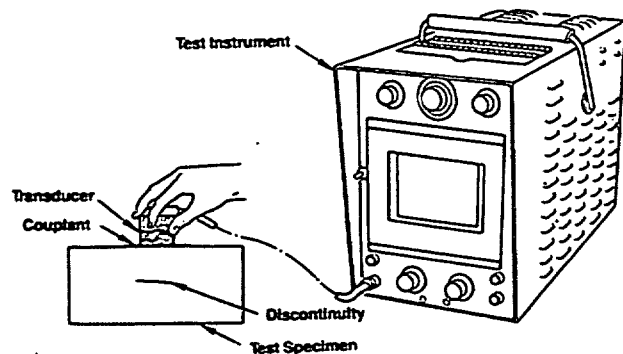


Figure 6-14. Contact Testing

method, but the difficulty of maintaining constant transducer alignment and uniform coupling during scanning reduces its desirability. Through-transmission pulsed longitudinal-wave testing is most applicable to the detection of planar defects and voids in materials, such as flat plates and bars having opposite parallel surfaces. Under certain conditions and transducer arrangements, surface wave modes may be employed. For example, large surface areas may be rapidly inspected for surface defects by positioning the transmitter and receiver on the same surface "looking" at each other. A similar technique may be used to inspect thin sheets for delamination defects by using plate waves.

In resonance-contact inspection a longitudinal-mode continuous wave is introduced normal to the surface of the specimen. Resonance testing is used mainly to measure the thickness of thin sheets. This test method is also applicable to the detection of large discontinuities, such as corrosion effects and laminar-type bond defects.

Table 6-13 is a list of military and industrial standards and specifications relating to ultrasonic inspection.

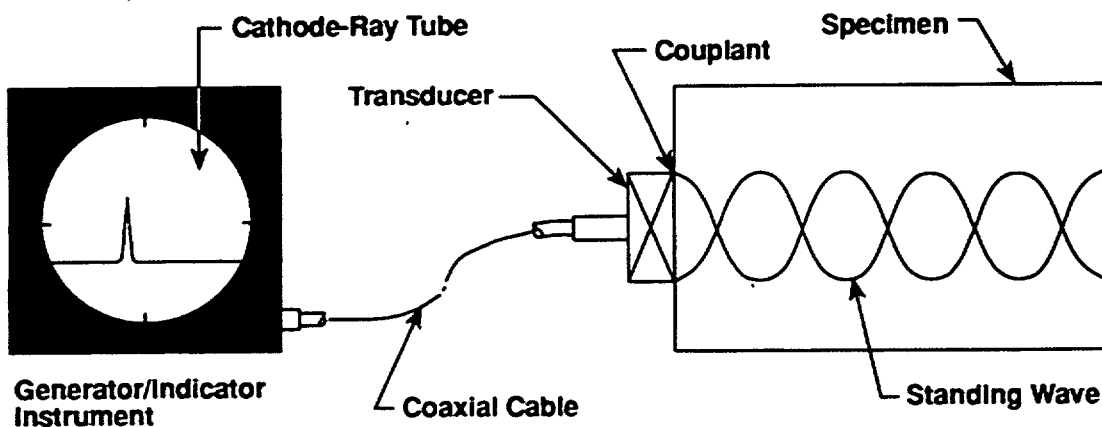


Figure 6-13. Resonance System

**MIL-HDBK-735(MR)****TABLE 6-13. STANDARDS AND SPECIFICATIONS FOR ULTRASONIC INSPECTION**

| ISSUED BY | DESIGNATION     | TITLE OR EXPLANATION   |
|-----------|-----------------|--|
| Air Force | TO-00-25-224    | Welding High-Pressure and Cryogenic Systems (Section 4, Nondestructive Inspection by Ultrasonic and Eddy Current Methods)                          |
| Air Force | TO 33 B-1-1     | Nondestructive Testing Methods, Chapter 4, "Ultrasonic Inspection Method"  |
| Navy      | NAVAIR 01-1A-16 |  |
| Army      | TM 43-0103      |  |
| ANSI      | B31.7           | Code for Pressure Piping, Nuclear Power Piping   |
| ANSI/SAE  | AMS 2630        | Ultrasonic Testing   |
| ASNT      |                 | Recommended Ultrasonic Acceptance Standards for Airframe Aluminum Alloy Plate, Forgings, and Extrusions  |
| ASNT      | SNT-TC-1A       | Recommended Practice for Nondestructive Testing Personnel Qualification and Certification: Ultrasonic Testing Method                               |
|           | Supplement C    |  |
| ASTM      | A376            | Specifications for Seamless Austenitic Steel Pipe for High-Temperature Central Station Service   |
| ASTM      | A388            | Recommended Practice for Ultrasonic Examination of Heavy Steel Forgings  |
| ASTM      | A418            | Method of Ultrasonic Testing and Inspection of Turbine and Generator Steel Rotor Forgings  |
| ASTM      | A435            | Specification for Ultrasonic Examination of Steel Plates for Pressure Vessels  |
| ASTM      | A503            | Specification for Ultrasonic Examination of Large Forged Crankshafts   |
| ASTM      | A531            | Recommended Practice for Ultrasonic Inspection of Turbine-Generator Steel Retaining Rings  |
| ASTM      | A556            | Specification for Seamless Cold-Drawn Carbon Steel Feedwater Heater Tubes  |
| ASTM      | A557            | Specification for Electric-Resistance-Welded Carbon Steel Feedwater Heater Tubes   |
| ASTM      | A577            | Specification for Ultrasonic Angle Beam Examination of Steel Plates  |
| ASTM      | A578            | Specification for Straight-Beam Ultrasonic Examination of Plain and Clad Steel Plates for Special Applications                                     |
| ASTM      | B594            | Practice for Ultrasonic Examination of Aluminum Alloy Wrought Products for Aerospace Applications  |
| ASTM      | E114            | Practice for Ultrasonic Pulse-Echo Straight-Beam Testing by the Contrast Method  |
| ASTM      | E127            | Practice for Fabricating and Checking Aluminum Alloy Ultrasonic Standard Reference Blocks  |
| ASTM      | E164            | Practice for Ultrasonic Contact Examination of Weldments   |
| ASTM      | E213            | Practice for Ultrasonic Inspection of Metal Pipe and Tubing  |
| ASTM      | E214            | Recommended Practice for Immersed Ultrasonic Testing by the Reflection Method Using Pulsed Longitudinal Waves                                      |
| ASTM      | E273            | Practice for Ultrasonic Examination of Longitudinal and Spiral Welds of Welded Pipe and Tubing   |
| ASTM      | E317            | Practice for Evaluating Performance Characteristics of Pulse-Echo Ultrasonic Testing Systems Without the Use of Electronic Measurement Instruments |
| ASTM      | E428            | Practice for Fabrication and Control of Steel Reference Blocks Used in Ultrasonic Inspection   |
| ASTM      | E500            | Terminology Relating to Ultrasonic Examination   |
| DOD       | MIL-I-6870      | Inspection Program Requirements, Nondestructive for Aircraft and Missile Materials and Parts   |
| DOD       | MIL-C-15726     | Copper-Nickel Alloy, Sheet, Plate, Strip, Bar, Rod, and Wire   |
| DOD       | MIL-S-16216     | Steel Plate Alloy, Structural High Yield Strength (HY-80-HY-100)   |

(cont'd on next page)

## MIL-HDBK-735(MR)

TABLE 6-13. (cont'd)

| ISSUED BY          | DESIGNATION      | TITLE OR EXPLANATION   |
|--------------------|------------------|--|
| DOD                | MIL-S-22698      | Steel Plate, Shapes and Bars, Weldable, Ordinary Strength and Higher Strength: Structural  |
| DOD                | MIL-S-23008      | Steel Castings, Alloy, High Yield Strength (HY-80 and HY-100)  |
| DOD                | MIL-T-23226      | Tube and Pipe, Corrosion-Resistant Steel Seamless  |
| DOD                | MIL-S-23284      | Steel Forging, Carbon and Alloy, for Shafts, Sleeves, Propeller Nuts, Couplings and Stocks (Rudders and Diving Planes)                             |
| DOD                | MIL-U-85067(AS)  | Ultrasonic Evaluation of Housing Welds for the Mark 71 Mod 0 Warhead   |
| DOD                | MIL-STD-271      | Requirements for Nondestructive Testing Methods  |
| DOD                | MIL-STD-410      | Nondestructive Testing Personnel Qualification and Certification (Eddy Current, Liquid Penetrant, Magnetic Particle, Radiographic, and Ultrasonic) |
| DOD                | MIL-STD-770      | Ultrasonic Inspection of Lead  |
| DOD                | MIL-STD-1875(AT) | Requirements for Ultrasonic Inspection   |
| DOD                | MIL-STD-2154     | Process for Ultrasonic Inspection of Wrought Metals  |
| Federal Government | FED-STD-151      | Test Methods, Metals   |
| NAS                | NAS 824 (Rev. 1) | Inspection, Ultrasonic, Wrought Metal  |
| NASA               | SP-3079          | Nondestructive Evaluation Technique Guide  |

#### 6-4.5 ELECTROMAGNETIC (EDDY CURRENT) METHODS

Nondestructive testing by electromagnetic (eddy current) methods involves inducing electric currents in a test piece and measuring the changes produced in those currents by discontinuities or other physical differences in the test piece.

The basic eddy-current test system is analogous to an electric transformer. The test coil serves as the primary winding of this transformer and produces a magnetic field that in turn excites current in the test material. The test material serves effectively as the one-turn, short-circuited secondary winding of this transformer, as shown in Fig. 6-15. The currents excited in the test material produce an opposing magnetic field. The net magnetic field existing at the surface of the material next to the test coil is the sum of the excitation field and the reaction field.

Measurements of the amplitude and phase of this net field, i.e., the vector sum of the magnetizing-coil field and the eddy-current-reaction field, provide the output signals for eddy current nondestructive tests. The controlled use and electronic analysis of these measurements permit direct indication of test object geometrical, electrical conductivity, and magnetic permeability factors. In many cases, other metallurgical, chemical, and mechanical properties of test materials can be correlated with these direct measurements. For example, material discontinuities, i.e., defects, that distort the eddy current flow patterns in the test material can often be detected.

Fig. 6-16 shows some arrangements of test probes and test objects in eddy-current tests. Optimum fre-

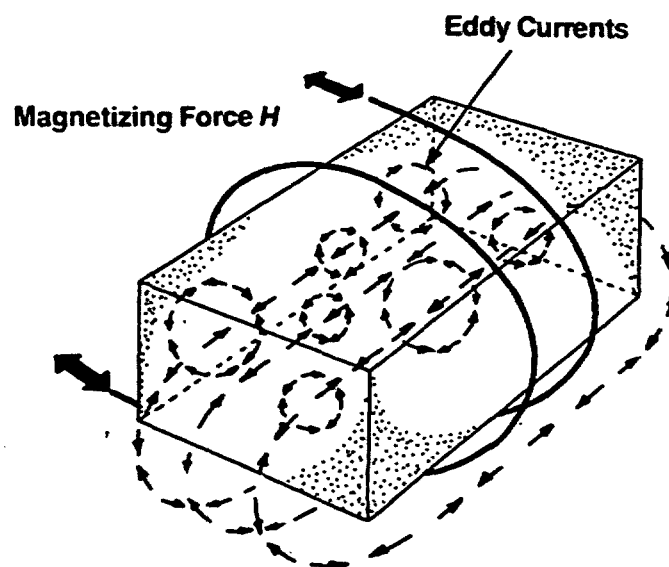
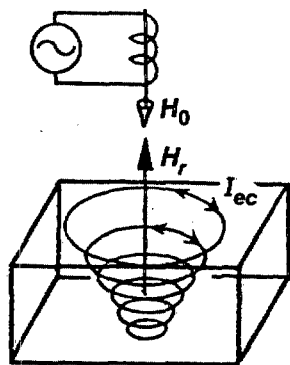


Figure 6-15. Production of Eddy Currents by an Alternating Field (Ref. 21)

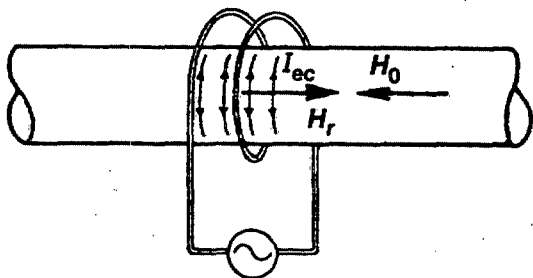
quency ranges are often determined experimentally. Examples of typical frequency ranges are illustrated in Fig. 6-17.

