MIL-HDBK-729
21 November 1983
SUPERSEDES
MIL-HDBK-724(MR)
1 October 1969
MIL-HDBK-721(MR)
1 November 1965

MILITARY STANDARDIZATION HANDBOOK

CORROSION AND CORROSION PREVENTION

METALS

NO DELIVERABLE DATA REQUIRED BY THIS DOCUMENT

/ AREA MFEP/

DEPARTMENT OF DEFENSE
WASHINGTON, D.C. 20301

MIL-HDBK-729
Corrosion and Corrosion Prevention-Metals
21 November 1983

1. This standardization handbook was developed by the Department of Defense in accordance with established procedure.

2. This publication was approved on 21 November 1983 for printing and inclusion in the military standardization handbook series.

3. This handbook provides basic and fundamental information on corrosion and corrosion prevention of metals for the guidance of engineers and designers of military material. This handbook is not intended to be referenced in purchase specifications except for informational purposes nor shall it supersede any specification requirements.

4. Benefical Comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: Director, Army Materials and Mechanics Research Center, Attn: DRXMR-SMS, Watertown, MA 02172, by using the self-addressed Standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document or by letter.

FOREWORD

This is one of a group of handbooks covering the metallic and nonmetallic materials and their characteristics, used in the design and construction of military equipment. This handbook replaces Military Standardization Handbooks MIL-HDBK-721(MR), "Corrosion and Corrosion Protection of Metals", dated November, 1965; and MIL-HDBK-724(MR), "The Stress-Corrosion Cracking and Hydrogen-Stress Cracking of Metals", dated October, 1969.

The intent of this handbook is to provide, in condensed form, a unified coverage of the factors influencing corrosion, forms of corrosive attack, and corrosion characteristics of metals and their alloys. Also provided are general methods of protecting metals and alloys from corrosion. Particular attention is given to the types of atmospheric corrosion encountered by military equipment. Generally, data regarding corrosion due to industrial type atmospheres, including effects of various chemicals, has been omitted. For information on this type of data, the reader is encouraged to consult the references listed in the bibliography.

The properties and data given in this handbook are not intended to be used for purposes of providing manufacturing or procurement specifications. Such requirements are adequately covered by applicable specifications.

Handbook draft preparation was accomplished by Battelle's Columbus Laboratories, Metals and Ceramics Information Center, in cooperation with and for the U.S. Army Materials and Mechanics Research Center. Figures 11, 13, 14, 15, 16, 20, 22 ,23, 24, 27, 29, 31 and 32 have been reproduced from various NACE publications with the kind cooperation of the National Association of Corrosion Engineers. Figure 26 has been reproduced by permission from Metals Handbook, Volume 7, copyright American Society for Metals (1972).

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CORROSION AND CORROSION PREVENTION OF METALS

SECTION 1. SCOPE

1.1 Purpose. MIL-HDBK-729 was developed for the Department of Defense (DoD) in accordance with standard procedure and in compliance with policies and requirements of the Defense Standardization Program (DSP).

DoD Directive 4120.3 establishes, and together with the Defense Standardization Manual 4120.3-M, "Standardization Policies, Procedures and Instructions," implements the DSP. Because of the comprehensive description of the DSP provided in these documents a detailed discussion is not presented here. However, the following definition of Standardization, taken from DoD Directive 4120.3, in effect summarizes the DSP.

"Standardization is the adoption and use (by consensus or decision) of engineering criteria to achieve the objectives of the DSP. These criteria are applied, as appropriate, in design, development, procurement, production, inspection, supply, maintenance, and disposal of equipment and supplies."

As implied in the preceeding definition, the mission of the DoD with respect to standardization is to develop, establish, and maintain a comprehensive and integrated system of technical documentation in support of design, development, engineering, procurement, inspection, maintenance, and supply management.

MIL-HDBK-729 is one of a group of standardization handbooks covering the metallic and nonmetallic materials used in the construction of military equipment. These handbooks are part of the previously referenced integrated system of technical documentation developed, established, and maintained by the DoD in support of the DSP.

The basis for the development of MIL-HDBK-729 then is the DSP. The specific purpose of MIL-HDBK-729 is to provide technical information and data on the many aspects of corrosion of metals for use in achieving the objectives of the DSP. The provisions of DoD Directive 4120.3 apply to all departments and agencies of the DoD, consequently, the data provided by the handbook are intended for application, as appropriate, in design, development, procurement, production, inspection, maintenance, supply, and disposal of military equipment and supplies.

1.2 Scope. MIL-HDBK-729 contains technical information and data pertaining to the corrosion and corrosion protection of metals and alloys. The factors influencing corrosion, forms of corrosive attack including stress-corrosion cracking and hydrogen-stress cracking (hydrogen embrittlement), corrosion characteristics of metals, and general methods of protecting metals and alloys from corrosion, are covered in condensed form, along with information on corrosion testing. Emphasis is placed upon the type of corrosion encountered by military equipment.

1.3 Definitions. A detailed list of definitions is given in Section 10, the Glossary, however, it is convenient at this point to define corrosion.

Corrosion is the deterioration (loss of desirable properties) of a material, usually a metal by a chemical or electrochemical reaction with its environment. In the traditional sense the word "metal" used in this context refers to all metals, alloys, or combinations of these.

The various forms of corrosion attack, the mechanisms by which corrosion occurs, are described in Paragraph 4. It will become apparent that although the presence of a corrodent (an aggressive species in the environment) is a necessary prerequisite for corrosion to occur, other non-chemical or non-electrochemical factors can aggravate the situation. One such factor is mechanical stress, which can lead to stress-corrosion cracking, and hydrogen-stress cracking. Mechanical action can also lead to erosion-corrosion, cavitation and fretting corrosion. The differences and similarities between the various identified types of corrosion will be made clear in subsequent paragraphs.

1.4 Contents. It is anticipated that this handbook will be used by personnel engaged in any of a variety of occupations, including engineering, design, development, procurement, manufacturing, supply, inspection, maintenance, and disposal of military equipment and materials. To satisfy the wide range of interest of this audience, the general characteristics of the various types of corrosion will be discussed, along with methods for detecting and measuring corrosion rates, and controlling or preventing corrosion. Stress-corrosion cracking and hydrogen-stress cracking service failures in general result from the presence of high residual stresses in the system acting alone or superimposed on design working stresses. The magnitude of residual stresses is usually unknown, hence, data on design allowables are not pertinent to this handbook. In a few instances threshold stresses (maximum stress at which stress-corrosion cracking will not occur in a given environment in a given time) are listed. These are for comparison only, and are listed for conditions where residual stresses are believed to be absent.

1.4.1 Section 1. Section 1 is an introduction in which the purpose and scope of the handbook are defined. A brief account of the benefits expected to be derived from the availability of information contained in this handbook is also included.

1.4.2 Section 2. Section 2 deals with the general nature of corrosion, and briefly describes the significance of corrosion, the nature of corrosion, the effect of design on corrosion, and protection against corrosion.

1.4.3 Section 3. In this section, the general nature of a corrosion process is described. Corrosion in solution, in the atmosphere, and in the soil are briefly addressed, along with the effects of environment, metal composition, and fabrication and assembly variables. The influence of film formation during the corrosion process is also discussed. To conclude this section, a classification is given of the various types of corrosion processes.

1.4.4 Section 4. The different forms of corrosion are described in this section. Topics covered include, apart from those already mentioned above, pitting corrosion, galvanic coupling corrosion and corrosion fatigue. Specific examples of the types of environment leading to each form of corrosion attack will be given. For the special cases of stress-corrosion

cracking and hydrogen-stress cracking, crack initiation, types and rate of crack propogation, and suggested mechanisms are described for specific alloy systems such as aluminum, copper, magnesium, nickel and iron based alloys including the medium and high-strength steels.

1.4.5 Section 5. This section contains a discussion of the susceptibility of engineering metals and alloys to corrode in a wide variety of environments likely to be encountered in military applications. Because of the many factors which can influence corrosion characteristics, such as composition of the material, exact nature of the environment, metallurgical and chemical treatments given to the material, the discussion will be general. Specific details or values which might be required by the design engineer will be found in the principal references cited in this handbook, and include the available handbooks in the Materials Handbook Series on aluminum, copper, magnesium and titanium, and appropriate materials standards and specifications.

1.4.6 Section 6. Section 6 deals with the various approaches which may be taken to control or prevent corrosion. Approaches such as modifying the environment, reducing or eliminating stresses, selecting more resistant alloy compositions, and applying protective coatings will be discussed. Where such methods are not practiced then the possiblity of substituting materials is considered.

1.4.7 Section 7. Methods applicable to measuring corrosion rates, determining the extent of corrosion attack, and screening metals for their susceptibility to various types of corrosion attack are described in this section. Also discussed is the important aspect of failure analysis whereby failed equipment due to corrosion attack, is subjected to a vigorous examination to determine the most probable cause of failure. Application of the results of a failure analysis can prevent that corrosion failure from happening again by utilizing the approaches delineated in Paragraph 6.

1.4.8 Section 8. Quality assurance and standardization in this handbook refer to materials failures rather than materials. A different connotation therefore is given and in this instance it is a general descriptive phrase that serves to identify any and all of the means available and used by the purchaser of both raw materials and finished products to assure himself that the materials ordered and received are of acceptable quality.

Further, it requires the designer and supervisor of structures of any size to use all diligence in design, selection of materials, and fabrication to (a) select materials or protective coatings that will be immune to all types of corrosion attack in the expected environment; (b) supervise fabrication so as to secure where applicable recommended shop heat-treatments, stress-relief treatments, correct assemblage, and proper coating procedures; and (c) inspect the finished structure for surface defects in material or coatings, or improper fastening practice.

1.5 Benefits. The expected benefits accruing through the use of this handbook are those resulting from alerting personnel responsible for the design, construction and maintenance of structures and equipment to the dangers of corrosion, so that conditions leading to dramatic failures may be averted, and so that costs of replacement or repair of damaged structures or equipment may be reduced.

The design engineer will receive guidelines for designing structures less susceptible to corrosion. For example, the avoidance of crevices in which chlorides can concentrate will minimize stress-corrosion cracking failures in austenitic stainless steels. If crevices cannot be avoided, an alloy with higher nickel content could be specified. Sharp bends in tubing through which flows a liquid containing suspended solids (some cooling waters in heat exchangers) should be avoided otherwise erosion-corrosion will occur. Similarly, sharp reductions in cross-sectional area should not be designed into a structure.

The fabrication supervisor should be aware of the dangers of residual stresses resulting in welded structures, and of the danger of overtorqueing threaded connections, particularly those involving tapered threads, or resulting in exposed cap screws or nuts. In certain environments such actions can result in stress-corrosion cracking. The contact of dissimilar metals in certain environments can also lead to galvanic corrosion, and loss of structure integrity.

Personnel involved in operations and maintenance should be alerted to potentially detrimental combinations of pH, chloride ion concnetration, temperature, oxygen concentration, humidity, and pressure, both intentionally contained in a structure, and outside the structure. The environment inside a structure is not necessarily the same as that surrounding it. Therefore, as far as practical, control should be exercised over both environments. For example, moisture and oxygen are usually present in environments producing stress-corrosion cracking. Reduction of these constituents to safe levels can prevent cracking under a number of conditions.

SECTION 2. CORROSION AND ENGINEERING DESIGN

2.1 Significance of Corrosion. The deterioration and destruction of metals as a result of reaction with the environment is a phenomenum that has been observed since the earliest use of metals. Corrosion, however, was not recognized as a serious problem until the development of modern industrial technology. Very likely, the monetary losses sustained by the military services as a result of corrosion amount to eight billion dollars a year, representing a substantial proportion of the estimated total of 70 billion dollars borne by industrial, community and military segments of the United States each year.(1) Because it affects both the economy and the military preparedness, corrosion and corrosion protection remains a subject of extensive research.

This research encompasses the causes and effects of corrosion, methods for diagnosing and predicting corrosion failures, and methods for controlling or preventing corrosion. Aspects of this research that are pertinent to the use of the more common structural metals are discussed in the ensuing sections of this handbook.

2.2 Nature of Corrosion. Earlier, corrosion was defined as the deterioration or loss of desirable properties, of a material by a chemical or electrochemical reaction with its environment, which could be compounded by the presence of mechanical stresses. Corrosive attack of metals involves complex processes and is evidenced by corrosion product build-up, tarnish, general attack, localized attack such as pitting or perforation, cracking, and in extreme cases, failure. The nature and extent of the attack varies with the material and with the environment and conditions to which the material is subjected. For any application the many variables and factors which are involved in the corrosive environment should be analyzed and understood as fully as possible, so that workable and dependable measures can be applied to count the corrosion process.

Corrosion may proceed at a rapid or slow rate. The rate is controlled by the nature of the material subject to attack, by the environment, by the concentration of reactants, and the prevailing temperature. Inasmuch as a metal may vary from high purity to an alloy containing various other elements, a wide variety of corrosion behavior is possible. Physical structure variability and composition heterogeneity, because of heat treatment, or cold working, also will influence the susceptibility to corrosion. Furthermore, the shape, form, or finish of the metal (e.g., concavities or sumps for the accumulation of corrodents, cast or wrought forms, and grit-blasted or mechanical finishes) will influence the rate of reaction. Environmental conditions, such as moisture contents, chemical contaminants and pollutants, and temperature can accentuate or moderate the rate of corrosion reactions to a significant degree.

Essentially, all reactions of metals in gaseous atmospheres (e.g., oxygen and water vapor) or in electrically conducting liquids or electroytes (commonly aqueous solutions of salts, acids or bases) are electrochemical in nature and in the past these have been called "wet" corrosion processes. High temperature gaseous corrosion (called "dry" corrosion) of metals is not generally considered as electrochemical, although charged ions can be present

and move in the oxidation products formed by the direct union of gas atoms or molecules with the metal (e.g., oxides in the case of oxygen or chlorides in the case of chlorine). The electrochemical nature of corrosion processes is discussed in Paragraph 3.1.

2.3 Protection Against Corrosion. In almost every application involving metals, some form of corrosion will be possible, necessitating the consideration of appropriate means of protection. The design engineer developing military equipment or structures involving metals, must, therefore, also prescribe measures for protecting them from corrosive attack.

The details of each application will be different but the approach is the same. The design engineer must know the functional requirements of the design; the most likely environmental conditions the item will meet in use; the metals and alloys which are available; and the protective methods which can be used to control corrosion attack. It follows, therefore, that in analyzing and correcting a potential or existing corrosive situation, four principal steps are involved. These are:

(1) Considering the metal(s) and ascertaining whether or not other metals might be a better choice for the application

(2) Determining the environmental condition which prevails, and altering it if possible, e.g., removing harmful species; using inhibitors; applying anodic and cathodic protection.

(3) Reviewing the design of the structure, and considering modifications which could alleviate or prevent the initiation of corrosion attack.

(4) Providing the metal(s) with a coating or treatment to protect it from the corrodent. The treatment can be a surface or bulk treatment, a chemical or mechanical treatment, or a combination of these.

For equipment in operation, step (2) is not always practical, however, it might be possible to accomplish a modification of the design or furnish a coating or treatment to achieve beneficial results.

Some metals effectively resist corrosion damage because of their ability to form and maintain on exposure to an aggressive environment an adherent and impervious film. The metals are then said to have become passivated. However, many of the common or structural metals are less efficient in producing such "passive" protective films, or are inherently devoid of the ability for such film formation. Consequently, protective coatings or treatments are applied to many common metals to prevent or diminish corrosion attack. One of the features of this handbook is the presentation of details concerning protective films and coatings.

2.4 Design Constraints. Even though the design engineer may be aware of the numerous aspects of a corrosive environment, and can recommend the appropriate protective measures, it is nevertheless difficult to achieve a design that satisfies all requirements. Metals or alloys which might possess superior resistance to corrosion might be unacceptable because of processing or economic factors, or both. The design engineer may be forced to sacrifice some corrosion resistance for mechanical properties, fabricability,

availability, cost or a combination of these. There are no strict rules for evaluating a design. The engineer must be guided by the priority of requirements after studying the problem. Thus, if corrosion resistance is the major design requirement, some alloys may be selected with excellent corrosion resistance despite their less desirable mechanical properties and fabrication characteristics.

In general, the only safe approach is to consider each application of a metal as unique. In unusual applications, or where substitute materials are being considered, simulated service tests may be necessary to determine the suitability of the material. To aid an engineer, much accurate and reliable information is available in published form. The bibliography at the end of this handbook supplements the specific references described in Paragraph 5, and will serve as a guide to further information. Several general texts are included together with certain references to extensive bibliographies on recent and detailed studies.

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SECTION 3. CORROSION PROCESS

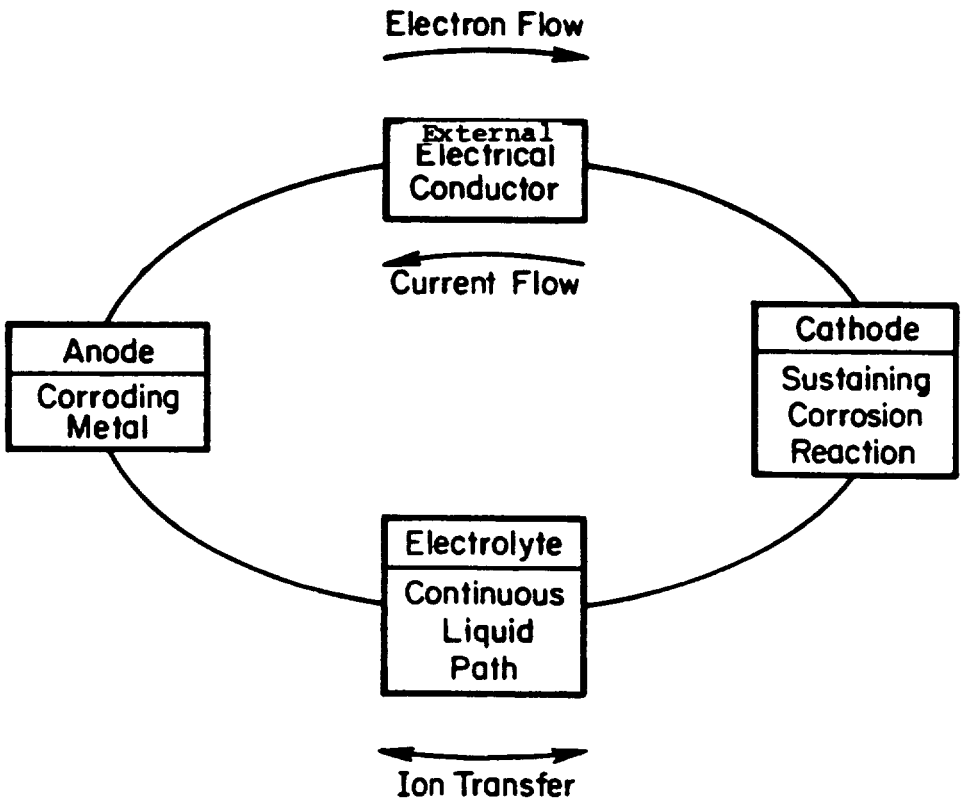
3.1 Corrosion as an Electrochemical Process. Corrosion, as defined for the context of this handbook, is a process involving the transformation of elemental metals or alloys of controlled composition to less desirable compounds of these metals through electrochemical reaction with their environment. The transfer of electrons during the reaction results in a flow of electrical current. A corrosion current is thus associated with a corroding metal. The mechanism of the basic process of corrosion applies to all metals, and can be described with the help of figure 1. For a corrosion reaction to occur, four conditions must be satisfied. There must be metallic sites at which an anodic (oxidation) reaction can occur to generate electrons. There must be metallic sites at which a cathodic (reduction) reaction can occur to consume the electrons released at the anode. There must be an external electrical conductor to transfer the electrons between anode and cathode in order to sustain the corrosion current. Finally, there must be a continuous liquid path (electrolyte) between the anode and cathode which permits the transfer of dissolved ions to the appropriate reaction sites, and allows the anode and cathode reactions to continue. The absence or removal of one or more of these four prerequisites means that corrosion attack through electrochemical action cannot occur. Also, as will be shown later, anodic and cathodic sites can exist on the same immersed metal surface in which case the electron conductor is the metal itself.

When a metal is immersed into an aqueous solution, it acquires an electrical potential related to the tendency for the metal to form metal ions, and at the same time releasing electrons, e.g., in the case of iron:

$$Fe \longrightarrow Fe^{++}+2e^{-}$$

where e- represents an electron with unit negative charge; and Fe^{++} represents a positivley charged iron atom having lost two electrons thereby becomming a divalent cation.

Because each metal has a different inherent ability to ionize, a table can be constructed which lists the metallic elements in order of the potentials generated in solution. Taking as a standard condition for such a comparison the potential of the metal in contact with an aqueous solution containing one equivalent weight per liter of the respective metal ion at 25°C, (77°F) such a list historically is called the Electromotive Series of Metals (see table 1).



Anode: The corroding metal which through an oxidation reaction donates electrons to the external circuit and produces metal ions in the electrolyte.

Electrolyte: The continuous liquid path (usually water in the form of condensate, salt spray, etc.) between anode and cathode.

Cathode: The site at which a reduction reaction occurs to utilize the electrons generated at the anode and sustain a corrosion current.

Electrical Conductor: External electrical conductor which transfers the electrons between anode and cathode in order to sustain the corrosion current.

FIGURE 1. The basic corroison process

TABLE I. The Electromotive Series of Metals

Metal	Ion Formed	Reactivity	Potential 1/
Sodium	Na^{+}	Less noble (reactive, anodic) ↑	-2.714
Magnesium	Mg^{++}		-2.363
Beryllium	Be^{++}		-1.847
Aluminum	Al^{+++}		-1.663
Titanium	Ti^{++}		-1.628
Manganese	Mn^{++}		-1.180
Zinc	Zn^{++}		-0.763
Chromium	Cr^{++}		-0.744
Iron (Ferrous)	Fe^{++}		-0.440
Cadmium	Cd^{++}		-0.403
Cobalt	Co^{++}		-0.277
Nickel	Ni^{++}		-0.250
Tin	Sn^{++}		-0.136
Lead	Pb^{++}		-0.126
Iron (Ferric)	Fe^{+++}		~-0.4
Hydrogen 2/	H^{+}	Neutral	0.000
Antimony	Sb^{+++}	More noble (unreactive, cathodic) ↓	+0.152
Copper (Cupric)	Cu^{++}		+0.342
Copper (Cuprous)	Cu^{+}		+0.521
Mercury	Hg^{++}		+0.788
Silver	Ag^{+}		+0.799
Palladium	Pd^{++}		+0.987
Platinum	Pt^{++++}		~1.2
Gold (Auric)	Au^{+++}		+1.498
Gold (Aurous)	Au^{++}		+1.691

1/ Standard electrode potential in volts at 25°C; data taken from References (2).

2/ Hydrogen electrode potential taken as a reference point and universally accepted as having a value of ± 0.000 volt.

The metals with the greatest tendency to form ions in solution (e.g., magnesium, aluminum, zinc) are said to be at the anodic, less noble or reactive end of the series. Conversely, the metals with little tendency to form ions (e.g., gold, platinum) are said to be at the cathodic, noble or unreactive end of the series. Thus it is evident that there is a relationship between the susceptibility of a metal to corrode and its position in this series.

A metal is usually capable of displacing from solutions any ions of another metal more noble than itself in the electromotive series. For example, when iron is immersed in a solution of a simple copper salt, iron enters the solution as ions and metallic copper is precipitated.

From an examination of the electromotive series, it may be predicted that metals on the more reactive side of hydrogen will dissolve in acids with the formation of gaseous hydrogen. The familiar example of zinc or iron dissolving in hydrochloric acid with the evolution of hydrogen illustrates this point.

The electrode potential of a metal is dependent on the concentration and type of ions in solution, which usually are quite different from the arbitrary conditions established for the electromotive series. Metal specimens immersed in solutions containing cations or that metal only, but of different concentrations, will have a higher potential (tendency to dissolve) as the concentration of cations in the solution decreases, and vice versa. Further, the non-metallic, negatively charged ions (anions) in solution will also influence the potential of the metal, depending on whether or not the anions will form chemical complexes with the metal cations and promote further dissolution of the metal. From table 1, iron would appear to be more active than tin because of its more negative standard electrode potential, and thus if both metals were in a solution in contact the Fe^{++} and Sn^{++} cations the iron would preferentially corrode. However, if the solution contained anions which formed complexes with one of these metals the above observation would not be true. For example, in dilute oxalic or citric acid solutions the concentration of tin cations is kept relatively small by the complexing power of the acid, and this situation promotes the corrosion (dissolution) of the tin metal. Under such circumstances, tin would corrode more rapidly than iron, reversing the position indicated by the electromotive series. In summary, the electromotive series should not be considered more than a general guide for establishing the relative corrosion behavior of metals in a particular environment.

Returning to table I, consider zinc and copper metal immersed in a dilute, non-complexing acid solution, such as shown in figure 2. Because zinc is a reactive metal it will tend to dissolve, releasing divalent zinc cations, leaving an excess of electrons in the metal. On the other hand, copper will displace hydrogen from the solution by donating electrons to the hydrogen ions resulting from ionization of the dilute acid. A deficit of electrons, or a net positive charge, will therefore result in the copper metal. Eventually, an equilibrium condition would be attained, and a potential (electron gradient) would exist between the two immersed metals. As mentioned earlier, if these two metals are now connected by an electrical conductor, the flow of electrons down the potential gradient completes the four prerequisites for a corrosion cell, and a corrosion current will flow, as shown in figure 3,

causing the electrolyte to become richer in zinc cations and poorer in hydrogen cations. Chemically, we may write:

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

if the above metals are immersed in a dilute hydrochloric acid solution. At the surface of the zinc metal the anode reaction can be expressed as:

$$Zn \longrightarrow Zn^{++} + 2e^-$$

and at the surface of the copper the cathode reaction can be expressed as:

$$2H^+ + 2e^- \longrightarrow H_2$$

where hydrogen cations are supplied by the dissocation of the acid:

$$2HCl \longrightarrow 2H^+ + 2Cl^-$$

Adding the anode reaction and the cathode reaction results in the overall corrosion reaction given above, namely, the formation of zinc chloride accompanied by the evolution of hydrogen gas.

In exactly the same way, a zinc specimen which contains copper inclusions will release electrons from the zinc areas to the copper areas, provided both are exposed to the solution, and zinc will go into solution and some constituent of the electrolyte will be reduced at the copper surface (see figure 4). Ordinarily, the most readily reducible species in naturally corrosive solutions are hydrogen ions or oxygen in solution.

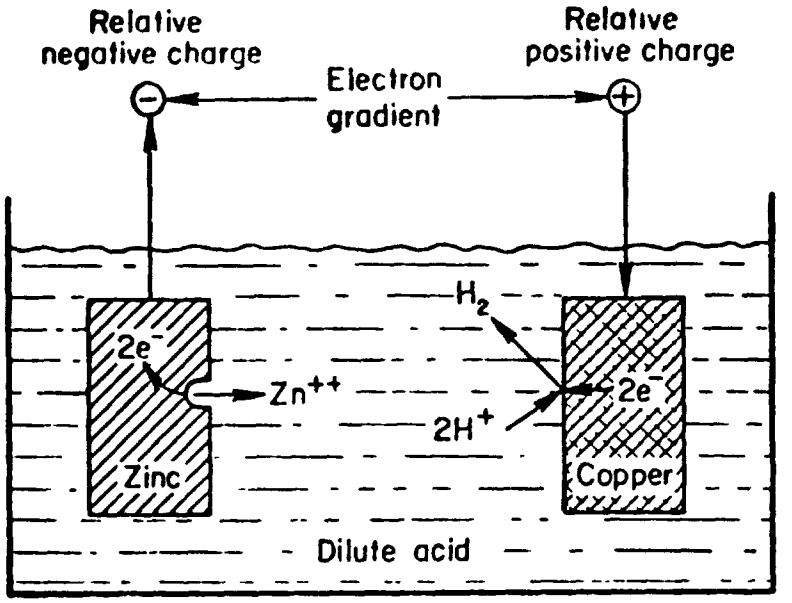


FIGURE 2. Formation of a potential gradient between zinc and copper immersed in dilute acid solution.

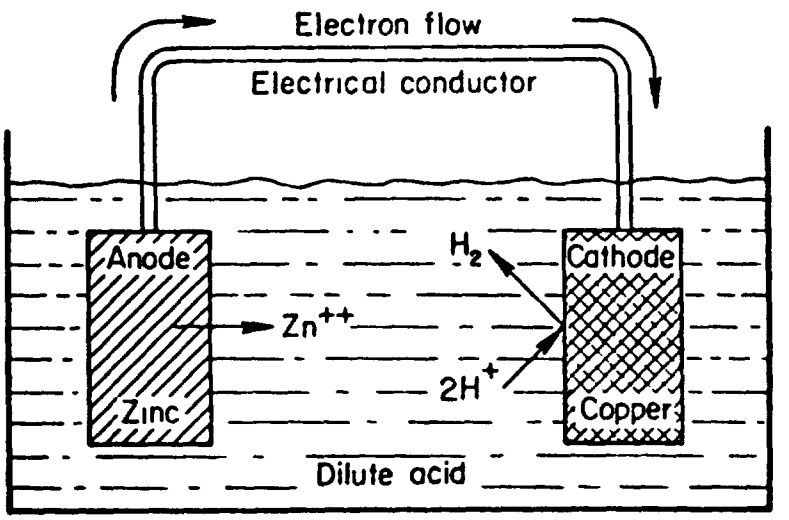


FIGURE 3. Corrosion of the anode and formation of hydrogen at the cathode in a corrosion cell due to electron flow.

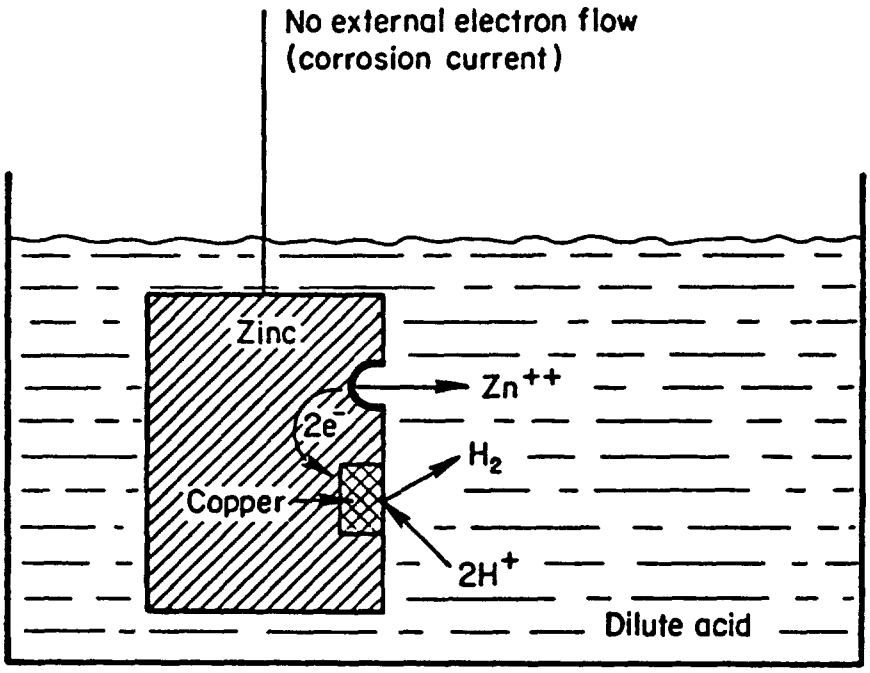


FIGURE 4. Corrosion of zinc containing a copper inclusion.

The flow of corrosion current between dissimilar metals in a conductive medium can be affected by differences in that conductive medium or by changes occuring at the metal surfaces as a result of the electrochemcial reactions.

During flow of the corrosion current, changes occur at both the anode and cathode such that the potential gradient is diminished, and the potentials approach each other. This process is known as polarization. When the anode potential equals the cathode potential the corrosion current will be maximized. These potential changes may be represented graphically[3] on a polarization diagram as shown in figure 5. With no current flow, under standard conditions described previously, E_a and E_c, the potential of the anode and cathode respectively, would correspond to the electrode potentials given in the electromotive series (see table I). When $E_a = E_c$ through polarization, the corrosion current is a maximum, I_{max}, and the resulting potential, E_m, is known as a mixed (corrosion) potential. Figure 5 represents the ideal case where the corrosion cell has no internal resistance. For a finite internal resistance the corrosion current measured, I_{corr}, would be less than I_{max} (see paragraph 3.9).

Anodic polarization usually takes the form of film formation or increased cation concentration. Cathodic polarization is usually associated with a change in pH, decrease in ion concentration or gas films because of slow bubble release. It is obvious that any conditions which enhance electrode polarization will result in a decreased corrosion current, hence rate of corrosion.

3.2 Characteristics of the Environment that Influence Corrosion. When a metal is exposed to an environment, there are certain characteristics of the environment that influence the progress of corrosion. Some of the more important ones are discussed below.

Acidic environments (low pH values) are generally corrosive to metals more active than hydrogen because of the tendency of the metal cations to displace hydrogen as the metal continuously dissolves. Metals such as aluminum or zinc may corrode in alkaline solutions because soluble salts are formed at anodic areas. Coupled with little tendency for the anode to polarize, these metals continue to corrode while immersed.

In acid solutions, hydrogen gas is generally evolved as a result of the cathodic reaction, as described earlier, and this is not a desirable corrosion product. Metals are not often used in environments which would produce excessive hydrogen gas. Fortunately, the corrosion which occurs in typical service environments is mitigated by a thin film of hydrogen gas formed over the surface of cathodic areas, which lessens the flow of current in the system by acting as an internal resistance, hence lowers the corrosion rate (see paragraph 3.1). This phenomenum is called hydrogen polarization. If a hydrogen depolarizer is introduced (usually dissolved oxygen form the air) the hydrogen film can be destroyed and the corrosion will proceed at a faster rate. As a result of the depolarizing effect of oxygen water is formed:

$$4Me.....H + O_2 \longrightarrow 2H_2O$$

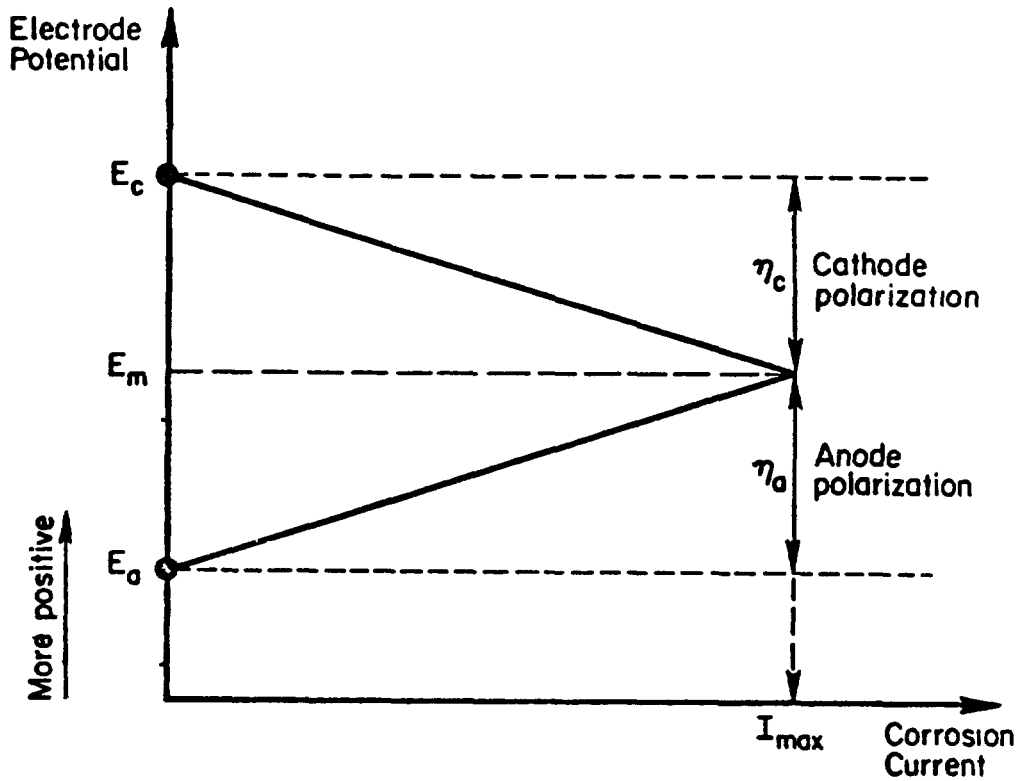


FIGURE 5. Idealized electrode polarization as a function of corrosion current flow.

where Me.....H represents a hydrogen atom sorbed on the surface of a metal to form the polarizing film. It is also possible for direct cathodic reduction of oxygen to occur. Thus in acidic solutions:

$$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$$

and in alkaline solutions:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$$

Mildly acidic solutions saturated with dissolved oxygen may give rise to corrosion rates up to 100 times those found under comparable conditions, but where dissolved oxygen was absent.

However, while oxidizing agents, such as dissolved oxygen, may markedly accelerate corrosion of some metals, they may retard the attack on others by hastening the development of protective films of oxides. Aluminum, chromium and titanium are protected in this manner by oxidizing agents. By combining sufficient quantities of these metals with other metals, to take advantage of this characteristic, the resulting alloys frequently will possess improved corrosion resistance.

Corrosion is usually accelerated by increasing the temperature of the environment. An increase in temperature results in increased electrolyte conductivity, and increased solubility and diffusivity of normally protective corrosion products. Cathodic depolarization by dissolved oxygen is increased by an increase in temperature because of the more rapid diffusion of the gas. On the other hand, at over 80°C (176°F) the solubility of oxygen in solution becomes very small, and the corrosion rate is decreased.

Corrosion is also accelerated by an increase in the velocity or agitation of the electrolyte with respect to the metal or vice versa. Because of the relative movement (1) the corrodents, including oxygen are brought to the surface of the metal where they react at a much higher rate, and (2) the resulting corrosion products are removed at a higher rate, preventing them from accumulating, and retarding corrosive action. As the velocity increases, any films on the surface of the metal will tend to become thinner, thus making the metal more vulnerable to destructive action. In circumstances where corrosion resistance is based on an accumulation of corrosion products on the surface of the metal, sudden movement or high velocity impingement will remove the films. Continued movement will often prevent their formation and deny the metal any surface protection. This condition is typical of small diameter tubes or pipes through which corrosive fluids are forced at high velocities, as well as in the area of bends in pipe lines, and on propellers, agitators, and centrifugal pumps (see also cavitation corrosion in paragraph 4.3.7).

3.3 Characteristics of the Metal that Influence Corrosion. Some of the more important characteristics of a metal that influence the progress of corrosion are outlined below.

Pure metals containing inclusions or impurities may show definite increases in electrochemical reactivity[4]. Similarly, grain boundaries and other imperfections in the crystal structure of a metal tend to behave as

anodic sites in a corrosive environment. The non-homogeneity of an alloy may also promote corrosion under some conditions where the differences in composition lead to the establishment of anodic and cathodic sites because of the different electrical potentials generated (see paragraph 4.3.1).

In highly deformed metals, the grains are deformed, and the grain structure is completely disrupted. In this condition the metal is more susceptible to corrosion attack. A stressed metal may corrode more rapidly than an unstressed metal under specific environmental conditions. Residual or applied tensile stresses can lead to severe localized corrosion and even spontaneous cracking of the metal (see paragraph 4.3.8).

In summary, a metal must be relatively free from impurities, imperfections, and stresses, and have a relatively large grain size (small percentage of grain boundary area) in order to present the best combination of properties to ensure resistance against corrosion. Generally, most metals and alloys must be properly heat-treated to derive the maximum corrosion resistance benefits. For example, martensitic steels are usually tempered after quenching to provide the desired corrosion resistant characteristics. Austenitic stainless steels are more resistant in the annealed condition, and must be properly treated to resist intergranular corrosion. Some aluminum alloys must be quenched rapidly. If quenched too slowly their corrosion resistance is decreased, and these alloys become especially vulnerable also to intergranular attack. An artificial aging treatment is required to restore resistance against corrosion.

3.4 Influence of Fabrication and Assembly on Corrosion. When fabricating and assembling metal equipment and structures, the primary problem is to avoid any physical or metallurgical property changes that will leave the product more susceptible to corrosion attack. It is impossible to generalize and declare that a certain operation such as bolting, brazing, casting, riveting, soldering or welding, will leave a metal more vulnerable to corrosion. The application, the environment, and above all, the characteristics of the metal or alloy will determine the relative resistance to attack. The design engineer must consult specialized sources for data on each metal and method. Nevertheless, a brief inquiry will indicate the intricacy of the problems that accompany the various operations.

The corrosion resistance of bolted joints is affected by the composition (and electrode potential difference) of the bolts and the joined parts, as well as the presence of trapped moisture, stress, the type of exposure in service, and by any possible faulty installation. Bolted joints are therefore susceptible to both galvanic and crevice (concentration cell) corrosion.

Soldered, brazed or welded joints are to be preferred to bolted joints, because if properly designed and fabricated, the former will not be susceptible to crevice corrosion if continous joints are used.

Brazing involves the use of a brazing metal that melts and flows at a temperature lower than that of the metals being joined. The effects of high temperature or resulting heat treatment on the chemical and physical characteristics of the metals in the area of the joint, and the effect of

heat-induced stress, may all alter the corrosion resistance of that joint. Compositional changes will lead to galvanic corrosion, while mechanical changes (stress) can lead to stress-corrosion cracking.

Soldering also does not require the joined metals to be heated to their melting points, and difficulties may arise due to the difference in potential between the solder and the joined metal. Various metals cannot be used in corrosive environments if soldered. In joining aluminum, for instance, the corrosion resistance of brazed or welded joints is generally superior to that of soldered joints.

Welding similarly requires careful consideration and adherence to appropriate procedures. In the welding of solid, corrosion-resistant materials, maximum resistance can be maintained if the filler rod has substantially the same corrosion resistance as the metal. Generally, it is necessary to select the proper welding rod and coating, to use the proper technique for depositing the weld metal, and to avoid gas pockets, laps, undercuts, and excessive nonmetallic (slag) inclusions. These welding defects may lead to localized corrosion. Precautions are doubly important when welding alloys that are vulnerable to corrosion. Correct welding temperatures, heat treatment after welding, careful attention to any defects in the area of the weld and removal of any weld spatters, are necessary to insure maximum corrosion resistance.

A recent development[5] is the use of plastic fittings for joining metal tubes. Because a plastic is an electrical insulator the fitting can isolate dissimilar metals such as copper and aluminum preventing galvanic corrosion from occurring. Although plastic fittings cannot tolerate extreme heat or high pressure, they cost less, deaden noise and can withstand a wide range of corrosive fluids. Brass fittings for galvanized pipe can be replaced by plastic fittings as a corrosion control measure.

3.5 Influence of Films from Corrosion. The extent or progress of corrosive attack is often determined by the nature of films and coatings on the surface of the metal. Films that form on metallic surfaces as a result of chemical reaction with the environment, are in reality the products of the corrosion. These products may be oxides, other compounds, or even adsorbed gases.

Films and coatings range in thickness from imperceptively thin films to relatively thick coatings. Normally, invisible films that cause a metal to become passive and to exhibit more noble behavior are continuous, nonporous films and protect the metal through barrier action and by diminishing the flow of current in electrochemical systems. In the medium in which they are formed, passive films are generally quite effective in protecting the metal against attack. Thin oxide coatings which characteristically can form on aluminum, titanium, chromium and stainless steels in air and in certain oxidizing electrolytes are typical examples of passive films and the phenomenon of passivity.

In general, thicker inorganic (oxide) films are somewhat porous and, although effective as protective barriers, have shortcomings. Virtually any film which is insoluble in the corroding medium will retard attack. However, permeable or porous films will permit localized access of the corrodent to the

metal and corrosion at the point of access. Porous and discontinuous coatings can cause differences of potential at the metal surface and accelerate localized attack (see paragraph 4.3.1). Porous films can retain moisture or other corrosive agents for longer periods, thus increasing the damaging action on the metal.

3.6 Corrosion in Solution. The process of corrosion in solution refers to the action that occurs when metals are immersed in a solution containing ions. In this form of electrochemical action, as differentiated from the corrosive action that follows exposure to the atmosphere or soil, there is an abundant supply of moisture while oxygen may or may not be plentiful, according to the particular circumstances. The supply of oxygen is one of several factors that may influence the rate and degress of attack in solution. These factors are outlined in table II. Later it will be seen that similar factors influence corrosion in soil and in atmosphere.

Since water is the most commonly encountered constituent in a corrosion environment, subsequent discussion treats the corrosive effects of waters of varying compositions.

The corrosive effect of water depends primarily on the type and number of other substances present in the water. Acids, alkalies, and dissolved oxygen in varying amounts will determine the rate of attack. At constant temperature, the amount of oxygen in solution (in the water) and the amount of corrosion that occurs primarily on ferrous metals are almost directly proportional. Also whether the water is stagnant or moving, and the velocity with which the water strikes the metal surface, influence corrosion. An increase in the velocity of the water may accelerate corrosion because the corrosive agents are brought into contact with the metal at a more rapid rate and the products of the action are removed more rapidly.

In general, sea water is more corrosive to common metals than fresh water. However, in non-saline waters of rivers or harbors near large industrial or urban areas, the presence of inorganic and organic contaminants may accelerate corrosion. Certain metals, moreover, may not be affected by particular substances or oxidizing agents present. For example, while waters with high acid content are invariably corrosive, waters low in acid or those which induce an alkaline reaction will vary in their effect; steel may be comparatively unaffected while aluminum, zinc, or tin may be corroded. Also, the presence of animal or vegetable life in the water may influence the type and rate of attack by consuming dissolved oxygen in normal decay processes. Various waters differ in dissolved oxygen content; surface waters may be saturated whereas waters contained in pipes or closed container may contain little, if any, dissolved oxygen content.

TABLE II. Factors Influencing Corrosion in Solution.

(1) Characteristics of the Metal
Composition and chemical homogeneity of the metal. Surface properties; inherent protective films. Effective electrode potential of the metal in solution. Overvoltage 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).
(2) Characteristics of the Solution (Environment)
Hydrogen-ion activity in the solution (pH). 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 Presence of dissolved gases. Presence of suspended particles. Presence of living organisms.
(3) 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. Scale formation on boilers is an example of this. The formation of oxides may consume the available oxygen where the supply of oxygen is limited. This action would lessen or retard further corrosion.

3.7 Corrosion in Atmosphere. The process of corrosion in the atmosphere refers to the action that occurs when metal is exposed to atmospheres containing varying amounts of corrosive substances. In this form of corrosion, as differentiated from corrosion in solution or soil, there is an abundant supply of oxygen while moisture and other factors are among the variables. Atmospheres range widely in content and characteristics, but can be classified as industrial, marine, urban, and rural. In many situations, a particular environment may be a combination of these types.

Climate, geographical region, type of animal and vegetable life, and form of human activity are general characteristics that will affect the corrosiveness of the atmosphere. These characteristics are indicated by such important factors as temperature, humidity, and moisture content, prevailing wind, particles carried by the winds, industrial contaminants, salt and chlorine content, etc. The atmosphere along a seashore (marine) will be characterized by high humidity, salt and chlorine compounds, and winds carrying various particles. Continental (rural) climates may vary from dry plateaus, to deserts, to areas of constant heavy fog and rain. The air over large cities and areas of industrial activity (urban and industrial atmospheres) contains solid particles, and industrial chemical contaminants that collect moisture and corrode metals rapidly.

Just as rapidly flowing solutions can prevent the build-up of protective films for metals corroding in solution, the abrasive nature of air-borne particles can prevent the formation of protective films in atmospheric corrosion. Under some circumstances the abrasive attack can be so severe that films already present, or protective coatings applied, can be removed leaving the bare metal to corrode freely.

Rain, can have both a beneficial and a detrimental effect. Heavy rains can wash away atmospheric pollutants, including hygroscopic particles that attract and retain moisture, which promote corrosion. On the other hand, rain can be a contributing factor to corrosion if it collects in pockets or crevices resulting from poor design, and sets up the conditions for electrochemical action to occur.

3.8 Corrosion in Soil. The process of corrosion in soil refers to the action that takes place when metal is placed on or buried in soil. The factors associated with soils that are most significant in determining the rate and type of corrosion are: (1) chemical content and pH, (2) moisture content, (3) oxygen content, (4) electrical conductance, (5) stray electrical currents, (6) compactness and size of agglomerates, (7) biological organisms, and (8) temperature gradients.

The corrodents commonly found in soils are salts, acids, alkalies and traces of other organic or inorganic compounds peculiar to certain regions. The concentration of acids may be high in wet, marshy soils and low in loose, well drained soils. Alkaline substances may be found in dry soils; coastal soils usually contain appreciable amounts of neutral salts. The amount of moisture in soil depends on the rainfall, drainage, type and consistency of the soil. In heavy, clay soils or muddy, loamy soils, the high content of water may produce a corrosive environment comparable to immersion in liquid.

Aeration or the access of oxygen is an important factor. If one area on a metal is less accessible to oxygen than an adjacent area, the imbalance will initiate a form of electrochemical action due to the difference is oxygen concentration. The surfaces deficient in oxygen will corrode more rapidly than surfaces richer in oxygen. In sand or gravel where air circulates rather freely, corrosion may approach the rates found in atmospheric exposure. Variable climatic conditions and great range of temperature will contribute to the corrosiveness of a soil.

In general, corrosiveness increases with higher acidity, or salt content, and lower electrical resistivity. Very dry soils, like very dry climates, produce low corrosion rates. Within certain limits, corrosion increases with low aeration and higher moisture content in heavy, poorly drained soils. Stray electrical currents which emanate from underground service installations may exert a strong influence on the rate of corrosion of metals in soils.

3.9 Influence of Anodic and Cathodic Processes on Corrosion Rate. Figure 5 shows idealized electrode polarization at the anode and cathode corrosion sites in relation to the corrosion current. This graphical method of showing how corrosion depends on the anodic and cathodic polarizations was originated by Evans,[6] hence such diagrams are often referred to as "Evans diagrams". The current-voltage relationships are shown as straight lines obeying the relationship:

$$I^{1}_{corr} = [(E_c - E_a) - (\ ^{1}_{c} + \ ^{1}_{a})]/(R_1 + R_2)$$

where $^{1}_{c}$ and $^{1}_{a}$ are the cathodic and anodic overpotentials at corrosion current, I^{1}_{corr}; R_1 and R_2 represent resistances due to the electrolyte, films on the corroding metals, and so on. Figure 5 may be modified to show this terminology and figure 6 results. As (R_1+R_2) approaches zero $(E^{1}_{c}-E^{1}_{a})$ approaches zero and the potentials of the anode and cathode become essentially equal (E_{corr}) at the corrosion, mixed, or steady-state potential of the system.

Although the Evans-type diagrams do not give an indication of the contributing factors to the polarizations on the corrosion cell internal resistances, they are useful tools for classifying different types of corrosion processes, and in a simplified manner pointing out the differences between thermodynamic and kinetic factors, as shown in figures 7 and 8. The thermodynamic tendency for a system to corrode is given by the E_c and E_a potential values. For a finite corrosion current to flow the anode and cathode become polarized, and the rate of corrosion, that is the kinetics of the corrosion process are governed by the factors which control the polarizations.

For a system under anodic control (see figure 7 (a)) it is the reaction occurring at the anode which primarily governs the corrosion rate. Conversely, for a system under cathodic control (see figure 7 (b)) the cathodic reactions are of prime importance. When both anode and cathode reactions contribute significantly to the determination of the corrosion current, the system is said to be under mixed control (figure 7 (c)). However, if the electrolyte has a high electrical resistivity, or resistive films or coatings are present, then its system is said to be resistance controlled (figure 7 (d)).

Figure 8 (a) shows how two systems with different thermodynamic tendencies to corrode may give the same corrosion current (I_{corr}) and mixed potential (E_{corr}). In figure 8 (b) it is shown how a system with a greater thermodynamic tendency to corrode can give a lower corrosion current (I_{corr}) than a system with a lesser tendency to corrode but different polarization behavior.

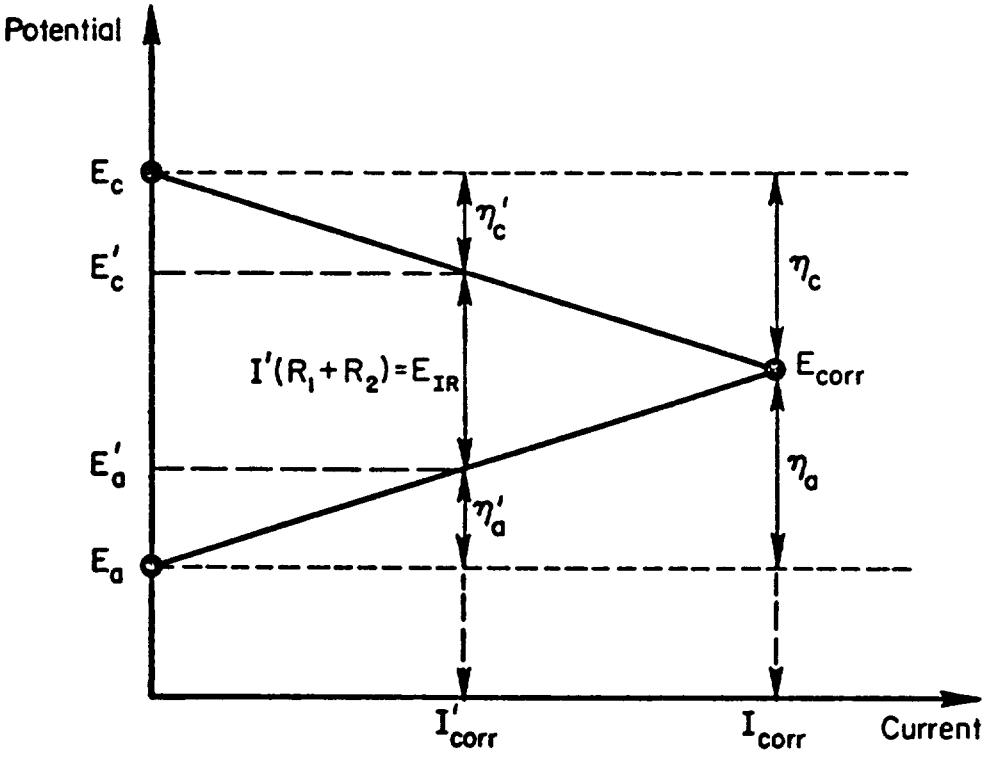


FIGURE 6. Evans-type diagram for depicting corrosion curent as a function of electrode polarization.

In later paragraphs, Evans-type diagrams will be used to illustrate the principles of corrosion control through the use of corrosion inhibitors, and to illustrate the use of anodic and cathodic protection for buried or immersed structures.

It is useful at this point to indicate the difference between corrosion current I, measured in amperes, and corrosion rate, i, measure in amperes per unit area. Although polarization strictly is a function of the current density, i, the measure of corrosion rate, Evans-type diagrams always show I as a function of n because according to Faraday's Law $\Sigma I_a = \Sigma I_c$, whereas Σi_a does not necessarily equal Σi_c. Also, in accordance with Faraday's law, at the intersection of the anodic and cathodic polarization curves $I_a = I_c$. Current density is a logarithmic function of η, and for future discussion Reference (7) should be consulted.

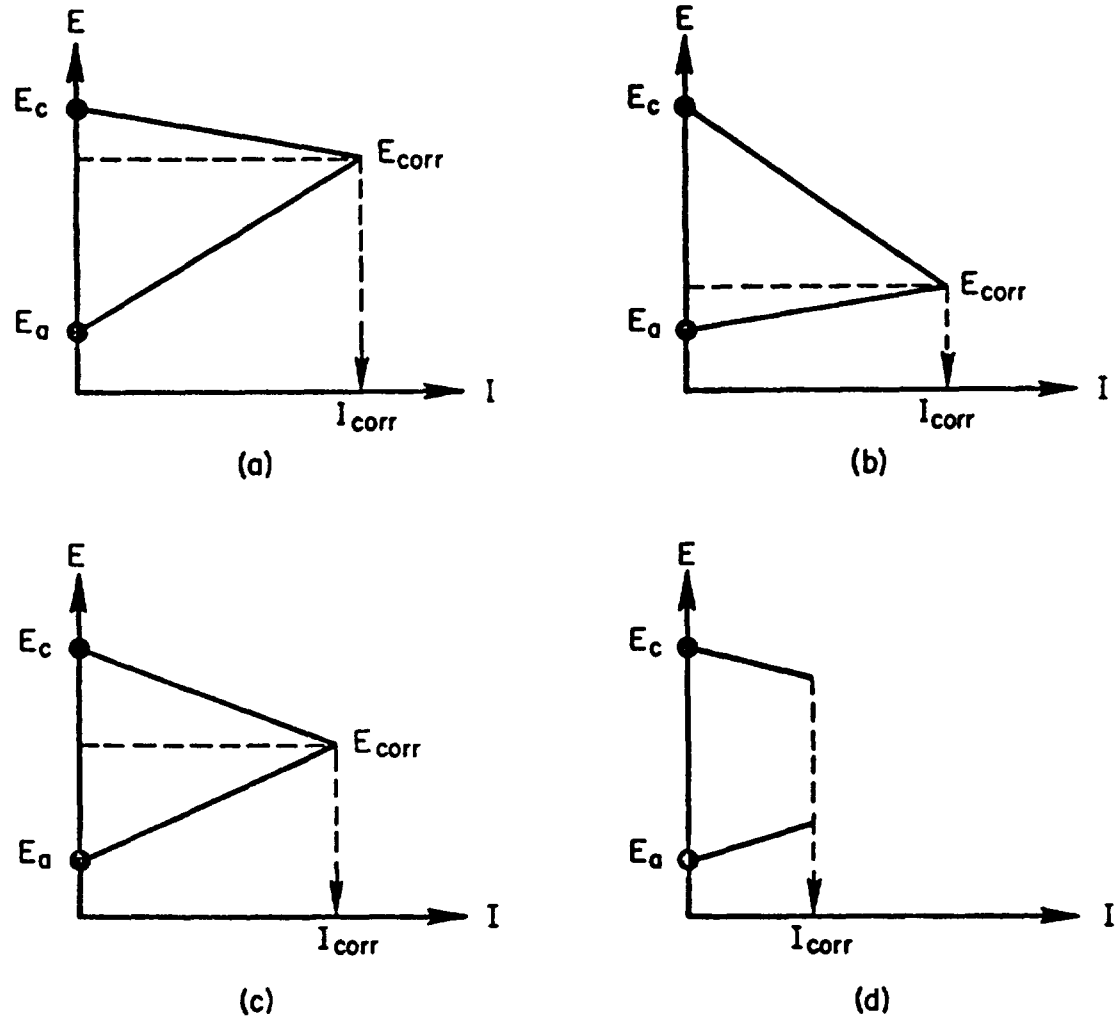
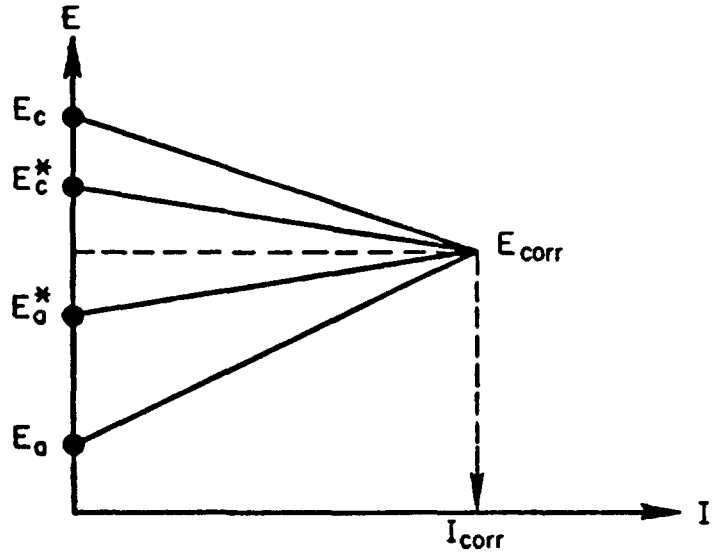
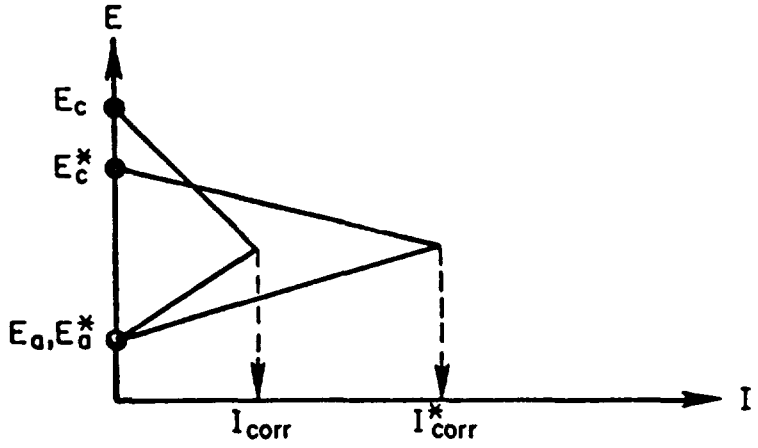


FIGURE 7. Evans-type diagrams showing (a) anodic, (b) cathodic, (c) mixed, and (d) resistance control of simple corrosion processes.



(a) Two systems with different thermodynamic tendencies to corrode (E_c/E_a and E_c^*/E_a^*) may give the same corrosion rate and mixed potential.



(b) A system with a large thermodynamic tendency to corrode (E_c/E_a) may give a lower corrosion rate than a system (E_c^*/E_a^*) with a lesser tendency.

FIGURE 8. Evans-type diagrams relating thermodynamic with kinetic corrosion parameters.

SECTION 4. CORROSION ATTACK

4.1 Types of Corrosion. There is no single universally accepted classification of the types of corrosion. One approach is to consider the form of the corrosion attack, as schematically presented in figure 9. Thus the attack may be seen to be uniform over the surface of the metal, as concentrated at local or isolated areas, in the extreme being apparent as cracking, pitting or perforation.

Corrosion of metals by uniform chemical attack is regarded as the simplest form of corrosion and may occur in the atmosphere, in liquids, or in soil. It occurs frequently under normal conditions of exposure and is relatively uniform over the metal surface, and generally proceeds at a fairly uniform rate if the products of corrosion are soluble in the corroding medium.

Uniform corrosion commonly occurs on metal surfaces having a good degree of compositional homogeneity; i.e., the microstructure of the metal surface is uniformly distributed. Access of the attacking environments to the metal surface is generally unrestricted and uniform. Microscopic anode and cathode areas are involved; consequently, uniform corrosion might be considered as localized corrosion occurring consistently and uniformly over the surface of a metal.

The rusting of iron, the tarnishing of silver, the fogging of nickel, and the high temperature oxidation of iron or stainless steels are typical versions of uniform corrosion.

Another approach is to consider three basic kinds of deterioration, namely electrochemical, chemical and physical, each kind being associated primarily with electrons, ions and atoms, respectively. Irradiation, or erosion (mechanical) attack would typically fall under the physical kind of deterioration, whereas high temperature oxidation exemplifies the chemical kind of deterioration.

High temperature oxidation can be experienced by military structures and equipment, therefore, the next section discusses this phenomenum briefly. Attention will then be given to the different forms of electrochemical corrosion attack in paragraph 4.3.

4.2 High Temperature Oxidation. The direct combination of an oxidizing agent, e.g. oxygen, sulfur dioxide, carbon dioxide, etc., with a metal at high temperatures is termed high temperature oxidation or dry corrosion. Specific types of high temperature oxidation to be found in the literature are Internal or Subsurface Oxidation; Metal Dusting; Green Rot; and Scaling, and these phenomena are briefly defined in the Glossary (see Paragraph 10.)

Dry corrosion is distinguished from usual corrosion processes which occur at ordinary temperatures in that it does not involve a liquid electrolyte as an integral link in the system.

Oxidation corrosion products form on the metal surface within certain temperature limits depending on the metal. If the film is continuous, nonporous, adherent, and thermally stable, the rate of oxidation will decelerate with time (see figure 10.) In this case the film is protective.

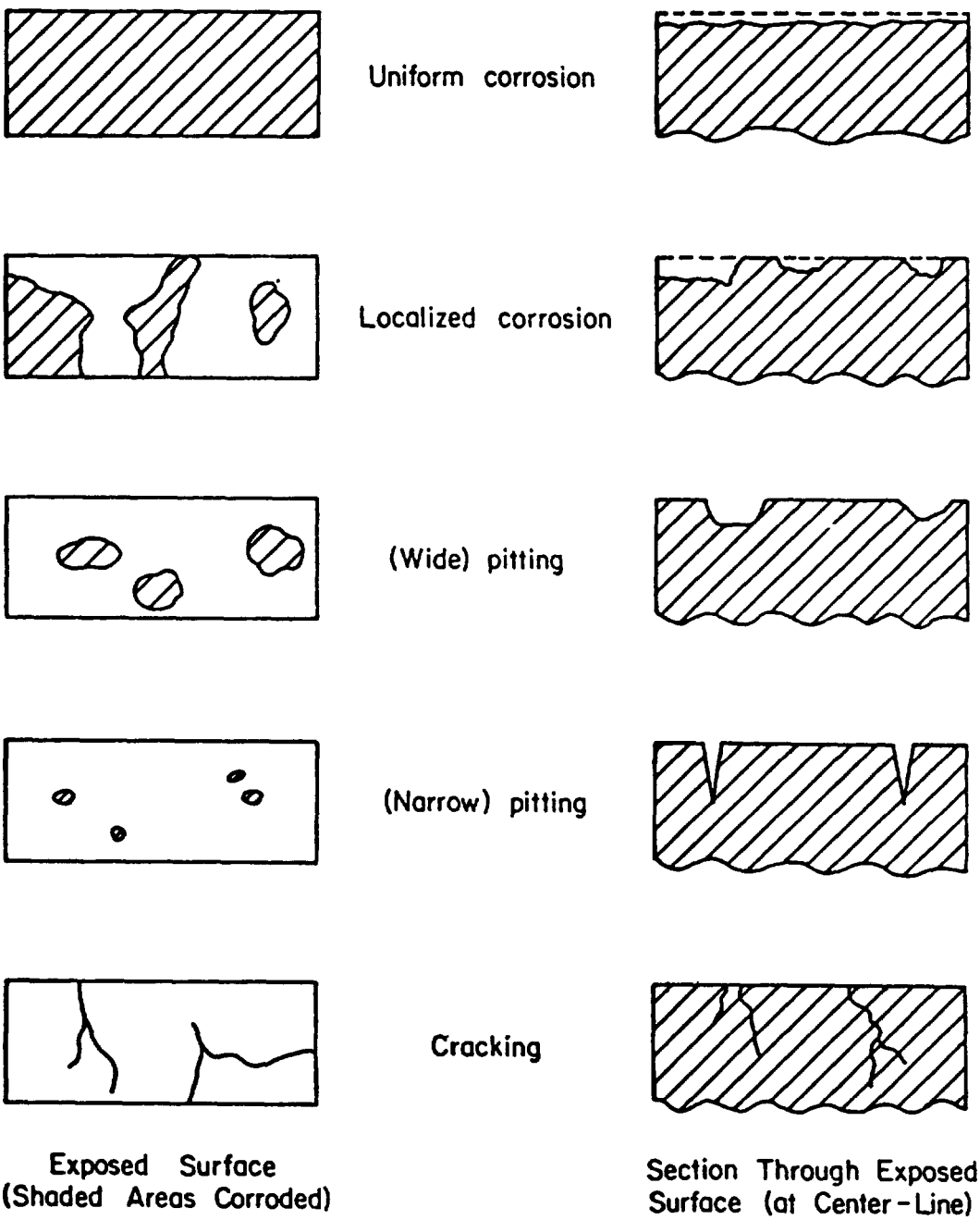


FIGURE 9. Physical Appearance of different types of corrosion attack.

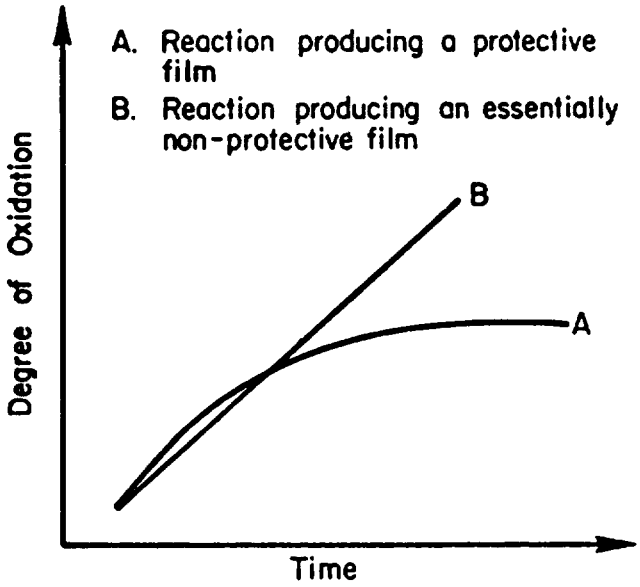


FIGURE 10. Effect of film properties on high temperature oxidation.

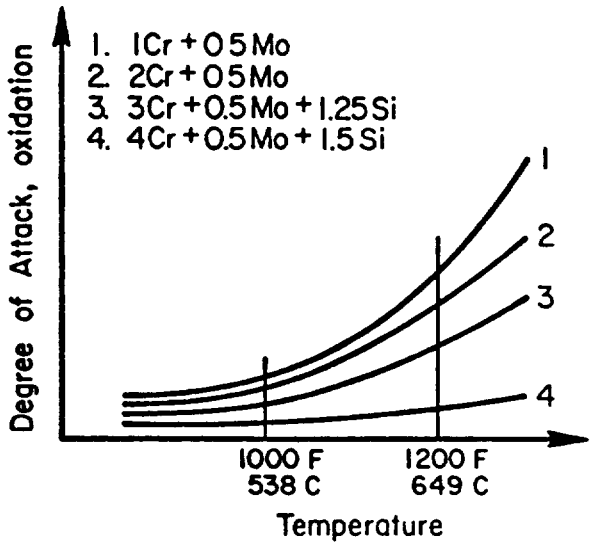
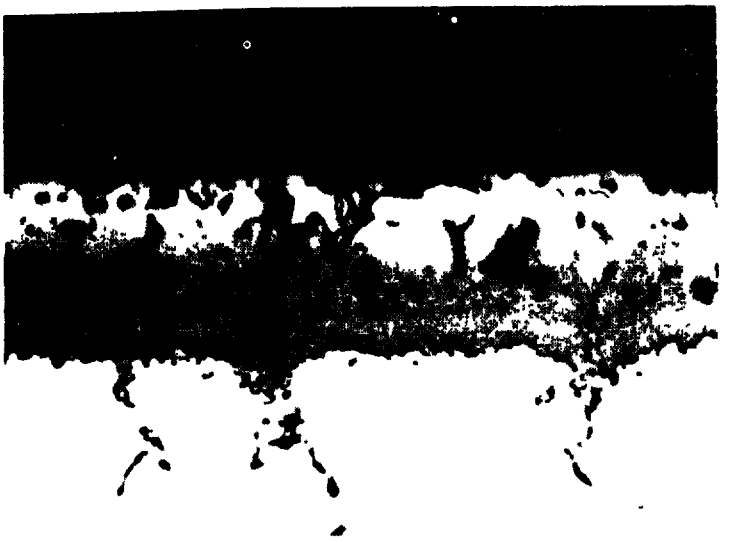


FIGURE 12. Effect of alloying on high temperature oxidation resistance of steel.



(a) Oxide coating formed on a 21% Cr + 25% Ni, balance Fe alloy after 20 cycles to 50°C.

(b) Oxide film formed on stainless steel in air at 980°C in the presence of traces of vanadium pentoxide vapor.

FIGURE 11. Protective and unprotective oxide corrosion films formed on metals.

If the film is porous or has a tendency to spall, the oxidizing agent will have access to the surface and oxidation will continue at a high rate. The film wil be essentially nonprotective and the metal will be severely attacked (see figure 11).

In addition to the nature of the film formed in high temperature reactions, the specific environment and the temperature conditions are some factors which should be taken into account in choosing metals for high temperature uses. Also the composition of the metal may be significantly important. To cite an example, the addition of 1 to 2 percent silicon to steels with low or intermediate content of chromium improves the resistance of chromium-steels to high temperature oxidations (see figure 12).

Further, a film such as the oxide formed on molybdenum at high temperature which is volatile at approximately 550°C (1020°F) will result in serious or possibly catastrophic loss of molybdenum.

Aside from dry oxidation at high temperature, metal damage at high temperatures is caused by molten salts (annealing and tempering baths), liquid metals, (liquid metal heat exchangers) and steam under pressure.

The designers of modern military equipment are confronted with many new requirements and demands for materials which can be serviceable under very high temperature use conditions. Technical advances in providing a variety of new materials and compositions to resist high temperature deterioration are noteworthy. Consultation with the current literature concerning new high temperature materials and their applications is urged. A good introduction to the subject is the Metals and Ceramics Information Center Report No. MCIC-72-07, entitled "Oxidation of Iron-Nickel-and Cobalt-Base Alloys", authored by I. G. Wright, and published in June, 1972.

With respect to military equipment, in particular gas turbine engines, corrosion problems have been encountered with the so-called "hot corrosion" of nickel base and cobalt base superalloys. Sodium salts, such as NaCl in marine environments, when ingested into the turbines have been thought to react with sulfur compounds in the combustion products, and cause a degradation of the air foils. The particular nature of hot corrosion or "sulfidation" is discussed below in more detail.

4.2.1 Hot Corrosion of Superalloys. This discussion will be limited to the hot corrosion of superalloys in military aircraft, although the mechanics of the degradation are similiar for land based and ship borne gas turbines. Hot corrosion is an accelerated deterioration mechanism caused by both high-temperature oxidation and sulfidation of the metal. Detailed discussions are given in References (8) and (9), however, the salient features will be given below. It should be pointed out that, although many turbine vanes and blades are coated with corrosion-resistant coatings containing aluminum and other metals such as chromium, the engine manufacturers prefer not to rely entirely on these coatings for hot corrosion resistance. High-strength, high chromium content, nickel base alloys have been developed for these applications in severe environments.(8) Chromia containing oxide scales have been found to be less susceptible to attack by sodium sulfate, the presence of which is detrimental for maintaining alumina-containing oxide scales stability. Protection against hot corrosion can only be achieved if a

protective film is maintained on the surface of the metal (whether it be an oxide, or in some cases a sulfide[8] film).

Early experiences with hot corrosion showed that the corroded parts were encrusted with a white deposit of primarily sodium sulfate, Ns_2SO_4. Tests with pure sodium sulfate indicated that there was little effect on the rate of oxidation (scaling), however, as little as 0.3 percent sodium chloride, or the presence of carbon produced a rapid increase in scaling rate, particularly for alloys which had borderline resistance to hot corrosion. More detailed observations showed that in the temperature range of interest, 750 to 1000 C (1380 to 1830 F), corrosion attack was associated with sulfur uptake and the formation of sulfides. There appears to be an incubation period before the detrimental reactions proceed rapidly. This period can be of the order of 100 to 1000 hours. Some data suggest that a form of hot corrosion (accelerated attack) can take place in the presence of sodium chloride alone, however, the mechanism of attack is likely to be different from that in the presence of sulfur compounds.

During normal gas turbine operation the conditions in the turbine should be oxidizing, and the protective scales on the vanes and blades should retain their integrity. However, if sulfur containing salts of sodium can condense on these surfaces, at the temperatures of operation it is thought that the condensed layers lead to an increase in sulfur acitivity at the surface of the alloy, and a decrease in oxygen activity. Both these factors lead to a destruction of the protective oxide scales. Thus although large chromium alloying additions may be detrimental with respect to mechanical properties the film-forming ability of the chromium improves the protective nature of the scales. Additions of aluminum also enhance the film-forming ability of the alloys (e.g., Ni-Cr-Al and Co-Cr-Al alloys). For the sulfidation reaction to be self-sustaining a reducing reaction must occur, either through the formation of double oxides, or by reaction with other contaminants, such as carbon.

With the assumption that hot corrosion results because of the destruction of protective scales, several mechanisms can be postulated for how this can occur.[10] First, solution of the surface scale can occur by either an acid or basic fluxing mechanism. The former occurs if tungsten or molybdenum are present in the nickel or cobalt alloys irrespective of whether chromium or aluminum is the major oxide film-forming element present. Basic fluxing occurs in the presence of sodium sulfate condensates for unalloyed nickel or cobalt, or when these are alloyed with aluminum. Second, a local reduction can occur due to the deposition of carbon particles or as a result of other reductants being present. Scale degradation can also result from mechanical erosion, or because of mechanical faults already present in the surface scale developed on the alloy. Thermal stresses or superimposed operating stresses can also cause scale failure. Finally, scale failure may occur due to contaminants (e.g., chlorides) reacting with the underlying metal causing a mechanical disruption of the surface scale. The role of mechanical, as opposed to chemical factors, had only recently received attention, and the possibility for conjoint action has now been recognized.

4.3 Electrochemical Corrosion Attack. As mentioned above, there is no single universally accepted classification of the various types of corrosion attack, however, traditionally in the U.S. it has been convenient to group

corrosion phenomena into eight arbitrary categories. These so-called eight forms of corrosion are described in the book by Fontana and Greene (listed in the Bibliography) and summarized below. Most of the known forms of attack are covered by one of the eight categories, and it will become evident that some of the forms of corrosion result purely from an electrochemical action, whereas others result from the conjoint action of electrochemical and mechanical factors. If the eight forms are classified as follows:

(1) Uniform corrosion, or general attack
(2) Galvanic corrosion or two-metal corrosion
(3) Pitting corrosion or localized attack
(4) Crevice corrosion
(5) Intergranular corrosion
(6) Selective leaching or parting
(7) Erosion-corrosion, and
(8) Stress-corrosion

then (7) and (8) above include conjoint action types of corrosion attack.

4.3.1 Uniform Corrosion. This is the most prevalent form of corrosion which is characterized by a reaction which proceeds uniformly over the entire exposed surface, or at least over a relatively large area exposed to the environment. As the attack proceeds the metal (or alloy) becomes thinner, and failure eventually occurs. With this form of attack it is possible to estimate the life of a metal based on comparatively simple immersion tests, hence the life of a structure or piece of equipment. Conversely, for a given life, a thickness can be specified. Thus uniform corrosion is usually of little concern from the practical standpoint.

Uniform corrosion can be prevented or ameliorated by applying protective coatings, or specifying more corrosion resistant metals of construction; by adding inhibitors to the environment; or by cathodic protection. These approaches are discussed in Section 6.

4.3.2 Galvanic Corrosion. Galvanic corrosion can occur on a macro-scale, such as when two dissimilar metals are joined together in a corrosive environment (see figure 13), or on a microscale on a single piece of metal, where inhomogeneities in composition or physical structure occur. In the former, the cathodic and anodic areas are easily discerned. In the latter case the anodic and cathodic areas can only be discerned by metallographic techniques, or deduced by inference or observation of the corroded metal. Usually, the coupling of two dissimilar metals is understood when the term galvanic corrosion is used, however, for both cases the principle of attack is the same.

When two dissimilar metals are immersed in an electrolyte and contacted electrically, a current will flow (see Paragraph 3.1). The more active metal (anode) of the couple beings to corrode and the less active metal (cathode) is protected. The limitations of the Electromotive Series which make it unsuited for practical use with many metals have been indicated (see Paragraph 3.1). Another relationship has been developed that takes into consideration over-all and practical aspects as well as theoretical principles, and is referred to as the Galvanic Series, shown in table III, in which sea water is used as the electrolyte. The metals grouped together can be joined with a minimum of

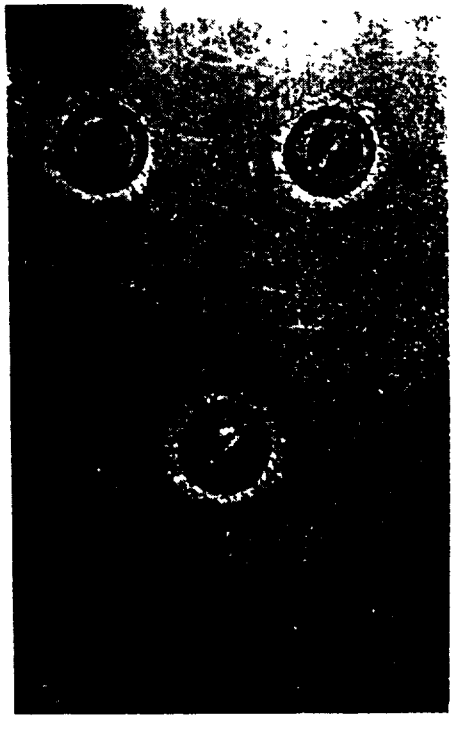


FIGURE 13. Galvanic corrosion attack associated with fasteners on steel sheet.

Note: galvanic attack on washers as well as on steel due to the contact of dissimilar metals in the presence of moisture.

galvanic corrosion; the coupling of metals from adjacent groups will exhibit a slightly greater galvanic effect; metals distantly located in the list will result in appreciable or intense galvanic action.

Factors which influence and control galvanic action are the effectiveness of the electrical circuit, the ratio of anode and cathode areas, and polarization of the electrodes.

Galvanic corrosion requires not only a conductive environment but also good electrical contact between the dissimilar metals. If this is not maintained, the galvanic action will decrease. Insulating materials such as non-wicking gasketing, paint and plastic films and certain inorganic coatings, at the juncture surfaces of dissimilar metals, will prevent or considerably reduce the flow of galvanic current and the progress of corrosion. Corrosion products which might form at contacting surfaces of dissimilar metals, particularly if wet, may serve as a conductor and promote further galvanic corrosion.