Eddy-current testing is primarily a surface inspection in which the currents are concentrated near the surface of the material that is closest to the eddy-current test coil. The penetration depth  $\delta$  is the theoretical boundary beneath the surface of the material that encloses 63% of the induced currents. The relationship between depth of penetration in various metals and test frequency are given in Fig. 6-18.

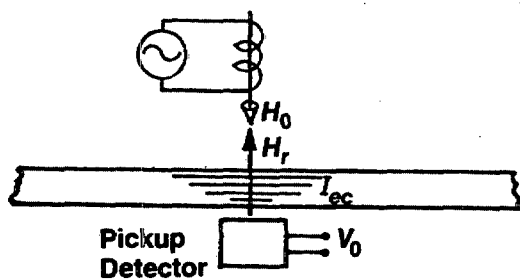
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(A) Probe on One Side of Object



(B) Probe Encircling Test Object



(C) Excitation and Pickup on Opposite Sides of Test Object

- $H_0$  = excitation field  
 $H_r$  = reaction field (produced by eddy currents)  
 $I_{ec}$  = eddy current paths in test object, normally circular and concentric

Figure 6-16. Arrangements of Test Probes and Test Objects (Ref. 20)

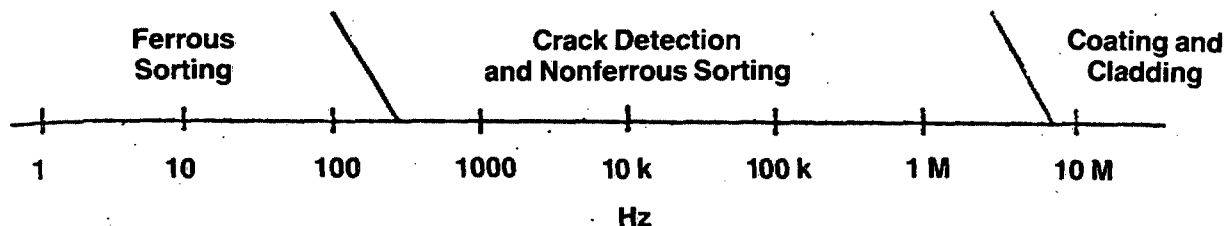


Figure 6-17. Frequencies Used for Various Test Problems (Ref. 21)

The eddy-current method can detect or measure a number of material variables that influence the electrical characteristics of materials. For example, eddy-current instruments are employed to detect cracks, corrosion, and pinholes in coatings. Other applications include measuring heat treatment, hardness, stress, chemical composition, cladding thickness, and the diameter of cylinders.

The eddy-current technique is a fast and accurate method of measuring thickness. The probe-type test coil is usually used for eddy current thickness measurement. However, the encircling coil also has been employed to measure the wall thickness of metal tubing and conductive coatings on solid cylinders.

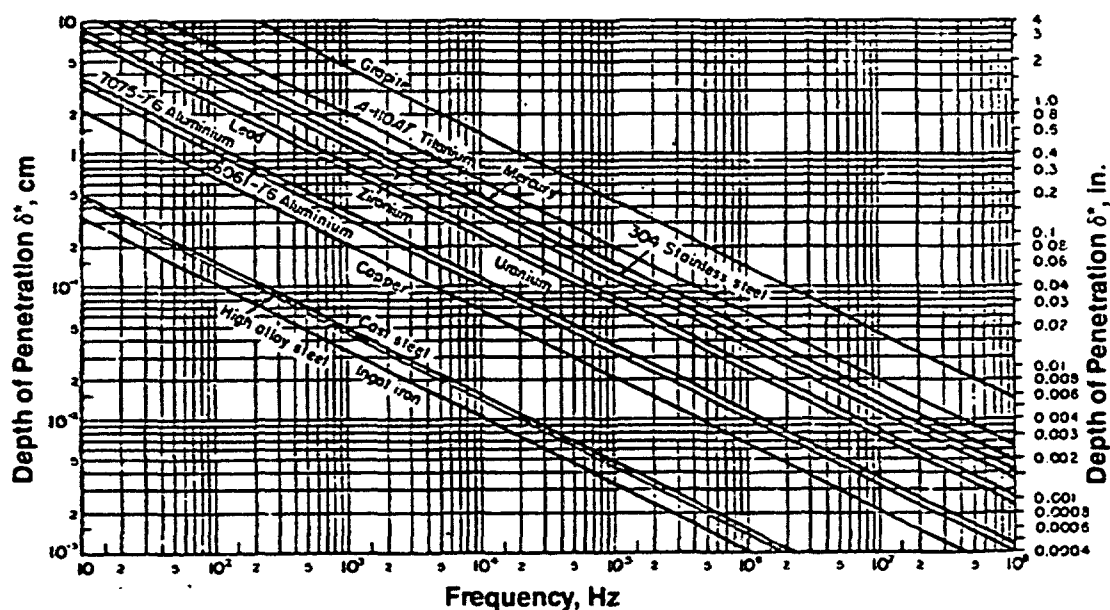
There are three basic types of material configurations for which eddy-current thickness measurements are employed, i.e.,

1. Nonconductors on conducting substrates
2. Conductors on nonconducting substrates
3. Conductors on conducting substrates.

Eddy-current measurement of nonconducting coatings on conducting material includes applications such as the thickness of anodized coatings on aluminum plate and the thickness of a variety of nonmetallic paints and lacquers on metal substrates. Eddy-current measurements of conductive coatings on conducting substrates require that the two materials differ significantly in electrical conductivity or magnetic permeability.

Table 6-14 lists standards and specifications for eddy-current testing.

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\* $\delta$  is the depth of penetration at which the eddy current density has decreased to  $1/e$  times its value at the surface.

Figure 6-18. Relationship Between Depth of Penetration in Various Metals and Test Frequency (Plane Case) (Ref. 21)

TABLE 6-14. STANDARDS AND SPECIFICATIONS FOR EDDY-CURRENT TESTING

| ISSUED BY | DESIGNATION               | TITLE OR EXPLANATION   |
|-----------|---------------------------|--|
| Air Force | TO 00-25-224              | Welding High-Pressure and Cryogenic Systems (Section 4, Nondestructive Inspection by Ultrasonic and Eddy Current Methods)  |
| Air Force | TO 33B-1-1                | Nondestructive Testing Methods, Chapter 3, "Eddy Current Method"   |
| Navy      | NAVAIR 01-1A-16           |  |
| Army      | TM 43-0103                |  |
| ASNT      | SNT-TC-1A<br>Supplement E | Recommended Practice for Nondestructive Testing Personnel Qualification and Certification: Eddy Current Test Method  |
| ASTM      | B244                      | Method for Measurement of Thickness of Anodic Coatings on Aluminum and of Other Nonconductive Coatings on Nonmagnetic Basic Metals With Eddy Current Instruments |
| ASTM      | E113                      | Recommended Practice for Ultrasonic Testing by Resonance Method  |
| ASTM      | E164                      | Standard Method for Ultrasonic Contact Inspection of Weldments   |
| ASTM      | E215                      | Practice for Standardizing Equipment for Electromagnetic Testing of Seamless Aluminum Alloy Tube   |
| ASTM      | E243                      | Practice for Electromagnetic (Eddy Current) Examination of Seamless Copper and Copper Alloy Tubes  |
| ASTM      | E268                      | Definition of Terms Relating to Electromagnetic Testing  |
| ASTM      | E309                      | Practice for Eddy Current Examination of Steel Tubular Products Using Magnetic Saturation  |
| ASTM      | E376                      | Practice for Measuring Coating Thickness by Magnetic Field or Eddy Current (Electromagnetic) Test Methods  |
| ASTM      | E426                      | Practice for Electromagnetic (Eddy Current) Testing of Seamless and Welded Tubular Products, Austenitic Stainless Steel and Similar Alloys                       |
| ASTM      | E566                      | Practice for Electromagnetic (Eddy Current) Sorting of Ferrous Metals  |

(cont'd on next page)



**MIL-HDBK-735(MR)****TABLE 6-14. (cont'd)**

| ISSUED BY          | DESIGNATION  | TITLE OR EXPLANATION   |
|--------------------|--------------|--|
| ASTM               | E571         | Practice for Electromagnetic (Eddy Current) Examination of Nickel and Nickel Alloy Tubular Products  |
| ASTM               | E690         | Practice for In-Situ Electromagnetic (Eddy Current) Examination of Nonmagnetic Heat Exchanger Tubes  |
| ASTM               | E1004        | Test Method for Electromagnetic (Eddy Current) Measurements of Electrical Conductivity   |
| ASTM               | F673         | Method for Measuring Resistivity of Semiconductor Slices With a Noncontact Eddy Current Gage   |
| DOD                | MIL-I-6870   | Inspection Program Requirements, Nondestructive for Aircraft and Missile Materials and Parts   |
| DOD                | MIL-STD-271  | Requirements for Nondestructive Testing Methods  |
| DOD                | MIL-STD-410  | Nondestructive Testing Personnel Qualification and Certification (Eddy Current, Liquid Penetrant, Magnetic Particle, Radiographic, and Ultrasonic) |
| DOD                | MIL-STD-1537 | Electrical Conductivity Test for Measurement of Heat Treatment of Aluminum Alloys, Eddy Current Method   |
| Federal Government | FED-STD-151  | Test Methods, Metals   |
| NASA               | SP-3079      | Nondestructive Evaluation Technique Guide  |

**6-4.6 LEAK TESTING**

Leak testing is a type of nondestructive test. The presence of a leak is an indication of discontinuity in a material or lack of a seal at an interface. A leak may result from fabrication processes, or it may be the result of operational wear including corrosion. Local corrosion, such as pitting and crevice corrosion, can result in a leak without significant general corrosion and at relatively mild environmental exposure conditions.

The correct choice of a leak testing method optimizes sensitivity, cost, and reliability of the test. In general, leakage measurement procedures involve covering the whole of the suspected region with tracer gas while establishing a pressure differential across the system by either pressurizing with a tracer gas or by evacuating the opposite side. The presence and concentration of tracer gas on the lower pressure side of the system are determined and then measured. Fig. 6-19 is a guide for selection of a leakage test method that illustrates the various options.

A dynamic test method can be performed in the shortest time. Static techniques increase test sensitivity, but the time for testing is also increased. Leak tests are performed on open units, which are accessible on both sides, and sealed units. Either evacuation or pressurization of one side of a unit that is accessible on both sides may be used to test for leakage.

Leak location can be accomplished with a tracer-probe or a detector-probe method. The tracer-probe method is used when the system is evacuated, and the tracer gas comes from a probe located outside the system. The detector probe is used when the system is

pressurized with tracer gas and testing is done at atmospheric pressure.

When using liquid penetrants for leak location, both surfaces must be accessible.

Table 6-15 is a list of ASTM standards and specifications related to leak testing.