The current flow and effective potential difference between dissimilar metals in an electrolyte may also be reduced by polarization. Polarization may occur at the anode (less noble metal) with the accumulation of corrosion products, or at the cathode (more noble metal) with the deposition of an insulating film of gaseous hydrogen. In either case, the result is a decrease in electrochemical action. The deposition of hydrogen, called cathodic polarization, is the more influential deterrent and may produce a strong barrier to galvanic corrosion. Oxygen in solution, however, may act as a depolarizer by uniting with the deposited hydrogen to form water.

Under actual service conditions many factors combine to modify normal corrosion expectations. The design engineer should be aware of all the contributing factors in order to determine which will be the most important for his considerations.

The ratio of the cathodic area to the anodic area influences the rate of attack. When there is a large cathode in contact with a small anode, the attack of the anode is more concentrated and corrosion is more rapid. For certain metals in contact, the rate of galvanic corrosion in specific electrolytes increases directly in proportion to the ratio of increase of the cathodic area over the anodic area.

Galvanic corrosion effects are usually greatest near to the junction between the dissimilar metals, and the extent of the attack decreases with increasing distance from the junction. The extent of the attack can be very localized, or more diffuse, depending on the electrical conductivity of the metals and the conductivity of the corrodent (electrolyte). In general, however, galvanic corrosion is readily recognized by the localized attack near the junction of the two metals, and the more aggressive the environment, the greater the amount of corrosion attack.

TABLE III. The Galvanic Series of Metals and Alloys.

Anodic End	Magnesium
	Magnesium Alloys
	Zinc
	Galvanized Steel
	Aluminum 1100
	Aluminum 6053
	Alclad
	Cadmium
	Aluminum 2024 (4.5 Cu - 1.5 Mg - 0.6 Mn)
	Mild Steel
	Wrought Iron
	Cast Iron
	13% Chromium Stainless Steel Type 410 (Active)
	18-8 Stainless Steel Type 304 (Active)
	18-12-3 Stainless Steel Type 316 (Active)
	Lead-Tin Solders
	Lead
	Tin
	Muntz Metal
	Manganese Bronze
	Naval Brass
	Nickel (Active)
	76 Ni-16 Cr-7 Fe Alloy (Active)
	60 Ni - 30 Mo - 6 Fe - 1 Mn
	Yellow Brass
	Admiralty Brass
	Aluminum Brass
	Red Brass
	Copper
	Silicon Bronze
	70:30 Cupro Nickel
	G-Bronze
	M-Bronze
	Silver Solder
	Nickel (Passive)
	76 Ni - 16 Cr - 7 Fe Alloy (Passive)
	67 Ni - 33 Cu Alloy (Monel)
	13% Chromium Stainless Steel Type 410 (Passive)
	Titanium
	18-8 Stainless Steel Type 304 (Passive)
	18-12-3 Stainless Steel Type 316 (Passive)
	Silver
	Graphite
	Gold
Cathodic End	Platinum

4.3.3 Pitting Corrosion. Pitting is a common and extreme form of localized corrosion attack. Thin metal sheets and plates are especially vulnerable to failure by this form of attack since penetration of the metal at pit sites can result in perforation, and possibly unserviceability (figures 14 and 15), when only a small percentage of weight loss has occurred.

Pits are isolated holes which may vary in shape as shown in figure 9, but which are often hemispherical in appearance and sometimes covered with a corrosion product. If pits are closely spaced together then the metal surface takes on a roughened appearance.

Pitting is usually initiated at highly anodic points on a metal surface. Such anodic areas may result from differences in chemical composition (e.g., at grain boundaries--see intergranular corrosion), discontinuities in coatings or protective films, in heavily mechanically worked regions, at surface scratches, and at point defects such as emerging dislocations. At these points an aggressive corrodent (such as a chloride solution) will cause local dissolution of the metal. Once dissolution begins, the process is self-sustaining, for example in a chloride electrolyte, as the metal dissolves an excess positive charge is built up locally while dissolved oxygen is being reduced on adjacent surfaces. The excess charge attracts chloride ions to maintain electroneutrality. In doing so, the aggressiveness of the electrolyte is locally increased and further dissolution occurs. The criteria for pitting to occur are thus (1) local anodic sites on the metal surface (2) an aggressive electrolyte, and (3) the presence of oxygen (from air) or any other easily reducible species (e.g., cupric or ferric ions). If the solution is flowing or in the presence of strong convection currents, there may be a lessened chance that pitting might occur if the solution flow makes it difficult to maintain the aggressive electrolyte composition within the pits. Similarly, pits are usually found on horizontal surfaces facing up, because this orientation favors retention in the pits of the aggressive electrolyte.

Several approaches may be taken to reduce the incidence of pitting corrosion. Alloying addition can reduce the susceptibility, and deaeration of the corrodent often helps. Inhibitors in theory can be useful, but in practice can be dangerous because below threshold values the rate of pitting may actually be accelerated.

4.3.4 Crevice Corrosion. The mechanisms of crevice corrosion and pitting corrosion are very similar. A metal susceptible to pitting will also be susceptible to crevice corrosion, although the converse is not true. Pitting corrosion may be thought of as a special form of crevice corrosion which is self initiating--a crevice is not required to start the localized anodic dissolution of the metal.

Crevice corrosion is usually characterized by intense localized attack in crevices or other shielded areas in contact with a corrodent, which because of the shielding effect, is stagnant (see figure 16). Holes, gaskets, lap joints, crevices under bolt and rivet heads, and surface deposits are corrosion sites. To maintain a stagnant condition, the crevices usually should be less than 0.5 mm (0.125 in.) in width or diameter.

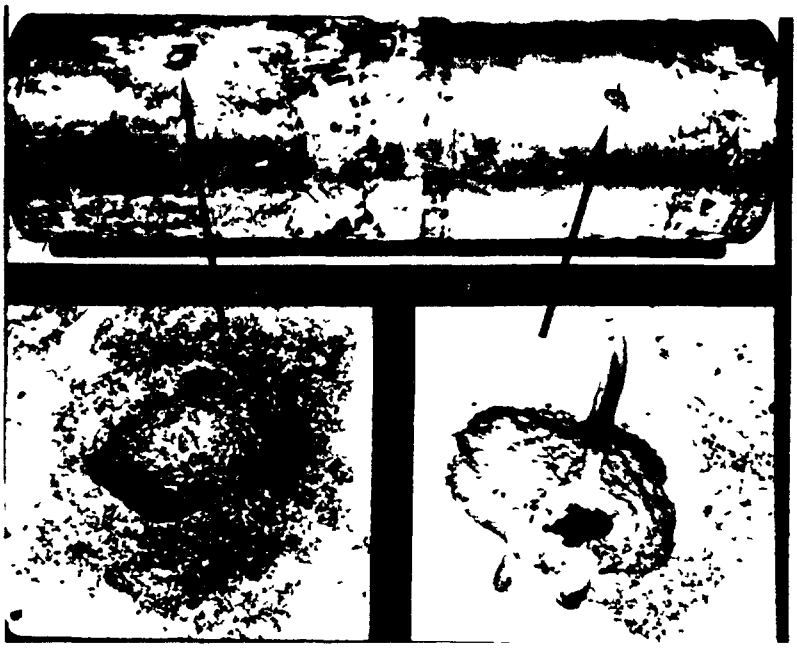


FIGURE 14. Pitting corrosion attack in an aluminum gas transmission pipe.

Enlarged view at right shows where metal has been perforated causing a leak to occur.

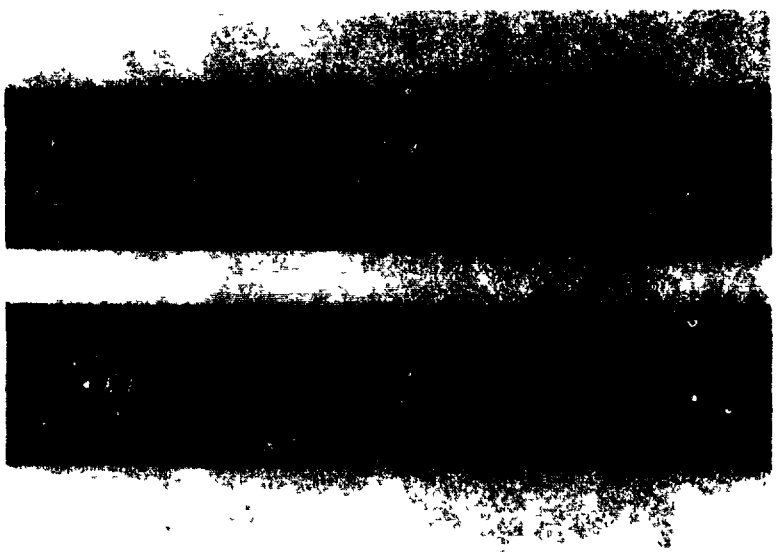


FIGURE 15. Pitting corrosion attack in hard temper copper water tubing.

Perforation has occured on the left-hand side of the bottom half of the sectioned tube.

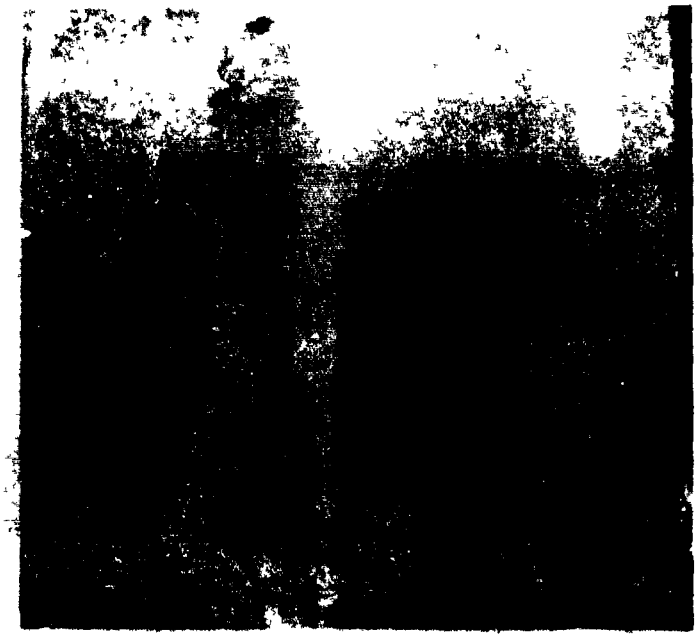


FIGURE 16. Corrosion attack at a crevice between a tube and a tube sheet.

Porous substances in contact with metal surfaces may also absorb or retain corrosive solutions and crevice corrosion may then result also.

Before discussing the probable mechanism of crevice corrosion it is convenient to describe metal-ion concentration cells and oxygen concentration cells, because the latter plays an important role in crevice attack.

When a metal goes into solution, there is some concentration of ions of that metal in the corroding solution. The lower the metal-ion concentration, the greater the tendency for the metal to go into solution as the metal ions. When the concentration of metal ions in the solution reaches saturation, the metal does not dissolve any further. If the concentration of metal ions in the solution is greater at one point on the metal than at another, then concentration cell action will occur. An electrical potential is established between the two points of different concentration; the metal surface in contact with the higher concentration of metal ions becomes the cathode, and the surface of the lower concentration is the anode. The flow of current is from the metal to the solution at the anode, and from the solution to the metal at the cathode. Therefore at the point of higher concentration, the cathode is protected while at the point of lower concentration, the anode is attacked. In actual service, metal-ion concentration variation may be due to differences in velocity or agitation. The metal ions in the corrosion products may be removed from one part of a metal at a higher rate; or they may not be removed at all from one part of the metal. In either case, such sustained action would lead to differences in metal-ion concentration.

Corrosion by oxygen concentration (differential aeration) cells may occur when the concentration of dissolved oxygen is greater at one point on the metal than at another point. As in the case of metal-ion concentration, a difference in potential is established between the two points of differing oxygen concentration. The point of the metal of higher oxygen concentration is the cathode, whereas the point of surface of the lower oxygen concentration is the anode. The current flows from the metal to the electrolyte at the point of lowest concentration and from the electrolyte to the metal at the point of highest concentration. This action results in accelerated corrosion at the area of lowest oxygen concentration in the cell (see figure 17). Water-line attack is a special type of oxygen concentration cell.

In some metals it is possible for metal-ion and oxygen concentrations in the cell to counteract one another. The development of an area of higher oxygen concentration may result in an increase of metal ions in the area of the anode. This would produce another set of potential differences that would counteract the original effect. Oxygen-cell concentration corrosion would then be retarded. This peculiar pattern may occur with many metals, especially copper and copper alloys.

Active-passive cell action may arise with alloys that develop a protective, passivating type of film. If an oxygen-cell type of condition develops, the absence of oxygen at the anodic area will prevent the protective film from reforming. Because of the incompleteness of the passivating (protective) film, corrosion at the exposed anodic areas is accelerated. This accelerated corrosion occurs because of the increased potential between the passive cathodic areas and the active sites.

Returning to the mechanism of crevice corrosion, initially attack occurs over the entire surface of the metal or structure, with metal ions going into solution, and dissolved oxygen being reduced to hydroxyl ions. However, the oxygen supply in the crevice is depleted if corrodant replenishment is not possible due to restricted convection. Oxygen reduction stops in the crevice while the overall rate of oxygen reduction on the remainder of the metal surface is virtually unchanged. If the metal continues to dissolve (corrode) in the crevice an excess positive charge is built up in solution, which in turn attracts anions to confer electroneutrality. As the concentration of metal cations and anions builds up, hydroysis often occurs to give insoluble metal hydroxides with the release of protons. The presence of protons (H^+) and anions (e.g., Cl^-) usually constitute an extremely aggressive environment, and the rate of corrosion attack is accelerated, and the process is self sustaining, like pitting.

Deposition corrosion (also known as gasket corrosion) is a special type of crevice corrosion, where a part of a metal surface is shielded or covered by foreign matter or nonmetallic structural members. An oxygen-deficiency type of concentration cell is established (figure 18) and corrosion proceeds. Figure 19 shows this type of attack on a carbon steel exposed to sulfuric acid. The metal surface need not be totally immersed in the electrolyte constituting the corrodent. Capillary action, absorption by porous deposits, or water uptake by hygroscopic deposits can establish the three-phase interface (corrodent: metal: deposit) necessary to promote attack.

Filiform corrosion is another special type of crevice corrosion which appears in the form of thread-like lines or worm-like strands. It has been noted to occur on metal surfaces under water-permeable coatings of clear lacquers and varnishes, under paints, and sometimes under thin noncontinuous electrodeposits. It is very likely to occur on surfaces of steel, although it has been observed to develop on other metal surfaces such as aluminum, magnesium and zinc (see figure 20). Chemical conversion treatments of the metals prior to applying organic coatings will materially inhibit filiform corrosion.

The individual threads of corrosion are considered to initiate at and radiate from discontinuities or nuclei of contaminants (corrosive salts) on the metal surface, and lengthen because of differences in concentrations of oxygen between the advancing head and the thread body. The head is considered to be more anodic; i.e., lower in oxygen concentration than the body. Water enters at the head by osmotic action, and diffuses out of the inactive tail. Relative humidity levels between 65 and 90 percent will promote filiform corrosion, while above 90 percent, blistering is more likely to occur. Moving, active threads can merge if they meet obliquely, however, an active thread cannot cross an inactive thread tail. The active head is reflected, or if meeting perpendicularly, is often divided into two new threads. The various possibilities are discussed in detail in Fontana and Greene's book referenced earlier.

Because attack is at the metal substrate/coating or protective film interface, this type of corrosion is also called "underfilm corrosion". Filiform or underfilm corrosion does not usually decrease or destroy the mechanical properties of a metal, but it does destroy the surface appearance, which might be an important factor in food and beverage applications.

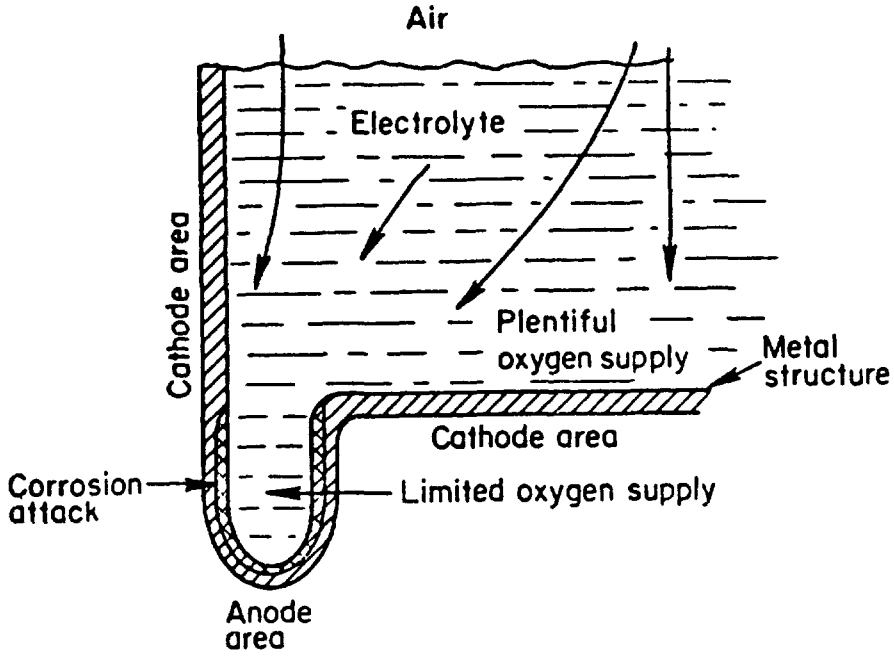


FIGURE 17. Example of crevice attack in an open vessel.

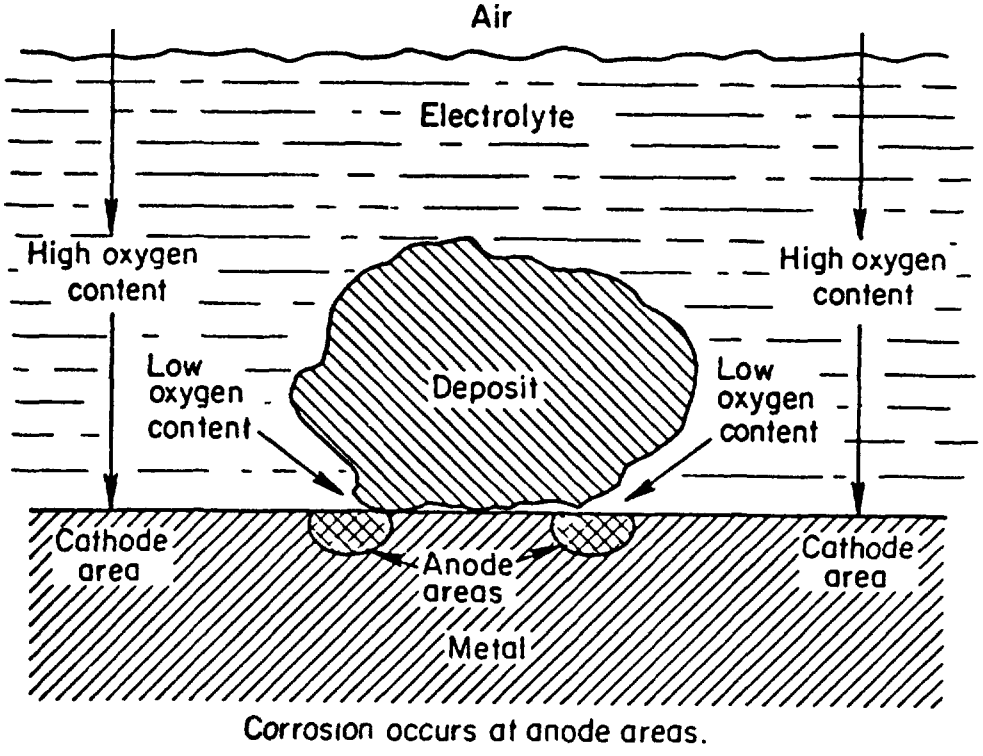


FIGURE 18. Example of deposit attack, a form of crevice corrosion.

FIGURE 19. Deposition-type attack of a carbon steel exposed to sulfuric acid at 30oC.

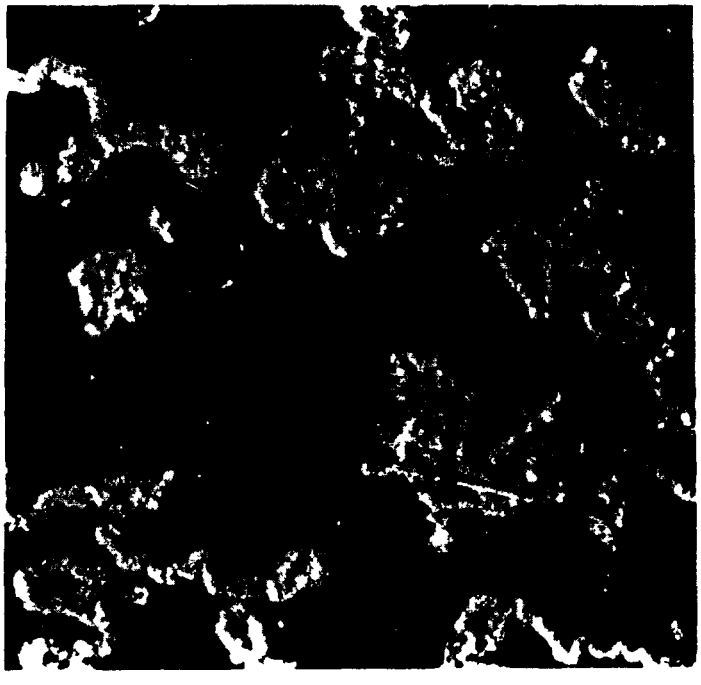


FIGURE 20. Filiform corrosion on aluminum under an organic coating.

4.3.5 Intergranular Corrosion. Intergranular corrosion occurs in boundaries between grains or crystals in metals. The boundary areas are usually anodic to the grains, often due to the presence of impurities or precipitates. Consequently in certain corrosive electrolytes, if sufficiently wide potential differences exist between the anodic grain boundaries and the cathodic grains, rapid and concentrated intergranular or intercrystalline corrosion will occur. Although many alloys are susceptible to some extent to intergranular corrosion, in very many cases this type of attack is of little significance. However, when the corrosion attack at grain boundaries is severe, the strength and other physical properties of the metal may be reduced out of proportion to the amount of metal consumed. Such is the case with some aluminum alloys which are susceptible to "exfoliation" (see paragraph 5.1.1 and figure 21) where flakes of metal are lifted from the surface due to this corrosion process. Die-cast zinc alloys containing aluminum in steam or marine environments, are also susceptible to intergranular attack, which has also been observed in ancient bronzes.

Of the structural alloys, the so-called nonstabilized stainless steels are singularly vulnerable to intergranular corrosion. When these alloys are heated in the temperature range of 482 to 816°C (900 to 1500°F) for a sufficient time, the carbon contained in the alloy will combine with chromium in the alloy to produce an iron chromium carbide which precipitates in the grain boundaries. This results in the lowering of chromium content in areas adjacent to the carbides. The chromium deprived portions of the alloy are susceptible to intergranular corrosive attack (see figure 22).

This increased susceptibility of intergranular corrosion due to heating is frequently referred to as sensitization to intergranular corrosion. If they are not followed by proper solution annealing treatment, welded nonstabilized stainless steels may be sensitized to grain boundary corrosion attack in the heat-affected zones on either side of the weld (see figure 23 and figure 24) sometimes referred to as weld decay. If the carbon content of the steel is lowered (e.g., ELC = extra low carbon steel) then excess carbon is not available for carbide precipitation, and weld decay cannot occur. An example of this approach to corrosion protection is shown in figure 24 (a).

Knife-line Attack is similar to weld decay, and is another type of intergranular corrosion. Knife-line attack, as its name implies, is characterized by a narrow band of corrosion (a few grains wide) on each side, and immediately adjacent to welds in stabilized stainless steels under certain conditions. If the niobium or titanium stabilizing additions, for example, fail because of an unfavorable thermal history to prevent chromium carbide precipitation by combining with the excess carbon, then the microscopic galvanic cells set up between the grains and grain boundary areas in a suitable corrodent will cause corrosion to take place. If stabilized steels are used, and welded, subsequent heat treatment should include as a final step heating to about 1065°C (1950°F) followed by cooling to dissolve chromium carbide and precipitate columbium carbide particles, for example.

4.3.6 Selective Leaching. Selective leaching, occasionally referred to as parting, is the removal of a single element from an alloy by corrosion processes. The most common example of selective leaching is the removal of zinc from brasses (e.g., "dezincification") however, aluminum, chromium, cobalt, iron, and some other elements may be selectively removed from specific alloys.

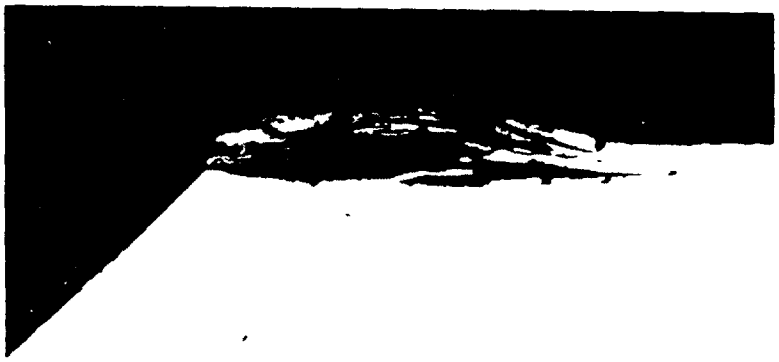


FIGURE 21. Exfoliation corrosion of a 2024 ST6 aluminum alloy.

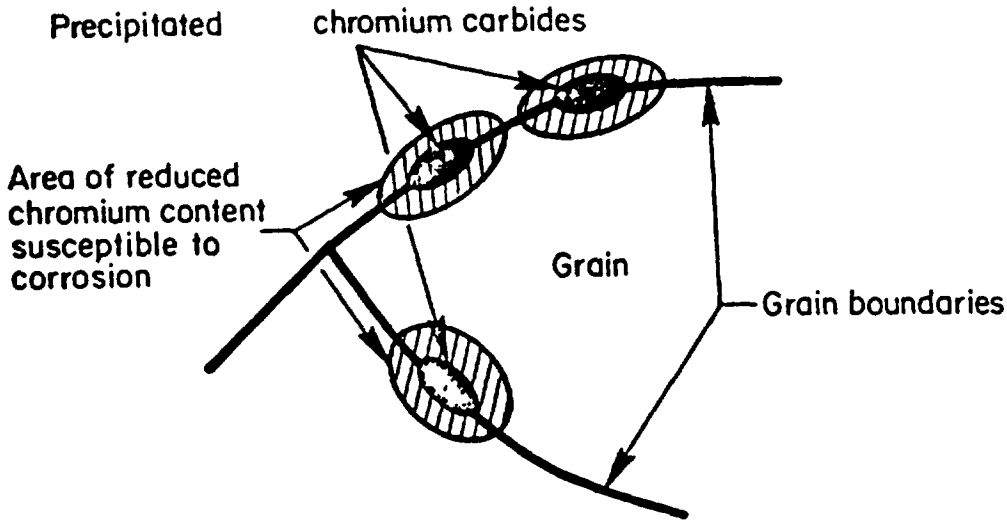


FIGURE 22. Conditions leading to the intergranular corrosion of stainless steel.

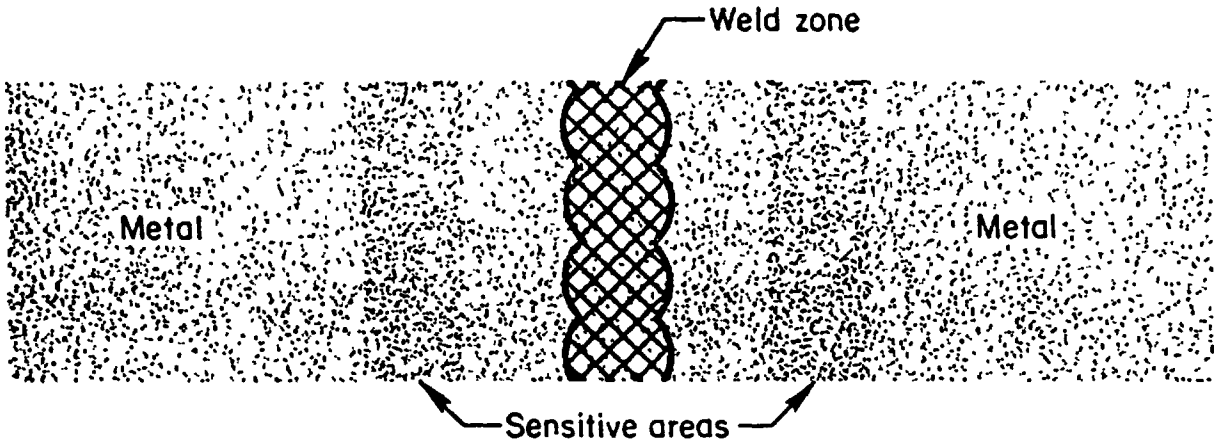
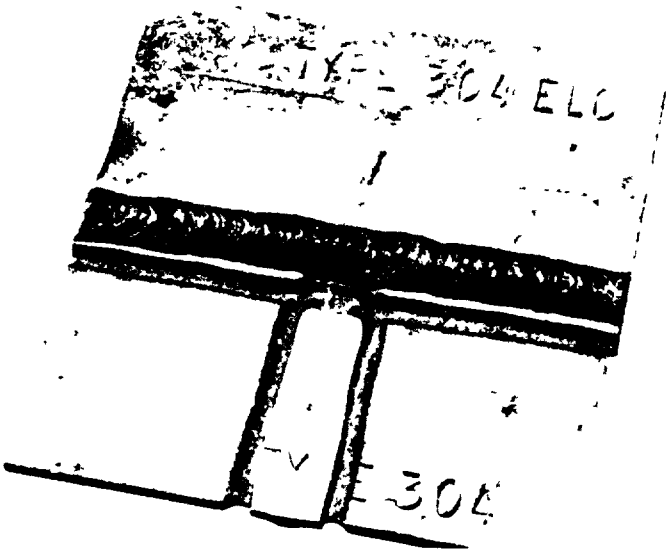
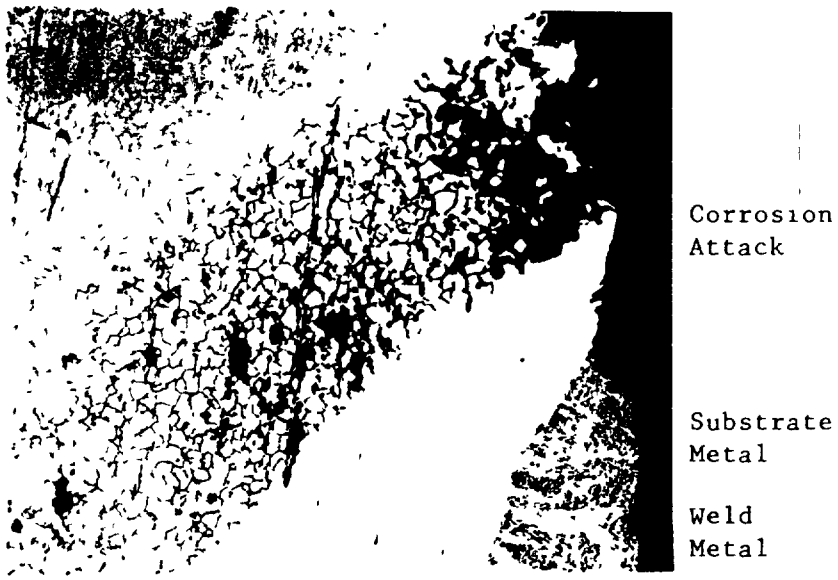


FIGURE 23. Sensitized areas resulting from welding stainless steel.



(a) Type 304 stainless steel sensitized by welding and exposed to boiling concentrated nitric acid to reveal regions of Weld Decay. Note that low carbon steel (top) is not attacked.



(b) Cross-section through a welded plate showing the corrosion attack along the sensitized region.

FIGURE 24. Appearance of Weld Decay on (a) macro-scale, and (b) a micro-scale.

Brasses contain two major constituents, copper and zinc. When dezincification occurs zinc is lost from the alloy, leaving a primary residue of copper. The copper remains or is redeposited in a porous and friable form on the surface of the metal, retaining the original shape and form of the part. The process is continuous. If the action is not arrested, the entire metal will be reduced to a weak, spongy mass.

Dezincification may be either the uniform or "layer" type, or the localized or "plug" type (figure 25). In general, the dezincification of brasses occurs during contact with sea water or fresh water containing a high concentration of oxygen and carbon dioxide. Stagnant or slow moving waters, foreign surface deposits, and elevated temperatures also contribute to promote the attack. The tendency toward dezincification of the layer type increases with an increase of zinc content in the alloy and acidity of the environment. On the other hand, brasses containing 85 percent copper are quite resistant to dezincification. However, brasses with relatively low zinc content in neutral alkaline or slightly acidic environments are prone to the plug type of dezincification. Alloying additions of arsenic, antimony or phosphorous reduce the tendency to dezincification of copper brasses, and arsenic is effective in aluminum brasses. For extremely corrosive environments, however, where dezincification occurs, cupro-nickels should be used. These copper alloys contain between 10 and 30 percent nickel.

Gray cast iron is subject to graphitic corrosion or graphitization, a reaction which is comparable to dezincification suffered by certain brasses. Graphitization occurs only under specific conditions and corrodes away the iron portion of the product, leaving a coherent matrix which is largely graphite. The shape of the product may not be changed, but the metal becomes porous and its mechanical and metallic properties are destroyed.

Aluminum leaching from aluminum bronzes, silicon from silicon bronzes, and cobalt from cobalt-tungsten-chromium alloys have all been reported in the literature.

4.3.7 Erosion Corrosion. This form of attack involves the acceleration of corrosion by erosive action. It is encountered when particles in a liquid impinge on a metal surface, causing the wearing away of protective films and exposing new reactive surfaces which are anodic to uneroded neighboring areas on the surface. This results in rapid localized corrosion, usually of a characteristic geometry, of the exposed areas as shown in figure 26. Virtually all flowing or turbulant corrosive media can cause erosion corrosion. Also, since all metals develop some surface film in mild corrosion environments which may retard the corrosive action, it is a fact that the corrosion of all metals can be promoted under erosive or flowing conditions. Metals (such as stainless steels, lead and aluminum) which normally develop a highly effective protective film (passive film) under usual conditions of use will undergo highly accelerated corrosion when subjected to even mildly aggressive environment when erosive conditions exist.

Impingement corrosion is a severe form of erosion corrosion. It is particularly noted to occur in turns or "ells" of tubes, or pipes, or on surfaces of impellers or turbine blades where impingement (change in direction of fluid flow) is encountered and erosion is more intense. Figure 27 shows impingement attack on copper tubing, and the characteristic "horseshoe" impressions formed.

(a) Plug-type dezincification of brass.

(b) Cross-section through a plug of corrosion product resulting from dezincification.

FIGURE 25. Appearance of dezincification of brass on (a) a macro sacle, and (b) a micro scale.

FIGURE 26. Erosion corrosion of a valve seat by escaping steam.

FIGURE 27. Impingement attack on copper tubing used in water service. Solution flow was from right to left.

Perhaps the severest form of erosion corrosion is cavitation corrosion (see figure 28). It occurs principally as the result of high impact on a metal surface by the liquid environment and is brought about by implosion of vapor bubbles. The vapor bubbles form because of high velocity movement of liquids on the trailing side of hydraulic impeller blades, for example. The high impact pressures result in damage and removal of surface protective films at the point of implosion, and the establishment of very severe erosive/ corrosive conditions.

Fretting corrosion is the term commonly applied to a type of metal damage which may occur when two metal surfaces are in contact, under load, and subjected to vibration, or slight relative motion.

Damage by fretting corrosion can occur between any two surfaces in contact, providing one is metal. The surfaces must be in relative motion - low or high frequency - and oxygen or air must be present. The surfaces may be wet or dry, and other conditions such as temperature or stresses may vary widely.

Surfaces of ball or roller bearings, couplings, knuckle connections and electrical contacts are subject to fretting corrosion. Bolts, flanges, key shafts, etc., which are intended to be fast but which might encounter vibration can be affected if the contacting surfaces undergo very slight relative motion. Attack by fretting corrosion may be rapid. Deep depression can form and may lead to stress or fatigue failure.

Fretting corrosion is characterized by the presence of surface discoloration, oxide debris and depressions or pits (see figure 29). In the case of ferrous alloys, brown to red iron oxide issues from the interface. On aluminum alloys, a black corrosion product is evident.

4.3.8 Stress-Corrosion Cracking. Stress-corrosion cracking of metals may be defined as the loss of load-carrying capacity of metals as the result of the combined action of stress and a corrosive environment.

The stress may be residual, or applied, or the superposition of the two. Stresses, with relation to stress-corrosion cracking are tensile, or must have a tensile component, and may increase in magnitude with the propagation of cracks, but are ordinarily nonfluctuating. Further, failures of structures as the result of reduction of load-carrying areas by general corrosion, as for example, that occuring in the rusting of a bolt, are not considered to be stress-corrosion cracking as it is defined here. However, if voluminous corrosion products are formed in a restricted space, such as on the threads, the build-up in pressure can be sufficient to cause stress-corrosion cracking. Aluminum alloy units have been known to fail because of general corrosion of the bolts in a structure (figure 30).

Factors controlling stress corrosion include the type and amount of stress in the metal, the nature, concentration, temperature of corrosive environment and the period of exposure. Any stressed metal or alloy might be considered vulnerable to stress-corrosion failure under appropriate conditions. The degree of tensile stress whether residual or applied is an important consideration as indicated by figure 31.

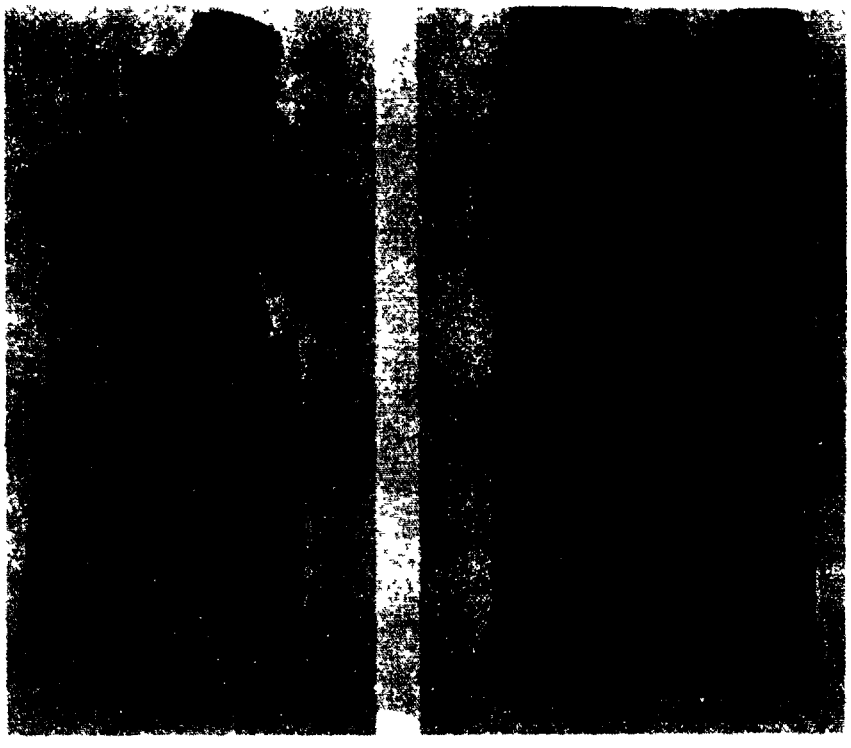


FIGURE 28. Cavitation corrosion attack on cast iron diesel engine cylinder liners.

FIGURE 29. Fretting corrosion of 7075 T651 aluminum alloy sheet in contact with a steel trap.

FIGURE 30 Stress-corrosion cracking of an aluminum alloy nut caused by corrosion of the bolt.

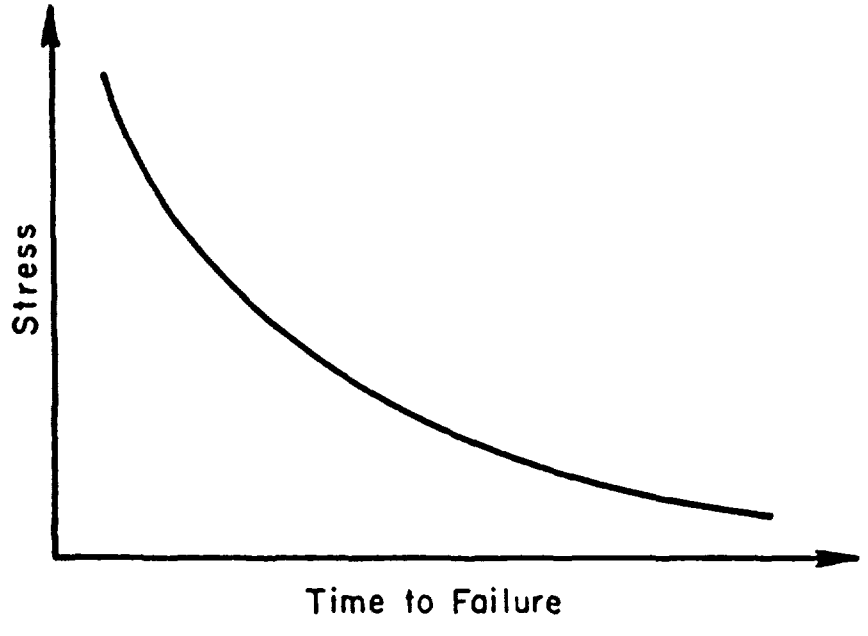


FIGURE 31. Relation of stress to failure time in a corrosive environment.