**6-4.7 THERMAL NONDESTRUCTIVE INSPECTION**

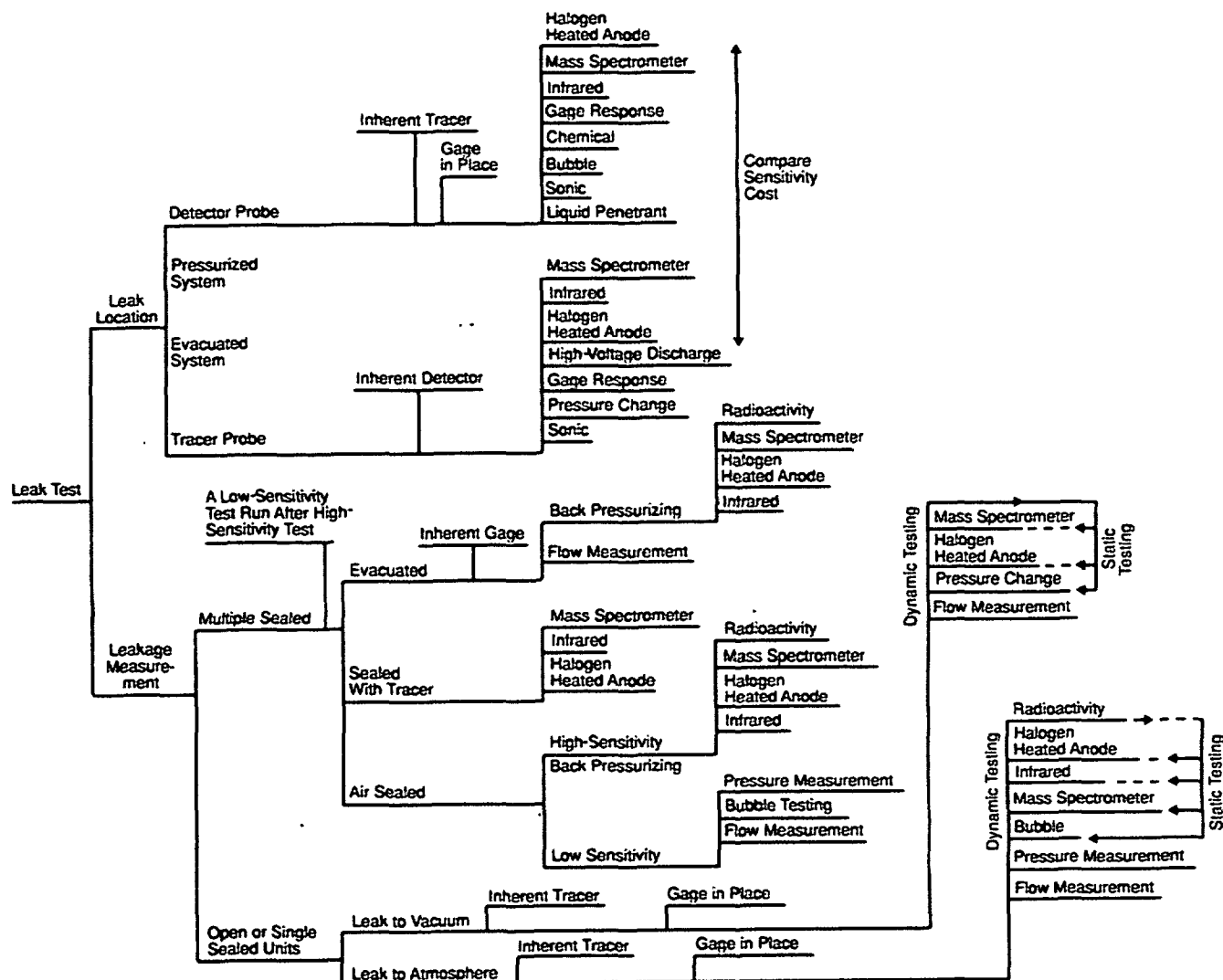
Thermal nondestructive inspection (TNI) is a process for determining the existence of discontinuities, anomalies, and malfunctions in test objects by virtue of their thermal properties.

If malfunctioning components of an operating test object may be detected because they generate excessive heat, the test is termed passive. An example of passive TNI is the measurement of the temperatures of components in electronic assemblies to determine whether the components are operating properly.

If discontinuities and anomalies are detected by their altering of the heat flow in the test object and heat must be added to detect them, the testing method is termed active. Flaws influence temperature gradients as a function of location or time. An example of active TNI is the inspection of honeycomb structures. Heat introduced on the surface flows less rapidly from the surface where cells are not bonded to the face sheet. This slower flow of heat results in a higher temperature on the surface above the anomaly.

Temperature is the variable that signals the existence of discontinuities, flaws, and malfunctions. An important method of classifying TNI temperature measure-

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Figure 6-19. Guide for Selection of Leakage Testing Method (Ref. 22)

ment methods is based on whether or not the temperature-measuring device contacts the surface of the test object.

Contacting methods may be classified as point measurements using thermocouples or thermistors or area measurements using coatings that change their properties in response to the temperature of the object. Coatings include cholesteric liquid crystals, thermochromic phosphors, and thermochromic paint.

It is not necessary to contact the surface of an object to measure its temperature. It is possible to sense the radiated energy emitted by the object and relate it to the temperature of the object. There are several types of noncontacting temperature detectors that are used in TNI. One type is the thermovoltaic device that responds to the total spectral range. The incident radiation heats a black-surface mass. A series connection of thermocouples (a thermopile) or a single thermocouple in

contact with the mass produces a voltage in response to the temperature of the absorbing element. The voltage is related directly to the incident radiant power. Another type of thermal radiation detector is the bolometer, which changes its resistance with changes in its temperature.

A type of infrared radiation detector that is significantly different from thermal detectors is the photon detector. Photon detectors do not respond equally to all wavelengths. There are two basic ways in which they respond to incident infrared light: (1) the resistance of a semiconducting element changes with changing incident light intensity (photon conduction) and (2) the semiconductor material generates a voltage in response to incident light (photovoltaic operation).

**MIL-HDBK-735(MR)****TABLE 6-15. ASTM STANDARDS AND SPECIFICATIONS  
RELATED TO LEAK TESTING**

| DESIGNATION | TITLE OR EXPLANATION   |
|-------------|--|
| D998        | Test for Penetration of Liquids into Submerged Loaded Shipping Containers  |
| D3078       | Test Method for Leaks in Heat-Sealed Flexible Packages   |
| E425        | Definitions of Terms Relating to Leak Testing  |
| E427        | Practice for Testing for Leaks Using the Halogen Leak Detector   |
| E432        | Guide for the Selection of a Leak Testing Method   |
| E493        | Test Methods for Leaks Using the Mass Spectrometer Leak Detector in the Inside-Out Testing Mode                          |
| E498        | Methods of Testing for Leaks Using the Mass Spectrometer Leak Detector or Residual Gas Analyzer in the Tracer Probe Mode |
| E499        | Methods of Testing for Leaks Using the Mass Spectrometer Leak Detector in the Detector Probe Mode                        |
| E515        | Method of Testing for Leaks Using Bubble Emission Techniques   |
| F37         | Test Method for Sealability of Gasket Materials  |
| F78         | Method of Calibration of Helium Leak Detectors by Use of Secondary Standards   |
| F97         | Recommended Practice for Determining Hemeticity of Electronic Devices by Dye Penetration                                 |
| F98         | Recommended Practices for Determining Hemeticity of Electronic Devices by a Bubble Test                                  |
| F112        | Test Method for Sealability of Enveloped Gaskets   |
| F134        | Recommended Practices for Determining Hemeticity of Electron Devices With a Helium Mass Spectrometer Leak Detector       |
| F586        | Test Method for Leak Rates Versus $y$ and $m$ Factors for Gaskets  |
| F730        | Test Methods for Hemeticity of Electron Devices by a Weight Gain Test  |

There are two variables to which temperature may be related: position and time. Position leads to the location of the anomalies. The important time period is the time difference between temperature measurement and initiation or cessation of heating. The most common way to interpret TNI data is by comparing temperature data for a structure under given heat flow conditions to an identical structure that is known to be free of defects or malfunctions under the same heat flow conditions.

### 6-5 FAILURE ANALYSIS

The quality engineering process described in par. 6-3 has the goal of fielding a quality product that satisfies the mission requirements. Therefore, it is important that feedback on service performance be part of the process. In particular, logistic support analysis is an iterative process that continually refines a product based upon testing and performance information. One aspect of this information feedback is failure analysis.

A failure is the event, or inoperable state, in which any item or part of an item does not, or would not, perform as previously specified (Ref. 23). Failure analysis occurs subsequent to a failure. It is the logical, systematic examination of an item, its construction, application, and documentation to identify the failure mode and determine the failure mechanism and its basic course (Ref. 23). This is in distinction to a failure mode and effects analysis (FMEA), which is a procedure

by which each potential failure mode in a system is analyzed to determine the results or effects thereof on the system and to classify each potential failure mode according to its severity (Ref. 23). The failure mechanism is the physical, chemical, electrical, electrochemical, thermal, or other process that results in failure (Ref. 23). The failure mode is the consequence of the mechanism through which the failure occurs, i.e., electrical short, open circuit, fracture, excessive wear, leakage, or rupture (Ref. 23).

Therefore, corrosion is a failure mechanism even though many types of corrosion are characterized by the consequences and not by the mechanism. In some situations the mechanisms for corrosion are not completely understood and the only convenient way to describe it is by the consequences. Electrochemical mechanisms are usually a salient feature of most corrosion processes. For example, the mechanism of corrosion may be responsible for the mode of failure—penetration and leakage—of an automobile radiator. However, the failure may manifest itself in overheating of the engine or perhaps seizure of moving parts.

Failure may be characterized in various ways (Ref. 23):

1. A catastrophic failure results in the sudden loss of an item.
2. A critical failure or combination of failures prevents an item from performing a specified mission.

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3. A dependent failure is caused by the failure of an associated item(s). An independent failure occurs without being caused by the failure of any other item.

4. An intermittent failure occurs for a limited time, after which the item recovers its ability to perform within specified limits without any remedial action.

5. A nonrelevant failure is (a) a failure verified as peculiar to an item design that will not enter the operational environment or (b) a failure verified as peculiar to an item design that will not enter the operational inventory. Thus a relevant failure is equipment failure that occurs in the operational environment.

6. A nonchargeable failure is (a) a nonrelevant failure or (b) a relevant failure caused by a condition previously specified as not within the responsibility of a given organizational entity. (All relevant failures are chargeable to one organizational entity or another.)

7. The occurrence of a random failure is predictable only in a probabilistic or statistical sense. This fact applies to all distributions of the universe.

Most failures are unexpected. Nevertheless, when a sufficiently large sample of similar failures has been accumulated, probabilities of failure can be assigned to the universe represented by the sample. It is important to draw the boundaries of the universe carefully. For example, the universe may consist of all similar items, only the items produced by one manufacturer, or only the items given a similar heat treatment.

An item may fail under test or operational conditions. A testing program follows a detailed test plan that is designed to provide information to the design process. Failures that occur during tests may result in design and material changes, modification of operating limits, and schedules for preventive maintenance. Tests are usually well documented. Test articles may be fitted with sensors that monitor operating conditions and indicate failure mechanisms. Test articles are available for detailed posttest examination. However, as realistic as a testing program might be, unanticipated failures should be expected under field operating conditions. All too often the information that is potentially available from field failures is not obtained, is poorly documented, or does not find its way to those who are in a position to correct a problem or to insure that similar mistakes are not made in the future. One reason for poor response from the field may be that people who report failures become discouraged if they perceive that nothing results from their reports.

As a failure mechanism, corrosion is often missed in testing programs because of the long time that can pass before evidence of significant failure mode damage is detected. Although the mechanisms associated with corrosion are operating continuously, the failure modes require extensive damage before they become apparent. Therefore, the first indication of failures occurring by corrosion mechanisms is often in the field after a

materiel item has been tested and "fielded". A failure analysis must be conducted to obtain useful information concerning these failures.

It is important that a failure analysis involving metal failure be conducted by someone who is familiar with corrosion manifestations and mechanisms. Some forms of corrosion are similar to mechanical wear and failure, and it is important to distinguish between the two. For example, a shaft may break as a result of mechanical overload or the breakage may be the result of a corrosion mechanism in which the shaft undergoes corrosion-assisted crack growth until the remaining uncracked portion is overloaded mechanically. When a corrosion mechanism is identified as contributing to the failure mode, the extent of corrosion, the mechanisms, and the exposure conditions responsible for corrosion should be determined. It is also important to identify the metal involved and the function of the part affected.

Although only a limited amount of failure analysis can be conducted in the field, it is important that even this be done. If corrosion is not suspected in the field examination, further examinations are not likely to be carried out. In the field the most important type of examination is visual.

Failed components should be examined for signs of corrosion products and corrosion attack. Conditions that could be conducive to corrosion, such as trapped water, wet mud and sand, corrosive working fluids, and environmental conditions, should be noted. The conditions of protective coatings should be assessed, and dimensions of corroded sections should be noted.