Applied tensile stresses are usually present because of the design of the structure or piece of equipment, or the manner in which it is used. Residual stresses may be present for a variety of reasons, either direct or indirect. Fabrication procedures may directly lead to residual stresses, e.g., rolling of tubes, improper heat treatments, mismatch in welding or riveting, over-torqueing of threaded joints, forcing oversized bushings or bearings in extruded fittings, and so on. Indirectly, stresses may result from the build-up or corrosion products in confined spaces, such as in the nut and bolt example given above.

The environment must contain specific corrosive agents, in many cases, in order to influence the initiation or acceleration of the stress-corrosion. For example, cold-worked brass containing residual stresses, will crack intergranularly when subjected to an ammoniacal environment. Other examples are given in table IV. Increasing the concentration of the corrosive agent or increasing the temperature will tend to increase the rate of stress-corrosion cracking. Environments that will produce stress-corrosion cracking are relatively mild, and if it were not for the applied stresses there could be no failure, and the metal could be considered resistant to corrosion.

There are two stages in the life of a metal failing due to stress-corrosion cracking, as illustrated in figure 32, adopted from Reference (11). During the first stage, or induction period, stress plays relative little part[3], except towards the end, pitting or crack initiation occurs, or a pre-existing flaw begins to enlarge. This first stage comprises the major part of the life of the metal. In the second stage crack propagation is rapid, in comparison, and failure results. Fracture mechanics studies have developed relationships from which, if the fracture toughness of the metal and the applied stress are known, a critical flaw size can be estimated. If defects in the metal itself, or cracks, notches, and other defects are built into the metal structure, and the applied stresses are such that the critical flaw size is exceeded, a running crack will develop, and the structure will fail by brittle fracture.

In failed structures metallographic examinations of the metal adjacent to the failed area will usually reveal fine cracks extending into the metal from the exposed (not from the fractured) surface. These cracks may be intergranular (intercrystalline), transgranular (transcrystalline), or a mixture of the two. (With intergranular cracking, high stress loads can be imposed on metal adjacent and communicating with the crack, and can lead to transgranular cracking.)

Intergranular cracks, as the term implies, follow the grain boundaries in the material. This is the usual type of cracking found in high-strength aluminum alloys, low-carbon steels, and in service failures in alpha-brass. Intergranular (Intercrystalline) cracking is shown schematically in figure 33(a).

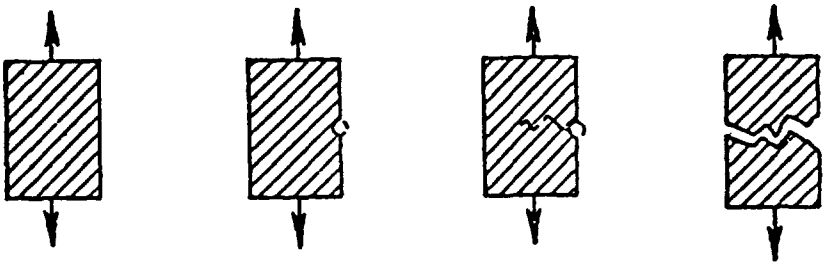
Transgranular cracks pass through the grains and sometimes are highly branched within the grains. This type of cracking is found in the chloride cracking of austenitic stainless steels. Cracks that are predominantly transgranular will and often do follow a grain boundary for a short distance. Predominantly intergranular cracks can and sometimes do cut through a grain rather than follow the boundary around it. Transgranular cracking is shown schematically in figure 33(b).

TABLE IV. Environments Reported to Have Produced Stress-Corrosion Cracking Failures in Selected Metals.

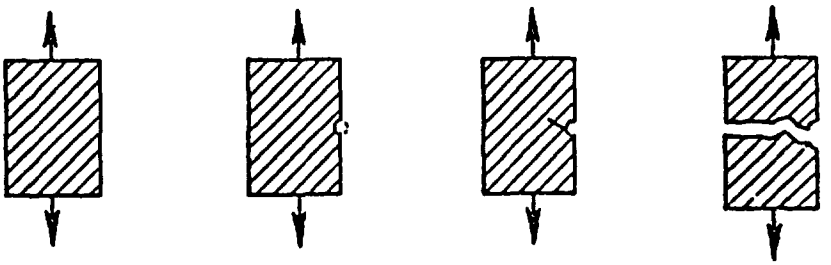
Alloy	Environment and/or Corrodent[a]
Aluminum	Marine, semi-industrial, and industrial atmospheres NaCl solutions; NaCl + H_2O_2 solutions; NaCl + K_2CrO_4 solutions; NH_4Cl solutions; $CaCl_2$
Copper	NH_3 vapors and solutions; moist SO_2; sea water amines; 1 g-mole/l NH_3+0.05 g-mole/l Cu (added as $CuSO_4$-5 H_2O)
Gold	Chloride solution; $FeCl_3$
Magnesium	Marine, industrial, tropical and rural atmospheres; NaCl + K_2CrO_4; aerated distilled H_2O; fluorides
Nickel	NaOH + KOH solutions; fused NaOH; steam; HF vapor + air; polythionic acids
Low-Carbon Steels	Nitrates and hydroxides; Co/Co_2 mixtures and carbonates; products of destructive distillating of coal; anhydrous liquid NH_3 + contaminants; molybdate and phosphate solutions; $FeCl_3$ solutions
Medium-strength Steels	H_2S solutions as well as those corrodents listed for low-carbon steels.
Martensitic Stainless Steels	High temperature water; chloride and sulfide solutions
Austenitic Stainless Steels	Severe industrial atmospheres; steam; chloride, hydroxide, Na)Cl solutions; polythionic acid solutions.
Titanium	Solid NaCl at elevated temperatures; chloride solutions at ambient temperatures; liquid NO_2 (N_2O_4); red fuming HNO_3; methanol liquid and vapor; H_g chlorinated hydrocarbons
Zirconium	$FeCl_3$ solutions; methyl alcohol + HCl, H_2SO_4 or HCOOH; ehtyl alcohol + 0.4% HCl

(a) A more complete list of alloy/corrodent combinations is to be found in Reference (18).

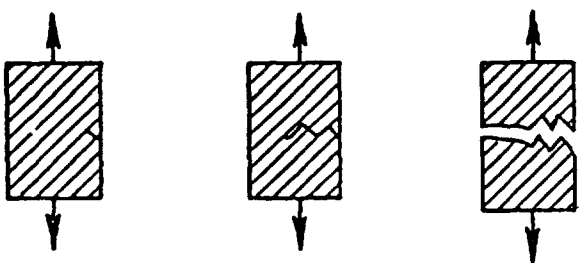
(b) Sensitized metals will crack in a wide variety of environments, including water.



(a) Metal with no pre-existing flaws, but developing a corrosion pit

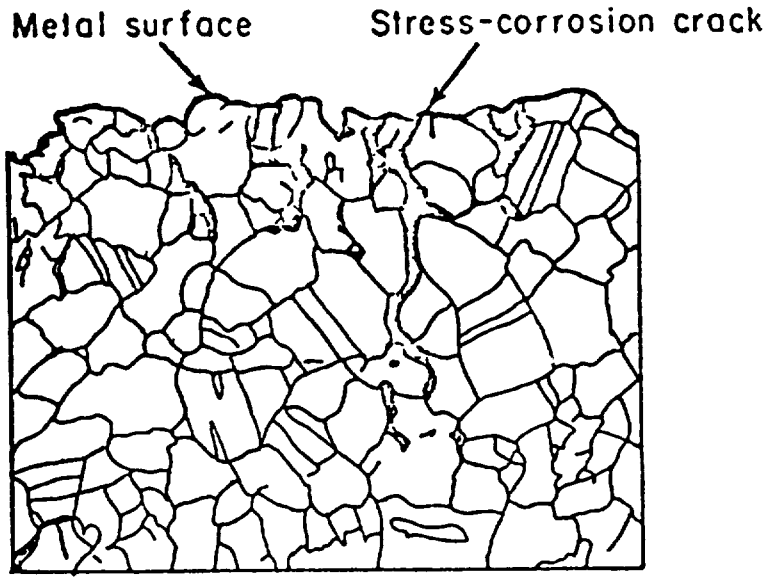


(b) Metal more brittle than (a) above.

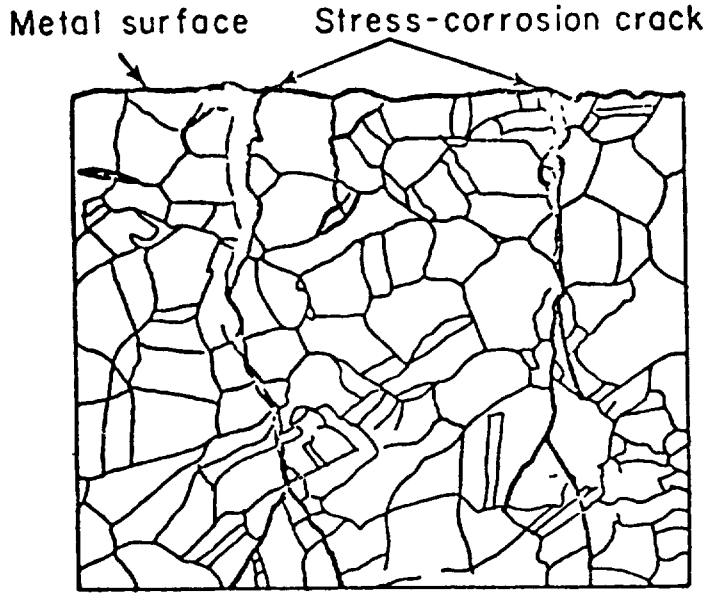


(c) Metal with pre-existing flaw

FIGURE 32. Sequence of events leading to failure by stress-corrosion cracking.



(a) Intercrystalline (Intergranular) Cracks



(b) Transcrystalline (Transgranular) Cracks

FIGURE 33. Types of crack morphology associated with stress-corrosion cracking.

Changes in the temperature and pH of the corrodent are reported to have changed the mode of cracking in particular metals. It has been stated that a change in temperature of a few degrees has changed the type of cracking of austenitic stainless steels exposed in a concentrated hydroxide solution (about 200°C) from transgranular to intergranular. Conversely, increasing the pH of a solution from the 6.5-7.3 range to 8.0 is stated to change the mode of cracking in cartridge brass (70 Cu + 30 Zn) from intergranular to transgranular.

Severe cold working of (Monel) nickel alloys is reported to change the type of cracking in hydrofluoric acid vapor from intergranular for the annealed material to transgranular for the severely cold worked alloy.

In very fine grained materials such as the high-strength steels it is difficult to localize the path of cracking by conventional metallographic methods. It has been suggested by some investigators that cracks follow prior austenitic grain boundaries. In some instances the examination of replicas of fractured surfaces, using the electron microscope, indicate that the cracking is intergranular.

Various mechanisms have been proposed to account for the different types of stress-corrosion behavior encountered. These mechanisms fall into two general categories (a) mechano-electrochemical and (b) sorption. In the former it has been proposed that in a metal there are paths susceptible to anodic dissolution when an electrochemical cell could be formed by a suitable set of circumstances. The role of the stress was to continuously open the cracks so produced, and prevent the corrosion products formed from restricting access of electrolyte to the newly exposed crack surface. With continued access the stress-corrosion process could be maintained. A "film-rupture" model has also been proposed in which the corrosion product forming on the surfaces of a crack is brittle, and when it reaches a certain thickness fractures, and exposes bare metal. The bare metal then reacts with the electrolyte/ environment to form a further brittle film, and a cyclic process develops. Another mechano-electrochemical mechanism postulates that the electrochemical reaction which occurs embrittles the metal directly behind the corroding metal surface. This embrittled metal could eventually fracture and expose fresh surfaces, and the cycle would proceed again through the electrochemical action. In the sorption hypothesis it is proposed that the surface energy of the crack surfaces is reduced by specific absorption of some species in the environment. This reduction in energy permits new surfaces to form, and stress-corrosion can proceed.

Because stress-corrosion cracking, and hydrogen-stress cracking, are both important factors of failure in service by corrosion, it is important that a clear understanding of these phenomena be developed. Having a better knowledge of why failures happen will assist designers and engineers in avoiding future occurrences.

4.3.9 Hydrogen-Stress Cracking. Hydrogen-stress cracking is defined as the failure of a metal as the result of the combined action of stress and the penetration of hydrogen into the metal. The term "hydrogen embrittlement" is frequently used in the literature. However, in its strictest sense hydrogen embrittlement denotes a loss in ductility of a metal as the result of hydrogen penetration. The source of hydrogen may be a chemical process, e.g., pickling, or it may be a by-product produced at the metal surface during electroplating. Hydrogen attack occurring in high-temperature chemical processes is not considered in this handbook.

As with stress-corrosion cracking, hydrogen-stress cracking leads usually to brittle failure, and the metals commonly involved are medium or high strength steels, and possibly titanium alloys. The stresses may be residual, applied, or a combination of these, and are usually nonfluctuating. Under a high-tensile stress the path of failure can be either inter or transgranular, and it is often difficult to distinguish between hydrogen-stress cracking and stress-corrosion cracking. Frequently a metallographic examination is required to definitely establish which one of these two types of corrosion attack was the cause of failure. As a rule of thumb, however, if specific corrodents are involved for a given metal, then hydrogen-stress cracking can be suspected. Of course, a knowledge of prior treatments, such as coating by electrolytic means, can serve to reinforce the judgment.

Hydrogen-stress cracking is generally considered to be restricted to the medium and high-strength steels; steels heat treated to a hardness of 22 Rockwell C or greater, and some of the titanium alloys. At normal temperatures the hydrogen atoms are absorbed into the metal, and diffuse through the grains, tending to collect at inclusions or imperfections in the crystal lattice.[12] The conjoint action of a tensile stress then favors transgranular cracking. On the other hand, at elevated temperatures the absorbed hydrogen tends to collect at the grain boundaries, and intergranular cracking will result.

Chemicals present in the environment can have an advantageous or detrimental effect with respect to hydrogen-stress cracking, depending upon whether or not the ingress of hydrogen atoms (or possibly portons) is facilitated. For example, sodium chromate inhibits the absorption of hydrogen, while sodium disilicate promotes absorption.[12] Some sulfur and arsenic compounds, and phosphorus also promote the uptake of hydrogen, and are often referred to as "poisons".

Failures of steels by hydrogen embrittlement have long plagued the petroleum industry. Steels having a yield strength in excess of 90,000 psi exposed in environments containing H_2S, moisture, and sometimes CO_2, will fail under engineering applied stresses with evidence of brittle fracture. A piece of steel tubing, exposed to such an environment showed, on superficial examination, no evidence of corrosion but an examination of the inner surface under low-power magnification revealed a fine network of cracks. Upon sectioning it was found that many of these cracks extended up to half way through the tube wall. This was a typical case of sulfide cracking or hydrogen cracking. The hydrogen sulfide in the presence of moisture is believed to react with the steel to form atomic hydrogen at the surface, while the sulfide ion present "poisons" at the surface of the steel so that some of the hydrogen atoms diffuse into the steel (rather than combining to form molecular hydrogen which does not penetrate steel).

4.3.10 Corrosion Fatigue. Corrosion fatigue is a form of fatigue failure aggravated by a corrosive environment. Although similar in some aspects to stress-corrosion, the differences are real, and this type of corrosion attack warrants receiving a separate classification. An example of corrosion fatigue is shown in figure 34.

In corrosion fatigue, the corrosive environment effects a lowering of the endurance limit (fatigue limit, fatigue strength for ferrous alloys) of the metal as it undergoes cycles of stress. On the other hand, the metal, if tested in air in the absence of corrosive agents, would undergo significantly many more cycles at the same stress before failure; i.e., it would attain the normal endurance limit of stress and number of cycles. Hence, maximum resistance to corrosion fatigue is attained when the alloy exhibits maximum corrosion resistance (see figure 35). Surface roughness, surface defects, the presence of corrosion products, and so on, all decrease the endurance limit when tested in air, and hence, will result in a lower corrosion fatigue life before failure. Some electroplated coatings have a more marked detrimental effect on corrosion resistance than others, because of larger amounts of codeposited hydrogen occluded in the coating. Thus, copper, nickel, or chromium plated articles will have lower resistance than lead, tin, zinc, or cadmium plated articles, for example. The situation can be somewhat improved by baking the article after plating to drive off the hydrogen.

A hot-dip galvanized coating has a more detrimental effect on corrosion fatigue resistance than an electroplated coating of zinc. Metallized articles in general have a lower resistance because of the high surface roughness needed to obtain a good bond. Shot-peening is frequently used to offset the adverse effects of electroplating. The peening action induces a residual compressive surface stress, which is desirable, rather than the tensile stress inherent in the electrodeposited coatings. Nitriding, carbonizing, and flame induction hardening are other methods of producing surface compressive stresses.

4.3.11 Biological Corrosion. Various types of microorganisms, bacteria, yeasts, molds, and algae can influence the electrochemical reactions that cause corrosion; these microorganisms can be found in soil, sea water, and fresh water. Several forms of microorganisms produce different effects and operate in different environments. Certain bacteria, for example, have an unusual metabolism that forces them to obtain part of their sustenance and energy from the oxidation of inorganic compounds such as iron, sulfur, hydrogen, nigrogen, and carbon monoxide. The chemical reactions that cause corrosion are part of the normal metabolism of these organisms. Another type (the sulfate-reducing bacteria) utilizes the cathodic hydrogen to reduce soluble sulfates to sulfides. In some cases the sulfides can precipitate metal ions accumulated at anodic sites and further increase corrosion. Sulfate- reducing bacteria are anaerobic; i.e., they thrive only when free oxygen is absent. Some microorganisms, including sulfate reducers, present as contaminants in jet fuel have caused perforation due to corrosion in wing tanks on aircraft.

Aerobic bacteria (bacteria that require oxygen in order to thrive) may also accelerate corrosion. For instance, sulfur bacteria oxidize sulfur to sulfuric acid, and nitrosifying bacteria together with nitrofying bacteria,

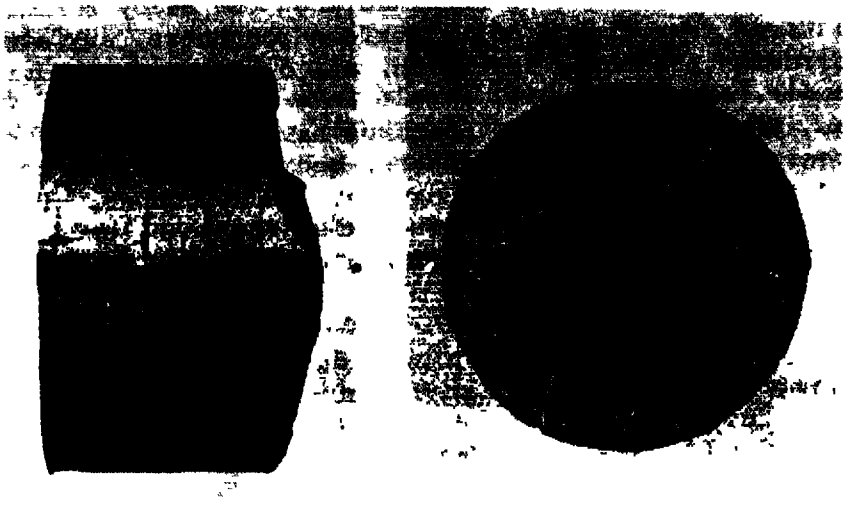


FIGURE 34. Corrosion fatigue showing characteristic fracture surface and localized surface attack.

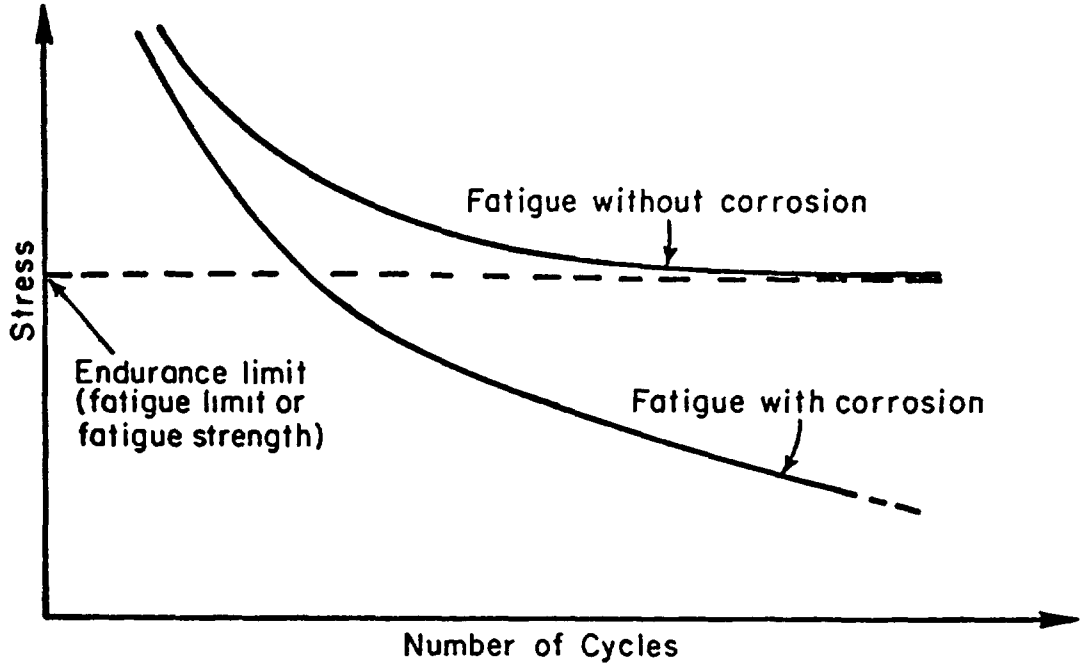


FIGURE 35. Comparison of fatigue and corrosion fatigue curves.

A corrosion fatigue failure is never associated with an endurance limit.

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SECTION 5. CORROSION OF SPECIFIC METALS

5.1 Aluminum and Aluminum Alloys. Aluminum and its alloys are used for many engineering applications because of their combination of strength with lightness, high thermal and electrical conductivity, good corrosion resistance, high heat and light reflectivity, and their non-toxic and hygienic properties. Alumunium and aluminum alloy stock is readily available in both cast and wrought forms in a variety of sizes, and is amenable to surface treatments (e.g., "anodizing") which can be dyed to impart attractive colors or improve corrosion resistance. Different heat treatments and/or mechanical treatments can give a wide range of mechanical properties, and conventional fastening techniques can be used in fabricating equipment or structures. Chemical compositions of some of the alloys discussed in the following sections are given in table V. Further details may be found in MIL-HDBK-694(MR), "Aluminum and Aluminum Alloys".

Aluminum and aluminum alloys generally exhibit good resistance to natural environments and various forms of corrosive attack. This is so although aluminum is inherently a highly active metal and is next to or very near magnesium in the Electromotive and the Galvanic Series (see tables I and III).

Aluminum exhibits passivity and is thus more resistant to corrosion in aerated or oxidizing media than in reducing or partially aerated environments. Moreover, substantial differences in resistance to various media appear with certain differences in alloy composition.

Aluminum and aluminum alloys may be subject to the following forms of attack: pitting (more usual), stress-corrosion, intergranular attack, crevice corrosion and corrosion fatigue. In addition, galvanic action may result from coupling with dissimilar metals. Pitting may occur in many corrosive situations, but especially in sea water and marine atmospheres. Stress-corrosion cracking may occur with aluminum alloys containing a substantial amount of such elements as copper, magnesium, and zinc. In such alloys, heat treatment may induce susceptibility. High strength, copper bearing alloys in corrosive environments may suffer intergranular attack. This attack is also associated with thermal treatment, as for example, slow quenching or aging beyond critical time periods at elevated temperature. Corrosion-fatigue of aluminum alloys may occur under the appropriate conditions in water.

As a group, aluminum and aluminum alloys are quite resistant to corrosion on exposure to air. When an aluminum surface is freshly exposed to the atmosphere, an oxide film forms instantaneously; this film protects the metal under most non-aggressive environmental conditions. In circumstances where there is free movement of air over the metallic surface, aluminum and the more resistant alloys exhibit superior resistance in rural, urban, industrial, and seacoast atmospheres. Much of this resistance is due to the effectiveness of the barrier surface film in inhibiting attack. When aluminum is exposed, moisture, dirt, and other foreign matter that collect on the surface, initiate corrosion that penetrates the weak spots on the oxide film, causing tiny pits; the metal from these pits is converted to hydrated aluminum oxide and becomes part of the surface coating. The coating may thicken and serve to retard further attack. As this action occurs, the metal may discolor or darken, but it will remain structurally sound.

TABLE V. Chemical Compositions of Varius Aluminum Alloys
(Composition given in nominal weight percentages.)

Alloy	Zn	Mg	Cu	Fe	Si	Mn	Cr	Ti	Total Others
				(1) Wrought					
2017	--	0.5	4.0	--	--	0.5	--	--	--
2024	0.25	1.2-1.8	3.8-4.9	0.50	0.50	0.30-0.90	0.10	--	0.15
2219	0.10	0.02	5.8-6.8	0.30	0.20	0.20-0.40	--	0.02-0.10	0.15
5083	0.25	4.0-4.9	0.10	0.40	0.40	0.30-1.0	0.05-0.25	0.15	0.15
5456	0.25	4.7-5.5	0.10	--0.40--		0.50-1.0	0.05-0.20	0.20	0.15
7039	3.5-4.5	2.3-3.3	0.10	0.40	0.30	0.10-0.40	0.15-0.25	0.10	0.15
7049	7.2-8.2	2.0-2.9	1.2-1.9	0.35	0.25	0.20	0.10-0.22	0.10	0.15
7075	5.1-6.1	2.1-2.9	1.2-2.0	0.50	0.40	0.30	0.18-0.35	0.20	0.15
7079	3.8-4.8	2.9-3.7	0.40-0.8	0.40	0.30	0.10-0.30	0.10-0.25	0.10	0.15
				(2) Cast					
319	1.0	0.50	3.5	1.2	6.0	0.50	--	0.20	0.50 1/
355	0.20	0.50	1.25	0.60	5.0	0.30	--	0.20	0.15
356	0.20	0.30	0.20	0.50	7.0	0.10	--	0.20	0.15
380	1.0	0.10	3.5	2.0	8.5	0.50	--	--	0.80 2/

1/ Includes 0.50% nickel.

2/ Includes 0.50% nickel and 0.30% tin.

Many aluminum alloys undergo little or no general attack when exposed to natural fresh water from most sources. Water containing dissolved oxygen and most aqueous solutions also have no significant effect, but soft water and water carrying a high content of carbon dioxide are more corrosive. Aluminum equipment is excellent for storing and handling distilled water of high purity, and has been used in municipal water systems. However, waters with a high content of acids or alkalies as well as waters that are polluted or carrying small amounts of cathodic metals, damage aluminum.

The aluminum alloys in which copper is the major additive are the least resistant to corrosive attack in fresh water and other natural media. High purity aluminum and aluminum alloys, which contain magnesium or magnesium and silicon in the proper proportions, possess fairly good resistance to unpolluted seawater and marine atmospheres. Most other alloys, especially those containing much copper, are attacked by both seawater and marine atmospheres; and in polluted harbor waters or in rapidly moving agitated waters, damage by pitting corrosion occurs readily. Even pure aluminum may be severely pitted under these conditions.

The corrosion of aluminum alloys buried in soils varies with the composition of the alloys and the type of soil. Corrosion is negligible in dry, sandy soils but may be severe in wet, acidic, or alkaline soils. Compositions which effectively resist corrosion in the atmosphere and various types of water should similarly resist corrosion in soil. To insure long life, a suitable protective coating is recommended.

Heat treatment has, in general, a more pronounced effect on the resistance of aluminum alloys than on most other metals and their alloys. The corrosion resistance of some aluminum alloys is decreased if these alloys are quenched slowly. They also become vulnerable to intergranular attack. Artificial aging after slow quenching is preferable to room temperature aging. In the case of thick sections, quenching in cold water may not be rapid enough to assure adequate resistance to intergranular corrosion.

In the atmosphere and in many fresh waters, aluminum is cathodic to iron, but in seawater the reverse is true and aluminum is attacked. Zinc is similarly anodic to aluminum in most neutral or acidic media, but in alkaline media the potential reverses and aluminum suffers galvanic corrosion. In general, aluminum should not be joined to copper or brass, or any other cathodic metal. Direct contact must be avoided, as well as any indirect contact caused by the flow of water saturated with the cathodic metal ions. Contact with stainless steel, despite its apparently more cathodic electrode potential, usually causes relatively slight galvanic attack on aluminum alloys because this action is limited by polarization of the stainless steel. Stainless steel exhibits a noble potential in environments in which it remains passive.

As far as applications for corrosion resistance are concerned, aluminum and its alloys ar divided into two broad classifications: (1) clad products, and (2) basic compositions that are especially resistant to corrosion.

The relative resistance to corrosion of wrought and cast aluminum alloys is presented in MIL-HDBK-694(MR) "Aluminum and Aluminum Alloys".

Clad products consist of a corrosion-resistant pure aluminum surface layer or cladding over a stronger but less corrosion-resistant alloy. This combination provides not only surface protection, but also a galvanic protection to corrosion; should the outer layer be penetrated, the inner layer would be protected because it is more noble than the cladding. Thus the core is cathodically protected in the same way iron is protected by galvanizing.

Some specific examples of different forms of corrosion attack are given in the following sections to supplement the general discussion given above.

5.1.1 Uniform Corrosion. General dissolution will occur in highly acid or alkaline solutions with a few exceptions. Concentrated nitric acid is able to maintain the protective surface film. Also, some inhibitors, such as silicates, will allow alkaline solutions to be used[14] with aluminum up to pH 11.5.

5.1.2 Pitting Corrosion. Pitting is the most commonly encountered form of aluminum and aluminum alloy corrosion (figure 14). It is initiated by a galvanic action typically in near neutral electrolytes. As a result of the galvanic corrosion cell activity the local pH decreases, and it becomes impossible for a protective film of alumina to be formed on the metal, instead aluminum ions migrate away from the cell to cathodic areas with subsequent film formation increasing the severity of the localized attack, and causing pit formation. Electrolytes containing chloride ions are very harmful, especially in the presence of good cathode depolarizers (e.g., "temporary hardness" or copper ions)[14]. Alkaline electrolytes give a kind of etching effect in that pits are formed at lattice defects in the metal.

With salts, such as chromates, dichromates, silicates, borates, and cinnamates, which have an inhibiting effect, and are used in closed-circuit water systems, care must be taken to ensure that sufficient quantity is added. If not all the exposed surface is covered then corrosion will be concentrated at these small, exposed anodic areas.

5.1.3 Crevice Corrosion. With cement and concrete under conditions of continuous immersion (condensation or otherwise) aluminum may be subject to attack through the setting up of differential aeration cells. Usually, however, the rate of attack decreases with time, and the integrity of the structure is not endangered. Bituminous protection of the metal may be advisable under these conditions, not so much to protect the metal, but to prevent cracking of the cement or concrete due to the pressures built up by the corrosion products[14]. Crevices in other types of structure should be filled with an inhibited sealant to prevent the occurrence of crevice corrosion. In static structures a rigid setting type of compound can be used, but a mastic type should be used where movement can occur. It is advisable to incorporate a chromate salt in these sealing compounds to inhibit corrosion attack by any moisture which might penetrate to the basis metal.

Filiform corrosion a type of crevice corrosion will occasionally be found with aluminum and its alloys. It appears as a random, nonbranching white tunnel of corrosion product on the metal surface, (figure 20) destroying its pleasing appearance. With clad materials, filiform corrosion can be severe enough to expose the more corrosive basis alloy with subsequent detrimental results.

5.1.4 Intergranular Corrosion. This form of corrosion is initiated at heterogeneities in alloy structure at the surface of the metal. For example, in aluminum alloys containing copper, particles of $CuAl_2$ are precipitated at the grain boundaries during heat treatment. These particles are cathodic with respect to the adjoining alloy grains and a galvanic corrosion cell is set up in a suitable environment. If the alloy contains enough magnesium that Mg_2Al_3 is precipitated at the grain boundaries, these particles are anodic with respect to the bulk alloy, and a galvanic corrosion couple can again be set up. If enough alloying addition is present to form a continuous grain boundary film, intercrystalline attack can be severe. In some alloys usually exposed to a marine atmosphere, and in structures containing metal with a highly directional grain pattern, attack can occur along grain boundaries parallel to the surface of the metal. Flakes of metal (elongated grains) are then separated or lifted up as a result of pressure exerted by the corrosion products formed, and this characteristic delaminated appearance gives rise to the name of exfoliation for this type of attack (figure 21). The alloys most prone to this type of attack are the 2000 (Al-Cu-Mg), 5000 (Al-Mg) and 7000 (Al-Zn-Cu-Mg) series, and cold-rolling and extrusion are the most likely fabrication processes to give the elongated grain structure.(15) Where there is corrodent access to the interior of the metal (e.g., bolt or rivet holes) exfoliation can occur inside the structure and is more difficult to detect.

5.1.5 Stress-Corrosion Cracking. This form of corrosion with aluminum and aluminum alloys is limited in occurrence, and found primarily associated with the high-strength alloys as used in aircraft and aerospace applications. Special aging techniques ("tempers") have been developed which reduce the tendency for intergranular attack, exfoliation and stress-corrosion cracking to occur. However, instances of stress-corrosion cracking still occur as the result of residual or applied tensile stresses acting in the short, tranverse direction (in relation to the grain structure at the metal surface) with 2000 and 7000 series alloys, for example. Because attack is usually along the grain boundaries, alloying additions or heat treatments do influence grain boundary composition and structure and can have a marked effect upon the susceptibility to stress-corrosion cracking.(16)

While the above generalities are sufficient for an introduction to this form of attack, it is appropriate to discuss in a little more detail (a) those alloys which are susceptible, (b) the environments found to cause stress-corrosion cracking, and (c) other factors such as fabrication procedures and heat treatments which have some sort of effect on susceptibility. Additional information is to be found in Reference (17) and will not be repeated here.

5.1.5.1 Susceptible Alloys. In the past, extruded 2017 and 2024 aluminum-copper-magnesium-manganese alloys were used in aircraft, and failures in structures exposed to marine atmospheres were attributed to stress-corrosion cracking. These structures contained residual stresses as the result of the presence of an oversized steel bushing or bearing that had been forced into them. Further, unless the extrusion had been rapidly quenched from the heat treatment temperature it was susceptible to intergranular corrosion in the unstressed condition. Thus, it should be pointed out that all failures by intercrystalline attack need not be the result of stress-corrosion cracking, and that stress-corrosion cracking failure is not always through intercrystalline attack. The 7000 series were developed to have

higher tensile properties than the 2000 series, and to be more resistant to stress-corrosion cracking, however, in some conditions of heat treatment both the 7000 and 2000 series are susceptible to this type of attack.

The wrought aluminum-magnesium alloys of the 5000 and 6000 series which also contain silicon can be strengthened by heat treatment to precipitate a $MgSi_2$ complex. These alloys and those aluminum-magnesium alloys containing less than 3% magnesium, strengthened by cold work rather than heat treatment, are generally quite resistant to stress-corrosion cracking.

Alloys containing more than 4% magnesium, the 5083, 5456, and the British alloy NP6-1/4H (4.5 Mg), coldworked and aged at elevated temperatures 100°C (212°F) or higher, are susceptible to stress-corrosion cracking in laboratory experiments. It has been recommended in the United States that the magnesium content of aluminum-magnesium alloys to be used in the temperature range of 60 to 205°C (140 to 400°F) be limited to 3%.

Cast aluminum alloys are in general more resistant to stress-corrosion cracking than the wrought alloys. However, an aluminum-zinc-magnesium casting alloy (5.5 Zn, 0.7 Mg, 0.32 Cr, 0.48 Fe, 0.15 Ti, and 0.10 Si) failed in storage by stress-corrosion cracking.[18] This alloy had been used for a hose connection. A tapered thread was involved in assembling the fitting, and it had been overtorqued, putting high hoop stresses in the outer fibers, in order to pass a hydraulic test. Failures occurred in as short a time as one month in weather exposure.

Numerous service failures of cast aluminum alloys containing 10% magnesium have also been reported.[19] It is believed that in most cases the alloys had not been properly heat treated and contained a magnesium-rich second phase that would be preferentially attacked in a corrosive medium. In other instances the original heat treatment had been satisfactory but long time aging at ambient temperatures, or much shorter periods of elevated temperatures, had resulted in a submicroscopic precipitation of the magnesium-rich phase at the grain boundaries.

Laboratory studies[20] of this same aluminum-magnesium alloy 220 (magnesium content ranging from 8.8% to 12.9%) in the -T4 condition indicated that it was susceptible to stress-corrosion cracking when stressed to 75% of its tensile yield strength and subjected to alternate immersion in a $NaCl/H_2O_2$ solution. The high silicon permanent mold castings, 355-T61 and 356-T6, were susceptible in some degree to stress-corrosion cracking in this same solution. The permanent mold casting 356 in the -T61 condition was the most resistant of those tested in the $NaCl/H_2O_2$ solution. A sand casting alloy (8 Cu + 6 Mg) was more resistant than most alloys studied, although less resistant than the 356-T61 permanent mold casting mentioned above.

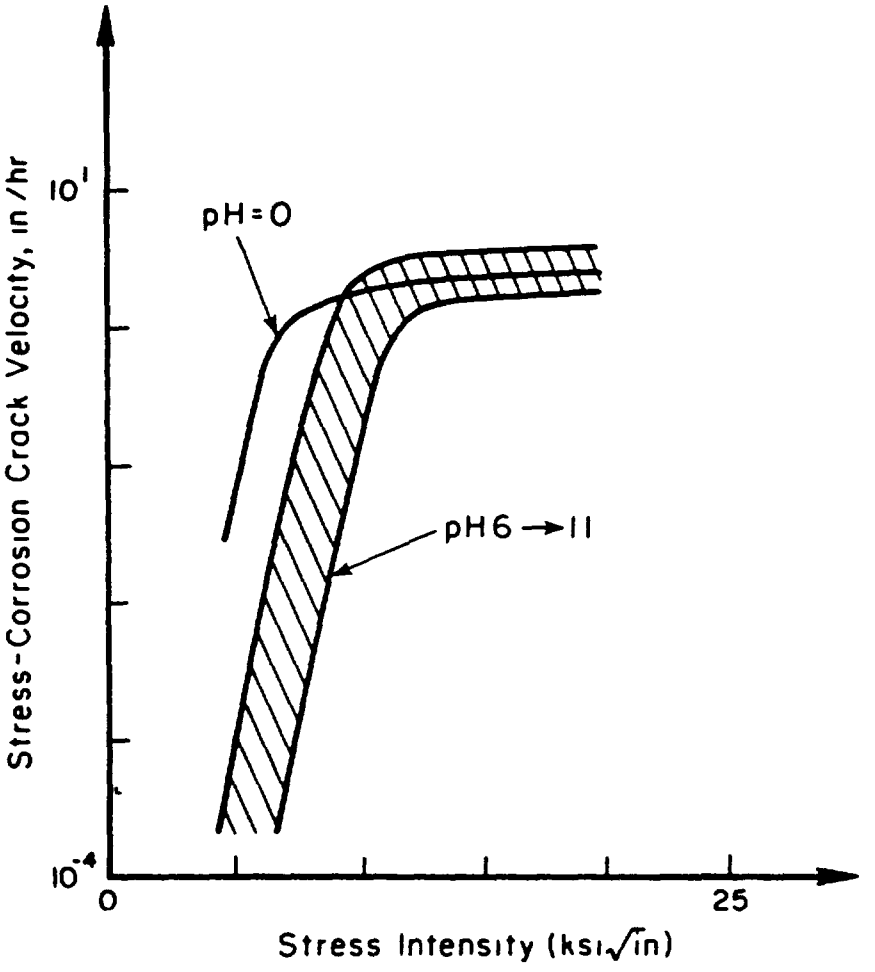
In another investigation[21] the 195 and B195 aluminum-copper-silicon alloys (-T6 condition) were reported to be moderately susceptible to stress-corrosion cracking. The aluminum-silicon-copper alloys 319 and 380 in the as cast condition, and the 355 alloy in the -T6 and -T61 conditions, were reported to be very resistant to stress-corrosion cracking.

5.1.5.2 Environments Favoring Stress-Corrosion Cracking. The environment needed to cause stress-corrosion cracking need not be very severe. As mentioned earlier, the most common environment is a marine atmosphere (NaCl + H_2O). However, because increasing amounts of salt have been used for snow removal on highways, stress-corrosion cracking of aluminum alloys is now not restricted to coastal regions. Large amounts of salt (or other chlorides) are apparently not required to initiate attack. In Reference (16) tests on five alloys stressed to 75 percent of their short tranverse yield strengths in various aqueous solutions (pH=7) are reported. At least one out of three specimens of 7039-T63 failed in less than 60 days when exposed to solutions (1N) of NaCl, NaBr, NaI, NaF, $NaNO_3$ and Na_2CrO_4. In contrast alloy 7075-T651 failed only in chloride and bromide solutions, while 2219-T37 failed only in the chloride solution. Alloys 2219-T87 and 7075-T73 did not fail in any solution, hence it is apparent that not only is the nature of the environment an important variable, but also the alloy composition and temper. In another laboratory test[17] alloy 7075-T651 is said to crack much more quckly in KI solutions than NaCl solutions when "double-cantilever-beam" specimens were used. Thus if data from References (12) and (17) are compared for the 7075-T651 alloy, it is also apparent that care should be exercised in interpreting different types of data from different types of experimental tests.

Chloride, bromide, and iodide anions appears to be specific for the stress-corrosion cracking of aluminum alloys.[16] Fluoride and thiocyanate anions do not appear to have the same accelerating effect as the above anions, while carbonate, sulfate, nitrate, bicarbonate, acetate, and dihydrogen phosphate anions appear to have little if any effect. Of the cations tested, Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Ca^{++}, and Al^{+++} do not appear to have a specific effect, except that they can influence the solubility product of the corrosion product in the electrolyte, hence can indirectly affect the anion concentrations. Mercury cations, in contrast, can cause rapid intergranular attack, and perhaps increase the susceptibility to stress-corrosion cracking. Hydrogen cations (protons, H^+) influence this type of corrosion attack by affecting electrolyte pH. As pH increases stress-corrosion cracking in chloride solutions is reduced considerably, and it may even be possible in some alkaline solutions (above a minimum pH value) to prevent this type of failure from occurring. The hydrogen cation concentration is thought to effect the rate of crack propagation as well as modify the stress intensity needed to initiate cracking. The relative importance of either of these effects depends on the region of the crack velocity versus stress intensity curve under consideration (see figure 36).

Stress-corrosion cracking of high-strength aluminum alloys is also possible in organic liquids such as engine oil, ethanol, and carbon tetrachloride. As the water or halide anion content of these liquids increase then the rate of crack growth has been found to increase.[16]

In dry hydrogen, argon, and air, aluminum alloys are not susceptible to stress-corrosion cracking, or hydrogen embrittlement in the case of hydrogen. However, traces of moisture will cause failure in those alloys which are susceptible (e.g., 7079-T651 very susceptible; 2219-T87 very resistant).



Conditions: 7079-T651 Alloy aqueous iodide electrolyte at 73°F held at -700 mV vs SCE (see Reference 12)

FIGURE 36. Relationship between crack velocity and stress intensity and pH for a 7000 series aluminum alloy.

5.1.5.3 Mechanical and Other Factors. Standard heat treatments for aluminum alloys are given in MIL-H-6088D. It has been found that the 2000 series must be slightly overaged to remove the susceptibility for cracking. Fortunately the mechanical properties are only slightly reduced by such treatments. More recently laboratory tests with the 7000 series alloys have shown that overaging reduces the crack growth rate, thereby improving the resistance to stress-corrosion cracking. If alloys from both the 2000 and 7000 series are to be immune from intergranular attack they must be cooled rapidly from the solution heat treating temperature. This is accomplished by a water quench which nominally sets up compressive stresses at the surface of a thick section and tensile stresses in the interior. The configuration of the structure and the temperature of the quenching water will affect the amount and distribution of the residual stresses. There are data to show that stresses resulting from quenching in water at 21°C (70°F) may be several times as large as those resulting from quenching the part in water at 82°C (180°F). The part quenched at the higher temperature is generally more susceptible to intergranular corrosion than if cooled at the higher rate.

Machining that exposes to the atmosphere material containing high quenched-in tensile stresses may cause stress-corrosion cracking in the highly stressed regions. In some instances rough machining of the part prior to heat treatment may solve this problem. This treatment is not always effective. The quenching of a complex part after it has been machined may produce more dangerous tensile stresses in some regions than if the structure had been heat treated prior to machining.

Theoretical work on the aluminum 5.7 zinc + 2.7 magnesium + 0.5 copper alloy suggests that deformation and aging that produce coherent precipitates of intermetallics with the matrix will be highly susceptible to stress-corrosion cracking, while alloys containing noncoherent precipitates will be immune.

Aluminum-magnesium alloys containing more than 5% magnesium can be made susceptible to stress-corrosion cracking by cold-rolling and aging at 100°C (212°F) for as short a time as 24 hours. Hence, it is to be expected that these alloys may become susceptible after long periods at ambient temperatures. It should be noted that metal exposed to the summer sun in temperate climates can reach temperatures much above those officially recorded. However, it was recently reported that an aluminum +7% magnesium alloy, stated to have good resistance to general corrosion, good welding characteristics, and to be easy to fabricate, had been exposed in a marine atmosphere (Kure Beach, N.C.) for six years without failure. This indicates that the aging time required to produce susceptibility to stress-corrosion cracking of this alloy at ambient temperatures is very much longer than had been expected.

It is now recognized that some metals are more susceptible to stress-corrosion when stressed in a direction normal to the rolling or extruded direction. This characteristic is very pronounced in aluminum alloy extrusions and plate. Material stressed in the direction of rolling of plate material or of extrusion is comparatively immune to stress-corrosion cracking. Specimens of the 7075-T6 alloy subjected to stresses of 50,000 psi

did not fail in exposure periods as long as 180 days when subjected to alternate immersion* in a 3.5% NaCl solution.(22) The tensile yield strength of the material in this orientation was approximately 85,000 psi. In the long transverse direction, yield strength approximately 80,000 psi, the threshold stress (stress below which stress-corrosion cracking does not occur) was approximately 32,000 psi. In the short transverse direction (thickness of a plate) with a somewhat lower yield strength than the long transverse material, the threshold stress was less than 10,000 psi.

Data also indicate that aluminum alloy forgings stressed normal to the parting line are much more susceptible to stress-corrosion cracking than those stressed parallel to the parting line.

The proprietary heat treatments, such as those designated by the Aluminum Company of America as -T73 for the 7075 alloy and -T611 for the 7079 alloy, materially increase the resistance of forgings to stress-corrosion cracking.

There has been considerable speculation and much research carried out to determine why aluminum alloy extrusions are so much more susceptible to stress-corrosion cracking when stressed in the short transverse than in any other direction.

In the extrusion or rolling process the grains are very much elongated in the direction of extrusion or rolling; their length is large compared to their width and very large compared to their thickness. Hence grains are long and narrow as viewed in longitudinal section, and much shorter and again narrow when viewed on a cross section, the narrow dimension of the grains of course corresponding to the thickness rather than the width of the plate or extrusion. Cracking is intercrystalline, and the attack at the grain boundaries does not appear to be orientation directed. Because of the grain structure just described, the probability that the attack on one grain boundary can link up with that on an adjacent boundary is very much greater in the short transverse direction than in any other. Further, the individual grain boundaries in the longitudinal and long transverse directions (normal to the short transverse direction) are relatively long and attack on these, particularly as it can join with attack on adjacent boundaries, is much more damaging than, for example, the attack on the end of an elongated grain (see figures 37 and 38).

To conclude this section on aluminum alloys the phenomenum of stress-accellerated intergranular attack should be briefly mentioned. If the 2024 aluminum alloy is slowly cooled (rather than quenched) from the solution heat treating temperature it has been postulated that a copper-aluminum intermetallic compound is precipitated at the grain boundaries.** This leaves the material adjacent to the boundaries impoverished in copper and in chloride solutions anodic both to the main body of the grain and to the boundary itself. Under these conditions this impoverished region will be dissolved by an electrochemical reaction. Since it is a very thin region and is adjacent

*Immersed 10 minutes, in air 50 minutes

**A short period of elevated temperature aging (for example one-half hour at 195 C) will produce a similar precipitate.

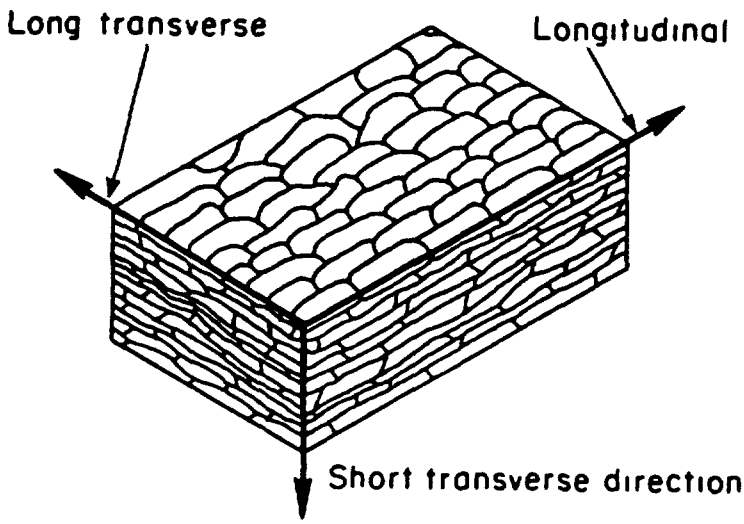


FIGURE 37. Schematic representation of grain structure in three orientations in an aluminum alloy extrusion.

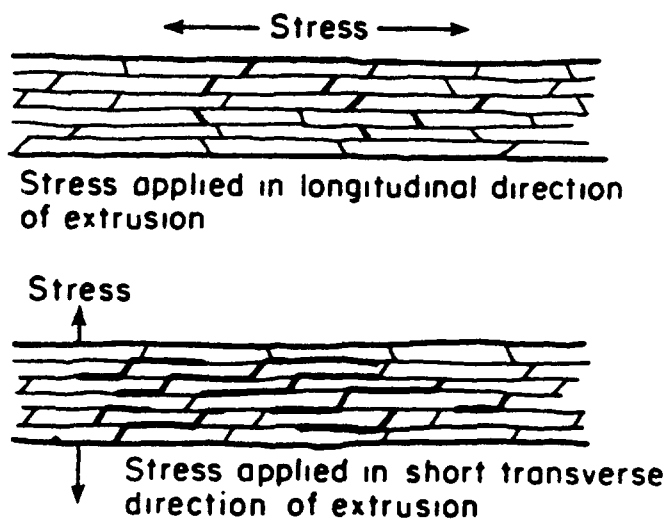


FIGURE 38. Schematic development of stress-corrosion cracking in an aluminum alloy extrusion (heavy lines represent stress-corrosion cracks.)

to the boundary, this corrosive attack is intergranular or intercrystalline. In some other alloy systems the grain boundary precipitate may leave the adjacent region impoverished in one or more components of the alloy and hence anodic to the great mass of the material, or the precipitate itself may be the anodic region.

In any case, the application of tensile stresses will tend to separate the material along intercrystalline paths, permitting the corrodent to reach anodic areas and accelerate the intergranular attack.

In other alloy systems susceptible to intergranular stress-cracking (particularly low-carbon steels and alpha-brasses), which are not susceptible to intergranular corrosion in the absence of stress, a pre-existing anodic grain boundary path has been postulated but not proven. Other mechanisms to explain the grain boundary path of attack, including a film-rupture mechanism, have also been suggested.

5.2 Beryllium and Beryllium Alloys. In the Electromotive Series (see table I) beryllium lies between magnesium and aluminum, hence may be classed as a reactive, or anodic metal. It should be noted that the physical properties of beryllium are markedly affected by changes in purity. Corrosion resistance is also influenced by the type and amount of impurities contained in the beryllium. Beryllium has a high modulus of elasticity, high specific heat, and like aluminum a high strength to weight ratio. Principal applications have been associated with nuclear reactors, and corrosion studies have mainly resolved around these applications. Powder metallurgy is a common approach for fabricating beryllium structures because of its brittle behavior at room temperature, and its mechanical anisotropy.

Beryllium is very resistant to oxidation in normal atmospheric conditions at room temperature, and will retain a lustre for many years. Beryllium may tarnish but resists gross oxidation in air when heated in the range of 400 to 500°C (750 to 930°F). Oxidation, resulting in thin films through heavy white scale, increases rapidly with increase in temperature in the range of 700°C (1290°F) to 1000°C (1830°F). In oxygen, similar reactions take place, but at lower temperatures. Beryllium reacts with nitrogen (at approximately 480°C), and the reaction rate increases with increasing temperature, forming the nitride. The metal also reacts with carbon dioxide (wet) at approximately 43°C (110°F) forming the carbide.

5.2.1. Uniform Corrosion. The general corrosion behavior of beryllium is similar to that of aluminum. Film-free metal surfaces are attacked readily, but in oxidizing conditions a stable, protective oxide film forms imparting passivity.

Beryllium is attacked by most acids at room temperature, however, it is resistant to concentrated nitric acid except at elevated temperatures, when it will react violently. Some organic acids, such as citric and acetic, attack beryllium initially, but the action ceases after a while because of the formation of a blocking surface of film.

Because it is amphoteric, beryllium is also attacked by alkaline solutions. The rate of attack is slow with dilute solutions, but is accelerated at higher concentrations. Hydrogen gas is evolved.

5.2.2 Galvanic Corrosion. The galvanic behavior of beryllium may vary, depending on whether the conditions of exposure are static or dynamic. For example, beryllium coupled to aluminum in demineralized water at a temperature of 85°C (185°F) may remain unattacked under static conditions, whereas under dynamic conditions it may be attacked. Galvanic corrosion is expected when coupled with copper or other similar metals, and corrosion has been observed when coupled with a (347) stainless steel in water at 85° (185°F) containing small amounts of hydrogen peroxide.

5.2.3 Pitting Corrosion. Beryllium generally undergoes little or no attack when subjected to fresh water, but in the absence of aeration and flowing conditions, it is susceptible to pitting attack. The presence of chlorides, fluorides, sulfates, cupric, and ferrous ions markedly increase corrosion and pitting of beryllium in aqueous media by causing breakdown of the protective film. Cupric ions at a concentration of less than 1 ppm have been found[23] to cause serious pitting in a dilute hydrogen perioxide solution at 85°C (185°F). Any factor which tends to maintain the protective character of the beryllium film will increase corrosion resistance, hence the addition of anodic inhibitors (e.g., up to 40 ppm of sodium dichromate) will suppress pitting attack.

5.2.4 Stress-Corrosion Cracking. Early attempts to produce stress-corrosion cracking of beryllium in the laboratory[18] in continuously circulating 0.005 M hydrogen perioxide solution (pH=6) at about 90 to 95°C (195 to 205°F), were not successful. Although specimens failed because of pitting, there was no evidence of the features associated with stress-corrosion cracking. Conversely, in aerated seawater (19,500 ppm of chloride) pH 8.2, and 25°C (77°F), and natural seawater at 15°F) stress-corrosion cracking has been reported for beryllium having a purity of 98.3 percent.

The stress-corrosion cracking behavior of copper-beryllium alloys is noted in the following section on copper.

5.3. Copper and Copper Alloys. Copper has been traditionally considered as a corrosion-resistant metal. It generally exhibits good resistance to the atmosphere, natural and salt water, and to many alkaline solutions and acids. Protective coatings are seldom used with copper or copper alloys because of the inherent resistance of the metal. Copper is rated below lead and above silver in the Electromotive Series, and is listed below tin and above the passive stainless steels in the Galvanic Series (see tables I and III).

While copper and copper alloys are broadly classed as corrosion-resistant, certain substances are destructive to them, and some of the alloys are susceptible to attack under special conditions. Oxidizing agents, ammoniacal solutions, and sulfur compounds are among the substances that affect copper and its alloys adversely. Also, when such solutions as salt water and brine strike copper at high velocities, damage can be serious. On the other hand, some alloys have been developed which are more resistant to such substances than the parent metal. In addition, certain brasses are subject to dezincification.

The rate of attack on copper and its alloys is generally least in rural atmospheres and most severe in industrial or marine atmospheres. In the latter areas, the metal develops a brown or black tarnish that turns to a green patina over a period of years. The patina is composed of basic copper sulfate and other compounds, and serves to protect the metal from further corrosion. Air that contains sulfur compounds will foster the development of the patina on "pure" copper compositions and brasses and bronzes as well.

The corrosion rates for copper and its alloys in natural fresh waters are usually low because these waters generally promote the formation of protective coatings on the metallic surface. In soft waters and in waters containing relatively large amounts of dissolved carbon dioxide, the corrosion rate is somewhat higher.

Copper and copper alloys are resistant to corrosion in seawater and, in the absence of dezincification, there is little practical difference in corrosion resistance to quiet seawater among the various alloys. When the water velocity is low, the corrosion rate of copper alloys may range from less than 0.0025 to 0.010 cm (0.001 to 0.004 inch) per year. Muntz metal, however, undergoes rapid dezincification and may show rates up to 0.022 cm (0.0085 inch) per year. Copper and high-copper alloys are also antifouling; that is, barnacles and other marine organisms do not generally collect on these metals or cause localized corrosion. Rapidly moving waters will alter these general corrosion-resistance ratings; high velocity seawater promotes extensive erosion corrosion.

Tests indicate that copper and its alloys are resistant to the corrosive action of most soils. Bronzes are notably resistant to soil corrosion and have been recovered in good condition after burial for several centuries. But the following conditions or characteristics will result in more severe corrosion: high content of organic matter; ammonium compounds, sulfates, or organic acids; soils containing much cinder; tidal-marsh soils; and soils subject to seepage by water with high content of dissolved carbon dioxide.

Copper and copper alloys are subject to these forms of corrosion under the appropriate conditions: uniform chemical attack or thinning, pitting, dezincification, stress-corrosion, corrosion-fatigue, and intergranular corrosion. A comprehensive review of these types of attack is contained in Reference (31).

The current specifications for various corrosion resistant copper alloys are listed in Department of Defense Index of Specifications and Standards. Table VI summarizes the chemical composition of some of the more common alloys.

5.3.1 Uniform Corrosion. Uniform chemical attack or thinning will result when copper and copper alloys are exposed to various types of atmospheres and waters, most soil types, neutral, alkaline or acid salts, and organic acids and most other chemicals. Resistance of various wrought copper alloys to atmospheric and seawater exposure is indicated in MIL-HDBK-698(MR) "Copper and Copper Alloys". The rate of corrosion under such conditions will vary depending not only on the medium, but also on temperature, velocity or agitation, aeration, oxidizing agents present, and similar factors. Aqueous ammonia, solutions of cyanides, oxidizing salts and acids, and salts or acids

TABLE VI. Chemical Compositions of Various Copper Alloys Discussed in This Handbook.
(Composition given is nominal weight percentage)

Alloy	Cu	Zn	Al	Fe	Mn	Ni	Pb	Sn	Notes
Admiralty Metal (Brass)	71	28	--	--	--	--	--	1	b
Aluminum Brass	76-79	Rem.	1.8-2.5	--	--	--	--	--	b
Cartridge Brass	70	30	--	--	--	--	--	--	b
Naval Brass 1	59-62	Rem.	--	--	--	--	0.20 (max)	0.5-1.0	c
Naval Brass 4	62-65	Rem.	--	--	--	--	0.20 (max)	0.5-1.0	c
Aluminum Bronze 1	86.0 (min)	--	8.5-9.5	2.5-4.0	--	--	--	--	d
Aluminum Bronze 3	83.0 (min)	--	10.0-11.5	2.0-5.0	0.5 (max)	2.5 (max)	--	--	d
Manganese Bronze A	55.0-60.0	Rem.	0.5-1.5	0.4-2.0	1.5 (max)	--	--	1.0 (max)	e
Manganese Bronze C	60.0-65.0	Rem.	3.0-7.5	2.0-5.0	2.5-5.0	--	--	0.2 (max)	e
Cupro-Nickels	65.0 (min)	1.0 (max)	--	0.4-0.70	1.0 (max)	29.0-32.0	0.05 (max)	--	f,g
	Rem.[a]	1.0 (max)	--	1.0-1.75	1.0 (max)	9.0-11.0	0.05 (max)	--	f,h
Muntz Metal	61	39	--	-	--	--	--	--	--

a Remainder
b Nominal composition, contains about 0.06% Sb or As
c Federal specification QQ-B-639a
d Federal specification QQ-B-671b
e Federal specification QQ-B-726d
f Federal specification MIL-T-15005B
g Nominal "70/30" alloy
h Nominal "90/10" alloy

in the presence of oxidizing agents are the most destructive because they prevent the formation of or dissolve protective films. Where these substances are absent, copper and copper alloys may be used for reasonably long periods of service despite slight thinning.

5.3.2 Galvanic Corrosion. Copper and copper alloys rarely undergo galvanic corrosion as a result of contact with other metals. The position of copper and its alloys in the Electromotive and Galvanic Series indicates that these materials are cathodic to the common structural metals (see tables I and II). Copper and the brasses can be joined to iron in cold fresh water without serious galvanic corrosion, but coupling in hot water and seawater will cause more serious attack on the iron. Coupling with stainless steels, tin, nickel, and Monel is usually satisfactory, while aluminum, zinc, and magnesium will be attacked when joined to copper and copper alloys. In addition, there are particular conditions that will alter expected corrosion rates that are based on measurements of potential (see Paragraph 4.3.2).

The effect of alloy composition on corrosion resistance is more important for some copper alloys than for others. For commercial "pure" coppers, small variations in composition have no significant effect on corrosion resistance. Among the brasses, red brass (85 copper + 15 zinc) is usually considered the most corrosion-resistant. In general, the alloys containing 85 percent or more copper resist dezincification, but are more susceptible to impingement attack. Exceptions have been reported[25] for alpha-brasses with 92 percent copper in marine and rural atmospheres which exhibited dezincification. Brasses are particularly resistant to attack by uncontaminated fresh waters, showing a rate that may range from 0.00025 to 0.0025 cm per year (0.0001 to 0.001 inch per year) (in the absence of dezincification). The various straight bronzes, silicon bronzes, and cupro-nickel alloys exhibit superior resistance to corrosion by fresh waters, whether polluted or unpolluted.

Of the various alloys, copper-tin and copper-nickel compositions are considered the most resistant to corrosion for marine applications. In harbors containing contaminants such as sulfur compounds, the straight bronzes, aluminum bronzes, and cupro-nickel alloys are more resistant than other copper alloys. In seawater, brasses with 65 to 85 percent copper are superior to those with more copper. The 70-30 copper-nickel alloys exhibit the best general resistance to aqueous corrosion. In atmospheric exposure tests, copper-beryllium alloys were the only ones found to pit.[24]

5.3.3 Pitting Corrosion. Pitting occurs when there is an incomplete protective film or corrosion product coating. In the great majority of situations, the pitting of copper and copper alloys is not sufficiently serious to interfere with their service, unless thin sections are used and perforation occurs (see figure 15). Such a situation often arises in domestic water supply systems.

5.3.4 Crevice Corrosion. In a comprehensive study of the corrosion behavior of copper and copper alloys immersed below the sea off the West Coast of California[26], some copper-nickel alloys were found to be susceptible to crevice corrosion. For example, the 70/30 alloy (CDA No. 716) exhibited pitting and crevice attack after 751 days at a depth of about 1830 m (6000 ft) while the 55/45 alloy was perforated by crevice attack after 1064 days of

immersion. Except for the 711 and 716 copper-nickel alloys, 653 and 655 bronzes and 102 copper specimens, the corrosion rates of the immersed specimens increased linearly with increasing concentration of oxygen in the seawater. The corrosion rates of 102, 653, and 655 alloys were insensitive to changes in oxygen concentration, while 711 and 716 alloys showed an irregular dependence upon the changes.

In marine environments, crevice corrosion can easily occur under dead barnacles or other shellfish. The decomposing organic matter can accelerate the rate of corrosion.

5.3.5 Selective Leaching. Some copper-zinc alloys corrode primarily by the process of dezincification which is the selective leaching out of the zinc leaving behind a porous copper-rich deposit of inferior mechanical and physical properties (see Paragraph 4.3.6 and figure 25). Alloys with increasing amounts of zinc, such as Muntz metal and several yellow brasses, are especially vulnerable, and under certain conditions (e.g., stagnant solutions) attack can be severe. But brasses containing upwards of 85 percent copper are practically immune to dezincification. Furthermore, the addition of tin or arsenic in small amounts to the alloys containing more than 15 percent zinc is quite effective in retarding or inhibiting dezincification. Nickel silvers are also noted for resistance to corrosion in most types of atmospheres and waters. Furthermore, the nickel constituent inhibits dezincification. Recent data[25] indicate that the method of dezincification may differ in marine and rural environments. The presence of chloride anions in the former case are throught to be the reason for this.

5.3.6 Stress-Corrosion Cracking. In general, of all the wrought copper alloys, the 70/30 copper-nickel alloys have high resistance to stress-corrosion cracking and impingement attack. In the latter, water moving past the metal, if fat enough, can cause local breakdown of the protective surface film. If air bubbles are entrained in the water and burst as they hit the surface, the mechanical action can accelerate the rate of attack. Clean, smooth, horseshoe-shaped pits result through the continual removal of cations and corrosion product (figure 27).

The straight bronzes or phosphor bronzes with up to 10 percent tin are less susceptible to stress-corrosion cracking than the brasses. These bronzes are also quite resistant to impingement attack. For applications inovlving corrosion fatigue under particular conditions, beryllium copper, cupro-nickels, aluminum bronze, and phosphor bronzes exhibit the most satisfactory performance.

The general corrosion resistance of the silicon bronzes is similar to that of the commercial coppers, with the silicon bronzes more resistant to stress-corrosion than the brasses. Table VII summarizes the resistance of copper and copper alloys towards stress-corrosion cracking. Data were taken from Reference (32).

As was done in earlier sections, more specific information will be given below about (a) materials susceptible to stress-corrosion cracking, and (b) environments which cause stress-corrosion cracking.

5.3.6.1 Susceptible Alloys. Season-cracking, the name given earlier to the stress-corrosion cracking of brasses, was first reported 70 years ago in connection with brass cartridge cases for small arms ammunition. These were made of (70 Cu + 20 Zn) cartridge brass which combined good deep drawing characteristics with the desired strength. The British had trouble in India during the hot humid season with cracks developing near the base of the cases. These rendered the cartridges completely unfit for use. The problem was solved by annealing the material following certain steps in the drawing process. These annealing operations were time consuming and expensive. Immediately following World Ware I, a symposium was held that was largely devoted to the stress-corrosion of brass. During World War II, stress-corrosion cracking of brass was again considered a problem and about half of a 3-day symposium on stress-corrosion cracking held in 1944 was devoted to the stress corrosion of brass.(27)

Cracking as it is normally observed in failed material is intergranular in alpha-brass and transgranular in beta-brass. In an alpha-beta-brass (Cu $<$ 65%) cracking will frequently follow the boundaries between alpha-crystals but pass through the beta-crystals.

The sensitivity of brasses to stress-corrosion cracking increases with the amount of zinc present in the alloy. While it is reported that brass containing as little as 5% zinc can be made to crack under laboratory conditions and a (90 Cu + 10 Zn) large-grained brass cracked quite readily in the laboratory, brasses containing 85% or more of copper have generally been quite resistant to cracking in service. It is reported, for example, that the problem of stress-corrosion cracking in automobile tail light receptacles drawn from 70/30 brass and used presumably without annealing was solved by substituting a 90/10 brass that could be used as drawn.

Copper, when alloyed with less than 1% of arsenic, antimony, aluminum, silicon, or phosphorus, is stated to be susceptible to stress-corrosion cracking in certain media. Copper containing 2% nickel, 1.8% beryllium and 0.3% cobalt may also be made to fail by stress-corrosion cracking in ammoniacal solutions in the laboratory.

The failure of commercial copper tubing used to connect gas mains with individual household units was attributed to stress-corrosion cracking penetrating into the metal from the side exposed to the soil.(28) Two failures (after approximately 4 years exposure) developed in more than 50,000 installations. Residual stresses were most probably set up in the tubing during installation. Chemical analysis of the tubing indicated that it contained 0.033% phosphorus. This was approximately eight times the minimum percent of phosphorus stated to have caused cracking in copper. Phosphorus is commonly used to deoxidize copper tubing and a maximum of 0.04% is permitted in ASTM specifications.

Many of the commercial copper alloys contain several elements as impurities or as specific additives. Some of these are given specific names and most are susceptible in some degree to stress-corrosion cracking.

TABLE VII. Resistance of Some Copper Alloys Towards Stress-Corrosion Cracking.

Relative Rating	Alloy System
1. Low Resistance	(a) Brasses with more than 20% Zn (b) Brasses with more than 20% Zn plus small amounts of Sn, Pb, or Al (e.g., leaded high brass; naval brass; admiralty brass; aluminum brass)
2. Intermediate Resistance	(a) Brasses with less than 20% Zn (e.g., red brass; commercial bronze; gilding metal) (b) Aluminum bronze (c) Nickel (12%)-Silver
3. High Resistance	(a) Silicon Bronze (b) Phosphor-copper (c) Phosphor-bronze (d) Nickel (18%)-Silver
4. Superior Resistance	(a) Cupro-Nickel Alloys (b) Tough-pitch Copper (c) High-purity Copper

Admiralty metal (28 Zn + 1 Sn) and aluminum brass (18.5 - 22.8 Zn + 1.8 - 2.5 Al) are used as condenser tubes. Stresses are, in some cases at least, believed to result from the order of assembling tubes in the tube sheet. There will be stresses, of course, set up as the result of rolling the tube into the tube sheet and there may be thermal stresses. Stress-corrosion has been reported in installations in which seawater was used as the coolant. The inference is that chlorides are the effective corrodent but there is usually no information as to possible pollution of the seawater.

Nickel-brass (65 Cu + 12 Ni + 23 Zn) wire parts of a telephone system exposed to dust containing about 8% by weight of a nitrate salt failed by stress-corrosion cracking after 2 years.(29) These salts were hygroscopic and it was postulated that the cracking was initiated and propagated during periods of high humidity. An alloy containing 18% Ni (55 Cu + 18 Ni + 27 Zn) appeared to be more susceptible to cracking under the conditions of exposure than the 12% nickel alloy.

Data indicate that the cupro-nickel alloys containing iron are generally very resistant to stress-corrosion cracking.

A number of stress-corrosion cracking failures of manganese bronze castings, Class A, have been reported in seawater in submarine and other service. In some instances, ammonia could have been present in the seawater. Castings used inboard did not fail. If the microstructure of the casting contained both alpha- and beta-phases the casting was generally immune to stress-corrosion cracking. In castings containing the beta-phase only, failure could occur along an intergranular path. One investigator suggests that the aluminum content of this alloy should not be above 0.80%. High aluminum content tends to shift the alloy structure into the beta-phase and increases its susceptibility to stress-corrosion cracking. The manganese-bronze casting alloy, Class C, is also reported to be susceptible to stress-corrosion cracking.

The failure of an aluminum bronze casting (12 Al + 1.5 Fe + 1.5 Ni) in seawater was also reported.(19) In this alloy stress-corrosion cracks followed a second phase network along the grain boundaries. Intergranular stress-corrosion cracking of a single phase aluminum-bronze alloy (8% Al) was reported in a steam atmosphere. It should be noted that these compositions fall outside the range given in Federal Specification QQ-B-671b.

5.3.6.2 Environments Favoring Stress-Corrosion Cracking. The ammonium cation has long been considered the specific corrodent that will cause stress-corrosion cracking in copper-base alloys. Brass specimens subjected to a tensile stress and exposed in an atmosphere containing ammonia gas, air, and water vapor will fail after exposure periods decreasing with increased stress. A blue to black film of Cu_2O forms on the surface of the brass and this is believed to contribute to the stress-corrosion cracking. Service failures may show this discoloration adjacent to the final tensile fracture. Recent laboratory work has shown that cracking can be produced very rapidly in a solution of 1 g mole/liter of NH_3 and 0.05 g mole/liter of copper (added as $CuSO_4.5\ H_2O$) maintained at a pH of 7.0 to 7.3. This solution produces the black or blue Cu_2O film on the surface of brass in this pH range. As was reported above, service failures have been reported in chloride, both for equipment used in sea water and in heat exchangers. In most cases, there is

no information as to whether the water could have been contaminated with ammonia. There are also reports of stress-corrosion cracks in brass exposed in air containing sulfur dioxide or oxides of nitrogen. Evidence has been presented[30] that citrates, tartrates, nitrites, carbonates, and phosphates may also produce cracking in some copper-base alloys. Any compounds which may be decomposed to give ammonium cations in solution (e.g., amines; animal hair felt lagging around pipes) are also candidate corrodents for this type of attack.

None of 46 different copper alloys exposed at two depths, 760 and 1830 m (2500 and 6000 ft) in the Pacific Ocean for periods of time varying from 123 to 1064 days were susceptible to stress-corrosion cracking in those environments. However, some of the alloys studies were not suitable for this type of service because of other types of corrosive attack,[26] described above.

Highly stressed copper-base alloys are particularly susceptible to liquid metal embrittlement when in contact with mercury. Mercury vapor from a mercury diffusion pump is believed to have caused leaks in a brass bellows some distance downstream in the vacuum system from the diffusion pump, but with no intervening cold trap. Copper-base alloys will displace mercury from aqueous mercury salt solutions, plating the mercury out on the metal. Hence, mercury in the liquid or vapor phase in contact with highly stressed copper-base alloys can produce failures by liquid metal embrittlement which is a form of stress-corrosion cracking.

5.4 Iron and Iron Alloys (Steels). There is no need to enumerate the desirable characteristics and applications of these most common engineering materials. Generally speaking, these metals may be grouped into three broad categories[29] according to the amount and type of alloying element(s) present. In the first group fall the cast irons, wrought irons and carbon steels to which no alloying elements have been deliberately added, and which are susceptible to corrosion. In the second group are the low-alloy steels which contain small percentages of added alloying elements such as chromium and copper, but which do not corrode as rapidly as those metals in the first group in many types of environment, particularly the atmosphere. The last group comprises steels with large alloying additions such as chromium and nickel of which the best examples are the various stainless steels. These alloys exhibit a high resistance to corrosion under a range of environmental conditions.

Basically, two chemical substances are responsible for the corrosion of iron and its alloys, namely, oxygen and water, and the corrosion product most often formed is "rust" a mixture of hydrated oxides. Other corrosive agents and environmental conditions, such as acidic vapors, and salts, and alternate wetting and drying and high temperature conditions accelerate the attack.

Ferrous alloys corrode quite differently in industrial, marine and rural atmospheres. Atmospheric corrosion will vary with the composition and types of contaminants present and the concentration of moisture. Corrosion rates are lowest in dry, uncontaminated atmospheres. Industrial atmospheres--because they usually contain some sulfur dioxide, acid vapors, and salts--may result in rapid attack of the metal. In marine environments, particularly because of condensate and salt spray, the corrosion rate of iron alloys can be quite severe.

Composition and heat treatment of iron alloys or steels will establish the degree of susceptibility to corrosion under a particular set of conditions. The common elements in steel (carbon, manganese, sulfur, phosphorous) when present in the normal proportions have no appreciable effect on corrosion in normally encountered environments. Studies indicate very little difference in corrosion rates among the various types of steels (excluding the stainless steels) except for the sulfur and phosphorous-bearing free-maching steels, and the copper-bearing steels. The former are more susceptible to rusting than the straight carbon steels. Steels with 0.2 to 0.4 percent copper content are several magnitudes more corrosion resistant to industrial and marine atmosphere conditions than the non-copper bearing steels. Low alloy steels containing small amounts of chromium, silicon and phosphorous also exhibit improved resistance to corrosion in industrial atmospheres. Gray cast iron is subject to graphitization when immersed in some types of water or buried in certain soils.

The corrosion rates of iron and steels in fresh waters are dependent upon the amount of dissolved oxygen in the medium. Moreover, in fresh water there may be organic contaminants which can accelerate attack. Hard water is generally less corrosive to steels than is soft water.

Iron and steel products are widely used in oils, e.g., buried pipe lines, pilings, etc. These products are subject to the many varieties and forms of corrosive attack and proper consideration should be given to their selection and protection in such use. Iron-base alloys containing 12 percent or more chromium (as well as other constituents) are the stainless steels. They are remarkably resistant to corrosion becuase chromium content in excess of 12 percent fosters the development of passivity (protective-film formation on the metallic surface). The use of these steels is governed by the oxidizing characteristics of the service environment. Where strong oxidizing conditions exist, stainless steels are superior to the more noble metals and alloys. But they are vulnerable to acidic reducing agents.

Corrosion resistant alloys for castings are those ferrous alloys capable of sustained service when exposed to normally corrosive agents at operating temperatures lower than 480°C (900°F). Many of the ferrous castings considered corrosion resistant are also used for their ability to withstand attack or structural damage at temperatures up to approximately 650°C (1200°F).

The stainless steels and the other corrosion resistant ferrous alloys exhibit varying resistance to general or uniform attack, pitting, intergranular attack, erosion-corrosion, and other forms of localized attack arising from contact between the alloy and another metal or nonmetallic surface. In general, resistance increases with increasing amount of chromium and decreases with higher carbon content. The actual behavior is exeedingly complex. For example, passivity, an important factor in the corrosion resistance of stainless steels, is not a constant state but exits only under certain conditions. The steels become "passive" and resistant under oxidizing conditions but can become "active" in the presence of reducing agents that inhibit film formation. The steels are often treated in a passivating solution to chemically enhance film formation. Active stainless steels are rated just below ordinary steels in the Galvanic Series; the passive stainless steels are listed just above silver (see table III).

The three principal types of wrought stainless steels in common use are austenitic chromium-nickel, martensitic chromium, and ferritic chromium. Their basic constituents, general corrosion characteristics, and common uses are listed in table VIII. The grades indicated are those for which corrosion resistance is mentioned in current military specifications.

In general, the austentic steels are satisfactory for most corrosive conditions, while the martensitic and ferritic types have more limited applicability. As previously mentioned, stainless steels exhibit excellent resistance to corrosion in oxidizing environments, but are not recommended for use in halogen acids or halogen salt soluutions. They are resistant to almost all atmospheres, fresh waters, and similar mild corrosive environments. Under more severe conditions, such as polluted atmospheres, only certain compositions may be resistant. Stainless steels are generally not resistant to sea water and will pit under such service. Type 316 is the most resistant of the common stainless steels. However, it too will pit in seawater after extended exposure.

Depending upon environmental circumstances, stainless steels may undergo various types of corrosive attack, including uniform chemical attack (rusting), pitting, galvanic, crevice, and intergranular corrosion. Stress-corrosion cracking has been reported, primarily in solutions containing chlorides.

Uniform chemical attack is typical of atmospheric exposure. Pitting occurs following exposure to seawater, neutral or near neutral halide salts, and heavy metal chloride solutions. Several compositions of stainless steels may fail by pitting in some types of soils, but this tendency is much less pronounced than in seawater. Generally, the resistance of stainless steels buried underground is good.

Almost all stainless steels require suitable heat treatment to develop maximum corrosion resistance. The martensitic steels are usually quenched and tempered to provide optimum resistance to corrosion, and normally they show maximum resistance in the fully hardened condition. Relief of quenching stresses, coupled with greatly improved ductility and toughness, may be obtained by tempering these steels at 370°C (700°F) or less, without seriously reducing their resistance to atmospheric corrosion. However, tempering between 370 and 593°C (700°F and 1100°F) should be avoided particularly when the carbon content is high, since this range of temperature imparts low toughness as well as low resistance to corrosion. The austenitic stainless steels are more resistant in the annealed condition. These steels are rendered susceptible to intergranular corrosion when heated in the range of 400 to 900°C (750°F to 1650°F) or on cooling slowly through this range. Steels so sensitized are vulnerable to severe attack at the grain boundaries even by relatively mild corrosive agents such as water. This same condition is developed when welding these steels. Resistance may be improved by annealing at about 1100°C (2000°F), followed by rapid cooling (water quenching), removal of the oxide scale, and repassivation. A number of alloys have been developed to resist intergranular corrosion. The titanimum or niobium stabilized alloys 321 and 347 are less susceptible to sensitization, but nevertheless may be subject to knifelike attack in areas adjacent to multiple-pass welds in strong nitric acid solutions.

TABLE VIII. Corrosion Resistance Characteristerics of Major Types of Stainless Steels.

Type	Corrosion Resistance Characterisitics	Alloying element, percent				Common Uses
		Grade	Carbon	Chromium	Nickel Other	
Austenitic	Ordinarily most resistant type; resists attack by rural, marine, industrial atmospheres, fresh waters, and wide variety of chemicals; 18-8 grades rarely rust in atmospheres; alloying aids resistance.	302[a]	0.08 to 0.20	17.0 to 19.0	8.0 to 10.0 Mn, 2.0	General-utility 18-8 alloy; food containers, utensils, and processing equipment; burner section furance parts.
		303[a]	0.15	17.0 to 19.0	8.0 to 10.0 P,S,Se, Zr,Mo	General-utility 18-8 alloy; bolts brushing, fasteners, nuts, and shafts; where seizing and galling must be minimized.
	Some grades vulnerable to intercrystalline corrosion at temperatures of 427 to 870 deg. C unless stabilized". Most grades pit in seawater.	304[a]	0.08	18.0 to 20.0	8.0 to 11.0 Mn, 2.0	General-utility 18-8 alloy; weldable; liners, drums, tubes, evaporators, cooling coils.
	Sensitized stainless steels will crack due to stress-corrosion even in water.	310	0.25	24.0 26.0	19.0 to 22.0 Mn, 2.0	Air heaters, gas turbine parts, heat exchangers, and carburizing boxes.
		316[a]	0.10	16.0 to 18.0	10.0 to 14.0 Mo, 2.0 to 3.0	Chemical and photographic equipment; brine tanks, piping, valves and fittings; and in tropical, marine, and polluted air.
		321	0.08	17.0 to 19.0	8.0 to 11.0 Ti	"Stabilized" 18-8 high-temperature service alloy; aircraft parts; welded equipment.
		347	0.08	17.0 to 19.0	9.0 to 12.0 Nb	"Stabilized" 18-8 alloy; chemical equipment; heat resistors; heavy wall welded equipment.