More detailed examinations can be carried out in the laboratory. It may not, however, be feasible under some conditions to provide specimens for laboratory examination. Examinations that can be conducted in the laboratory are

1. Microscopic examination of the failure zone to confirm the presence of corrosion and the type and extent of corrosion attack

2. Metallographic examination of the failure surface and adjacent zones

3. Measurement of the strength properties of the metal to determine changes that may have resulted from the service exposure

4. Instrumental and wet-chemical analysis of corrosion film and scale and the corroded surface of the metal

5. Instrumental and wet-chemical analysis of protective coatings

6. Electrochemical measurements of the effectiveness of protective films and coatings and the corrosion characteristics of galvanic couples

7. Chemical analysis of possible corrodents, if available.

By themselves, the results of this examination are incomplete. They should be related to service history, operating conditions, maintenance, and assembly configuration. This information must come from the field

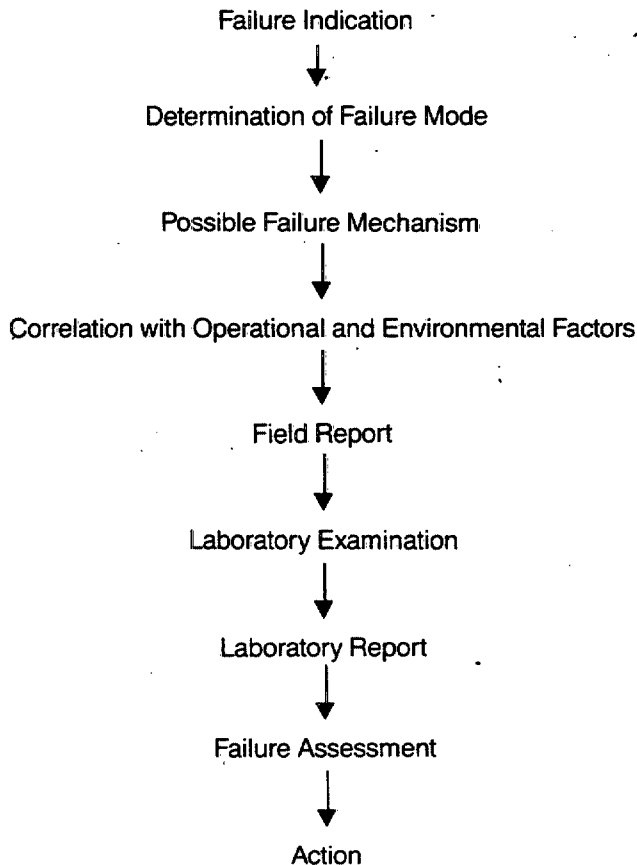
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examination. The operating elements responsible for the field examination will have some relevant information. Unfortunately, it may be difficult, if not impossible, to reconstruct a complete history of the item.

The failure examination and its interpretation should be compared with information available on similar failures. The objective is to determine whether there is some common element that would indicate one or more of the following:

1. Design deficiency
2. Material inadequacy
3. Fabrication defects
4. Inadequate quality assurance
5. Damage in shipment
6. Deterioration in storage
7. Inadequate or improper maintenance
8. Unusually severe operating conditions.

Fig. 6-20 indicates the general progression of the failure analysis process.



**Figure 6-20. Failure Analysis Process**

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6.6 SUBJECT TERM (KEY WORD) LISTING

Aluminum and Aluminum Alloys  
Beryllium  
Chemical Conversion Coatings  
Coatings, Inorganic, Metallic, and Organic  
Cobalt and Cobalt Alloys  
Copper and Copper Alloys  
Corrosion, Chemistry and Types  
Corrosion Considerations, Design and Material Selection  
Corrosion Prevention  
Dry Film Lubricants  
Environments  
Ion Implantation  
Inhibitors  
Laboratory and Field Testing  
Lead and Lead Alloys  
Magnesium and Magnesium Alloys  
Molybdenum  
Nickel and Nickel Alloys  
Packaging  
Powder Metallurgy  
Tantalum and Tantalum Alloys  
Titanium and Titanium Alloys  
Tungsten and Tungsten Alloys  
Uranium and Uranium Alloys  
Zinc and Zinc Alloys

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## GLOSSARY

## A

**Acceptable Quality Level (AQL).** The maximum percent effective that, for purposes of sampling inspection, can be considered satisfactory as a process average.

**Acceptance Number.** The maximum number of defects or defective units in the sample that will result in acceptance of the lot.

**Acid Media.** Liquids having a pH less than 7.

**Acid Mine Drainage.** Drainage from bituminous coal mines that contains large concentrations of acidic sulfates, especially ferrous sulfate.

**Acid Pickling.** Treatment of a metal, usually steel, with an acid, usually sulfuric acid with an added inhibitor, to remove mill scale, rust, and other impurities from the surface.

**Acid Salt.** A compound that is derived from an acid and a base and in which only part of the hydrogen is replaced by a basic radical, e.g., the acid sulfate  $\text{NaHSO}_4$ .

**Acoustics.** The transmission of energy to an object by sound waves.

**Acrylic.** Resin polymerized from acrylic acid, methacrylic acid, esters of these acids, or acrylonitrile.

**Active.** A state in which a metal tends to corrode.

**Active-Passive Behavior.** The formation of a passive protective film on an otherwise active metal surface.

**Aeration.** Introducing air into a solution.

**Aerobic.** Living, active, or occurring only in the presence of oxygen.

**Aging.** A second heat treatment of an alloy at a lower temperature that causes precipitation of the unstable phase and increased hardness, strength, and electrical conductivity.

**Alkaline Solution.** A solution having a pH greater than 7.

**Alkyd.** Resin used in coatings; reaction products of polyhydric alcohols and polybasic acids.

**Alkyl Halide.** A compound consisting of an alkyl group and a halogen, e.g., ethyl bromide.

**Allotropic.** The property of a substance to assume different forms or structures under different conditions, such as temperature.

**Alloy.** A substance composed of two or more metals intimately united, usually by being fused together and dissolving in each other when molten.

**Amphoteric.** Having both acidic and basic characteristics.

**Amphoteric Metal.** A metal that dissolves in both acid and alkaline solutions.

**Anaerobic.** Living, active, or occurring in the absence of free oxygen.

**Anion.** A negatively charged ion of an electrolyte. An anion migrates toward the anode under the influence of a potential gradient.

**Anisotropic.** Showing different properties in different directions.

**Anode.** The electrode at which oxidation or corrosion occurs.

**Anodic Coating.** A film of oxide produced on a metal by electrolysis with the metal as the anode.

**Anodic Protection.** An appreciable reduction in corrosion achieved by making a metal an anode and maintaining this highly polarized condition with very little current flow.

**Anodize.** To subject a metal to electrolytic action as the anode of a cell in order to coat with a protective or decorative film.

**Anodizing.** Forming an oxide coating on a metal surface (generally aluminum) by an electrolytic process.

**Antifouling.** Prevention of the attachment of marine organisms or growth on a submerged metal surface that is generally achieved through chemical toxicity caused by the composition of the metal or coating layer.

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**Antifouling Paints.** Coatings designed to release slowly a biocide such as copper over a period of time. This release prevents fouling of painted underwater surfaces by marine organisms.

**Antiseizing Compound.** A lubricant used to prevent metals from cohering or binding in sliding or rolling contact.

**Applied Stress.** A stress system within a solid that is the result of external forces.

**Armored Vehicle.** Wheeled or track-laying vehicle, with armor hull or body and with or without major armament, that is used for combat, security, or cargo.

**A-Scan Display.** An ultrasonic testing time versus amplitude display. From the signal location on a cathode-ray-tube (CRT) screen, the depth of a defect within a material and an estimate of its size can be determined.

**As-Cast Surface.** The surface of a metal object that results from a casting process.

**Aspect Ratio.** The ratio of length to width of an item such as a metallic grain.

**Asymptote.** A straight line associated with a curve such that as a point moves along an infinite branch of the curve, the distance from the point to the line approaches zero and the slope of the curve at the point approaches the slope of the line.

**Atomic Hydrogen.** A free, unassociated atom of hydrogen.

**Attributes, Inspection by.** Inspection whereby either the unit of product is classified simply as defective or nondefective or the number of defects in the unit of product is counted with respect to a given set of requirements.

**Austenite.** Gamma iron with carbon in solution.

**Austenitic.** The name given to the face-centered cubic crystal (FCC) structure of ferrous metals. Ordinary iron and steel have this structure at elevated temperatures. Also certain stainless steels have this structure at room temperature.

**B**

**Babbitt Metal.** Any of the white alloys, composed primarily of tin or lead and of lesser amounts of

antimony, copper, and perhaps other metals, used for bearings.

**Ballistic Property.** The characteristics of a metal that affect the motion of a projectile made from it in the bore, through the atmosphere, and during target penetration.

**Base (Basis) Metal.** The underlying structural metal.

**Bearing Race.** A track or channel in which bearings roll or slide.

**Beta Particle Backscatter.** The rebounding of incident beta particles from a material in the direction of the beta particle source.

**Beta Particles.** High-speed electrons emitted from the nuclei of materials undergoing radioactive decay nuclear transformation.

**Bimetallic Corrosion.** Corrosion resulting from dissimilar metal contact, i.e., galvanic corrosion.

**Binary Chemical Munition.** An artillery shell or bomb in which the two liquid components, which are individually nontoxic, are separated by a membrane that ruptures on firing and allows the two components to mix, react, and form a toxic compound.

**Black Light.** Electromagnetic radiation in the ultraviolet (UV) end of the light spectrum.

**Boiler Water.** Water in the steam-generating section of a boiler unit.

**Bolometer.** A very sensitive resistance thermometer used in the detection and measurement of feeble thermal radiation and specially adapted to the study of infrared spectra.

**Borescope.** An optical device for examining internal surfaces not directly accessible; initially developed for examining the bored surfaces of gun tubes and barrels.

**Brackish Water.** Water having salinity values from approximately 0.50 to 17.00 parts per thousand.

**Braze.** To solder metals by melting a nonferrous filler metal such as brass or brazing alloy (hard solder) with a melting point lower than that of the base metals at the point of contact.

**Breakaway Corrosion.** The sudden change in corrosion from a slow to a fast rate.



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**Bronze.** To solder with a nonferrous alloy that melts at a lower temperature than the metals being joined.

**B-Scan Display.** An ultrasonic testing presentation of a cross-sectional view of the material being examined. The front and back surfaces and relative location of defects within the material are shown.

**Burning.** Permanent damage to a metal caused by heating beyond the temperature limits of the treatment. Also the tendency of materials to burn at given temperatures in contrast to melting or disintegrating.

## C

**Camouflage.** The disguising of military equipment or installations with paint, nets, or foliage.

**Carbon Brush.** A conductive carbon block used to make sliding electrical contact with a moving part.

**Carburize.** To surface-harden steel by converting the outer layer of low-carbon steel to high-carbon steel by heating the steel above the transformation range in contact with a carbonaceous material. The carbonaceous material may be solid or gaseous.

**Carnauba Wax.** The hardest natural wax, having a melting point of 85°C, exuded from the leaves of the carnauba palm.

**Cast Alloy.** Alloy that is formed into a fixed shape from a liquid by letting it cool in a mold.

**Catastrophic Corrosion.** Continuous and rapid corrosion leading to complete destruction of the metal.

**Catastrophic Failure.** A failure that results in the sudden loss of function of an item.

**Cathode.** The electrode at which reduction (and practically no corrosion) occurs.

**Cathodic Protection.** Reduction or elimination of corrosion achieved by making the metal a cathode by means of an impressed direct current or attachment of a sacrificial anode.

**Cation.** A positively charged ion of an electrolyte. A cation migrates toward the cathode under the influence of a potential gradient.

**Caustic Embrittlement.** Cracking as a result of the combined action of tensile stresses and corrosion in alkaline solutions.

**Cavitation.** Formation and sudden collapse of vapor

bubbles in a liquid; usually results from local low pressure, e.g., as on the trailing edge of a propeller. This action develops momentary high local pressure that can mechanically destroy a portion of a surface on which the bubbles collapse.

**Cavitation Corrosion.** Corrosion damage resulting from cavitation and corrosion: metal corrodes, pressure develops from collapse of cavity and removes corrosion product, and thus exposes bare metal to repeated corrosion.

**Cavitation Damage.** Deterioration of a surface caused by cavitation—sudden formation and collapse of cavities in a liquid.

**Chargeable Failure.** All relevant failures chargeable to one organizational entity or another.

**Chemical Agents.** Chemical substances used in warfare to disable enemy forces.

**Chemical Conversion Coating.** A metal surface layer intentionally developed by chemical reaction to protect or to improve appearance.

**Chemical Milling.** Controlled removal of metal by chemical dissolution.

**Chemical-Vapor-Deposited Carbon.** Carbon formed from carbonaceous material that is condensed from a vapor phase.

**Chemically Pure.** The grade of metal that is highly refined to be essentially free of impurities.

**Chemisorption.** The adsorption of a chemical species on a surface with strong binding forces that are comparable with those leading to the formation of a chemical compound.

**Cholesteric Liquid Crystal.** A liquid crystal material in which the elongated molecules are parallel to each other within the plane of a layer, but the direction is twisted slightly from layer to layer to form a helix through the layers.

**Clad Alloy.** A base metal bonded to a layer of another more corrosion-resistant metal.

**Clad Metal.** A metal substrate to which a different metal surface layer has been fixed by physical means.

**Cladding Alloy.** The overlapping metal in a clad metal.

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**Cold Working.** Plastic deformation of a metal below the annealing temperature in order to cause permanent strain hardening.

**Combustion Gas.** The gas resulting from the oxidation of a fuel.

**Commercial Grade.** The grade or purity of a chemical material that is commonly used in industry and that is readily available.

**Commercially Pure.** The grade of metal normally sold as "pure".

**Commutation.** The process of reversing every other half-cycle of an alternating current so as to form a unidirectional current. In the case of a generator, this process is achieved by a series of bars or segments so connected to armature coils that rotation of the armature in conjunction with fixed brushes results in unidirectional current output.

**Commutator.** That part of a direct current motor or generator that serves the dual function, in combination with brushes, of providing an electrical connection between the rotating armature winding and the stationary terminals and of permitting reversal of the current in the armature windings.

**Complex Ion.** A complex, electrically charged group of atoms or radical.

**Composite.** A structural shape in which more than one discrete component is intimately united so that the properties exhibited reflect those of the components.

**Compressor Stall.** The aerodynamic condition in which the compressor section of a gas turbine engine loses its effectiveness.

**Concentration Cell.** A cell involving an electrolyte and two identical electrodes, with the potential resulting from differences in the chemistry of the environments adjacent to the two electrodes.

**Concentration Gradient Mass Transfer.** The transfer of material between a concentrated and a less concentrated region at the same temperature.

**Conductivity.** The property of a metal to transmit electrical current.

**Conformal Coating.** A viscous formulation that forms a dry, thick, adherent, and water-repellent coating on irregularly shaped surfaces.

**Continuous Casting.** A technique in which an ingot, billet, tube, or other shape is continuously solidified and withdrawn while it is being poured so that its length is not determined by mold dimensions.

**Copper Strike.** A thin electroplated copper film applied prior to depositing the principal electroplate.

**Core Alloy.** Metal that is overlaid on one or both sides with a different metal.

**Corrosion.** The deterioration of a material, usually a metal, caused by a reaction with its environment.

**Corrosion Fatigue.** The combined action of corrosion and fatigue, i.e., cyclic stressing, that causes metal fracture.

**Corrosion Fatigue Strength.** The maximum stress that a corroded material can withstand from a given number of stress reversals.

**Corrosion Resistant.** Exhibition of resistance to corrosion attack in specific environments.

**Cost-Effectiveness.** A measure that relates cost to physical and performance characteristics.

**Creep.** Time-dependent strain occurring under stress.

**Creep Resistance.** The resistance of a metal to a time-dependent strain caused by stress.

**Creep Rupture Strength.** The stress that at a given temperature will cause a material to rupture at a given time.

**Crevice Corrosion.** Localized corrosion resulting from the formation of a concentration cell in a crevice formed between a metal and a nonmetal, or between two metal surfaces.

**Critical Defect.** A defect that is likely to result in hazardous or unsafe conditions for individuals using, maintaining, or depending on the product or that is likely to prevent performance of the tactical function of a major end-item.

**Critical Failure.** A failure or combination of failures that prevents an item from performing a specified mission.

**C-Scan Display.** An ultrasonic testing presentation of a plan view of the material being examined. It outlines the contour of the specimen.

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**Cube Dimension.** The volume of a unit package expressed as the length of an equivalent cube.

**Cutting Oil.** A type of cutting fluid used in machining metals to lubricate the tool and workpiece; this lubrication reduces tool wear, allows increased cutting speeds, and decreases power needs.

**Cyclic Loading.** The repeated application of stress separated by periods of reduced or zero stress.

## D

**Damping Capacity.** Capability of a material to absorb vibrations.

**Damping Factor.** The ratio of the logarithmic decrement of any underdamped harmonic motion to its period.

**Dealloying.** The selective corrosion (removal) of a metallic constituent from an alloy, usually in the form of ions.

**Dealuminification.** Dealloying corrosion in which aluminum is preferentially removed from an alloy.

**Decomposition.** The more or less permanent breakdown of a molecule into simpler molecules or atoms.

**Decontaminants.** The substances used to remove or detoxify a chemical or biological hazard.

**Deep-Drawing.** Capability to form shapes with large depth-to-diameter ratios by considerable plastic deformation of sheet or strip metal in dies.

**Defect.** An imperfection that impairs worth or utility.

**Defective.** A unit of product that contains one or more defects.

**Demineralized Water.** Water from which mineral constituents have been removed.

**Density.** The mass of a given substance per unit volume.

**Dessicant.** A material that will absorb moisture by physical or chemical means.

**Dezincification.** Corrosion of brass in which both components of the alloy are dissolved and the copper is redeposited as a porous surface residue.

**Die Casting.** A metal-casting process in which molten metal is forced under pressure into a permanent mold.

**Dielectric.** A material that is an electrical insulator.

**Differential Aeration Cell.** An electrolytic cell in which the difference in electromotive force (EMF) between the anode and cathode is established by different concentrations of air or oxygen in the electrolytes.

**Diffusion.** Movement of a chemical species within a liquid, solid, or gaseous medium from a region of high to low concentration or from a high temperature to a low temperature.

**Diffusion Coating.** A coating developed on a metal surface by a high-temperature diffusion process, such as carburization, colorizing, or chromizing.

**Dislocation.** Large lattice disturbance of the crystal structure of a metal.

**Diurnal Temperature Variation.** Daily variation of the atmospheric temperature at a given location.

**Double Cantilever Beam Specimen.** A fracture-mechanics-type tensile specimen having a relatively high aspect ratio that is cracked across a short dimension and loaded by equal and opposed stresses in order to open the crack.

**Double Sampling Plan.** Sampling inspection in which inspection of the first sample leads to a decision to accept, to reject, or to take a second sample. Inspection of the second sample leads to a decision to accept or reject the lot.

**Dry-Film Lubricant.** A formulation applied to a surface that has lubricating properties when dry.

**Drying Oil.** An oil capable of conversion from a liquid to a solid by slow reaction with oxygen in the air.

**Ductility.** Property of a metal to deform under tensile stress without fracture.

**Duplex Alloy.** An alloy comprised of two metallurgical phases.

## E

**Eddy.** A vortex-like motion of a fluid running contrary to the main current.

**Eddy Current.** An electric current induced by an alternating magnetic field.

**Elastomer.** A material, such as synthetic rubber or plastic, that at room temperature can be stretched under low stress to at least twice its original length and upon immediate release of the stress will return with force to approximately its original length.

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**Electrical Bonding.** An electricity-conducting joint between two conductors.

**Electrical Conductivity.** A measure of the capability of a metal to transmit electricity.

**Electrical Discharge Machining.** A process by which materials that conduct electricity can be removed from a metal by an electric spark.

**Electrode.** A metal in contact with an electrolyte that serves as a site where an electrical current enters the metal or leaves the metal to enter the solution.

**Electroless Coatings.** Metallic coatings formed on a surface by chemical reaction in comparison to electroplated coatings.

**Electroless Plating.** Deposition of a metal coating by immersion of a metal or nonmetal in a suitable bath containing a chemical reducing agent.

**Electrolyte.** An ionic conductor (usually in aqueous solution).

**Electrolytic Cleaning.** The process of degreasing or descaling a metal by making it an electrode in a suitable bath.

**Electromagnetic Radiation.** Radiation consisting of oscillating electric and magnetic fields and propagated with the speed of light. It includes gamma radiation; X rays; ultraviolet, visible, and infrared radiation; and radar and radio waves.

**Electromagnetism.** Magnetism developed by a current of electricity.

**Electromotive Force Series (EMF Series).** An orderly listing of elements according to their standard electrode potentials relative to the hydrogen electrode, which is given the value of zero.

**Electron.** An elementary particle consisting of a charge of negative electricity equal to about  $1.602 \times 10^{-19}$  coulomb and having a mass when at rest of about  $9.107 \times 10^{-29}$  gram or 1/1837 that of a proton.

**Electron-Beam Physical Vapor Deposition.** Deposition of a material from the vapor phase by the action of a narrow stream of electrons that move in the same direction, have about the same velocity, and focus on the target part.

**Electron Probe Microanalysis.** A technique in analytical chemistry by which a finely focused beam of

electrons is used to excite an X-ray spectrum characteristic of the elements in the sample; can be used with samples as small as  $10^{-11}$  cm<sup>3</sup>.

**Electron Probe Microanalyzer.** An instrument used to determine the elemental composition of a small sample. A finely focused beam of electrons is used to excite an X-ray spectrum characteristic of the elements in the sample. It can analyze samples as small as  $10^{-11}$  cm<sup>3</sup>.

**Electrophoresis.** The movement of suspended particles through a fluid under the action of an electromotive force applied to electrodes in contact with the suspension.

**Electroplated Coatings.** Coatings formed by electro-deposition of a metal or alloy from a suitable electrolyte solution. The article to be plated is connected as the cathode in the electrolyte solution; direct current is introduced through the anode, which consists of the metal to be deposited.

**Electrorefining.** Purifying metals by electrolysis using an impure metal as the anode, from which the pure metal is dissolved and subsequently deposited at the cathode.

**Encapsulant.** A formulation that sets to enclose completely a component. *See also* Conformal Coating and Potting Compound.

**Environment.** The surrounding circumstances, conditions, or objects.

**Epoxy.** Resin formed by the reaction of bisphenol and epichlorohydrin.

**Erosion.** Deterioration of a surface by the abrasive action of moving fluids. This action is accelerated by the presence of solid particles or gas bubbles in suspension. When deterioration is further increased by corrosion, the term "erosion-corrosion" is often used.

**Eutectic.** The composition of a mixture, such as an alloy, having the lowest melting point possible.

**Exfoliation.** A thick, layer-like growth of loose corrosion products.

**Exfoliation Corrosion.** A type of corrosion that progresses parallel to the metal surface so that underlying layers are gradually separated.

**Explosive Exfoliation.** Exfoliation at an extremely rapid rate.

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## F

**Failure.** The event, or inoperable state, in which any item or part of an item does not or would not perform as specified.

**Failure Analysis.** The logical, systematic examination of an item, its construction, application, and documentation to identify the failure mode and determine the failure mechanism and its basic course.

**Failure Mechanism.** The physical, chemical, electrical, electrochemical, thermal, or other process that results in failure.

**Failure Mode.** The consequence of the mechanism through which the failure occurs.

**Failure Mode and Effects Analysis (FMEA).** A procedure by which each potential failure mode in a system is analyzed to determine the results or effects thereof on the system and to classify each potential failure mode according to its severity.

**Faraday's Law.** The electrical energy available per mole of chemical reactants equals  $zEF$ , where  $z$  is the number of equivalents per mole,  $E$  is the EMF of the cell, and  $F$  is equal to 96,494 coulombs.

**Fatigue.** A process by which fracture results from repeated stress cycles well below the normal tensile strength. Such failures start as tiny cracks that grow to cause total failure.

**Fatigue Cracks.** Fracture resulting from repeated stress cycles well below the normal tensile strength.

**Fatigue Strength or Limit.** The maximum stress a material can endure without breaking for a given number of stress cycles.

**Faying Surfaces.** The surfaces of materials in contact with each other and joined or about to be joined together.

**Ferrite.** Relatively pure metallic iron phase present in steel or cast iron.

**Ferritic.** Pertaining to the body-centered cubic crystal (BCC) structure of many ferrous metals.

**Ferromagnetic Material.** A substance with high magnetic permeability, a definite saturation point, and appreciable residual magnetism and hysteresis.

**Fiber, Filament.** A long, flexible object with a small cross section.

**Filiform Corrosion.** Corrosion that occurs under lacquers and other organic films in the form of randomly distributed hairlines.

**Filler Alloy.** The rod used to deposit metal in a joint during brazing, soldering, or welding.

**Fillet.** A concave transition surface between two otherwise intersecting surfaces.

**Film.** A thin surface layer that may or may not be visible.

**Fissionable Isotopes.** Those isotopes of a material whose nuclei are capable of undergoing fission.

**Flash.** An electroplated coat with a thickness less than  $25.4 \times 10^{-5}$  mm ( $10^{-5}$  in.) thick.

**Flashing.** Electrodeposition of a thin film of metal.

**Flue Gas.** Gaseous combustion products from a furnace.

**Flue Gas Environment.** The environment created by burning fossil fuels in air.

**Fluorescent Dye.** A dye that emits visible light when excited by light in the ultraviolet spectrum (black light).

**Flux.** A substance applied to surfaces to be joined by soldering, brazing, or welding to clean and free them from oxide and to promote their union.

**Flux Dust.** Fine particles of flux material.

**Flux Material.** Low-fusion materials used to extract impurities from molten metals and to prevent the formation of metal oxides.