TABLE VIII. Corrosion Resistance Characteristerics of Major Types of Stainless Steels (Continued).

Type	Corrosion Resistance Characterisitics	Alloying element, percent					Common Uses
		Grade	Carbon	Chromium	Nickel	Other	
Martensitic	Less resistant than other two types; may form rust in industrial and polluted atmospheres after short exposures; generally resistant to mild corrodents, fresh waters, mild atmospheres. Pits in seawater and often in marine atmospheres.	410[a]	0.15	11.5 to 13.5	--	--	Common inexpensive items; hardware keys, caps, trays, scissors, brackets, and valves.
		416[a]	0.15	12.0 to 14.0	--	P,S,Se,B Zr,Mo	General-purpose, common items; suitable for automatic screw machines; pump and valve parts; machined outboard motor parts.
		420	Over 0.15	12.0 to 14.0	--	--	Cutlery, surgical instruments, valves, ball-bearings, magnets, springs, and valve seats.
		440C	0.95 to 1.20	16.0 18.0	--	Mo,0.75	Cutlery, instruments, valves; when high hardness and resistance is desired.
Ferritic	More resistant than martensitic but not as resistant as austenitic; satisfactory for mild atmospheres, fresh waters, and mild corrodents; may form rust in industrial and polluted atmospheres after short exposure. Pits in seawater and sometimes in marine atmospheres.	430[a]	0.12	14.0 to 18.0	--	--	Trim on vehicles; chemical equipment; when formability is desired.

[a] Most commonly used alloys of the class.

The characteristics of the corrosive environment and the requirements of the application should be carefully evaluated when specifying a particular composition. The complexity of the problem of selecting the correct alloy makes it necessary for the design engineer to consult the available data. These data, however, should be used only as a guide. In many instances, the selection of a stainless steel must be based on tests under actual operating conditions.

5.4.1 Galvanic Corrosion. Stainless steels will be subject to galvanic action coupled with other metals in an electrolyte. If the solution in which the contact occurs produces an active condition, metals like copper and bronze will accelerate the attack on stainless steel, particularly if the area of steel is smaller than the area of copper and bronze. However, when the steels are passive, they are quite stable in contact with these metals. Passive stainless steels are cathodic too, and will initiate attack on, metals such as carbon steel, cast iron, and aluminum alloys, especially when the area of stainless steels is larger than the area of the other metal. The influence of relative size of areas is important. Where there is a small anode and a large cathode, small differences in potential under these conditions may result in extensive corrosion because of increased current density in the anodic areas.

During the hot rolling of non-stainless steels, an oxide scale ("millscale") forms on the surface containing essentially three components. Next to the metal is a layer of FeO (comprising about 70% of the total thickness) followed by a layer of Fe_3O_4 (20%) and finally by a layer of Fe_2O_3 (10%). Unless this millscale is deliberately removed, corrosion attack will occur on this scale and not on the metal. However, because millscale does not form a good protective coating, in a suitable electrolyte, galvanic attack will occur locally at any bare metal exposed due to the fact that millscale has a potential more noble than the bare steel by about 0.3 volt. The large cathode area coupled to small anode areas causes appreciable local attack (e.g., pitting) as mentioned above. For applications where bare metal is to be exposed to aqueous electrolytes, such as boiler tubes, it is desirable, therefore, to remove all millscale before use.

Galvanic corrosion can also occur when ferrous and non-ferrous metals are part of the same structure but not in direct contact. For example, copper or bronze may corrode in a flowing electrolyte and the copper may be redeposited on the iron or steel surface setting up local galvanic cells. Alternatively, mechanical action could cause particles of a nonferrous metal to fall by gravity and settle on the ferrous surface causing the same attack.

5.4.2 Pitting and Crevice Corrosion. Localized attack of this type can develop where there are cracks or crevices and scales or other surface deposits. The types of cells most frequently encountered are the oxygen and active-passive cells (see Reference (37) and Paragraph 4.3.4). The action of such cells may produce severe attack and pitting, especially in solutions containing chlorides. When these conditions are to be encountered, it is customary to institute precautionary measures such as periodic surface cleaning, uniform surface exposure, and cathodic protection.

Corrosion cells can also be formed when steel is exposed to electrolytes of different compositions. For example, "long line" corrosion has been observed[34] in a lock gate in contact with a layer of fresh river water

flowing over a layer of seawater. Corrosion may also occur when sections of a long pipe line run through areas of dissimilar soil, or as a result of a stray current entering the pipe at one point, and leaving at another.

Crevice corrosion is a common form of corrosion attack with ferrous materials in a wide range of applications[37], such as: (1) under a rubber sealing gasket on an iron diesel cylinder liner, (2) under a rubber/asbestos gasket on a Type 316 stainless steel flange, (3) on Type 304 stainless steel bolts and washers exposed to nonflowing seawater, and (4) on a stainless steel orthopedic nail implant in contact with body fluids. It has been found[28] with high purity, ferritic stainless steels, at least, that increasing the chromium or molybdenum content, or both, will increase the resistance towards this type of corrosion attack. The most resistant alloy contained 25 Cr + 5 Mo, and showed no evidence of crevice corrosion in 1N NaCl solution at up to 50°C (122°F) in experimental tests.

5.4.3 Intergranular Corrosion and Selective Leaching. Graphitic corrosion in certain types of cast iron has been recorded for buried pipes.[34] This is a form of galvanic attack in which a cell is set up between flakes of graphite (cathodes) and adjacent iron (anodes) resulting in the formation of localized plugs of corrosion products. Intergranular corrosion is encountered with 18-8 type low-carbon stainless steels in particular circumstances. This type of attack is associated with welding or heat treatment (see figure 24) and can be eliminated by the use of stabilized compositions, e.g., alloys 321 and 347 (see table VIII) which incorporate additions of titanium or niobium to form carbides (see paragraph 4.3.5) and prevent chromium depletion at grain boundaries. A further discussion is given in References (35) and (36).

5.4.4 Stress-Corrosion Cracking. Because of the importance of ferrous alloys as engineering materials, their wide range of compositions and properties, their failure by stress-corrosion cracking (including hydrogen-stress cracking) will be discussed by types of alloy. For convenience, as before, the following general classification is used:

(a) Cast irons; wrought irons; steels (no deliberate alloying)
(b) Low alloy steels (medium strength)
(c) High alloy steels (high strength, e.g., stainless steels; precipitation hardening steels; maraging steels).

In the following discussion, emphasis will be placed upon (b) and (c) above.

5.4.4.1 Low Carbon and Low Alloy Steels. The low carbon steels referred to will have a Rockwell C Hardness Number of less than 22, and a tensile yield strength of less than 75,000 psi. Applications of these steels are mainly the construction of low pressure boilers; non-pressurized tanks and steel conduits. An early example of stress-corrosion cracking was found in steam locomotive boilers and low pressure, stationary boilers constructed by riveting. It was postulated that extremely small leaks developed at riveted joints and that the leaking water evaporated, precipitating any dissolved material in the fraying surfaces between the two connected plates. If this solid material was alkaline and if there were high stresses in the steel at the riveted joint, from mis-match of rivet holes or even from caulking to stop

leaking, stress-corrosion cracks could develop in the steel. It is believed that in some instances boiler explosions have been triggered by stress-corrosion cracks as a result of this so-called "caustic embrittlement".

A wide variety of inhibitors, inorganic and organic, have been suggested to prevent failures of this type. A water treatment that will maintain zero free caustic in the boiler water is reported to be the most satisfactory method of preventing failures from caustic embrittlement.

Caustic embrittlement can occur in a variety of alkaline environments. Failures have been reported in low-carbon steel tanks containing hot, concentrated hydroxide solutions such as those used to de-enamel steels and for the treatment of bauxite ores. Cracks were also associated with welds that had not been stress relieved. Recommendations have thus been made that no low carbon steel tanks should be put into service with 50% or higher caustic soda without a careful stress-relief anneal, preferably at 650°C (1200°F). It was reported that in England, cast iron had successfully replaced low-carbon steels in plants treating bauxite with sodium hydroxide.

Reports of failures of tanks used for storage and distribution of agricultural ammonia were common during the middle 1950's. Failures occured in tanks of all sizes from 1900 liters (500 gallon) distribution tanks to 113,550 liters (30,000 gallon) storage tanks. Most of these failures, where data were obtained, were within 5 to 8 cm (2 to 3 inches) of welds and in vessels that had not been stress relieved following welding. The tanks had generally been constructed of ASTM A-212 (now A-515) and ASTM A-285 steels, which are commonly used for pressure vessels.

Laboratory investigations indicated that contaminants such as air containing a normal amount of carbon dioxide were the most important of any of those studied in producing stress-corrosion cracking. Water in amounts greater than 2.0% appeared to be an effective inhibitor.(39)

It has been reported that similar tanks without stress-relief annealing have been successfully used to store other liquified compressed gases such as propane. For ammonia storage, however, it was recommended that all tanks having a diameter greater than about 1 meter (36 inches*) be stress relieved or be fabricated with heads that were hot formed or stress relieved before they were put in service, and tanks that were in service should be purged to remove any residual air before they were refilled.

The British have reported extensive stress-corrosion cracking in structures used in the production of illuminating gas (by the destructive distillation of coal). The carbon monoxide and dioxide constituents of this gas are thought to be responsible for the cracking.

The stress-corrosion cracks in the very large tank used to contain radioactive wastes discussed earlier were believed to be due to the presence of nitrates.(40) Hot concentrated solution of ammonium nitrate is used to produce stress-corrosion cracking in low-carbon steels in the laboratory. While some authorities limit the range of carbon content in which cracking may

* No failures were reported in tanks having smaller diameters.

occur from 0.02 to 0.22% carbon, cracking has been produced with a 20% boiling NH_4NO_3 solution in a decarburized steel having a bulk carbon content of 0.01% and, presumably, a much lower surface carbon content. Cracking has also been produced in a normalized 4130 steel with a carbon content of 0.31%. Thus, the probability that the catastrophic failure of the steel pipeline mentioned earlier, which had an average carbon content of 0.30%, was due to stress-corrosion cracking is not ruled out on the basis of the carbon content.

Stress-corrosion cracking in low-carbon steels is primarily intercrystalline whatever the corrodent. The mechanism of crack propagation has been studied extensively in nitrate solutions. Evidence indicates that it is propagated by an electrochemical-mechanical process.

The failure by hydrogen-stress cracking of medium-strength steels (hardness > 22 Rockwell C scale or tensile yield strength > 90,000 psi) is a continuing problem in the petroleum industry.

As little as 0.46 gram of hydrogen sulfide per cubic meter (0.2 grain/cubic foot) of natural gas can produce failures in a 4130 steel casing. The interior of the casing in one failure appeared to be free from corrosion, but on examination using a low-power binocular microscope, it was found to contain a network of cracks, some of which extended approximately half way through the 0.63m (1/4-inch) wall of the tube.

The mechanism of the reaction is not clear. Under slightly acid conditions and with moisture present, some of the hydrogen atoms generated at the steel surface by the corrosive reaction do not combine to form molecular hydrogen but diffuse into the steel as atomic hydrogen. If the steel is subject to high tensile stresses, it will fail by hydrogen-stress cracking or hydrogen embrittlement.

Extensive studies to determine what steels are most resistant to cracking in hydrogen sulfide environments have not been particularly successful. It has been suggested that steels in the quenched and tempered condition are more resistant to this type of failure than those in the normalized condition.

General recommendations are that steels for service where hydrogen sulfide is involved should have a tensile yield strength of less than 90,000 psi. For special purposes, such as valve components, springs, etc., Inconel, K-monels, Hastelloys, Stellites, and cemented carbides have been recommended.(41)

High strength, low alloy steels are also susceptible to failure under certain circumstances. The low alloy steels to be discussed (see table IX) include D6AC, 4137Co, 433OM, Vascojet, and H11 hot work die steel. The resistance of these steels to failure under stress in a variety of corrodents has been investigated in several laboratories. Some of them also have been exposed to the weather in industrial and marine atmospheres. The mechanism of failure is not always well understood, but involves hydrogen in the metal. Depending on the environment, failure is sometimes attributed to stress-corrosion cracking, and sometimes to hydrogen-stress cracking. For example, there is some evidence(47) that AISI 4340 will fail by the former in some environments, but by the latter mode of attack in dilute NaCl solutions.

The results of two major laboratory investigations will be discussed. In one of these[43] specimens were stressed in a modified U-bend manner to 50, 75, and 90% of their respective yield strengths. It was claimed that stresses were uniform over the specimen length. Specimens were immersed in a 3.5% NaCl solution for 10 minutes of each hour and were permitted to dry for the remaining time. In addition to intercomparison of alloys, the effects of machining processes and protective coatings were also investigated.

In the other investigation[42], conventional U-bend specimens were used in which stresses in excess of the yield strength of the material were applied in forming the specimen. Specimens were also precision cut to length and stressed as bent beams (ends restrained) to produce a stress of 75% of the yield strength in the outer fiber of the specimen. Specimens were exposed in 1 molar aqueous solutions of the following salts:

(a) sodium chloride $NaCl$

(b) sodium nitrate $NaNO_3$

(c) sodium sulfate Na_2SO_4

(d) sodium phosphate $NaPO_3$

(e) sodium sulfide Na_2S

These solutions were aerated regularly during the tests.

Certain general conclusions can be drawn from data from these investigations. At a given percentage of the yield strength of the various steels, for example 75%, the exposure period to failure decreases as the yield strength of the material increases. For a steel with a given yield strength, the exposure period to failure decreases as the applied stress increases. There may be threshold stresses, that is, stress levels below which cracking will not occur in some given exposure period, for some of these steels. The fact that steeels do not develop cracks after some arbitrary exposure period in the laboratory or in weather does not preclude the possibility that cracking may occur if the exposure period is extended. This is particularly true if the steel pits in the environment. Pits can act as regions of stress concentration and the resulting stress at the bottom of a pit may be much higher than the nominal stress on the specimen.

Generally, specimens whose long axes were perpendicular to the direction of rolling were more susceptible to failure than those whose long axes were parallel to the direction of rolling.

Optical and electron microscopic observation indicated that fractures were generally intercrystalline, with fractures following prior austenitic grain boundaries.

The data from the two investigations indicated that the D6AC and the 4330M and 4340M alloys were more resistant than other alloys of this group. In the alternate immersion tests, the H-11 alloy was grouped with the 4340 alloy in the 170,000 to 190,000 psi yield strength range, while in the constant immersion tests the die steel, H-11, was reported to be highly susceptible to failure above a stress level of 175,000 to 200,000 psi.

TABLE IX. Chemical Compositions of Low Alloy and Hot Work Die Steels for which Data are Available.
(Compositions are nominal weight percentages)

Steel	C	Mn	Si	Ni	Cr	Mo	V	Other
4137 Co*	0.42	0.77	0.90	0.12	1.14	0.26	0.15	Co 1.10, Al 0, 0.2
D6AC	0.46	0.70	0.20	0.60	1.10	1.00	0.1	
4330M	0.30	0.90		1.80	0.85	0.42	0.07	
4340	0.40	0.75	0.30	1.80	0.80	0.25		
4340 M*	0.40	0.75	1.65	1.80	0.82	0.40	0.07	
H11	0.40	0.30	0.90		5.00	1.00	0.5	
Vascojet*	0.39	0.28	0.90		5.10	1.30	0.5	

* Compositions of steels used in Reference (42).

One interesting result of the constant immersion tests using solutions of five different salts listed above was that there were no failures in the sodium sulfide solution and exposure periods to failure were much longer in nitrate solutions than in the chloride, sulfate, or phosphate solutions.

Various machining techniques were used to prepare specimens for the alternate immersion tests. Specimens finished by electro-polishing, chemical milling, or grinding (nominal 32RHR finish) were more susceptible to failure than specimens prepared by face milling or face milling followed by sand blasting or shot peening. Sand blasting or shot peening would put the surface layer of the material into compression and would thus be expected to increase the resistance of the material to failure. Manual and automatic fusion welding reduced the resistance of several of these steels to failure in the intermittent immersion tests.

Two of these steels were stressed and exposed to the weather. Uncoated specimens of a 4137 Co steel heat treated to a yield strength of approximately 215,000 psi and subjected to stresses of 160,000 psi failed in a few days, both in a marine atmosphere and in a semi-industrial environment. Specimens having yield strengths of 170,000 to 175,000 psi and subjected to applied stresses of 130,000 psi, did not fail in 462 days in a marine atmosphere and in 335 days in the semi-industrial environment.

The effectiveness of coating protection on the resistance to failure of a 5.0% chromium steel was also investigated in marine and semi-industrial environments.(44) Uncoated specimens stressed, to 75% of their yield strength, failed in exposure periods of 1.5 to 3 days in the marine atmosphere and in 20 days or less in the semi-industrial atmosphere. An aluminum coating, applied after austenitizing, a zinc-dust dibutyl titanate, and a nickel-cadmium electroplate markedly increased the resistance of the material to failure in both environments.

Aluminum applied before austenitizing, aluminum-pigmented silicon applied both before and after austenitizing, a rust preventive grease, and a zinc-chromate, iron oxide alkyd paint all improved the resistance of the steel to failure in the semi-industrial environment. The aluminum applied before austenitizing and the aluminum-pigmented silicon applied after austenitizing increased the resistance of the steel to cracking in a marine environment, but were less protective than the coatings listed above.

5.4.4.2 High Alloy Steels. The steels to be discussed in this section (see tables X and XI) include the stainless steels, the precipitation hardening, semiaustenitic stainless steels such as the 17-7PH, 17-4PH, PH15-7 Mo, AM350, AM355, and similar alloys; the nickel-cobalt-molybdenum, the nickel-cobalt, and nickel-chromium-molybdenum steels. Some of these steels may be heat treated to have tensile yield strengths of greater than 200,000 psi. All will fail by delayed fracture when exposed to specific corrosive media under sufficiently high residual applied tensile stresses.

Martensitic stainless steels contain 12 percent or more of chromium, and up to 2.5% nickel, and are normally quenched from a hardening temperature (e.g., 925 to 1040°C) then subsequently tempered. As quenched, the hardness ranges from 30 to 43 Rockwell C (AISI Type 410) to 53 to 56 Rockwell (AISI)

Table X. Chemical Compositions of Martensitic and Austenitic Stainless Steels

(Compositions given in nominal weight percentages)

Steel	C[a]	Mn[a]	Si[a]	Cr	Ni	Mo	Other
			(1) Martensitic Steels				
410	0.15	1.00	1.00	11.5-13.5			
420	over 0.15	1.00	1.00	12.0-14.0			
422[b]	0.20	0.65	0.5	12.0			
431[b]	0.20	1.0	1.0	15.0	1.5		
436[c]	0.16	0.50	0.45	12.67	2.10	0.18	3.04 W
			(2) Austenitic Steels				
201[b]	0.15	5.5-7.5	1.0	17.0	4.5		
202	0.15	7.5-10.0	1.0	17.0-19.0	4.0-6.0		
301	0.15	2.0	1.0	16.0-18.0	6.0-8.0		
304	0.08	2.0	1.0	18.0-20.0	8.0-12.0		
304L	0.03	2.0	1.0	18.0-20.0	8.0-12.0		
310	0.25	2.0	1.5	24.0-26.0	19.0-22.0		
316	0.08	2.0	1.0	16.0-18.0	10.0-14.0	2.0-3.0	
321	0.08	2.0	1.0	17.0-19.0	9.0-12.0		Ti 5 x C
347	0.08	2.0	1.0	17.0-19.0	9.0-12.0		Cb 10 x C

a Maximum unless otherwise indicated.
b Nominal composition.
c P. Lillys and A.E. Nehrenberg, Trans. ASM, 48(1956)327. Minimum.

TABLE XI. Chemical Compositions of Corrosion Resistant, Precipitation Hardening Steels.

(Compositions given in nominal weight percentages)

Steel	C	Mn	P (max.)	S (max.)	Si	Cr	Ni	Al	Mo	Other
17.6 PH[a]	0.09 (max.)	1.0 (Max.)	0.040	0.030	1.00 (max.)	16.0-18.0	6.50-7.75	0.75-1.50		
17-4 PH[c]	0.04	0.40			0.50	16.50	4.25			0.25 Cb 3.60 Cu
PH 15-7[b] Mo	0.09 (max.)	1.0 (max.)	0.040	0.030	1.00 (max.)	14.0-16.0	6.50-7.75	0.75-1.50	2.00-3.00	
AM350[d]	0.07-0.11	0.50-1.25	0.040	0.030	0.50 (max.)	16.0-17.0	4.00-5.00		2.50-3.25	0.07-0.13 N
AM355[d]	0.10-0.15	0.50-1.25	0.040	0.030	0.50 (max.)	15.0-16.0	4.00-5.00		2.50-3.25	0.07-0.13 N

a Military specification MIL-S-25043C.

b Military specification MIL-S-8955 (ASG).

c Nominal composition.

d Military specification MIL-S-8840B (ASG).

Type 420). Applications are usually found in high temperature nuclear reactors. Early failures were in both industrial and marine environments, and in the laboratory. They were attributed to hydrogen-stress cracking (e.g., Types 410 and 431).

Results of several investigations indicate that some of these steels will crack in high temperature water. Cracks in U-bend specimens of Type 431 steel having a hardness of 46 Rockwell C scale and of a Type 410 steel tempered at 343°C (650°F) were reported to follow prior austenitic grain boundaries. In the latter case, the austenite at the grain boundaries had transformed to untempered martensite which provide an easy path for crack propagation.

In another investigation involving Types 410, 420, 422, and 436 steels, the tempering temperature appeared to determine whether or not specimens failed. Specimens tempered at 482°C (900°F) were the most susceptible to failure. Specimens tempered at 370°C (700°F) or lower and at 593°C (1100°F) did not fail. These experiments were apparently carried out at ambient temperatures, which may explain the difference in results from those discussed earlier. Cracks, if they developed, again followed prior austenitic grain boundaries.

Service failures have been reported of 12% chromium martensitic stainless steels used for valve spindles and valve seats in marine boilers. These failures have usually been attributed to high chloride content of the water but they have also occurred where only very small amounts of chloride ions were believed to be present.

A steel designated 12 MoV* was exposed in a dilute chloride solution at ambient temperatures and the effect of applying both anodic and cathodic currents was determined. Specimens failed quite rapidly when made the anodes but were protected by a very small cathodic current. This behavior suggests stress-corrosion cracking. However, when the cathodic current was increased, specimens again failed, this indicated hydrogen-stress cracking.

There are reports that some of these steels have failed in laboratory tests in which they were exposed to a boiling magnesium chloride solution, a corrodent used in investigating the resistance of austenitic stainless steels to stress-corrosion cracking. Specimens have also failed in solutions containing sodium chloride and hydrogen sulfide. This solution is used to determine the resistance of steels to hydrogen-stress cracking.

Evidence would indicate that these steels are subject to hydrogen-stress cracking. Unless complete information as to conditions producing failure is known, it is difficult to say whether a failure results from stress-corrosion cracking or corrosion produced hydrogen-stress cracking.

Ferritic stainless steels are used at lower strength and hardness levels than the martensitic steels, and hence, may be expected to exhibit a greater resistance to stress-corrosion and hydrogen-stress cracking than the martensitic stainless steels. Ferritic steels are normally given a stress-relieved anneal after cold work or welding which also increases their resistance.

* U.S. Steel Co.; composition 0.25 C, 0.50 Mn, 0.45 Si, 0.63 Ni, 12.16 Cr, 0.98 Mo, and 0.33 V.

Austenitic stainless steels contain 16% or more of chromium and greater than about 4.5% nickel, with higher levels also of manganese than the martensitic steels (see table X). Type 300 series steels are commonly used in heat exchangers for the chemical and petrochemical industries, sometimes where the river water used for cooling may contain as much as 1000 ppm of chlorides on the East and Gulf Coasts at certain seasons of the year.

These steels have very good resistance to general corrosion in many inorganic as well as organic media. They are used where the presence of corrosion products would be objectionable. Unfortunately, they are susceptible to stress-corrosion cracking in chlorides at elevated temperatures. Failures in hydroxides at elevated temperatures have been reported, and also in polythionic acids at ambient temperatures. The latter have been formed during "down-time" of equipment in petroleum refineries in the presence of air (oxygen). Cracking is reported to be transcrystalline (as in the case with chlorides) if the steel is in the annealed condition, but intercrystalline if the steel has been sensitized by heat treatment.(41)

Failures of stainless steels in chlorides are usually not as catastrophic as boiler or pipeline failures described earlier in low-carbon steels. Chlorides simply produce leaks in stainless steel equipment. Nevertheless, such leaks are of great economic importance in that they cause down time, loss of product, and expensive replacement of capital equipment. They may occur at any point where chlorides in water can concentrate on a stressed and heated area. These would include tiny leaks, crevices of all kinds, hot spots on container walls, areas where there is drip, and area where chlorides can leach out of insulation on a hot water tank or pipeline carrying hot liquids.

The effect of the nickel content on the resistance of the chromium-nickel steels to failure in chlorides has been determined by varying the amounts of nickel in steels containing 18 to 20% of chromium. Data from Reference (45) are plotted in figure 39. It is seen that the exposure period to failure is a minimum for steels containing 8-10% nickel and that up to 40% of nickel must be added if the steel is to be resistant to stress-corrosion cracking in the media used, boiling 42% $MgCl_2$, for as long as 1000 hours.

It is the general opinion that if a steel containing 18 Cr + 8 Ni will develop stress-corrosion cracks under a given set of exposure conditions then a higher alloy steel, for example a 25 Cr + 20 Ni steel, will also fail, but after a longer exposure period.

Small grained steels appear to be more resistant to cracking than large grained steels. This is believed to be due to a longer incubation period before cracking is initiated in the fine-grained material than in the coarse. The crack propagation rate was independent of grain size.

Steels having a nominal composition of 18% Cr and 8% Ni may become "sensitized" when heated in the temperature range of 427 to 816°C (800 to 1500°F). Sensitization may occur in as short a period as 1 hour in the range of 650 to 705° (1200 to 1300°) and may occur during slow cooling following welding. In this condition, chromium carbides are believed to be precipitated at the grain boundaries, leaving the material immediately adjacent to the boundaries impoverished in chromium and more susceptible to

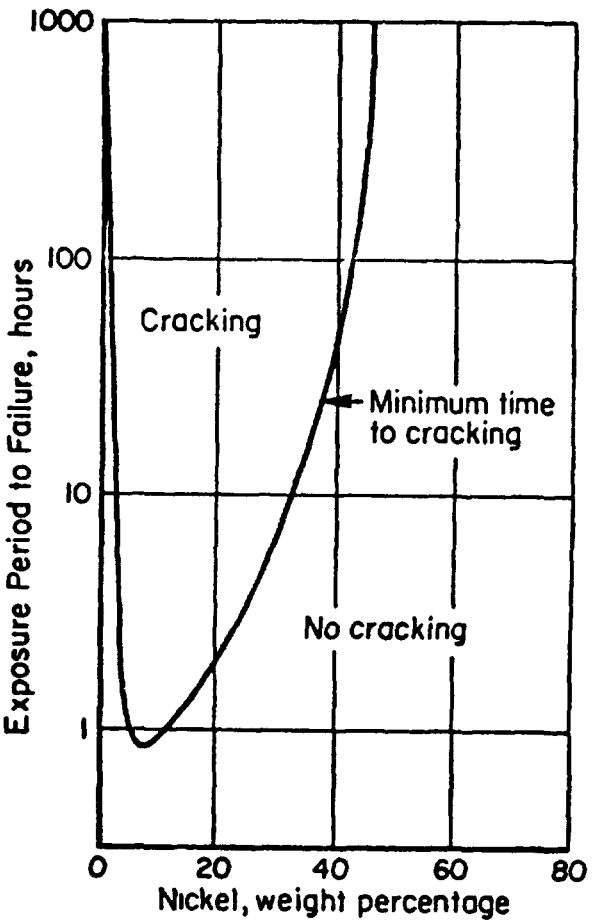


FIGURE 39. Effect of increasing nickel content on the susceptibility of stainless steel wires containing 18 to 20% chromium.

Tests were performed in a boiling 42% magnesium chloride solution (Reference 45).

corrosion in some media than the matrix. The result is intercrystalline corrosion, as shown in figure 24. Stress-corrosion cracking of sensitized material in chlorides will usually be primarily intercrystalline as compared to transcrystalline for quench-annealed material. In polythionic acids, cracking in sensitized material is intercrystalline.

A very low-carbon stainless steel, 304L, maximum carbon content 0.03%, may be used to avoid sensitization from welding (see figure 24a). The carbide formers, molybdenum, titanium, or niobium have been added to other steels to render them resistant to sensitization and intergranular corrosion. These steels are no more resistant to transcrystalline stress-corrosion cracking in chlorides than steels of approximately the same chromium and nickel contents, with higher carbon contents, or that do not contain the carbide forming additives.

Extensive attempts are in progress to develop steels having the desirable characteristics of the chromium-nickel stainless steels and that are immune to stress-corrosion cracking in chlorides.

The austenitic stainless steels will crack when exposed under stress in concentrated hydroxide solutions. Data obtained for a whole range of hydroxide concentrations indicate that, except for concentrations of about 35 to 65% hydroxide, cracking will occur at temperatures slightly above the boiling point of the hydroxide at that concentration (that is, under conditions where the solution can be heated above its normal boiling point).

One investigator reports that cracking can be either transcrystalline or intercrystalline, depending upon the carbon content of the steel. Cracks in steels containing 0.03% carbon were transcrystalline, while they were intercrystalline in steels containing 0.07 to 0.11% carbon. It was suggested that there was a submicroscopic grain boundary precipitate in the higher carbon steels.

Precipitation hardening stainless steels (see table XI) may be heat treated to give tensile strengths in excess of 300,000 psi, however, the heat treatment process is complex and lengthy. Semiaustenitic steels of this type have been found to fail in service in both industrial and marine environments. Laboratory tests to determine the resistance of these to delayed stress failure have been carried out in various corrosive media, including distilled water, tap water, and various salt solutions. The results indicate that distilled water may be the most damaging of these corrodents.

A survey was made of the resistance of several of these steels to high temperature water at 290°C (550°F). Steels included were 17-4PH (yield strength, 150,000-185,000 psi), 17-7PH (yield strength, 185,000-195,000 psi), and AM350 (yield strength, 150,000-170,000 psi). Specimens were subjected to stresses from 30,000 psi to greater than the yield strength. The 17-4PH in the H900 condition failed and cracking was intergranular. Addition of oxygen even in small amounts (0.2 ppm) appeared to promote the cracking. The same steel aged at 593°C (100°F) did not fail at stresses greater than the yield strength. Other materials studied did not fail in exposure periods of 2900 hours or more.

In another investigation, specimens of the 17-4PH steel, aged 1 hour at 482°C (900°F) or cold worked 48% and aged 1 hour at 482°C (900°F), failed on exposure to heavy water at 240°C (464°F).

The 17-4PH steel subjected to a stress below its yield point did not develop stres-corrosion cracks in 123 days exposure at a depth of 1850 m (5640ft) in the Pacific Ocean.(46)

The susceptibility of the AM350 to delayed failure in salt spray is stated to depend on the microstructure of the steel. Steels heat treated so as to produce a continuous carbide precipitate at the grain boundaries are reported to be susceptible to intercrystalline corrosion and failure. Steels in which carbide precipitation is more uniform and not confined to the grain boundaries are much more resistant to cracking.

Failures by stress-cracking of the AM350 alloy in the SCT condition have been reported in a marine atmosphere at stresses as low as 30 to 40% of the yield strength. Cracking was reported to be severe at 80 to 90% of the yield strength. In another investigation, specimens of the AM350 alloy stressed to 80% of its 164,000 psi yield strength did not fail in 1700 hours in a semi-industrial atmosphere; nor were there any failures of the 17-4PH alloy (yield strength, 185,000 psi) in 1700 hours in this same atmosphere. Two specimens of the Am355 alloy (yield strength, 195,000 psi), however, failed after 720 hours in this semi-industrial atmosphere while a third specimen had not failed in 2048 hours.

It should be noted that failures occurred under these exposure conditions after periods of 1500 to 2856 hours for the D6AC specimens (yield strength, 233,000 psi) and 1946 to 2091 hours for the 4340 specimens (yield strength, 215,000 psi).

The transverse grain direction of the AM350 sheet material was more susceptible to cracking than the longitudinal direction. This finding is in keeping with results for other high-strength steels. Both the AM350 and the AM355 steels are also susceptible to hydrogen embrittlement.(43)

Three steels are to be considered next in this section. Two of these, the 18 Ni + 9 Co + 5 Mo and the 12 Ni + 5 Cr + 3 Mo, are classified, because of their compositions and heat treatment as "maraging steels". The third steel is a 9 Ni + 4 Co steel containing either approximately 0.20 or 0.40% carbon.

Most of the data on the maraging steels have been obtained on the 18 Ni steel with the cobalt content varying from 7 to 9%. By making minor changes in composition, this steel can be obtained with yield strengths of 200,000, 250,000 or 300,000 psi.

The susceptibility of the 18/9/5 steel to delayed stress failures has been determined in several media. At a given stress level, the expected life of this maraging steel was found to be considerably longer in aerated distilled water than that of the H11 die steel; and for a given expected life in this corrodent, the stress required to produce failure was of the order of 100,000 psi higher for the maraging steel.

In another investigation in which the 18/9/5 maraging steel was compared with a number of other high strength steels by alternate immersion in a 3.5% NaCl solution, the maraging steel was reported to be the most resistant in the yield strength range of 210,000 to 270,000 psi.(43)

The 18% Ni maraging steel was also reported to be more susceptible to cracking in aerated distilled water than in 3% salt water. The steel showed a marked increase in susceptibility to cracking with increased temperature of the corrodent and decreased with alkalinity.

The resistance of this steel to stress-corrosion cracking is said to be strongly affected by its structure and thermal history. All cracks followed prior austenitic grain boundaries. Heat treatments that cause precipitation reactions or establish composition gradients at these boundaries are harmful. Coarse grain size is detrimental to resistance to stress-corrosion cracking. This, as has been pointed out in regard to other materials, is the usual situation.

Cathodically protected specimens in seawater were said to fail by hydrogen-stress cracking. It was further suggested that stress-corrosion and hydrogen-stress cracking were different phenomena in this steel.

Welded and aged 18% Ni maraging steel has a resistance comparable with the H11 tool steel, but lower than in either the cold worked and aged or annealed and aged conditions. (In general, strength will determine whether a metal will fail or not: if the metal has a strength in excess of about 180,000 psi failure will normally occur).

The 18% Ni maraging steel did not develop any stress-corrosion cracks when subjected to a stress less than its yield strength and exposed for 123 days at a depth of 1850 m in the Pacific Ocean.(46)

The tensile properties of the 12 Ni + 5 Cr + 3 Mo steel are appreciably lower than those of the 18% nickel maraging steel. At a 185,000 psi yield strength, the 12% Ni steel was reported to be more resistant to Hydrogen-stress cracking than a 4340 steel heat treated to the same strength level. Reports of other investigations indicated no failures of U-bend specimens of the 12 Ni + 5 Cr + 3 Mo steel after 200 days exposure in seawater. Specimens containing welds had failed in a shorter time. The base metal could be protected cathodically, using mild steel or zinc anodes, against both general and stress-corrosion cracking. Welds were stated to have been protected using mild steel anodes, but to fail by hydrogen-stress cracking if zinc anodes were used. Another investigation showed no failures of U-bend specimens of either the 12% Ni or the 18% Ni maraging steels in 750 days exposure in seawater, but prenotched specimens of both of these steels failed in a sodium chloride solution, in artificial seawater, and in natural seawater.

The 9 Ni + 4 Co steels containing 0.26 and 0.38 carbon were included with other high strength steels in an early investigation.(43) The 9 Ni + 4 Co + 0.26 C steel was listed along with the 4330M steel as having good resistance to failure at the 220,000 psi yield strength level when tested by alternate immersion in a 3.5% NaCl solution (specimens were of the modified U-bend type, stressed to 80% of the yield strength). The lower carbon steel (0.26) also appeared to be more resistant to cracking than the steel containing 0.38% carbon. Further, the 9/4 steel (0.26%C) specimens had not failed in 2630 hours in a semi-industrial atmosphere while specimens of a 4340 steel having approximately the same yield strength and subjected to the same stress had failed after an average exposure period of approximately 2000 hours.

5.5 Lead and Lead Alloys. One of the most important reasons for the wide-spread use of lead in industry is its resistance to corrosion. The wide range of uses for lead are indicative of its resistance; these uses include piping, protective sheathing on electrical cables, storage battery grids, bases for structural columns, roofing, and equipment in the chemical industry. Lead is resistant to corrosion by atmosphere, water, and a great many of the common corrosive chemicals, such as sulfurous, chromic, phosphoric, and hydrofluoric acids. The resistance of lead is due to the formation of protective coatings of lead compounds which are insoluble in the corrosive medium. These protective coatings or films readily form on lead in a wide variety of environments. In the Galvanic Series, lead is midway, above copper but well below iron, and is grouped together with tin and the lead-tin solders (see Table III).

Lead is equally resistant to atmospheric corrosion in almost all types of atmospheres. Moreover, this resistance is generally unaffected by the usual contaminants in the air (e.g., SO_2, SO_3, H_2S, CO_2).

Lead exhibits good resistance to corrosion by natural fresh water and seawater, with higher resistance in hard fresh water than in soft fresh water. In seawater, the rate of attack on lead after lengthy exposure was recorded as 0.000127 cm per year (0.00005 inch per year). The rate of attack on a babbitt (80:15:5 lead, antimony, tin) under identical conditions was 0.00152 (0.0006) and of a soft solder (50:50 lead, tin) 0.00533 cm per year (0.0021 inch per year). Lead should not be used, however, as a container for distilled water, because of its finite corrosion rate.

The use of lead under certain conditions is limited. For instance, lead is vulnerable to soils that contain organic acids from wood. Aerated acetic acid is very corrosive, even at room temperature, and dilute alkalies generally attack lead rapidly. Lead is readily attacked by nitric acid and should not be used in contact with nitrate or nitrate radicals.

The softness of lead and low melting point results in ease of fabrication, however, as a corollary, its lack of strength means that if often must be supported in structures. In these cases, care should be taken to avoid galvanic attack.

Lead-antimony, and lead-calcium-tin alloys are used for the grids in lead-acid battery plates, indicating their resistance to dilute acids, even in the presence of evolved oxygen.

Lead and lead-tin compositions, including terne alloys, are utilized as protective coatings for other metals. As in the case of electroplates and metallic coatings in general, the thickness of the coating is an important factor in the corrosion resistance of terne plates and hot-dipped cast iron and steel plates. The lead-tin coatings applied to steel provide an inexpensive and satisfactory means of protection under most conditions. But soldered joints may corrode in the presence of moisture that accelerates galvanic action between the dissimilar metals. Bearing metals are protected from attack in typical installations by the lubricating oil present on the surface.

The current specifications for lead and lead alloys are listed in Department of Defense Index of Specifications and Standards.

5.5.1 Galvanic Corrosion. The use of lead-tin coatings may be limited because both lead and tin are cathodic to iron and will accelerate corrosive action on steel at bare points, pores, and other discontinuities in a coating. Lead-tin coatings for steel are useful in atmospheric applications (both indoors and outside), but they are not recommended for products that will be immersed in aqueous solutions or in soil. The galvanic corrosion of both copper and iron is accelerated when coupled to lead in acid solutions, but in alkaline solutions, the reverse is true. The galvanic corrosion of copper may be accelerated by lead in a situation where solder is applied at high temperature, causing a noble copper-tin compound to form. By avoiding excessive heat, this tendency can be minimized.

In atmospheric corrosion, normally protective films are formed, which are electrically insulating, and offer resistance against galvanic attack in contact with other metals. However, if the film formed is electrically conductive (for example in sewage applications where H_2S is present, lead sulfide may be formed, which is also more noble than bare (or carbonate-covered lead) local galvanic cells are set up causing localized attack.(48)

In certain circumstances, galvanic action can have a beneficial effect. The addition of antimony, small amounts of silver and other metals can lead to the formation of a passivating film of lead dioxide under anodic polarizations in seawater below a current density of about 10 A/dm^2 (12 A/ft^2). Small pieces of platinum buried in the surface of lead can cause the same effect, and such metals can be used for cathodic protection in seawater.(48)

5.5.2 Crevice Corrosion. This type of attack occurs often in underground applications where lead pipes are used, and results because of chemical inhomogeneity of the soil, or local changes in the environment caused by aeration, water content, stray currents, packing and backfill (cinders, broken chalk, cement) or even bacteria. Potential differences of as much as 1.5 volt have been measured for pipeline passing through soils of different composition. The worst combination of soil is said to be wet clay and cinders, where the carbon present acts as an efficient cathode.