**Fly Ash.** Fine particulate, essentially noncombustible refuse, carried in a gas stream from a furnace.

**Fouling.** A term used to describe the covering of submerged surfaces by marine growth, such as barnacles.

**Fractography.** The microscopic examination of fractured metal surfaces.

**Fracture Mechanics.** The science of the cracking behavior of a cracked body under stress.

**Fracture Toughness.** The ability of a metal to absorb energy and deform plastically before fracturing.

**Fracture Toughness (strength).** The minimum tensile stress that will cause fracture.

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**Free Energy.** The internal energy of a system minus the product of its temperature and its entropy.

**Free-Machining Steel.** Steel incorporating distributed lead particles that provide lubrication for the cutting tool in machining processes.

**Fretting.** Metal deterioration caused by repetitive slip at the interface between two surfaces. When metal loss is increased by corrosion, the term "fretting corrosion" should be used.

**Fuming Sulfuric Acid.** Concentrated sulfuric acid containing dissolved sulfur trioxide. Also known as oleum.

## G

**Galling.** Surface damage on mating, moving metal parts due to friction caused by local welding of high spots.

**Galvanic Cell.** A cell consisting of two dissimilar metals in contact with each other and with a common electrolyte.

**Galvanic Compatibility.** The property of having sufficiently small difference in potential (EMF) in a solution so that electrochemical corrosion is negligible.

**Galvanic Corrosion.** Corrosion that is increased because of the current caused by a galvanic cell.

**Galvanic Potential.** The electrolytic potential resulting from dissimilar metal contact.

**Galvanic Series.** A list of metals arranged according to their relative corrosion potentials in some specific environment. (Seawater is often used.)

**Gamma Ray.** A photon or radiation quantum emitted spontaneously by a radioactive substance.

**Gas-Shielded Arc Welding.** A welding process in which the arc is flooded by an inert gas to prevent oxidation.

**Gate Valve.** A valve with a disk-shaped closing element that fits tightly over an opening through which water passes.

**Gauge.** The thickness of a metal sheet, a rod, or a wire.

**General (Uniform) Corrosion.** A form of deterioration that is distributed more or less uniformly over a surface.

**Globe Valve.** A device for regulating flow in a pipeline that consists of a movable disk-type element and a stationary ring seat in a generally spherical body.

**Grain.** A portion of a solid metal (usually a fraction of an inch in size) in which the atoms are arranged in an orderly pattern. The irregular junction of two adjacent grains is known as a grain boundary.

**Grain Boundary.** Surface between individual grains in a metal.

**Grain Structure.** The arrangement of grains in an alloy.

**Grain Structure Orientation.** The directional orientation of anisotropic aluminum alloy grains with reference to the direction of rolling or extrusion or to the axis of forging. The orientation of the fracture plane with respect to grain texture and the direction of propagation on that plane is important to stress-corrosion cracking.

**Graphite.** A mineral consisting of a low-pressure allotropic form of carbon.

**Graphitization.** The formation of graphite-like material from organic compounds.

**Graphitizing Carbons.** Carbonaceous material that forms graphite under appropriate conditions.

**Gumbel's Distribution.** A mathematical expression that is based upon extreme value probability techniques and that provides a correlation of maximum pit depths in a series of corrosion test specimens.

## H

**Halide Ion.** An ion of fluorine, chlorine, iodine, bromine or astatine.

**Halogenated Organic Compound.** An organic chemical containing one or more halogen atoms, usually chlorine and fluorine.

**Hard-Drawn Condition.** Drawn to produce great hardness and strength, especially copper tubing and wire.

**Hard Facing.** A layer of hard, abrasion-resistant metal applied to a less resistant metal part by plating, welding, spraying, or other techniques.

**Heat-Affected Zone.** Refers to the area adjacent to a weld braze, or cut, where the thermal cycle has caused microstructural changes that generally affect corrosion behavior.

**Heat Capacity.** See Thermal Capacity.

**Heat of Combustion.** The amount of heat released in the oxidation of one mole of a substance at constant pressure or constant volume.

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**Heat Shield.** Any protective layer that gives protection from heat.

**Heat Sink.** A substance or device used to absorb or dissipate unwanted heat.

**Heat Treating.** Elevating the temperature of a metal followed by some cooldown schedule to achieve some desired property. *See also* Solution Heat Treatment.

**Heavy Metal.** A metal whose specific gravity is approximately 5.0 or higher.

**Hexavalent Chromium Ions.** Chromium ions with a positive six charge, such as the dichromate ion  $(Cr_2O_7)^{-2}$ .

**Hydride.** A compound containing hydrogen and another element.

**Hydrofoil.** A motorboat that has metal plates or fins attached by struts fore and aft for lifting the hull clear of the water as the boat attains speed.

**Hydrogen Blistering.** Cracks or blisters caused when atomic hydrogen penetrates metal, becomes molecular hydrogen, and develops internal pressure.

**Hydrogen Embrittlement.** Embrittlement of a metal caused by hydrogen; sometimes observed in cathodically protected steel, electroplated parts, and pickled steel and other metals.

**Hydrolysis.** A chemical decomposition process that involves the splitting of a bond and the addition of the elements of water.

**I**

**Icing Inhibitor.** A chemical added to fuels of various kinds to prevent the formation of ice from water in suspension, in solution, or in a layer.

**Ignition Temperature.** The lowest temperature at which combustion begins and continues in a substance in air.

**Illuminating Gases.** Flammable mixtures of gases suitable for illuminating purposes. They contain hydrogen, methane, ethane, carbon monoxide, and some nitrogen and oxygen.

**Impingement.** Collision of liquid drops or solid particles in a flowing fluid with a solid surface.

**Impingement Attack.** Localized erosion-corrosion

caused by turbulence or impinging flow at certain points.

**Impressed Current.** Electrical current applied to an electrolytic cell from an external source.

**Inertial Guidance.** Guidance by means of accelerations measured and integrated within the craft.

**Infrared Radiation.** Electromagnetic radiation with wavelengths in the range of 0.7 to 12  $\mu$ m. These wavelengths are longer than those of visible light.

**Inhibited Acid.** An acid containing an inhibitor to reduce the reaction of the metal with the acid when used to remove mill scale from the metal surface.

**Inhibitor.** A substance that sharply reduces corrosion when added to an environment in small amounts.

**Inorganic.** Referring to the chemical elements and their compounds but excluding compounds of carbon to which hydrogen is attached.

**Inspection.** Examination or testing of supplies and services to determine conformance to technical and contractual requirements.

**Inspection by Attributes.** *See* Attributes, Inspection by.

**Inspection by Variables.** *See* Variables, Inspection by.

**Integrated Logistic Support (ILS).** A disciplined approach to the activities necessary to (a) cause support considerations to be integrated into system and equipment design, (b) develop support requirements that are consistently related to design and to each other, (c) acquire the required support, and (d) provide the required support during the operational phase at minimum cost.

**Intercalation.** Corrosion reactions between layers of a metal.

**Intergranular Corrosion.** Corrosion that occurs preferentially at grain boundaries.

**Interlamellar Compound.** Material formed or placed between laminae.

**Intermetallic Compound.** Alloy of two metals in which a progressive change in composition is accompanied by a progression of phases that differ in crystal structure.

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**Intermittent Failure.** A failure that occurs for a limited time, after which the item recovers its ability to perform within specified limits without any remedial action.

**Internal Oxidations.** The formation of isolated particles of corrosion products beneath the metal surface.

**Investment Casting.** A casting method designed to achieve high dimensional accuracy for small castings by making a mold of refractory slurry, which sets at room temperature and surrounds a wax pattern that is then melted to leave a mold without joints.

**Ion.** An electrically charged atom or group of atoms.

**Ion Implantation.** A process of introducing impurities into the near-surface regions of metals by directing a beam of ions at the metal.

**Ion Vapor Deposition.** A process in which vaporized aluminum is ionized and attracted to the negatively charged part to be coated. The trade name for the process is Ivadizer®.

**Ionizing Radiation.** Particles or photons that have sufficient energy to produce ionization directly in their passage through a substance.

**Isocorrosion.** Refers to lines on a graph that show constant corrosion behavior with changing concentration.

**Isocorrosion Diagram.** A plot of corrosion versus concentration, temperature, or some other property in which lines of constant corrosion are shown.

**J**

**JP-4R Fuel.** Jet engine test fuel made up of 35% light petroleum distillates and 65% gasoline distillates.

**K**

**Kaolin.** Any of a group of clay minerals with a two-layer crystal in which silicon-oxygen and aluminum-hydroxyl sheets alternate.

**Kevlar.** High-strength and high-modulus aramid fiber used in ropes, cables, and fabrics and as reinforcement for resins, tires, hoses, and belts.

**Kovar.** A trade name for an iron-nickel-cobalt alloy used to make metal-to-glass seals.

**Kure Beach, NC.** The location of an extensive ocean atmosphere corrosion testing facility.

**L**

**Land.** One of the raised ridges in the bore of a rifled gun barrel.

**Lanolin Grease.** The hydrous sheep's wool wax, primarily cholesterol esters of highly fatty acid, derived as a by-product from the preparation of raw wool for the spinner.

**Lap Joint.** A simple joint between two members made by overlapping the ends and fastening them together with bolts, rivets, or welding.

**Latent Heat of Fusion.** The quantity of heat necessary to change one gram of solid to liquid with no change in temperature.

**Leaching.** The dissolving, by a liquid solvent, of soluble material from its mixture with an insoluble solid.

**Life Cycle.** The various phases an item undergoes from concept to retirement from use.

**Life Cycle Costs.** The sum of all costs associated with an item of materiel through the phases of its life from concept exploration through disposal.

**Limiting Quality (LQ).** The worst quality that the consumer is willing to accept.

**Liquid Crystal.** A liquid that is not isotropic. It is birefringent and exhibits interference patterns in polarized light. In a liquid crystal display a voltage applied across a thickness of liquid disrupts the orderly arrangement of the molecules and darkens the liquid enough to form visible characters even though no light is emitted. Increasing temperature will also disrupt the orderly arrangement of crystals providing a temperature-sensitive display.

**Liquid Metal.** A metal that is liquid, usually at room temperature.

**Liquid Metal Embrittlement.** The decrease in ductility of a metal caused by contact with a liquid metal.

**Logistic Support Analysis (LSA).** The selective application of scientific and engineering efforts undertaken during the acquisition process, as part of the system engineering and design process, to assist in complying with supportability and other integrated logistic support (ILS) objectives.

**Longitudinal or Compression Ultrasonic Waves.** Simple compression-rarefaction waves in which the particle displacement is in the direction in which the waves are traveling.



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**Lot or Batch.** A collection of units of product from which a sample is to be drawn and inspected to determine conformance with the acceptability criteria.

## M

**Machined Surface.** The surface resulting from a machining operation on metal.

**Magnetic Flux.** Lines of force used to indicate magnetic induction.

**Major Defect.** A defect, other than critical, that is likely to result in failure or to reduce materially the usability of the unit of product for its intended purpose.

**Marine Atmosphere.** The atmosphere near seacoasts.

**Marine Organisms.** Organisms whose natural habitat is the ocean and other bodies of water.

**Martensite.** A supersaturated solid solution of carbon in iron characterized by a needlelike microstructure.

**Martensitic.** The type of steel that results from the formation of a nonequilibrium phase by quenching from the austenite (FCC) region. It is extremely hard, strong, and often brittle.

**Martensitic Structure.** Having the structure of martensite, i.e., an interstitial, supersaturated solid solution of carbon in iron having a body-centered tetragonal lattice. The microstructure is characterized by an acicular, or needlelike, pattern.

**Materiel.** Equipment, apparatus, and supplies used by the Armed Services.

**Matrix.** The continuous material in a composite.

**Mattson's Solution.** An ammoniacal copper sulfate solution used in stress-corrosion cracking testing of brasses.

**Mean Stress.** The algebraic mean of the maximum and minimum values of a periodically varying stress.

**Melting Point.** The temperature at which a solid becomes liquid.

**Metabolic Product.** The residue of metabolism.

**Metabolism.** The physical and chemical processes by which nutrient-containing substances are synthesized into complex elements, complex elements are trans-

formed into simple ones, and energy is made available for use by an organism.

**Metal.** Any of the various opaque, fusible, ductile, and typically lustrous substances that are good conductors of electricity and heat, form cations by the loss of electrons, and yield basic oxides and hydroxides.

**Metallography.** The study of the structure of metals and alloys by various methods, especially by the optical microscope, the electron microscope, and X-ray diffraction.

**Metastable.** Characterized by a slight margin of stability.

**Microorganism.** A microscopic organism including bacteria, protozoans, yeast, viruses, and algae.

**Microporosity.** Extremely fine porosity visible only with the aid of a microscope.

**Microstructure.** The grain structure of a metal as revealed by a microscope with a magnification of over 10 times.

**MIG Welding.** A gas-shielded arc welding process in which a metal filler is used.

**Mill Products.** Products, such as ingots, billets, sheet, plate, and bars, that are available from metal producers.

**Mill Scale.** The heavy oxide layer formed during hot fabrication or heat treatment of metals and alloys.

**Minor Defect.** A defect that is not likely to reduce materially the usability of the unit of product for its intended purpose or is a departure from established standards having little bearing on the effective use or operation of the unit.

**Modulus of Elasticity.** The ratio of the increment of some specified form of stress to the increment of some specified form of strain.

**Mole.** An amount of substance of a system that contains as many elementary units as there are atoms of carbon in 0.012 kilogram of the pure nuclide carbon-12. The elementary unit must be specified.

**Multiphase Alloy.** An alloy comprised of more than one metallurgical phase.

**Multiple Sampling Plan.** Sampling in which a decision to accept or reject an inspected lot or batch is reached after one or more samples from the inspection lot have

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been inspected. The decision will always be reached after not more than a designated number of samples have been inspected.

## N

**Neutral Media.** Liquids having a pH of 7.

**Neutron.** An uncharged elementary particle that has a mass nearly equal to that of the proton and is present in all known atomic nuclei except the hydrogen nucleus.

**Neutron Cross Section.** An expression of the neutron interaction property of an isotope as an area measure.

**Nitridation.** The absorption of nitrogen atoms by a metal to form metal nitrides.

**Nitroguanidine (NG).** An explosive.

**Noble Metal.** A metal that is not very reactive, e.g., silver, gold, and copper, and that may be found naturally in metallic form on earth.

**Nonchargeable Failure.** A nonrelevant failure or a relevant failure caused by a condition previously specified as not within the responsibility of a given organizational entity.

**Nongraphitizing Carbons.** Carbonaceous material that cannot be treated to form graphite.

**Nonrelevant Failure.** A failure verified as peculiar to an item design that will not enter the operational environment, or a failure verified as peculiar to an item design that will not enter the operational inventory.

**Normal Inspection.** Inspection used when there is no evidence that the quality of the product being submitted is other than the specified quality.

**Nuclear Radiation.** Particulate and electromagnetic radiation emitted from the nuclei in various nuclear processes. The important nuclear radiations from the weapon standpoint are alpha and beta particles, gamma rays, and neutrons.

## O

**Oleum.** See Fuming Sulfuric Acid.

**Operating Characteristics (OC) Curve.** OC curves indicate the percentage of lots or batches that may be expected to be accepted under the various sampling plans for a given process quality.

**Organic Chemical.** Carbon-chain or carbon-ring compounds or mixed chain-ring compounds.

**Organic Coatings.** Protective coatings derived from naturally occurring and synthetic organic chemicals.

**Orthogonal Squares.** A type of experimental design in which two  $n \times n$  Latin squares are superimposed such that any letter of the first occurs just once with every letter of the second. This array forms the basis for the design of efficient experiments involving several variables.

**Outgassing.** The release of absorbed or occluded gases or water vapor, usually by heating.

**Overlay Coating.** A coating applied over another coating, usually to protect the base coating.

**Oxidation.** The combining of a material with oxygen.

**Oxidizing Acids.** Nitric acid and acid solutions of ferric and cupric ions.

**Oxidizing Gases.** Gaseous atmosphere in which oxidation of a metal occurs.

**Oxidizing Salts.** Any salt solution containing ions that can add electrons.

**Ozone.** A triatomic form of oxygen that is formed naturally in the upper atmosphere by a photochemical reaction with solar ultraviolet radiation.

## P

**Pack Cementation.** High-temperature impregnation of a metal with another material in the form of a powder that is packed around the part being treated.

**Paint Coating.** A coating consisting of primer and topcoat on a prepared surface.

**Paint Coating Systems.** Metal coatings consisting of surface treatment, primer, and topcoat.

**Parabolic Oxidation.** The pattern of the variation of oxidation with time exhibited by a metal whose oxidation is controlled by diffusion through a continuous adherent film.

**Passivation.** A reduction of the anodic reaction rate of an electrode involved in electrochemical action, such as corrosion.

**Passive.** The state of a metal when its behavior is much more noble (resists corrosion) than its position in the EMF series would predict. This is a surface phenomenon.

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**Passive-Active Cell.** A cell composed of a metal in the passive state and the same metal in an active state.

**Passive Oxide Film.** An oxide surface film formed on a metal surface by natural processes or by immersion in a passivating solution that makes the metal resistant to corrosion.

**Patina.** A green coating that slowly develops on copper and some copper alloys consisting mainly of copper sulfates, carbonates, and chlorides, after longtime exposure to the atmosphere.

**Penetrators.** High-density artillery components designed to penetrate armor.

**Permanent Mold.** A reusable metal mold used for the production of many castings of the same kind.

**Petroleum Coke.** A carbonaceous solid material made by the destructive heating of high-molecular-weight residues from petroleum refining.

**pH.** A term used to describe the hydrogen-ion activity of a system. A solution of pH 0 to 7 is acid, pH of 7 is neutral, pH over 7 to 14 is alkaline.

**Pickle.** Removing mill scale or other corrosion products from a metal by immersion in or treatment with a solution, usually an acid.

**Pitting.** Corrosion of a metal surface confined to points or small areas in the form of cavities or pits.

**Plasma.** The region in an ionized gas discharge that contains nearly equal numbers of positive ions and electrons. This is achieved at very high temperatures.

**Plasma Spraying.** Applying a metallic coating by spraying droplets of metal from a gun in which the metal is atomized in an extremely high-temperature gas stream.

**Plastic Deformation.** Deformation of a metal under applied stresses without fracture.

**Plate or Lamb Ultrasonic Waves.** Ultrasonic vibrations transmitted into a thin sheet or plate whose thickness is comparable to the wavelength of the ultrasonic energy. The pattern of particle displacement is very complex.

**Platform.** The device or structure that carries and interfaces with an item in testing or in operation.

**Polar Substance.** A substance whose molecules form permanent electric dipoles.

**Polarization.** The deviation from the open circuit potential of an electrode resulting from the passage of current.

**Polarization Curve.** A plot of current density versus electrode potential for a specific electrode-electrolyte combination.

**Polycrystalline Graphite.** Graphite characterized by variously oriented crystals.

**Polymer.** Substance made of giant molecules formed by the union of simple molecules (monomes).

**Porcelain Enamel.** See Vitreous Enamel.

**Portland Cement.** A hydraulic cement made by pulverizing the clinker produced by calcining to incipient fusion a mixture of argillaceous and calcareous materials.

**Potentiostat.** An electronic device that maintains an electrode at a constant potential. It is used in anodic protection by an impressed electrical voltage.

**Potting Compound.** A polymer compound used to fill completed electronic assemblies to provide resistance to shock and vibration and exclusion of moisture and corrosive agents. The compound is initially liquid but forms a solid upon application.

**Powder Metallurgy Products.** Components made from pressed and sintered metal powder.

**Prealloyed Powders.** Powdered alloys of uniform composition, not powder alloys made from mixtures of powders of different metals.

**Precipitated Phases.** Phases in a metal structure representing material precipitated from solid solution.

**Precipitation Hardening.** Increasing the hardness of an alloy by a relatively low-temperature heat treatment that causes precipitation of components or phases of the alloy from the supersaturated solid solution.

**Primer Coat.** First coat of paint applied to a surface. It is formulated to have good bonding and wetting characteristics, and it may or may not contain inhibitive pigments.

**Process Average.** The average percent defective of product submitted by the supplier for original inspection.

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**Proton.** An elementary particle that is identical with the nucleus of the hydrogen atom. It carries a positive charge numerically equal to that of an electron and has a mass of  $1.672 \times 10^{-24}$  g.

**Pulse-Echo Testing.** A mode of ultrasonic testing in which pulses of ultrasonic sound are generated by the test instrument. The pulse travels through the material and is reflected back to the transducer from the opposite side or from any location in the material where there is an abrupt change in acoustic impedance.

**Purple Plague.** A compound formed by intimate contact of gold and aluminum, which appears on silicon planar devices and integrated circuits using gold leads bonded to aluminum, thin-film contacts and interconnections.

**Pyrolysis.** The breaking apart of complex molecules into simpler units by the use of heat.

**Pyrolytic Carbon.** Carbon that is formed by breaking apart complex organic molecules by the use of heat.

**Pyrolytic Graphite.** Graphite that is formed by breaking apart complex organic molecules by the use of heat.

**Pyrophoric Alloy.** An alloy that in powder form spontaneously oxidizes in air and reaches high temperatures.

**Q**

**Quality.** The composite of all attributes or characteristics, including performance, of an item or product.

**Quality Assurance.** The management function by which conformance of materiel to contract and specification is assured.

**Quality Control.** That function of management relative to all procedures, methods, examinations, and tests required during procurement, receipt, storage, and issue that are necessary to provide the user with an item of the required quality.

**Quality Engineering.** Specifying and documenting technical requirements for materiel.

**Quenching.** Rapid cooling of metal from heat-treatment temperatures.

**R**

**Random Failure.** A failure that is predictable only in a probabilistic or statistical sense.

**Random Sampling.** Any procedure used to draw units

from an inspection lot so that each unit in the lot has an equal chance without regard to its quality of being included in the sample.

**Rare Earth.** The elements having atomic numbers 57 through 71. These elements are so similar that generally it is extremely difficult to separate two succeeding elements.

**Reagent Grade Chemicals.** High-purity chemicals used for chemical work where impurities must either be absent or at a known concentration.

**Red Fuming Nitric Acid.** Concentrated nitric acid containing dissolved nitrogen dioxide.

**Red Plague.** Corrosion of small-diameter copper electrical wire that is plated with silver and insulated with Teflon®.

**Reduced Inspection.** Inspection that may be instituted in accordance with established rules when it is evident that product quality is very good.

**Reducing Acids.** Hydrochloric acid, sulfuric acid, and phosphoric acid.

**Reducing Atmosphere.** An atmosphere of hydrogen, or other substances that readily provide electrons, surrounding a chemical reaction or physical device.

**Reducing Gases.** Gaseous atmosphere containing hydrogen or other substance that readily provides electrons and in which a reduction reaction takes place.

**Reduction.** Gain of electrons, e.g., when copper is electroplated on steel from a copper sulfate solution.

**Refraction Metal Oxides.** Metal oxides that exhibit high-temperature melting points.

**Refractory.** A material of high melting point. The property of resisting heat.

**Refractory Coating.** A coating composed of heat resisting or high melting point material.

**Refractory Metals.** Metals capable of withstanding high temperature.

**Refractory Oxide Coating.** A coating composed of high melting point metal oxide.

**Rejection Number.** The minimum number of defects or defective units in the sample that will cause rejection of the lot.

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**Relevant Failure.** Failure of an item in the operational inventory in an operational environment.

**Reliability.** The probability that an item will perform its intended function for a specified interval under stated conditions.

**Residual Stress.** A stress system within a solid that is not dependent on external forces.

**Resin.** Any of a class of solid or semisolid organic products of natural or synthetic origin, generally of high molecular weight with no definite melting point. Most resins are polymers.

**Resistivity.** The longitudinal electrical resistance of a uniform body of unit length and unit cross-sectional area.

**Resonance Testing.** A mode of ultrasonic testing in which a longitudinal mode continuous wave is introduced normal to the surface of the specimen. It is used mainly to measure the thickness of thin sheets because at resonance the frequency of these waves is related to the thickness and acoustic velocity of the material.

**Reversion.** Decomposition of a synthetic substance into its component substances.

**Rework.** Reprocessing of defective units.

**Rockwell Hardness Test.** One of the arbitrarily defined measures of resistance of a material to indentation under static or dynamic load.

**Rotating Band.** A band of soft metal around an artillery projectile that seals the annular space between the inside diameter of the gun tube and the outside diameter of the shell.

**RTV Silicone Rubber.** A heat-stable, water-repellent rubber formed by semiorganic polymers of organic radicals attached to the silicones. The material vulcanizes in the presence of air at room temperature.

**Rusting.** Corrosion of iron or an iron-base alloy to form a reddish-brown product that is primarily hydrated ferric oxide.

**Rust-Preventive Compound.** Several types of coating formulations that are applied to vehicle frames and inner- and underbody panels to provide corrosion protection.

**Rustproofing.** Treating inner portions of the sheet metal

of a motor vehicle with a heavy, gel-like material that flows into crevices and sets up as a pliable coating providing protection against corrodents.

## S

**Sacrificial Anode.** A metal that protects from corrosion the metal to which it is galvanically coupled in an electrolyte. The sacrificial anode is more anodic than the protected metal, so it preferentially corrodes.