The most successful method for protecting covered or bare lead underground is cathodic protection. This must be carefully controlled, however, to maintain an acceptable potential at the lead surface. If the potential exceeds normal limits, hydrogen can be formed, and the surrounding environment

will become more alkaline. Adjacent lead structures, in the relatively more acid environment, may then become prone to a form of concentration cell corrosion.

5.5.3 Stress-Corrosion Cracking. Failure of lead as a result of stress-corrosion cracking has not been reported in the literature. However, because of its low tensile strength, coupled with the large grain size often found, failure by intercrystalline cracking can be observed under some conditions of mechanical stress. Alloying can be employed to improve the mechanical as well as corrosion resistance properties of lead. Certain alloys can be dispersion-strengthened, and this characteristic is taken advantage of in the lead-acid battery industry for the manufacture of plate grids.

5.6 Magnesium and Magnesium Alloys. Magnesium is a highly active metal in the Electromotive Series and is rated just above aluminum in the Galvanic Series (see tables I and III). It is generally not regarded as a corrosion-resistant metal and has a great tendency to corrode by galvanic action. The extent of corrosion is largely determined by the purity of the metal and the characteristics of the environment. Furthermore, the degree of aeration of the media is not the important factor in the corrosion of magnesium, as it often is with other vulnerable metals. Rather, corrosion proceeds largely by hydrogen evolution.

Magnesium alloys in general are susceptible to the usual types of corrosive attack, including direct chemical attack, pitting, stress-corrosion cracking, corrosion fatigue, intercrystalline, and galvanic corrosion. Some of the current commercial alloys are considered to be less susceptible to intergranular corrosion.

Pure magnesium is considerably more resistant than commercial magnesium and almost all of its alloys. For example, the corrosion rate for pure magnesium under conditions such as exposure to seawater or mildly acidic solutions may be only 1 percent of that encountered with common binary magnesium alloys. Pure magnesium, however, exhibits relatively low strength values, and therefore invariably is used as an alloy. In general, commercial alloys with impurities such as copper, iron, nickel, below certain limits, exhibit satisfactory resistance on exposure to mild atmospheres but corrode more rapidly in other environments. The relative resistance to corrosion of magnesium cast and wrought alloys is indicated in MIL-HDBK-693(MR) "Magnesium and Magnesium Alloys". The current specifications for magnesium and magnesium alloys are listed in Department of Defense Index of Specifications and Standards.

Despite the general tendency for magnesium alloys to be less resistant than pure magnesium, certain high-purity alloys that exhibit comparatively good corrosion-resistance are available. But in these compositions, impurities such as iron, nickel, copper, zinc, and silver are held to a minimum. Nevertheless, magnesium and its alloys are ordinarily given suitable surface protection, even for shipment or temporary storage. It is customary to recommend protective measures for magnesium (by suitable chemical surface treatment or paint systems) because of the oxide film inherently developed by magnesium provides little or no protection. This film is attacked by water containing carbon dioxide and solutions that are even mildly acidic. The film is resistant to alkaline agents, but in most natural environments, it is

dissolved or undergoes chemical reaction. Hence, should the barrier protection (paints and lacquers, etc.) be removed or damaged, the bare metal would be vulnerable to corrosion.

Atmospheric corrosion rates are dependent on the type of atmosphere and the alloying elements present. Interior atmospheres and rural outdoor atmospheres are relatively harmless. During interior exposure, magnesium alloy, M1, containing one percent manganese, is more resistant than the alloys containing aluminum, but the reverse is true for outdoor exposures. As the aluminum content increases to about 9 percent, there is less tendency for tarnish to develop during outdoor exposure. Zinc, in excess of 5 percent, and small amounts of silver will increase the rate of tarnishing. Humidity is also a major factor in atmospheric attack on magnesium and its alloys. Even at 30 percent humidity, tarnish and a small amount of oxide will develop after extended exposure. Corrosion will be severe in areas where high humidity conditions prevail.

Magnesium alloys containing impurities may be attacked in industrial and marine atmospheres suffering an extensive loss of tensile strength. Controlled-purity alloys are more resistant, and when considered in relation to aluminum and steel under the same conditions, compare favorably with aluminum alloys and are slightly superior to low-carbon steels.

The attack of magnesium in various types of water and aqueous solutions is affected by the purity of the alloy, the presence of carbon dioxide, alkalinity or acidity, and temperature. Magnesium is resistant to alkalis but ordinarily is attacked by most acids. As the alkalinity increases above the point at which magnesium hydroxide is formed (pH 10.2), the effect of cathodic alloying impurities and of salts in the environment is overshadowed by the stronger tendency for films to form. The effect of temperature is modified by the purity of the metal. But higher temperatures approaching the boiling point of the solution will increase the rate of corrosion considerably.

Fresh water, in general, is much less corrosive to magnesium alloys than seawater. For short-time exposure, the rate of attack on controlled-purity alloys in tap water is about 0.0025 to 0.0050 cm per year (0.001 to 0.002 inch per year). Higher rates, and possibly pitting, might be expected with ordinary alloys under the same conditions. On the other hand, all the commercial magnesium compositions are attacked by seawater. Pitting normally occurs and the attack may be quite severe. In warm water, impure alloys corrode rapidly. Test on controlled-purity alloys exposed in alternate immersion to seawater showed loss of tensile strength up to 59 percent in about 8 months. Satisfactory protection of magnesium and magnesium alloys against seawater is difficult to achieve even if suitable anodic treatments and post treatments are applied. The latter are generally effective in protecting magnesium from corrosion in other environments. Therefore, the use of these materials for structural purposes under conditions of continuous or intermittent immersion is limited.

In addition to the causes of corrosion already mentioned, surface contamination due to foreign particles imbedded in the metal can give rise to localized corrosion. This surface contamination may be caused by shot or sand blasting, some types of welding, or fabricating operations. Where magnesium

is highly stressed, it is vulnerable to stress corrosion during exposure to water and atmosphere. Many of the corrosion problems involving magnesium in actual service are galvanic and can be eliminated by proper design and other appropriate measures.

5.6.1 Galvanic Corrosion. In a conducting solution, almost all common metals in contact with magnesium act cathodically and hence accelerate the attack on magnesium. Moreover, under conditions where galvanic corrosion may occur, both magnesium and an amphoteric metal to which it is joined, such as aluminum, may be attacked. This tendency may prevent the use of magnesium in applications where the high conductivity of the media induces rapid galvanic action. On the other hand, use under conditions of atmospheric exposure where conductivity of the medium is low, reduces the probability of galvanic action.

The rate of galvanic attack does not differ greatly if magnesium alloys are used instead of magnesium metal. The type of electrolyte rather than the composition of the magnesium metal in contact with the dissimilar metal is the governing factor.

5.6.2 Pitting Corrosion. Galvanic attack on a microscopic scale occurs with magnesium alloys exposed to clean but humid atmospheres. Differences in potential between the metal and local cathodic areas (e.g., impurities at the surface) cause irregular pitting to occur. Below a R.H. of about 60 percent, under similar conditions, the magnesium will retain its lustrous appearance. With magnesium alloys, a reverse form of intergranular attack can also occur. In this case the grain boundaries are cathodic with respect to the bulk (interior) of the grains, and the grain interior is preferentially corroded, initially along the area adjacent to the boundary. In the extreme case for coarse-grained materials, the grain can be undercut and the center be dislodged or fall out.[49] Unlike true intergranular attack, the corrosive action described above is always limited to the first layer of grains in contact with the electrolyte, and rapid penetration cannot occur.

5.6.3 Crevice Corrosion. Although this type of general attack, which includes deposition corrosion, is possible in theory, specific examples are difficult to find in the literature. The high electrochemical reactivity of the metal usually results in a galvanic type of attack under conditions which, with less activity materials, would cause true crevice attack, for example (see paragraph 4.3.4). Filiform corrosion, however, has been reported[51] to occur on magnesium in chloride electrolytes.

5.6.4 Stress-Corrosion Cracking. In the 1930's, laboratory studies performed in Germany showed that alloys containing more than 2.5% aluminum were susceptible to stress corrosion cracking. Later in the 1940's, failures were observed with AZ61A alloy* (see table XII) containing 6.5% aluminum fabricated into airplane booms.[50] These booms were subjected to static loads until buckling occurred, and then were stored in the open, exposed to the weather. Subsequent examinations revealed stress-corrosion cracking in the buckled areas. Because of their light weight, magnesium alloys were being considered for extensive use in aircraft. The finding of the stress-corrosion

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* Federal Specification QQ-M-316.

TABLE XII. Chemical Compositions of Some Wrought Magnesium Alloys.

(Compositions in nominal weight percentages)

Alloys	Al	Zn	Mn	Si	Cu	Ni	Fe	Ca	Total Others
M1A	--	--	1.2-1.76	0.10-0.30	0.05	0.01	--	0.30	0.30
AZ31B	2.5-3.39	0.6-1.4	0.20	0.10	0.05	0.005	0.005	0.04	0.30
AZ51	5.1	1.0	--	--	--	--	--	--	--
AZ61A	6.5	1.0	--	--	--	--	--	--	--
AZ80A	7.8-9.2	0.2-0.8	0.12	0.10	0.05	0.01	--	0.30	0.30
AZ60A	--	5.7	--	--	--	--	--	--	0.55 Zr

cracks in the airplane booms lead to extensive investigations in the United States of the susceptibility of the magnesium alloys then available to stress-corrosion cracking. An investigation was also undertaken in England under the sponsorship of the Director of Scientific Research (Aircraft) Ministry of Supply.

There was general agreement, as the result of these investigations, that the M1A alloy was immune to cracking, but that alloys containing more than 2.5% aluminum were susceptible to cracking. These include AZ31B; AZ51, AZ61A; and AZ80A. A magnesium-zinc-zirconium alloy, ZK60A, was more resistant to stress-corrosion cracking than the magnesium-aluminum-zinc alloys but did fail when subjected to stress in weather exposure. Russian investigators have recently studied the resistance of magnesium alloys, including some containing small amounts of rare earth additives. Published Russian results are in general agreement with those obtained elsewhere.(50) The statement has recently been made in this country that "magnesium alloys, including those containing manganese, rare earths, thorium, zinc, and zirconium are not sensitive to stress-corrosion".

Following the success in improving the corrosion resistance of aluminum alloys by cladding them with aluminum or an aluminum-very low zinc alloy, an attempt was made to improve the resistance of the AZ31 sheet by cladding it with thin layers of the M1A alloy. These clad sheet materials* proved very resistant to stress-corrosion cracking. Specimens loaded in direct tension to approximately 90% of their yield strength did not fail in more than 600 days exposure in a marine atmosphere.

The conventional magnesium-base alloys have a hexagonal crystal structure and have more anisotropic mechanical properties than metals with face-centered cubic or body-centered cubic structures. Hence, there has been some interest in the magnesium-lithium alloy system because both components have low densities and alloys containing more than approximately 12% by weight of lithium have a body-centered cubic structure.

Alloys containing 14% lithium and 1 to 1.5% aluminum, with the balance magnesium, failed by stress-corrosion cracking in laboratory tests. Alloys containing 14% lithium with small amounts of zinc and/or silicon and/or silver, but no aluminum, did not fail in the laboratory.

The data given above are for wrought alloys. The cast magnesium alloys are considered to be more resistant to stress-corrosion cracking than wrought alloys.

Although magnesium alloys can be made to fail readily in KHF_2 solutions, the conventional corrodent used to test the resistance of magnesium alloys to stress-corrosion cracking is a 3.5%NaCl, 2%K_2CrO_4 aqueous solution used at room temperature. This is strictly a "go-no-go" test. Specimens that do not fail in 5 minutes will probably not fail in 24 hours. A much more satisfactory test method is weather exposure. Average exposure periods to

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* The AZ31 alloy sheet was sandwiched between two very thin layers (each approximately 3% of the total thickness of the sheet) of the mechanically weaker but more corrosion resistant M1A alloy.

failure at given stress levels have been approximately the same for specimens exposed in marine and in rural inland environments. Failures occur during or after rain. A specimen that showed no evidence of stress-corrosion cracks prior to a rain may fail completely as the result of the rain. There is a question then as to just what the corrodent is. Certainly moisture and oxygen are involved. Slight solubility of corrosion products formed on specimens may have contributed to the stress-corrosion cracking.

In one laboratory investigation, specimens were immersed in deaerated water and sealed from the air. Companion specimens were immersed in water open to the air. The specimens protected from the atmosphere had not failed after four times the average exposure period to failure for the specimens exposed in water that contains some oxygen.

The paths of stress-corrosion cracks in magnesium alloys are primarily transcrystalline. The cracking mechanism is believed to be electrochemical-mechanical. The fact that the M1A clad AZ31 alloy had a very much longer life than the bare AZ31 alloy indicates that cracking is, in part at least, electrochemical. The M1A clad layer acts to cathodically protect the AZ31 core material. Application of cathodic protection using an external electrode to bare magnesium alloy specimens exposed in the $NaCl/K_2CrO_4$ solution stopped the propagation of stress-corrosion cracks in the material. Upon removal of the cathodic protection cracking was immediately reinitiated. The rate at which cracks propagate in the $NaCl/K_2CrO_4$ solution would require a very high current density if crack propagation were entirely by an electrochemical process. Hence, the mechanism is thought to be electrochemical-mechanical as described earlier.

5.7 Nickel and Nickel Alloys. Nickel and nickel alloys posses excellent resistance to corrosion and are severely attacked only under particular conditions. Nickel itself is relatively noble; in the Electromotive Series it is ranked below iron but above copper, while in the Galvanic Series, it is grouped with the common copper alloys (see tables I and III). Nickel does not readily evolve hydrogen from solutions and common reducing acids. Hence, the presence of oxidizing agents, such as dissolved oxygen, is necessary for the corrosion of nickel to proceed. As a result, nickel and its alloys generally are most resistant to acid corrosion under reducing conditions and are most vulnerable in the presence of oxidizing acids and compounds. Moreover, nickel has the ability to protect itself from certain forms of attack by the formation of a protective, passive, oxide film. A detailed discussion about general corrosion resistance in specific corrodents is given in Reference (52).

The following discussion examines the resistance and vulnerability of nickel and several nickel alloys to corrosion. The alloys discussed include the Monels, Inconels and Hastolloys, approximate compositions of which are given in table XIII.

In general, Monel exhibits the widest range of resistance to mineral acids, and salts under most exposure conditions. Nickel is almost, but not quite as resistant to acids, although it is more resistant to alkalis.

Inconels and Hastelloys were developed for special resistance characteristics. Inconels resist corrosion and tarnishing by foods and dilute organic acids, while Hastelloys posses excellent resistance to hydrochloric

TABLE XIII. Chemical Compositions of Some Proprietary Nickel Alloys.

(Composition in nominal weight percentages[a,b])

Designation[d]		Ni	C	Mn	Fe	Si	Cu	Cr	Al	Ti	Other
Nickel	200	99.5	0.08	0.18	0.2	0.18	0.13	--	--	--	--
Duranickel[c] alloy	301	96.5	0.15	0.25	0.30	0.5	0.13	--	4.38	0.63	--
Monel[c] alloy	400	66.5	0.15	1.0	1.25	0.25	31.5	--	--	--	--
Monel alloy	K-500	66.5	0.13	0.75	1.00	0.5	29.5	--	3.00	0.63	--
Inconel[c] alloy	600	76.0	0.08	0.50	8.00	0.25	0.25	15.5	--	--	--
Inconel alloy	X-750	73.0	0.04	0.50	7.00	0.25	0.25	15.5	0.70	2.50	Nb, 0.95
Incoloy[c] alloy	800	32.5	0.05	0.75	46.0	0.50	0.38	21.0	0.38	0.38	--
Incoloy alloy	804	41.0	0.05	0.75	25.4	0.38	0.25	29.5	0.30	0.60	--
Incoloy alloy	825	42.0	0.03	0.50	30.0	0.25	2.25	21.5	0.10	0.90	Mo, 3.0
Hastelloy	C	54.0	0.08	1.0	5.0	1.0	--	15.5	--	--	Mo,16;W,4; Co,2.5
	C-276	56.0	0.01	--	5.5	0.03	--	15.5	--	--	Mo,16;Co, 2.5;W,4.0; V, 0.25

a The International Nickel Co., Inc., Handbook of Huntington Alloys (1968).

b Sulfur content, 0.005 to 0.015%.

c Trademark, The International Nickel Co., Inc.

d Corrosion characteristics of all Monels, Inconels, etc., will be similar, e.g., Incoloys 600, 800, and 825 will all behave similarly in a given corrodent.

acid and other corrosive chemicals over a wide range of concentrations and exposure conditions. The resistance of all these alloys, even to substances considered noncorrosive, is subject to the effects of variations in concentration, aeration, temperature, stress, and other metal-environment factors.

In ordinary indoor exposures, nickel, nickel-plate, and nickel alloys remain relatively bright and free from corrosion. In outdoor atmospheric exposures, the rates of attack vary, but are rarely severe, Inconels are usually more resistant than Monels or nickel, and are relatively free from the "fogging" that sometimes appears on Monel and nickel after lengthy exposure to damp, sulfurous atmospheres. This fogging is characterized by the appearance of a brown or greenish film that consists essentially of nickel sulfate. Fogging takes place in an atmosphere having a relative humidity averaging above 70 percent and containing sulfur dioxide.

In all but rural atmospheres, nickel will tend to lose its luster, but corrosion rates are never more than 0.0025 cm (0.001 inch) penetration per year even under adverse conditions. Nickel electrodeposits are inherently porous and to help reduce porosity plated nickel often is applied in thicknesses of 0.005 cm (0.002 inch) or over. The protection afforded by nickel electroplate is a function of its thickness. Ordinarily, nickel is not used for providing protection other than against atmospheric corrosion. Chemical plating of nickel, e.g., electroless nickel, can be accomplished on most surfaces. Physical properties of electroless nickel differ from those of electroplated nickel; the mode of plating provides uniform coating of intricately shaped metal parts. Chemically deposited nickel generally offers more corrosion resistance for equivalent films of electrodeposited nickel under 0.0025 cm (0.001 inch) thickness.

Nickel is resistant to corrosion in water, including distilled water, natural fresh water, water containing free carbon dioxide and hydrogen sulfide, and seawater. In seawater, pitting may occur under areas covered by barnacles or other foreign substances, especially in stagnant waters. Monels are likewise resistant to fresh and distilled waters, steam condensate, and particularly to seawater under high velocity. They resist cavitation and impingement, and even under strongly aerated and agitated water, the corrosion rate ordinarily does not exceed 0.0025 cm (0.001 inch) per year. Pitting may occur under particles lodged on Monel surfaces in stagnant waters, but Monels are generally superior to nickel in resisting pitting when submerged. Inconels are as resistant to all types of water as nickel, but are only moderately resistant to rapidly flowing seawater. And, while subject to pitting under the appropriate conditions, Inconels are more resistant to corrosion under typical mild conditions of exposure to the atmosphere, fresh water and seawater.

5.7.1 Pitting and Crevice Corrosion. Micro-inhomogeneities in surface chemical composition can cause pitting, which was mentioned in the general discussion above. Crevice corrosion can occur with nickel alloys, particularly in marine environments, under areas covered by barnacles or other surface deposits, particularly in stagnant waters. This type of corrosion attack is first evidenced by small pits, which can subsequently enlarge and coalesce resulting in a significant loss of metal, and impairing the mechanical properties. The resistance towards crevice corrosion varies with

the alloy composition. For example, Hastelloy C is considered resistant to this type of attack, whereas Incoloy 825 is slightly susceptible. A Carpenter 20 Cb 3 alloy is very susceptible to this type of corrosion in chloride solutions.[37] Additions of molybdenum apparently increase the resistance to pitting in seawater, hence, the effectiveness of the Hastelloy C alloy.

5.7.2 Intergranular Corrosion. This can be found on many nickel alloys, and in many respects the behavior is similar to that found with stainless steels containing appreciable amounts of nickel. Both types of alloy are capable of being sensitized through improper heat treatments, but as the nickel content of the alloy increases, the susceptibility to intergranular attack is decreased. Thus, a 65/35 nickel-chromium alloy is essentially immune to intergranular corrosion adjacent to welds in concentrated nitric acid or nitric/hydrofluoric acid mixtures, whereas a niobium-stabilized 18/13 chromium-nickel steel is much less resistant. A vanadium-stabilized 30/6 molybdenum-iron alloy (Corronel 220) has also been developed for use with hot concentrated mineral acids. Heat treatments are not required to prevent carbide precipitation at the grain boundaries with this alloy, hence, it does not suffer from intergranular attack. It has not yet been found possible to stabilize the nickel-chromium-molybdenum-iron alloys,[52] thus, these alloys will be susceptible to attack next to welds.

Proper consideration of tables I and III will prevent detrimental galvanic corrosion attack due to the contact of bulk, dissimilar metals in a corrodent.

5.7.3 Stress-Corrosion Cracking. Alloys found to be susceptible to this type of attack, and discussed in this section, include those containing appreciable amounts of nickel with relatively small amounts of iron (see table XIII). Cupronickels have been discussed in Paragraph 5.3.6.

There has been much interest in the possibility of replacing the austenitic stainless steels, which are susceptible to stress-corrosion cracking in high temperature water, with alloys having higher nickel contents than the stainless steels. The resistance of nickel alloys 600, 800, 804, and 825 to stress-corrosion cracking was investigated[53] in water containing 100 ppm of chloride and 50 ppm of oxygen at 300°C (572°F) and at a pH of 2.8, 6.5, or 10.5. The 800 and 825 alloys developed cracks at the lower pH's in exposure periods ranging from 1000 to 2000 hours. However, cracking of the 600 alloy has been reported in other experiments. At this time there is a difference of opinion as to whether alloy 600 would develop stress-corrosion cracks in pressurized water at approximately 315°C (600°F) unless contaminants such as lead or lead compound were present or an acid condition could develop in a crevice due to the presence of oxygen.

In another investigation, pipes of alloys 400, 600, and 825 and a stainless steel were bent into semicircular arcs, heated with steam to 154°C (310°F) and sprayed with potable water (3 to 6 ppm chloride). Cracks developed in the stainless steel specimens after 1000 hours (unless they had been annealed 677°C (1250°F) and cold water quenched. None of the nickel alloys developed stress-corrosion cracks under these conditions.

Nickel, nickel-clad steel, and the nickel-copper alloy 400 are considered the most satisfactory materials for handling hot concentrated caustics.

Nickel-copper alloys, such as Monel 400, are also the preferred material for the construction of salt plants. Evaporators are commonly lined with this alloy, which is resistant to concentrated salt brines at temperatures of 130°C (265°F). Stainless steels could fail rapidly under these conditions.

There have been reports of failures in cold drawn nickel tubes (99.4% nickel) exposed to caustic soda solutions at temperatures above ambient. These tubes had been given a low temperature anneal but were believed to contain residual circumferential stresses of 11,000 to 50,000 psi. They contained aqueous solutions of various concentrations of caustic soda. Cracking was stated to be intergranular. Failures started on the outer surfaces of some of these tubes were attributed to volatile sulfides carried over in steam from an earlier process. At temperatures above 135 to 370°C (600 to 700°F), nickel is subject to both general and intergranular corrosion by compounds and gases that contain sulfur.

Investigations of the reaction of fused anhydrous hydroxides with nickel alloys had produced some failures in internally stressed nickel and in the 400 and 600 alloys. A stress relief anneal at 850° (1560°F) is recommended for nickel welds prior to their exposure to hot caustics. For high temperature exposure to caustics, a low-carbon nickel (0.02% carbon maximum) is recommended. If the carbon content is higher than 0.02% and the material is held at temperatures above 455°C (850°F) for a prolonged period, graphite is said to form at the grain boundaries and produce a brittle structure. The suggestion has been made that some failures of stressed nickel in fused caustics and steam were due to this cause.

Failures of the nickel-copper alloy 40 in contact with hydrofluosilicic acid (H_2SiF_6) have been reported at temperatures up to 50°C (120°F). The resistance to cracking of nickel alloys 400 and K500, 301, 600, X-750, 85 Ni + 15 Cu, and nickel in hydroflouric acid vapor was investigated in the laboratory. U-bend specimens of the various materials were exposed over 48% hydrofluoric acid at 60°C (140°F). Materials were exposed in hot rolled, annealed, cold rolled, or aged conditions. The hot rolled 301 and the hot and cold rolled X-750 alloys did not fail before the experiment was terminated. The cold rolled and the aged 301 and the aged X-750 and other alloys in all conditions failed. Cracking in the annealed 400 alloy, in the cold rolled nickel, and in the age hardened 301 and X-750 materials were reported to be intergranular. It is interesting that cold rolling changes the crack path from intergranular to transgranular in the 400 alloy.

The 400 alloy has been used widely and successfully in hydrofluoric acid service. Failures have been reported[54] where the material was in contact with the acid vapor, air, and moisture, as would be expected from the results of the laboratory investigation. It has been recommended, therefore, that the 400 alloy for hydrofluoric acid service be kept totally immersed. In one application reported in the literature, the system was continuously flushed with nitrogen to prevent cracking.

A nickel-copper alloy 400 screen exposed in well water containing 5 ppm oxygen and 40 ppm carbon dioxide with a pH of 6.2 and Langelier index of -2.0, failed as the result of intergranular corrosion, most probably accelerated by stress The mechanism of failure was believed to have been selective

dissolution of copper at the grain boundaries and redeposition on grain surfaces. In some instances of failure of the 400 alloy in hydrofluoric acid vapor, copper is also reported to have been plated out.

The 400 alloy and the cupro-nickel alloys, 70 Cu + 30 Ni and 90 Cu + 10 Ni, containing high residual tensile stresses exhibit marked sensitivity to cracking when exposed to mercury or aqueous solutions of mercury salts. These failures are, of course, liquid metal embrittlement, a form of stress-corrosion cracking. They may occur, however, with no detectable evidence of the presence of mercury. In the event of apparently inexplicable stress-corrosion cracking of one of these materials in a closed system, the possible breakage somewhere in the system of a mercury thermometer or manometer should be investigated.

A newly developed, high-strength alloy "Multiphase" (35 Ni + 35 Co + 20 Cr + 10 Mo) is capable of exhibiting strengths as high as 300,000 psi. Although the general rule of thumb is that the stronger and/or harder the alloy the more susceptible it is to stress-corrosion cracking, this particular alloy has been shown to be highly resistant to this type of attack in seawater and marine atmospheres(54) which rapidly promote cracking in maraging and low alloy, high strength steels.

In general, nickel-base alloys, particularly Inconel 600, have found increasing use in high temperature water and steam, especially in nuclear reactor applications because of their better resistance to stress-corrosion cracking than austenitic stainless steels when chloride contamination is a problem. Resistance to cracking depends on the composition of the alloy as well as the environment. Thus, in studies simulating boiler water applications(54) (260°to 320°C, 40 to 300 ppm phosphate anion, pH 10 to 11; and 25 C, 0 to 500 ppm chloride anion, 0 to 8 ppm oxygen) Nickel 200, Inconel 600, Monel 400, Inconel X-750 and Hastelloy C did not crack in tests running for several thousand hours although the Nickel 200 and Monel 400 did pit. Incoloy alloys (e.g., 804, 825) in similar tests did crack, particularly at lower pH values, whereas Inconel 600 was resistant.

Nickel and nickel-base alloys have been shown to be resistant to corrodents known to initiate cracking of other alloys. For example, nickel alloys, even those containing copper, are resistant to nitrate solutions (which cause attack with low carbon steels) and ammonia solutions (which are responsible for season cracking with brasses). Nickel alloys are also resistant to sulfide cracking, which affects some steels, however, nickel corrodes readily in the presence of sulfur compounds at elevated temperatures, and the mechanical properties are affected. Failure in sulfur environments is because of the general corrosive attack, and not stress-corrosion cracking, although an exception to this statement may be the reported failure of Inconel 600 in sodium sulfide liquor.(54) Metallographic examination showed severe intergranular attack, however, carbides were present at the grain boundaries, and the material had been cold worked. Thus, failure may have been due to a form of galvanic attack, such as is found with weld decay.

5.8 Titanium and Titanium Alloys. Although titanium is an inherently active metal, it exhibits excellent resistance to corrosion. It is equal to or better than most metals in resistance to direct chemical corrosion by a

wide variety of chemicals, and is generally resistant to stress-corrosion, erosion-corrosion, galvanic corrosion, corrosion fatigue, and oxidation. Titanium is highly resistant to attack in various types of atmospheres and waters, even after long exposures. The corrosion resistance of the various titanium alloys has not been investigated as extensively as that of the commercially pure grades, because the development and availability of this metal is comparatively recent. Available data, however, indicates that the general resistance characteristics of titanium are not impaired by alloying.

When exposed to various types of atmosphere for extended periods, commercially pure titanium retains its luster.

The corrosive resistance of titanium is ascribed to a thick, stable, continuous film of oxide or adsorbed oxygen which readily forms at low temperatures in the presence of water vapor. As a result, the metal withstands reducing media and is more resistant to corrosion in the presence of oxidizing agents.

In general, titanium is almost unaffected by inorganic salts, organic reagents, and low concentrations (less than 5 percent) of inorganic acids. It is completly resistant to stress-corrosion when subjected to the common test reagents, although hydrobromic acid and red fuming nitric acid, especially at elevated temperatures, will lead to severe stress-corrossion. In those few instances where titanium is susceptible to corrosive substances (e.g., hot concentrated caustic solutions, molten NaOH) the rate of corrosion is usually severe and the action uniform. Titanium is completely resistant to aqueous solutions of ammonia irrespective of concentration and temperature.

Long term studies indicate that titanium in seawater and marine environments is resistant to pitting, stress-corrosion, galvanic corrosion, crevice corrosion, erosion, and corrosion fatigue. Titanium tested for effects of flowing seawater showed a thinning rate corresponding to 0.000075 cm (0.00003 inch) per year. No thinning could be detected in similar tests conducted in quietly moving seawater. In salt spray tests, titanium alloys were not attacked after exposure for 1000 hours. Even after severe testing for 60 days in rapidly moving seawater, titanium showed negligible attack. Testing under conditions which usually accelerate attack (stagnation in crevices, under fouling organisms, under moist salt crystals) failed to damage the metal.

The tensile properties of titanium alloys are generally unaffected by prolonged exposure to a marine environment. Tensile test specimens with yield strengths of 105,000 psi have withstood static loads of up to 80,000 psi in sea air for over 4 years without sign of failure. Specimens tested in seawater and in marine air maintained an endurance limit of 60,000 psi.

Titanium is probably one of the most corrosion resistant materials that can be utilized by the design engineer. However, titanium is relatively expensive and has certain basic limitations that have yet to be completely overcome. Information is continually being compiled on this relatively recently developed metal, and the design engineer is urged to consult other Government sources and data released by industrial and scientific groups.

The current specifications for titanium and titanium alloys are listed in Department of Defense Index of Specifications and Standards.

5.8.1 Galvanic Corrosion. Titanium is considered a noble metal in the same category as the passive stainless steels (see table III). When coupled with aluminum and zinc in acid solutions, titanium, like the stainless steels, does not form soluble corrosion products that can accelerate attack on these metals by a plating-out action. When coupled to titanium, accelerated galvanic attack of less noble metals is likely to result because titanium acts as an efficient cathode material. Under corrosive conditions, the coupling of titanium to a Monel may result in slight corrosive attack on the latter.

The resistance of titanium to corrosion, particularly galvanic corrosion, has certain limitations. With increasing temperatures, the thickness and permeability of the protective oxide film increases to the point where oxygen diffuses into the metal and produces embrittlement and corrosion. This tendency limits the use of titanium where high temperatures are encountered.

5.8.2 Pitting and Crevice Corrosion. As mentioned above, titanium is rarely susceptible to this type of attack, and examples of pitting and crevice corrosion have not been reported for seawater and marine environments.(55) Titanium is superior to stainless steels and cupronickels for applications where concentration cell corrosion situations may be encountered.

5.8.3 Stress-Corrosion Cracking. Because of their high strength to weight ratios and comparative inertness to most corrosive environments, titanium alloys have been considered for applications in which these properties will justify the cost of these materials. Stress-corrosion cracking was first reported in commercial titanium tanks and tanks made of the titanium + 8% manganese alloy (see Table XIV) used as containers for red fuming nitric acid. Cracking of a number of alloys in contact with chlorides at elevated temperatures (hot salt cracking) has been reported. Failures of titanium alloy tanks containing N_2O_4 and methyl alcohol have also occurred in the Appolo program. The use of titanium and its alloys in contact with either liquid oxygen or gaseous oxygen at cryogenic temperatures should be avoided, since either the presentation of a fresh surface (such as produced by tensile rupture) or violent impact may initiate a violent stress-corrosion reaction.

Stress-corrosion cracking of commercial titanium and also of the Ti + 8 Mn alloy was first reported in containers for red fuming nitric acid. Cracking occurred at room temperatures, but could be prevented if the acid contained less than 6.5%NO_2 and more than 0.7%H_2O.

Other failures pointed to the susceptibility of titanium alloys to cracking in contact with chlorides at high temperatures. For example, a welded tank constructed of the Ti + 5 Al + 2.5 Sn alloy developed stress cracks on being tested hydrostatically at 370° (700°F) with a chlorinated hydrocarbon as the pressurizing medium. Some of the hydrocarbon was believed to have broken down in the presence of moisture to form HCl.

In a second case parts formed from the same alloy and degreased in trichlorethylene frequently developed stress-corrosion cracks during subsequent heat treatment.

Some of the titanium alloys were considered for use in supersonic aircraft where at Mach 3 leading edges of wings might be heated to 260° (500°F). Hence, it became important to determine whether these alloys coated with a chloride, stressed, and heated to elevated temperatures would develop stress-corrosion cracks.

Extensive investigations(56) were carried out in a number of laboratories. Specimens were coated in various ways with ASTM salt, natural sea salt, and C.P. sodium chloride, and stressed at various elevated temperatures. There was general agreement from these experiments that most alloys would develop stress-corrosion cracks when coated with a chloride, stressed, and heated for 1000 hours at temperatures of 260°C (500°F) or higher. Cracking was generally found to be more severe in C.P. sodium chloride than in mixtures containing added salts. Cracking increased in severity with increased temperature.

While cracking occurred quite rapidly in a liquid eutectic mixture of LiCl and KCl melting at 355°C (670°F), cracking did not occur as readily in either of these salts separately as in CP grade NaCl. It has been suggested that cracking occurs because a liquid phase is formed at the contact of salt crystals with the titanium oxide, but, in spite of the results obtained with the LiCl-KCl mixture, this idea is not generally accepted. It is now believed that failure is the result of taking up hydrogen from the environment.

Oxygen or an oxide coating on the metal surface must be present for cracking to occur in the Ti + 8 Al + 1 Mo + 1 V alloy. There is a question as to the importance of moisture. Cracking has been reported under conditions where at most very small amounts of moisture are present.

Data obtained in one laboratory indicated that the Ti + 8 Al + 1 Mo + 1 V, one of the prime candidates for use in supersonic airplanes, was severely cracked when subjected to stresses of 50,000 psi at 290°C (550°). Another observer reports the Ti + 4 Al + 3 Mo + 1 V alloy to be the most resistant to hot salt cracking and the Ti + 5 Al + 2.5 Sn the least resistant.

There has been some experimental work in which the effectiveness of coatings in preventing hot salt cracking has been investigated. Anodizing does not appear to be helpful. Metal coatings of aluminum, nickel, and zinc have shown promise.

In other environments, cracking has occurred in tanks made of the Ti + 6 Al + 4 V alloy containing liquid N_2O_4. Various inhibitors have been tried to prevent this, and recently shot peening (with glass shot) of the interior surfaces of tanks before they are put in service has been recommended. This process puts the surface layer of metal in compression and reduces the probability of the initiation of stress-corrosion cracks which require tensile stresses.

The problem of failure of tanks made of the Ti + 6 Al + 4 V alloy and containing methanol is a serious one. It is stated that subcritical flaws 0.025 cm (0.01 inch) deep (too shallow to be readily detected by usual inspection techniques) in a tank wall can grow in methanol, even at relatively low stresses, to critical size with the result that the tank will fail.

TABLE XIV. Chemical Composition of Some Titanium Alloys Discussed in This Handbook.

(Composition given in nomainal weight percentages)

Alloy	Al	Cr	Mn	Mo	Sn	V	C[b]	Fe[b]	H[b]	N[b]	O	Other
75 A[c]	--	--	--	--	--	--	0.026	0.16	0.003	0.020	0.30	--
Ti - 0.15 Pd[c]	--	--	--	--	--	--	0.022	0.06	0.003	0.01	0.15	0.14 Pd
Ti - 5 Al - 2.5 Sn	4-6	--	--	--	2-3	--	0.15	0.5	0.20	0.07	--	--
Ti - 8 Al - 1 Mo - 1 V	7.3-8.3	--	--	0.75-1.25	--	0.75-1.25	0.08	0.30	0.015	0.05	--	--
Ti - 8 Mn	--	--	6.5-9.0	--	--	--	0.15	0.50	0.015	0.07	--	--
Ti - 4 Al - 3 Mo - 1V	3.75-4.75	--	--	2.5-3.5	--	0.75-1.25	0.10	0.35	0.015	0.05	--	--
Ti - 6 Al - 4 V	5.5-6.75	--	--	--	--	3.5-4.5	0.10	0.30	0.015	0.07	--	--
Ti - 13 V - 11 Cr - 3 Al	2.5-3.5	10-12	--	--	--	12.5-14.5	0.05	--	0.25	0.08	--	--

[a] Military specification, MIL-T-9046D, except as noted.

[b] Maximum values except for alloys 75 A and Ti - 0.15 Pd.

[c] Reference (55).

Commercial titanium sheet and Ti + 8 Al + 1 Mo + 1 V alloy sheet material stressed as U-Bend specimens will fail in methyl alcohol in the laboratory. One group of experimenters found that failures occurred much more readily in the vapor phase than when the specimens were immersed in the alcohol. Failures occurred after a much shorter exposure period in methyl alcohol than in any of the higher alcohols. The mechanisms by which cracking is initiated and propagates in titanium and its alloys exposed to hot salt, red fuming nitric acid, N_2O_4, and the alcohols is not understood at this time.

Using precracked specimens, a number of titanium alloys can be made to fail in chlorides or natural seawater in laboratory tests at ambient temperatures.(57) Bar specimens are notched, subjected to alternating stresses until fatigue cracks develop at the roots of the notches, and then loaded as cantilever beams. The notched and cracked regions are enclosed in plastic cups containing the corrodent. Data reported indicated that alloys containing aluminum with molybdenum, or molybdenum and vanadium were most resistant to cracking in seawater under these conditions than those containing aluminum with niobium, or niobium and tin. It has been suggested that hydrides of titanium form ahead of the advancing cracks and that failures are a form of hydrogen-stress cracking.

In recent works,(55) butt-welded specimens of the Ti + 13 V + 11 Cr + 3 Al alloy stressed to 75% of their yield strengths failed after periods of 35, 77, and 105 days exposure at the surface of the Pacific Ocean. The residual stresses induced in this same alloy by a 7.5 cm (3-inch) diameter unrelieved weld on a plate about 15 by 23 cm (6 by 9 inches) were sufficient to produce cracking after 181 days exposure at the surface, 402 days at a depth of 723 m (2370 ft) and 403 days at a depth of 2068 m (6780 ft) in the Pacific Ocean. Other alloys, 75A; Ti + 0.15 Pd; Ti + 5 Al + 2.5 Sn; Ti + 7 Al + 2 Cb + 1 Ta; and Ti + 6 Al + 4 V, containing similar welds were not susceptible to stress-corrosion cracking at the surface or at depth.

Chlorides and other halogens may be present in the environment from unexpected sources. Thus, sealants are used on fuel tanks in aircraft to prevent leaks at joints, and many of these sealants contain halogen radicals or hydrocarbons. In laboratory tests,(58) polyimide sealants were inert towards Ti + 8 Al + 1 Mo + 1 V; Ti + 6 Al + 4 V, and Ti + 13 V + 11 Cr + 3 Al alloys, and stress-corrosion cracking did not occur. However, fluorinated hydrocarbon and fluorinated silicon sealants caused cracking to occur, particularly for precracked specimens at temperatures of 177 to 316°C (350 to 600°F). The fluorinated hydrocarbon sealants were the most aggressive, and the beta alloy (Ti + 13 V + 11 Cr + 3 Al) was the most susceptible.

5.8.4 Erosion Corrosion and Corrosion Fatigue. Titanium exhibits excellent resistance against erosion corrosion and impingement attack, and has found application in condenser tubes and turbines, displacing conventional iron and nickel alloys. Titanium has good resistance against corrosion fatigue also, and failures occur very infrequently. The fatigue limit for titanium wetted with seawater is very similar to the value obtained in air, which is about half its tensile strength.(59) Valve springs and plates of titanium are often used in compressors because of this corrosion characteristic.