**Sacrificial Protection.** Reduction or prevention of corrosion of a metal in an electrolyte by galvanically coupling it to a more anodic metal (sacrificial anode).

**Salt Fog Test.** An accelerated corrosion test that exposes test specimens to a salt-bearing spray.

**Sample Size.** The number of items to be selected from a given lot size for inspection.

**Sand Casting.** A casting process using molds made of sand and binder. The mold is broken to remove the solidified component.

**Scaling.** High-temperature corrosion resulting in formation of thick corrosion product layers.

**Scaling Rate.** The rate at which high-temperature corrosion product forms on a metal surface.

**Seize.** To cohere to a moving part through excessive pressure, temperature, or friction.

**Selective Leaching.** The selective corrosion of one or more components of a solid solution alloy. (Also known as parting or dealloying.)

**Semiconductor Photon Detector.** A semiconductor device that responds to incident infrared radiation by changing resistance with changing light intensity (photon conduction) or by generating a voltage in response to incident light (photovoltaic operation).

**Sensitization.** A heat treatment whether accidental, intentional, or incidental (as during welding) that causes carbide precipitation at grain boundaries and often causes the alloy to be susceptible to stress-corrosion cracking.

**Sequential Sampling.** The sample units are selected one at a time. After each unit is inspected, the decision is made to accept or reject the lot, or to inspect another sample. An accept or reject decision terminates the sampling.

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**Shear or Transverse Ultrasonic Waves.** Waves in which particle displacement occurs at right angles to the direction of propagation.

**Shot Peening.** Shot blasting with small steel balls or glass beads driven by a blast of air in order to impart surface compressive stresses on the article being treated.

**Single Sampling Plan.** A sampling plan in which the results of a single sample from an inspection lot are conclusive in determining its acceptability.

**Slip Ring.** A conductive rotating ring that, in combination with a stationary brush, provides a continuous electrical connection between rotating and stationary conductors.

**Slurry Fusion.** The bonding at elevated temperatures of a coating on a metal surface formed by application of a slurry on the surface.

**Solar Radiation.** The electromagnetic radiation and particles (electrons, protons, and atomic nuclei) emitted from the sun.

**Solder.** An alloy, such as of tin and lead, used when melted to join metallic surfaces.

**Solder Flux.** A chemical substance that aids the flow of solder, removes oxides, and prevents the formation of oxides on the pieces to be joined.

**Solid Solution.** Metals uniformly distributed in one another in the solid state.

**Solution Annealing.** Heating and holding an alloy at a temperature at which one or more constituents enter into solid solution. This action is followed by cooling the alloy rapidly to prevent the constituent from precipitating.

**Solution Heat Treatment.** Heating a metal to a suitable temperature, holding it at that temperature long enough for one or more constituents to enter into solid solution, and then cooling rapidly enough to retain the constituents in solution. *See also* Heat Treating.

**Spalling.** The separation of a surface layer caused by thermal or mechanical stresses. An example is the breaking off of the high-temperature corrosion product from a metal.

**Specific Heat.** The quantity of heat required to raise a unit mass of homogeneous material one degree in temperature.

**Specification.** A document prepared specifically to support acquisition that clearly and accurately describes the essential technical requirements for purchased materiel. Procedures necessary to determine that the requirements for the purchased materiel covered by the specification have been met shall also be included.

**Standard.** A document that establishes engineering and technical requirements for processes, procedures, practices, and methods that have been adopted as standard. Standards may also establish requirements for selection, application, and design criteria for materiel.

**Standard ASTM Tensile Specimen.** A specimen specified by ASTM for tensile testing. (*See* ASTM E8-81, *Tensile Testing of Metallic Materials.*)

**Stiffness.** The ratio of the force acting upon a metal to its displacement.

**Strain Hardening.** Increasing the hardness and tensile strength of a metal by cold plastic deformation.

**Stray Current Corrosion.** Corrosion resulting from direct current flow through paths other than the intended circuit, e.g., any extraneous current in the earth.

**Stray Direct Current.** Current flow through paths other than the intended circuit.

**Stress-Corrosion Cracking.** Failure by cracking under the conjoint action of a tensile stress and certain chemical environments specific to the metal.

**Stress Intensifier.** *See* Stress Raiser.

**Stress Raiser.** A notch, hole, or other discontinuity in contour or structure that causes localized stress concentration.

**Stress Relief.** A schedule of heating to relieve residual stresses in a metal component.

**Stress-Relief Anneal.** Heating to reduce residual stress.

**Sulfidation.** The reaction of a metal with a sulfur-bearing compound to form a metal sulfide product. An example is the high-temperature reaction of alloys with sulfur-bearing gases.

**Sump Area.** The lowest point in a system to which liquids drain.

**Superalloy.** A thermally resistant alloy for use at elevated

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temperatures where high stresses and oxidation are encountered.

**Supersaturation.** Greater than equilibrium concentration of a metal solute in a solid solution.

**Surface-Effect Ship.** A transportation vehicle with fixed side walls, which is supported by low-pressure, low-velocity air and operates on water.

**Surface or Rayleigh Ultrasonic Waves.** Waves traveling over the surface of a solid material and penetrating it to a depth of about one wavelength. Particle displacement is elliptical in the vertical plane along the direction of travel.

**Sustained Load Cracking.** Cracking under the application of a constant stress.

**Swaging.** Tapering a rod or tube or reducing its diameter by any of several methods, such as forging, squeezing, or hammering.

**Switching Rule.** The means by which decisions are made to change from normal to tightened inspection and back again or from normal to reduced inspection and back again.

**T**

**Tactical Vehicle.** A motor vehicle used in direct support of combat or tactical operations including vehicles in combat, combat support, and combat service support tables of organization and equipment.

**Tailoring.** A process of modifying existing benchmark environmental tests to assure that military equipment is designed and tested for resistance to the environmental stresses it will encounter during its life cycle.

**Tapped Hole.** A drilled hole in which a tap has been screwed to cut an internal thread.

**Tarnish.** Discoloration of a metal surface due to the formation of a thin film of oxide, sulfide, or some other corrosion product.

**Tedlar.** A Du Pont Company trademark for polyvinyl fluoride film. It is tough and flexible with outstanding weathering resistance.

**Teflon.** A trademark of the Du Pont Company for polytetrafluoroethylene, fluorinated ethylene propylene copolymer, and perfluoroalkoxy resins. They are tough, heat resistant, and corrosion resistant.

**Temper.** The heat treatment given to a metal to affect its strength and hardness.

**Temperature Gradient.** The rate of change of temperature with thickness.

**Temporary Hardness.** The portion of the total hardness of water that can be removed by boiling whereby the soluble calcium and magnesium bicarbonate are precipitated as insoluble carbonates.

**Tensile Strength.** The resistance of a metal to deformation and fracture under the influence of a tensile stress.

**Thermal Barrier Coatings.** Coatings that exhibit insulating properties.

**Thermal Conductivity.** The quantity of heat that passes in unit time through a unit area of plate whose thickness is unity when its opposite faces differ in temperature by one degree.

**Thermal Cycling.** Varying the temperature of an object between a high and a low value.

**Thermal Diffusivity.** The quantity of heat passing normally through a unit area per unit time divided by the product of specific heat, density, and temperature gradient.

**Thermal Expansion Coefficient.** The fractional change in length or volume of a material for a unit change in temperature.

**Thermal Gradient Mass Transfer.** The transfer of material between a hot surface and a cooler surface separated by a fluid.

**Thermal Spray.** A metal coating process that sprays molten droplets of metal upon the base metal.

**Thermochromic.** Having the property of color variation with changing temperature.

**Thermopile.** An apparatus that consists of a number of thermoelectric couples combined so as to multiply the effect and used to determine the intensity of thermal radiation.

**Thermoplastic.** A plastic material that melts and solidifies reversibly.

**Thermosetting.** A plastic material that takes a permanent set upon heating.

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**Through Transmission Testing.** A mode of ultrasonic testing operating on the principle of transmitting sound waves through a test specimen with one transducer and receiving them with a second transducer.

**Throwing Power.** The ability to deposit a plating on a surface of irregular shape.

**Tightened Inspection.** Inspection instituted in accordance with established rules when it is evident that product quality has deteriorated.

**TIG Welding.** A gas-shielded arc welding process in which the electrode is tungsten and no metal filler is used.

**Topcoat.** Paint coating applied over the primer coat. It is formulated to provide color and gloss and to form a hard and highly impervious film.

**Topographic Features.** The physical appearance of a land area.

**Tracer Gas.** A gas or vapor sensitive to a convenient means of detection and used to detect leaks.

**Tracked Vehicle.** Vehicle that travels on two or more endless tracks mounted on each side of the vehicle. It has high mobility and maneuverability, is usually armed and frequently armored, and is intended for tactical use.

**Trade Names.** Names by which certain alloys are widely known.

**Treated Wood.** Wood that is impregnated with a chemical to reduce deterioration of the wood.

**Tube Sheet.** A mounting plate for tubes of heat exchangers, coolers, or boilers.

**Turbulence.** Departure in a fluid from a smooth flow to a condition in which local velocities and pressures fluctuate irregularly in a random manner.

**Turbulent Flow.** Flow in which there is complete cross-sectional mixing of the individual particles of liquid.

**U**

**Ultrasonic Waves.** Sound waves with frequencies above that which the human ear can detect. For purposes of nondestructive inspection, ultrasonic waves have frequencies in the millions of hertz in liquid and solid media.

**Unified Numbering System.** A numeric system for designating alloys.

**V**

**Vacuum Distillation.** Liquid distillation under reduced pressure, i.e., less than atmospheric pressure.

**Vacuum Hot Pressing.** Hot pressing of metal under reduced pressure, i.e., less than atmospheric pressure.

**Valve Trim.** The internal components of a valve excluding the body.

**Vapor Degreasing.** A type of cleaning procedure for metals that removes grease, oils, and lightly attached solids. A solvent such as trichloroethylene is boiled, and its vapors are condensed on the metal surfaces.

**Vapor-Phase Inhibitor.** A substance that sharply reduces corrosion when present in the gaseous environment of a metal.

**Vapor Plating.** A coating, usually of a metal, that deposits on a surface from the vapor phase.

**Variables, Inspection by.** Inspection in which a quality characteristic of each unit of product in a sample is measured on some cardinal scale.

**Vitreous Carbon.** Carbon in which the atoms or molecules are not arranged in any regular order, as in a crystal.

**Vitreous Enamel.** A glass coating applied to a metal by covering the surface with a powdered glass frit and heating until fusion occurs.

**Volatile Oxide.** A metal oxide that exerts considerable vapor pressure at a given temperature, which can be below the melting point for some metals.

**W**

**Water Trap.** A shape that collects water under the force due to gravity.

**Weathering Atmospheres.** External ambient environments, such as industrial, urban, rural, and marine.

**Weibull Function.** A mathematical expression that gives the distribution of a random time-to-failure variable of a series of test specimens. It is useful in failure analyses, such as the analysis of stress-corrosion cracking.

**Weld.** To unite metallic parts by heating and allowing the metals to flow together or by hammering or compressing with or without previous heating.



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**Weld Bead.** A deposit of filler metal from a single welding pass.

**Weld Decay.** A term applied to areas adjacent to welds of certain alloys that have been subjected to intergranular corrosion because of metallurgical changes in the alloy.

**Weld Penetration.** The inward extent of the zone of metal fusion.

**Weldment.** An assembly or structure whose component parts are joined by welding.

**Wet Primer.** A primer coating of a paint finishing system that has not dried.

**Whiteout.** A surface weather condition in an arctic area in which no object casts a shadow, the horizon cannot be seen, and only dark objects are discernible.

**Wire Thread Insert.** A spring-like component that fits inside a threaded hole to prevent seizing of the bolt and to provide a more reliable holding force.

**Work Hardening.** Increased hardening accompanying plastic deformation of a metal below the recrystallization temperature range.

**Wrought Alloy.** An alloy that has been mechanically worked after casting.

### X

**X Ray.** Electromagnetic radiation produced by bombarding metallic targets with fast electrons in a vacuum or by transition of atoms to lower energy states.

### Y

**Yield Strength.** The stress at which a material exhibits a specified deviation from proportionality of stress and strain.

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| 3. DOCUMENT TITLE<br>Material Deterioration Prevention and Control Guide for Army Materiel, Part One, Metals              |  |                                     |
| 4. NATURE OF CHANGE (Identify paragraph number and include proposed rewrite, if possible. Attach extra sheets as needed.) |  |                                     |
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