5.9 Zinc and Zinc Alloys Zinc maintains relatively good surface stability when exposed to natural environments, particularly atmospheres of various types. In the Electromotive Series, zinc is listed just below aluminum. In the Galvanic Series, zinc is ranked between aluminum and magnesium. Thus, zinc is anodic to many metals (see tables I and III). Zinc is used structurally in the unalloyed or alloyed forms and as a coating for steel. Commercial zinc is utilized largely in sheet form, while the alloys are usually in the form of die castings. As a coating for steel, zinc provides protection in two ways: (1) it acts as a mechanical barrier against the environment, and (2) since zinc, when coupled to iron, is anodic, the zinc protects the steel by galvanic action at breaks or discontinuities in the coating.

Zinc and its alloys may be fairly resistant to atmospheric exposures. The rate of attack will vary depending on the type of atmosphere, contaminants present, the nature of the film formed, and similar metal-environmental factors. In general, the rate of attack is lowest in dry rural atmospheres and becomes higher, proceeding from marine to semi-industrial and industrial atmospheres. Time of wetness is an important parameter in determining the extent of corrosion.

Zinc coatings, galvanized or plated, behave much the same as commercial grade zinc in their resistance to a corrosive atmosphere, except as limited by the coating thickness. The rapid attack of zinc and zinc coatings in industrial atmospheres is due to the presence of sulfur dioxides, which increases the acidity of any moisture condensed on the metal. Tropical marine climates are not as destructive as temperate marine atmospheres. Zinc and zinc alloys characteristically develop a dark gray color on prolonged atmospheric exposure.

Corrosive attack on zinc and zinc coatings is ordinarily uniform in all types of atmospheres. Deep pitting is rare. In particularly corrosive environments, the durability of a zinc coating on steel depends primarily on its thickness and uniformity. The method of application (whether hot dipped or electroplated) apparently does not modify resistance characteristics.

In ordinary indoor exposure, zinc tarnishes slowly with the formation of a dulling film. The extent of dulling or of corrosion is affected by the humidity in the surrounding air. For a given locality or climate, the life of a zinc coating exposed indoors may be as much as five times longer than that of a similar coating exposed outdoors.

The corrosion of zinc and zinc coatings in natural water varies considerably according to the salts and gases carried in the water. The rate of corrosion in water, in general, is much lower than that of iron. However, the presence of oxygen, carbon dioxide, elevated temperatures, strong aeration, and agitation will increase the rate of attack. The corrosion of zinc is accelerated in strongly acid or alkaline solutions, but becomes relatively low in the pH range of 7 to 12.5. Increasing concentrations of oxygen result in higher corrosion rates, and very low oxygen concentration such as found in stagnant water will initiate pitting. Hard water is usually less corrosive than soft water. Zinc coatings have been widely used in the piping and containers of water supplies, but rolled zinc and zinc die castings are less commonly used in contact with water, especially hot water. Zinc castings should not be used in continuous contact with steam.

Both zinc and zinc alloys may corrode in some types of soils. Strongly alkaline soil, with high chloride content, and high acid content soil exert more rapid attack than neutral soils. Nevertheless, zinc coatings provide corrosion protection for steel and are the coatings used most extensively for underground coating applications. With steel gas and water lines, the results have been good. In contrast, bare steel may corrode from three to six times faster than galvanized steel in certain soils. The degree of protection is generally proportional to the thickness of the zinc coating. Zinc anodes are also used in the protection of steel ship hulls and similar applications.

When zinc is attacked, corrosion is primarily direct uniform chemical attack or pitting. Waterline and ground-line surfaces, as well as submerged sheeting, are vulnerable. But the pitting that may be characteristic of submerged zinc sheets does not appear on submerged galvanized steel sheets. Stress-corrosion cracking and corrosion fatigue are rare.

The corrosion rate of zinc is not appreciably affected by variations in composition, although antimony in amounts of 0.03 to 0.07 percent may result in increased atmospheric corrosion. Normal impurities in zinc and zinc coatings will not impair resistance. Copper added in amounts of less than 0.06 percent will often increase corrosion resistance, while variations in the content of lead, cadmium, and iron have no significant effect.

Corrosion resistance of zinc is improved by the use of a chemical or electrolytic treatments.

When zinc or zinc coatings are confined in atmospheres in which organic vapors can accumulate, rapid corrosion of the zinc surfaces can occur. Organic materials which liberate gaseous constituents or degradation products, such as halogens, some sulfur containing vapors, phenolic, ammoniacal, and ester compounds can prove highly damaging. Hydrogen chloride from vinyl resins, sulfur oxidation products from sulfur bearing resins, phenolic constituents from molded phenolic resins, ammoniacal vapors from molden resins and from certain vapor phase corrosion inhibitors employed for steels, and esters or organic acid vapors from plasticized resins such as plastic wire coverings and plastic insulating materials have been known to attack zinc. Therefore, use of zinc in closed spaces with organic materials requires taking precautionary steps to preclude such attack of zinc.

The current specifications for zinc and zinc alloys are listed in Department of Defense Index of Specifications and Standards.

5.9.1 Uniform Corrosion. On a microscopic scale, impurities in zinc greatly affect the corrosion rate. For example, pure zinc is attacked slowly in dilute sulphuric acid, but impure zinc is attacked readily, displacing hydrogen gas. When ordinary commercial zinc is placed in dilute acid, at first it corrodes slowly, but as attack proceeds, the impurities (e.g., lead and tin) are reprecipitated on the surface, which accelerates the rate of attack, particularly as the surface area is increased and the individual corrosion sites become less polarized. Some impurities (e.g., aluminum) may help to slow the rate of attack by helping to form protective films.

5.9.2 Galvanic Corrosion. On a microscopic scale, galvanic corrosion couples can be set up, as for most of the other common metals. However, as mentioned above, in some circumstaces, this property is used with beneficial results. The technique is known as cathodic protection, and the zinc is referred to as a sacrificial anode. Originally, zinc anodes were attached to the copper-sheathed hulls of ships and an electrical connection made.(60) Remembering that material is only lost at anodic sites (see Paragraph 3.1) the copper cathodic areas are protected from attack. With material of suitable purity and composition, the zinc will corrode slowly and uniformly, conferring protection in the presence of the electrolyte. When all the zinc (alloy) has been consumed, new sacrificial anodes are installed. The technique is effective because zinc is a readily available, inexpensive, easily fabricted metal with suitable electrochemical properties. Of course, nowadays, the main use is as sacrificial anodes for ferrous materials and structures. About 11 to 12 kg (24 to 26 lb) of zinc will cause a corrosion current flow of 1 Ampere per year, and the size (area) of the structure which will be protected by such a current flow can be calculated. Although the current flow is appreciable, the associated driving potential difference is less than 250 mV, hence, zinc is suitable in electrolytes of low electrical resistivity such as seawater, but large structures in a highly resistive environment (e.g., buried underground) may be more practically protected by sacrificial anodes of magnesium alloys. Cathodic protection will be further discussed in Paragraph 6.3.3.

5.9.3 Crevice Corrosion. Various examples of this type of corrosion attack (e.g., crevice corrosion, water-line attack in seawater) have been described. If a newly prepared zinc surface is allowed to stand with large droplets of water on it, such as dew, in a closed place, a differential aeration cell can form between the edges and the centers of the drops. A porous form of zinc oxide gradually builds up which, in combination with carbon dioxide in the air, forms a basic carbonate known as "white rust". This type of attack can be prevented by storing the zinc in a dry environment not subject to wide temperature fluctuations in order to build a protective layer of corrosion products. Alternatively, the zinc surface may be coated with oils or lanolin, or given a chromate treatment.

In stagnant solutions containing dissolved oxygen, usually the protective corrosion products are not formed over the entire surface, leaving particles of bare zinc. These patches are anodic with respect to the products and local attack occurs, resulting in pitting. One reason suggested for this behavior is that parts of the surface are shielded from the dissolved oxygen by particles of corrosion product which have fallen there, resulting in a form of deposition corrosion. By making oxygen access uniform over the whole surface (e.g., by agitating the zinc, or stirring the solution) a protective layer of zinc hydroxide is formed over the entire surface, and pitting attack is avoided.

5.9.4 Stress-Corrosion Cracking. Zind and zinc-rich alloys are usually considered not to be susceptible to stress-corrosion cracking and corrosion fatigue. Copper-based alloys containing up to 30% zinc are discussed in Paragraph 5.3.6.

5.10 Miscellaneous Metals and Alloys. In this section, the corrosion properties of some less common metals and alloys will be presented only briefly because of their relatively limited engineering applications. The refractory metals molybdenum, tantalum, tungsten, and zirconium; the noble metals, gold and silver; and some electrodeposits used to confer corrosion resistance, such as cadmium and chromium, will be discussed.

5.10.1 Refractory Metals. Refractory metals are those having very high melting points (greater than 1925°C) and which are capable of retaining structural strength at high temperatures. Three major refractory metals of principle interest in industrial applications are molybdenum, tantalum, and tungsten. These metals and their alloys, when unprotected, resist corrosion by many environments at ordinary low temperatures and resist oxidation up to certain elevated temperatures (approximately 315 to 540°C depending on the metal).

Molybdenum has good resistance to hydrofluoric and hydrochloric acids under practically all conditions, providing oxygen or oxidizing agents such as hydrogen peroxide, nitrates and chlorates are not present. It has good resistance to sulfuric acid except at high concentration and high temperature. It is tarnished by exposure to the atmosphere and also by exposure to fresh and salt water. Alkaline solutions in presence of oxygen or oxidizing agents are corrosive to molybdenum. Molybdenum is not suitable for continued service at temperatures above 500°C (930°F) in an oxidizating atmosphere, unless protected by adequate coatings.

Tantalum is highly resistant to most acids, chemical solutions and organic compounds. It is not resistant to hydrofluoric acid and hot concentrated phosphoric and sulfuric acids. Resistance to alkali attack is satisfactory only when the alkalies are weak as in dilute solution. Tantalum oxidizes slowly in air above 300°C (570°F). In oxygen, and at a temperature of 350°C (660°F) tantalum suffers severe embrittlement. Natural fresh water and seawater have no action on tantalum. Tantalum has excellent resistance to salt solutions.

Tungsten resists attack by most dilute acids and alkalies at room temperature, and is attacked only slightly by concnetrated acids at room temperature. It is rapidly attacked by hot concentrated acids and also by hot alkali, especially if oxidizing agents are present. It suffers no attack from the atmosphere at room temperature or from hot or cold water. Tungsten corrodes during prolonged storage with phenolic materials if sufficient moisture is present. It does not oxidize appreciably in air below 595°C (1100°F) or in oxygen below 510°C (950°F).

Zirconium and zirconium alloys primarily have found application in nuclear reactor applications, but also in the chemical industries for small, but vital pieces of equipment (e.g., value stems, floats in rotameters, small heat exchangers). Cost is a deterrent to more widespread application. Like titanium, zirconium relies on the formation and subsequent integrity of a surface layer, usually an oxide, for its corrosion resistance. However, it is resistant to concentrated non-oxidizing acids and especially alkalies at elevated temperatures, and ranks second to tantalum in resistance against hydrochloric acid. It is only slowly attacked by fused alkalies and liquid sodium. Corrosion resistance in mineral acids is good except when chlorides

are present. Attack is rapid in neutral sodium chloride solution if an anodic potential of 2 volts is applied,(59) otherwise dilute metal chloride solutions are not very corrosive. Zirconium is not considered resistant to hydrofluoric acid; aqua regia or hot, concentrated nitric or chromic acids. It is resistant to attack by a wide range of organic acids except at elevated temperatures if chloride anions are present.

There are a few accounts of stress-corrosion cracking of zirconium.(61) In general, zirconium is expected to fail in the same types of environment responsible for failures with titanium. The first account of these was reported to have been produced in material containing about 1250 ppm of oxygen and lesser amounts of iron and other elements. The material developed stress-corrosion cracks when exposed in a 10% solution of $FeCl_3$ and subjected to stresses of more than one-half its yield strength of approximately 39,000 psi. The susceptibility of the metal apparently did not depend on whether it had been cold rolled, hot rolled, or vacuum annealed.

Other workers reported stress-corrosion cracking in zirconium in contact with methyl alcohol containing HCl, H_2SO_4, or HCOOH. They also reported cracking in ethyl alcohol containing HCl. Cracking could be prevented in a 0.4% HCl-methyl alcohol solution by the addition of 3% of water as an inhibitor. A stress-relief anneal at a temperature above 450 C ($\sim$ 850°F) to remove high residual stress was recommended to prevent cracking in these solutions. Cracking has also been reported in iodine containing environments.(11)

Zirconium, like tantalum and titanium, will readily absorb hydrogen over a wide range of temperatures, to form brittle hydride phases. Hydrogen embrittlement (hydrogen-stress cracking) is, therefore, possible with these metals.

5.10.2 Noble Metals. In general, the noble metals exhibit an excellent resistance to corrosion, particularly at elevated temperatures when base metals would be rapidly oxidized. Usually, the resistance can be attributed to the inert chemical nature of the metals, even though very thin oxide films may be present on the surface. However, the presence of a protective film is necessary for silver and its alloys to be resistant in hydrochloric of hydrobromic acids. Because of their relatively high cost and poor mechanical properties these metals are used mostly as coatings on suitable supporting materials. Exceptions are the use of silver and platinum for specialized applications in the chemical and petroleum industries.

The earliest report of stress-corrosion cracking in any material was in a gold-copper-silver alloy. Occasional reports of stress-corrosion cracking failures in gold alloys have appeared in the literature but most investigations have been theoretical.

In an early symposium, stress-corrosion failures of bridges and nose pieces of eyeglasses and also of 10K solid gold eyewire (that part of the eyeglass frame that holds the lens in place) were reported.(61) Failures were believed to be due to chlorides in perspiration. It has been shown that stress-corrosion cracking of gold alloys containing up to about 40 atomic percent of gold can be produced in ferric chloride solutions in the

laboratory. The gold-silver-copper alloys (green, yellow, and red golds) of the compositions most used for jewelry are the compositions that are most susceptible to stress-corrosion cracking.

5.10.3 Electrodeposited Coatings. Electroplating is the deposition of one metal upon a conductive surface, usually another metal, or metallized nonconductor, by the process of direct current electrolysis. Some applications are for decorative purposes, others for protection against corrosion, some may combine both these desirable characteristics. In this section, the concern is primarily with metals electroplated on other metals for corrosion protection purposes.

The largest percentage of commercial plating is applied to iron and steel; however, copper, brass, nickel-brass, zinc, zinc-base die castings, aluminum, and other metals are also plated. The metals normally used for plating include zinc, cadmium, chromium, copper, nickel, tin, lead, gold, silver and their alloys. The properties of zinc, copper, nickel, and lead presented in earlier paragraphs pertain also to these electroplates. The properties of cadmium, chromium, tin, gold, and silver are presented below.

While corrosion resistance is a major function of electroplated coatings, it is not the sole reason for their use. Such coatings may also be applied to improve appearance, hardness, electrical and other properties.

Electrodeposited coatings that are continuous and nonporous have about the same resistance as the wrought metals of the same composition; however, most electrodeposited coatings are more or less porous and accordingly may not afford complete protection. Porosity in electroplates is greatly reduced after a few micrometers (few tenths of a mil) are deposited. Cracking may be promoted by applying excessively thick deposits.

The protective characteristics of cadmium plate are very similar to those of zinc (see Paragraph 5.9). It is satisfactory for almost all types of atmospheric exposure except industrial air containing sulfur compounds. Zinc coatings are more resistant to industrial atmospheres than cadmium but cadmium is more resistant in sea spray and alkaline solutions.

Chromium plate has excellent corrosion resistance. It remains bright in the atmosphere because a thin, transparent oxide layer forms on the surface. This prevents further oxidation of the underlying chromium metal. However, chromium plate generally is very porous, and at these pores it actually promotes corrosion of the base metal. This attack, however, is not entirely detrimental because many very small pits are formed as opposed to a few large pits which could penetrate the underlying metal. Chromium is used extensively in heavy deposits for wear resistance, low coeffient of friction, resistance to corrosion, greater hardness, and heat resistance. It is particularly resistant to erosion-corrosion and abrasion, providing protection from chemical (except chlorides) attack in the surrounding medium. Chromium is also used to provide an attractive surface finish and to increase the dimensions as well as the resistance of undersize or worn parts.

Tin electroplated coatings are used primarily on steel sheet which is formed into containers, since tin is resistant to food and beverages. However, its protective value against exposure to weather is poor unless the

tin-plate is painted. Tin is cathodic to steel, and localized attack of the underlying metal will occur at pores or discontinuities in the coating. Tin-plate is also used to impart solderability to electrical equipment, as an anti-seize coating, and as a stop-off during nitriding.

The precious metals, gold and silver, have limited application as plates for corrosion resistance on articles normally used for military purposes. Silver and gold plate are principally used for imparting specific electrical properties (e.g., r-f shielding), specific emmissivity or reflectivity, and improved solderability. Corrosion resistant properties are generally sought from thicker deposits of low porosity.

Silver tarnishes readily in atmospheres containing sulfur compounds, but this has little effect on its electrical conductivity except in low voltage electrical contacts. Gold does not tarnish in the atmospere. Under high potentials and humid atmosphere, silver may migrate across insulators and cause short circuits. Silver preplate under gold, under conditions of high temperature use, may diffuse through the gold plate and result in surface tarnishing.

When gold or silver electroplates are used for both decoration and protection, they are usually applied over copper or nickel, and the noble metal plates should be virtually free from pores or pinholes. Otherwise, in the presence of an electrolyte, there would be intense galvanic action betwen the gold or silver and the basis metal due to the large potential difference between them.

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SECTION 6. PREVENTION OF CORROSION

6.1 Types of Protective Measures. In this Paragraph, the various forms of corrosion prevention and protection against corrosion, will be discussed. As suggested in Paragraph 2.3, in analyzing and correcting a potential or existing corrosive situation, few principal approaches can be used: (1) alternate or substitute materials may be considered where the originally specified metal cannot withstand the environment, (2) the environment may sometimes be changed to render it less aggressive, e.g., by adding a corrosion inhibitor, or applying cathodic protection, (3) modification of the original design, to avoid moisture traps and highly stressed regions may sometimes be possible, and (4) protective coatings can be provided to prevent access of the corrodent or to separate dissimilar metals. These few approaches are described below, followed by some general recommendations for protective measures against common types of corrosion attack.

6.2 Substitution of Materials. In the individual treatment of metals and alloys in Paragraph 5, numerous examples of alloy development to improve corrosion resistance were given. A few additional examples will be given here. It should be remembered that in the selection of any metal for a given application, a compromise is usually necessary between: (1) chemical properties, (2) mechanical properties, (3) toxicity (safety precautions), (4) cost, (5) availability, and (6) ease of fabrication. Quite often a material that corrodes will be selected for service in a given environment in order to meet criteria (1), (2), (3), (5) and (6) above, provided that the rate of corrosion is slow enough to meet the life requirements, and the nature of the attack is such that it does not cause an appreciable change in the mechanical properties. In this respect, uniform attack is preferred, while localized attack or attack leading to cracking or abrupt failure is to be avoided. Sometimes, a less expensive metal can be selected for an application provided it is given a protective coating. This approach is discussed in Paragraph 6.1(4). Some preventive maintenance may be necessary with this approach, but often the economics are more favorable than a significantly higher capital outlay for materials of construction which will not corrode.

Substitution by metals or non-metals, such as glass or plastics, is usually most frequently encountered and publicized in cases where dramatic failures have occurred, and health is endangered directly, but also indirectly when failure did not occur (e.g., toxic metals entering foodstuffs or potable water). As an example, consider failures which result from stress-corrosion or hydrogen-stress cracking. Once a failure has been diagnosed as due to stress-corrosion cracking, frequently, replacing the material with one known to be immune in the environment is an easy solution. This change requires that the substitute material have the desirable characteristics of the original material, is resistant to stress-corrosion cracking, and can be justified economically.

An example of this is the use of high nickel alloys in place of the austenitic stainless steels in reactors. Failures at high stress levels have been reported in these materials exposed under reactor conditions, and it has been suggested that service failures have not developed because these alloys are used at relatively low stress levels.(62-64)

An interesting example of substituting a relatively immune material for one subject to stress-corrosion cracking was in automobile stoplight receptacles. These were deep drawn of 70 Cu + 30 Zn cartridge brass and were installed without annealing. Some of them developed stress-corrosion cracks which prevented the light from operating. The problem was solved by deep drawing the receptacles from a 90 Cu + 10 Zn brass that was much more resistant to stress-corrosion cracking than the 70/30 alloy.

Cast iron and nickel tanks have been suggested to replace welded steel tanks as containers for hot concentrated caustic solutions.(65)

In Europe there is a trend toward the use of stainless steels in the production of potassium, ammonium, sodium, and calcium nitrates. Low-carbon steels are particularly susceptible to stress-corrosion cracking in hot concentrated ammonium and calcium nitrates. The cost differential is a factor in this trend, and some plants are reported to be using a low-alloy 2-4 Cr + 0.9 Al steel that is less susceptible to cracking than the low-carbon steels and less expensive than the stainless steels.

6.3 Modification of the Environment. Protection against corrosion attack, or decreasing the rate of corrosion attack, can be accomplished in two ways, which are best explained by referring to figure 1. This figure shows that in order for corrosion to occur, there has to be an anode, a cathode, an electrical conductor, and an electrolyte forming a continuous path for the corrosion current. If one of these components is removed, such as the electrolyte, then corrosion cannot take place. The other possibility is to interpose a barrier between two or more of the components to impede or halt the electron transfer, hence, corrosion current. The barrier can physically affect the corrosion rate if it is a coating, for example, or the barriers can be induced electrochemically by a modification of the surface potential of the anode or cathode through the use of an external source of current (e.g., cathodic protection). In this section, both types of approaches will be discussed, with the exception of coatings acting as physical barriers. Coatings are discussed in Paragraph 6.5.

6.3.1 Modifying the Electrolyte. Ideally, if the electrolyte component can be removed from the environment, then corrosion cannot occur. Unfortunately, for many applications this cannot be done because equipment is used to contain various types of solution, or is immersed in solutions, such as seawater, in its normal operating mode. In some circumstances, however, in atmospheric environments it will be possible to control the relative humidity. If the water vapor is removed, or lowered and the temperature not allowed to fall below the Dew Point, water cannot condense to form droplets on a metallic surface, and provide an electrolyte path. It will also be desirable to ensure that no hygroscopic or deliquescent particles (e.g., dust, salt) are present on the metal surface to retain moisture. The control of relative humidity (RH) is only successful in closed environments. The approach taken to reduce the RH to 50 percent, or lower, will depend on the volume under consideration. For small volumes, such as packages, shipping containers or storage cabinets, dessicants will suffice, however, for larger volumes, moisture is extracted by condensation, or the enclosure is heated, along with incoming air, to be above the Dew Point. Common dessicants are silica gel, activated alumina, and calcium oxide (quicklime). The latter is less easy to handle but is relatively less expensive.(66) With either approach, the container or enclosure walls must be effective moisture barriers in order to maintain the desired level of RH.

In situations where bulk aqueous solutions are present then controlling the pH and the dissolved oxygen content will serve to modify the corrosion rate. For metals (e.g., steels) which depend on impervious surface oxide films, the level of dissolved oxygen should be high, the pH high, and the chloride (or other agressive anion) concentration low. For other metals (e.g., copper) the presence of dissolved oxygen, in acid solutions particularly, can lead to increased rates of anodic dissolution. Further, details are given for individual metals in Paragraph 5. In those sections will also be found a discussion of the effects of temperature. In general, as the temperature rises the rate of corrosion increases. However, the effect of temperature changes on the solubility of dissolved gases must also be considered. For example, in an open system, where oxygen is free to escape, the corrosion rate of steel in water is a maximum at 80°C (176°F), and decreases rapidly above this temperature, as the oxygen is driven off.

Controlling the degree of agitation or speed of electrolyte flow can also influence corrosion behavior or rates. Differential aeration cells can be largely avoided in agitated or flowing electrolytes, provided the system has been well designed to avoid blind corners and crevices. On the other hand, rapidly flowing solutions, especially those containing particulate matter or entrained gas bubbles, can accelerate certain forms of corrosion attack such as erosion-corrosion, impingement attack and cavitation. Slowing the rate of electrolyte flow, filtering out particulate matter and removing dissolved gases all will be beneficial in reducing the rate of corrosion for these types of attack.

Removal of specific corrodents in a solution is a method of reducing corrosion attack in general, but is especially important where stress-corrosion cracking can occur. Often, removal is difficult, but nevertheless sometimes possible in closed systems where the specific corrodent has been identified. In reactors, it has been shown that at high temperatures water containing as little as 1 ppm of both oxygen and chloride can produce cracking in austenitic stainless steels. If, in a closed system, the oxygen and chloride contents can be kept in parts per billion, cracking should be avoided.

In several instances, limits have been placed on the amount of a suspected corrodent that could be tolerated in a given environment without producing stress-corrosion cracking: for example, the amount of air that could be tolerated in agricultural ammonia, and the amount of NO_2 in red fuming nitric acid. In these instances, it was specified that a minimum amount of H_2O should also be present. The water in this case could be an inhibitor.

One of the simplest cases of eliminating the active corrodent was the requirement that cleaning solutions for titanium alloy machined parts to be subsequently heat treated be free from chlorine in any form.

If cracking of Monel in hydrofluoric acid service is to be avoided, it must be kept submerged at all times; that is, air and oxygen must be eliminated. This is sometimes accomplished by purging the acid with nitrogen.

In a closed system, the pH of the effluent can sometimes be changed to prevent stress-corrosion cracking.

Control of the pH of the environment where possible has been particularly successful in copper-base alloys. A problem of stress-corrosion cracking in admiralty metal (Cu 71 + Zn 28 + Sn 1) in a refinery was solved by maintaining the pH of the material being processed in the range of 8 to 8.5.

The recommended method for preventing damage to stainless steel and high nickel alloys from polythionic acids in refinery service during shutdown is first to neutralize the acid. Where oxygen in the air is an important factor in the stress-corrosion cracking of a metal, preventing the contact of oxygen with the surface by blanketing it with nitrogen has proved an effective method of preventing corrosive attack. This technique has been used, following the neutralizing of any acid present on the surface by washing it with water containing ammonia, in preventing the polythionic acid cracking of austenitic stainless steels and high nickel alloys in refinery units during the time they are not in use.

6.3.2 Corrosion Inhibitors. Metals that do not naturally form protective coatings or films under ordinary service conditions may be protected in aqueous environments by the use of inhibitors. An inhibitor may be defined as a chemical or mixture of chemicals which can be added to an environment, usually in small quantities, that will decrease corrosion. An inhibitor should be clearly differentiated from a passivator which is a special form of inhibitor that produces a relatively thin and inert film on the metallic surface, causing the metal to behave as a more noble metal.

Inhibitors are classed as anodic or cathodic, according to their effect in retarding the anodic or cathodic reaction of the particular corrosion process. If added in sufficient amount to the corrosive medium, anodic inhibitors may stop corrosion completely. But if an insufficient amount is added, the rate of attack may be accelerated, compared to the uninhibited system. Apparently, the inadequate amount serves to increase localized corrosion and results in severe pitting. Copper, for instance, may be protected from general attack by such inhibitors, but these substances often markedly increase the rate of stress-corrosion cracking when used improperly. Cathodic inhibitors are not as efficient as anodic type, but they are safer to use. They are less likely to stimulate attack when added in insufficient quantity.

Inhibitors may be employed in various ways. They may be used to form conversion coatings and to seal the pores of these coatings. Also, they may be incorporated in a priming paint, sealing compound, or insulating material. As indicated above, inhibitors introduced by application to the metal to render the metal more cathodic are classed as passivators. When inhibitors are added to the environment, they similarly protect the metal by initiating the formation of a protective film on the metal, but the process of protection is not the same. A passivator may cause the metal to behave as a more noble metal, while the general inhibitor produces a film that acts more or less as a simple barrier against the corrosion medium. The addition of an inhibitor to a completely aqueous recirculating system, as for example automobile radiators and engine blocks, may decrease corrosion sharply. The type of inhibitor that is most effective is normally specified for a particular metal or alloy in a given medium.

There are a number of anodic inhibitors which react to protect ferrous and nonferrous metals in aqueous systems. Some of the more common types are soluble chromates, phosphates, carbonates, sulfonates, naphthenates, amines, nitrates, borates, silicates, and hydroxides. By acting to form or restore a protective film on the metal, these substances increase anodic polarization. Salts of zinc, magnesium, or nickel may function as inhibitors with steel that is aqueous media. Various other metals and alloys including aluminum, magnesium, copper, brass, lead, zinc, and galvanized products may also be protected under some conditions by specific inhibitors. Manufacturers' data, Government specifications, and test reports often provide information on the use of inhibitors in specific circumstances.

Priming paints for metals ordinarily contain inhibitors or passivators. Zinc chromate pigment also is extensively used as an inhibitor. This substance is somewhat soluble in water and the moisture which diffuses through the paint film brings about a concentration of chromate ions at the metal surface, thus passivating the metal. The most widely used corrosion-inhibiting pigments are compounds of lead or zinc. For use with steel, red lead is commonly compounded in primers to inhibit anodic solutions. Zinc chromate, iron oxide and basic lead silico-chromate primers are also used extensively. Other inhibiting primers may also include zinc tetroxy chromate, strontium chromate, zinc dust and zinc oxide.

A class of materials, mostly long chain nitrites, which volatilize and sublime slowly at ordinary temperatures are known as volatile corrosion inhibitors. When a material of this type is used in a closed container or package, the sublimed vapors form a film on the enclosed item. The sublimed film has the effect of preventing formation of rust on iron or steel surfaces, even in the presence of high humidity. The VCI's are usually introduced into the closed space in the form of a loose powder or may be held in a suitable carrier such as paper or fiberboard. In some applications, the inhibitors are impregnated in transparent, flexible plastic film. The VCI carrier in other applications is a petroleum base oil for use in closed systems such as interior engine surfaces, hydraulic systems and transmissions.

The military services utilize VCI's primarily in the packaging and storage of ferrous and aluminum items. Parts, subassemblies, and assemblies containing zinc plate, cadmium, zinc base alloys, magnesium base alloys, lead base alloys, and alloys of other metals (including solders and brazing alloys) containing more than 30.0 percent zinc and 9.0 percent lead must not be packaged with VCI's. Direct contact of VCI with nonferrous metals, except aluminum and aluminum base alloys, must be avoided unless specific permission is granted. When packaging assemblies consisting of metallic and non-metallic parts, additional limitations on the use of VCI's must be observed. For example, when the metallics are to be used with or near certain plastics, natural or synthetic rubber, painted or similarly coated surfaces, the contractor must furnish proof that the VCI is compatible with the non-metallic material in accordance with requirements of the applicable specification. Unless otherwise notified, the VCI's are not to be used to protect assemblies containing optical systems or precision moving parts which have already been coated with a preservative or lubricant. The VCI's are classed as preservative P-18 in Specification MIL-P-116. Specification MIL-I-8574 covers utilization of the volatile inhibitors and constitutes an expansion of MIL-P-116.

Some of the various types of volatile corrosion inhibitors used in the military services are presented in table XV.

Unfortunately, recent emphasis on environmental protection has focused on an undesirable aspect of corrosion inhibitors, namely most are objectionable from a point of view of contaminating the environment. Many inhibitor formulations contain compounds of lead or zinc or contain polyphosphates, chromates, nitrates, benzotriazoles, mercaptobenzothiazoles, ferrocyanides and phosphonates, to name some of the most common. Some of these chemicals are toxic, whereas others are undesirable (e.g., phosphates) because they are nutrients for biological growths, which cause other undesirable problems.

Effluents containing appreciable concentrations of chromates should not be directly discharged into surface supplies, such as streams or lakes. Chromate can be removed by chemical reduction with ferrous sulfate, sulfur dioxide, sulfurous acid or its salts, followed by separating out alkaline solution the resulting chromium hydroxide. Another method is to use an ion-exchange bed to selectively remove the chromate ions. The chromate can be released, and the bed regenerated at periodic intervals. Cyanides must be removed, not only because they are toxic, but also because they interfere with the effective precipitation of other metals such as copper and zinc. Cyanide is destroyed by oxidation treatments, usually with ozone, chlorine or hypochlorite before precipitation treatments. The hypochlorite may be generated electrolytically, so may the ozone.

Polyphosphates and phosphates in theory are more easily removed by precipitation with lime, alum or iron salts, or by adsorption on activated alumina, or sludge floc (from sewage treatment plants). However, work still needs to be done to optimize these procedures.

Lead can be removed by precipitation as the sulfide, followed by filtering. Zinc is permitted at levels of up to 5 mg/l in potable waters but is toxic to some fish at levels of 1 mg/l or less. In normal operations the zinc level in inhibitor treatments is often below 1 mg/l, and only temporarily found in the range of 2 to 3 mg/l for new systems where protective films need to be built-up. In the event that the zinc has to be removed, this can be accomplished by adsorption on calcium carbonate or silt.

Procedures for removing other contaminants are similar to those employed in the Meal Finishing (Electroplating) industry, for which the Environmental Protection Agency will issue guidelines for effluent limitations. New techniques being investigated to remove contaminants from process waters include electrodialysis, reverse osmosis, ion flotation and freezing.

Much of the current research work relating to corrosion inhibitors is directed towards formulating innocuous inhibitor treatments, capable of being easily disposed when necessary, and being economical to use. Treatments have been proposed for cooling water applications, for example, which do not include chromates. The inhibitor formulation consists of a mixture of polyphosphate, orthophosphate, and phosphonate salts, with an organic polymeric dispersant sometimes added.(91) Such a treatment will only work if the carbonate content of the cooling water is above 25 ppm minimum, and preferably above 100 ppm, and also if larger quantities of biocidal agents, such as chlorine or acrolein, for example, are present. The biocidal agent itself should not be an environmental contaminant.

TABLE XV. Listing of Specifications for Volatile Corrosion Inhibitors

Specification Number	Title
MIL-P-3420	Pakcaging Materials, Volatile Corrosion Inhibitors, Treated, Opaque
MIL-I-8574	Inhibitor, Corrosion, Volatile, Utilization of
MIL-F-22019	Film, Transparent, Flexible, Heat Sealable, Volatile, Corrosion Inhibitor Treated
MIL-B-22020	Bags, Transparent, Flexible, Heat Sealable, Volatile Corrosion Inhibitor Treated
MIL-I-22110	Inhibitors, Corrosion, Volatile, Crystalline
MIL-I-23310	Inhibitors, Corrosion, Volatile, Oil Type
MIL-L-46002	Lubricating Oil, Contact and Volatile Corrosion Inhibited

Stress-corrosion cracking occurs under conditions where corrosion is almost, but not completely, inhibited. Hence, an inhibitor may do more harm than good when used to prevent stress-corrosion cracking. Nevertheless, attempts have been made to use inhibitors to prevent stress-corrosion cracking.

The possibility of using inhibitors to prevent chloride stress-corrosion cracking of austenitic stainless steel in high temperature water has been widely investigated. At a pH of 6.5 and temperatures of 200 to 300°C (340 to 570°F), 100 ppm or chromate ion to 20 ppm of chloride ion produced only slight inhibition; nor did a ratio of 300 ppm of the phosphate ion to 100 ppm of choride at a pH of 2.8 and a temperature of 300°C (570°F) prevent cracking.(69) At higher pH levels and lower temperatures, attempts to inhibit cracking with phosphates were more successful. Another investigator reported that at 300°C, pH not given, ratios of Na_3PO_4/NaCl of 1/1 would inhibit cracking but that 1/1 ratios of NaCl and K_2HPO_4, $Na_2H_2PO_4$, $NaNO_2$, $NaNO_3$, Na_2SO_4, $Na_2Cr_2O_4$, and Na_2SiO_3 did not inhibit cracking.(68)

6.3.3. Cathodic Protection. Earlier it was shown (see Paragraph 3) that a flow of electric current is associated with the corrosion of a metal, and the tendency for a metal to enter aqueous solution as metal ions is indicated by the electrical potential generated and by the relative position of the metal in the electromotive series. Further, when two dissimilar metals are coupled, or are joined by an electrical conductor, the more reactive metal becomes the anode (where the anions are produced), while electrons left on the anode surface pass through the conductor to the surface of the more noble metal, the cathode, where they reduce some substance in the electrolyte. It was shown that the flow of galvanic current results not only from dissimilar metals in contact in an electrolyte, but also because of relative differences in the composition of the environment or of the surface of the metal.

It is at the anodic sites that deterioration or loss of metal occurs. At the cathodic sites, a change in the environment is produced. If all the anodic sites could be removed from a structure or piece of equipment, and the whole system made to act as a large cathode, then corrosion attack would not occur. Achieving this objective is called cathodic protection, and there are two approaches to transferring the anodic sites to another metal which is permitted to corrode at a controlled rate in order to maintain the protected structure as a large cathode site.

In the first approach, a direct current, I_{app}, is impressed on the system to oppose the galvanic corrosion current flow, I_{corr}. When I_{app} is less than I_{corr}, the potential of the cathode, E_c, will be partially depressed towards that of the anode, E_a, and the corrosion current will fall to a lower value I_{corr} as shown on figure 40. The system is said to be partially cathodically protected. When I_{app} equals I_{corr}, the system will be marginally protected (i.e., stable provided the environmental conditions do not change). However, when I_{app} exceeds I_{corr}, the system is fully cathodically protected, and the corrosion occurs at an auxiliary anode. Because this auxiliary anode, necessary to complete the electrical circuit as shown in figure 41, is allowed to corrode in order to protect the system, it is referred to as a sacrificial anode.

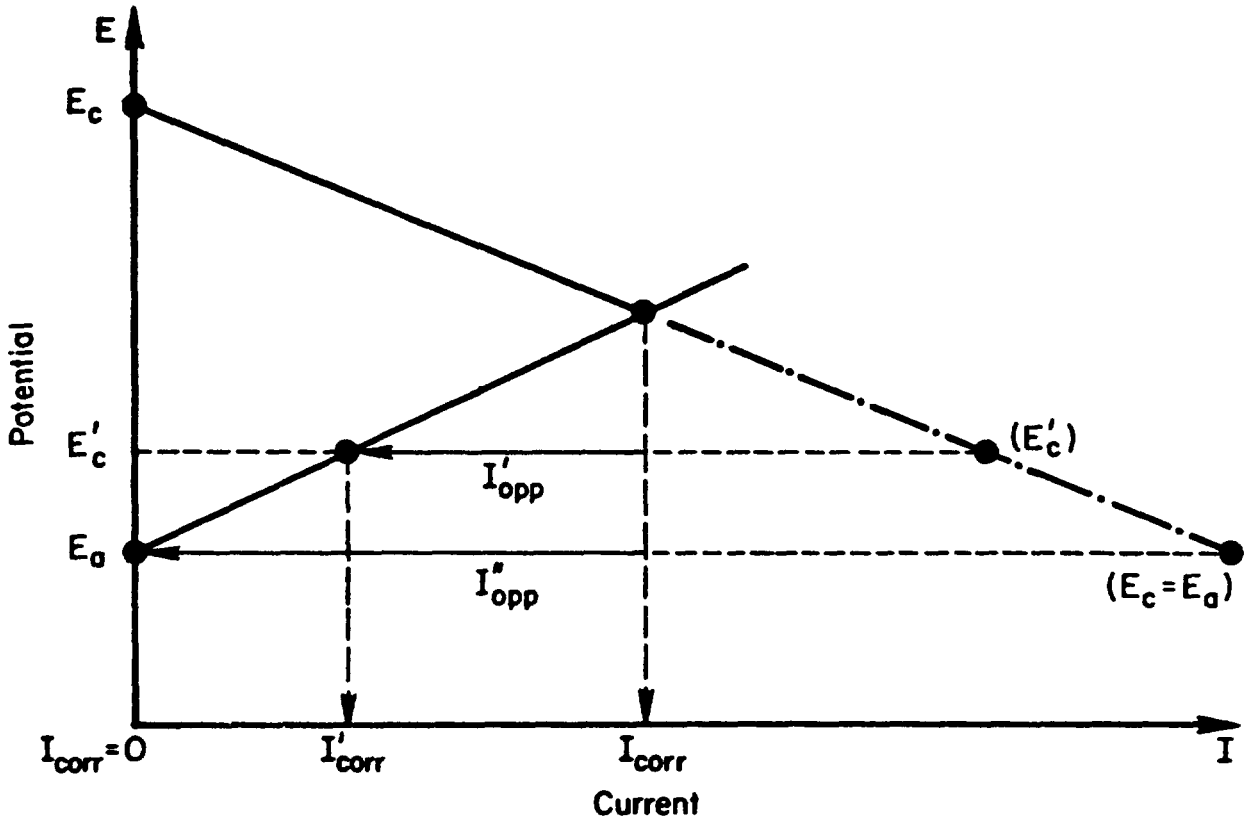


FIGURE 40. Evans-type diagram showing how an impressed current, I_{cpp}, opposing the galvanic corrosion current, I_{corr}, can reduce or halt the rate of corrosion by a process known as cathodic protection.

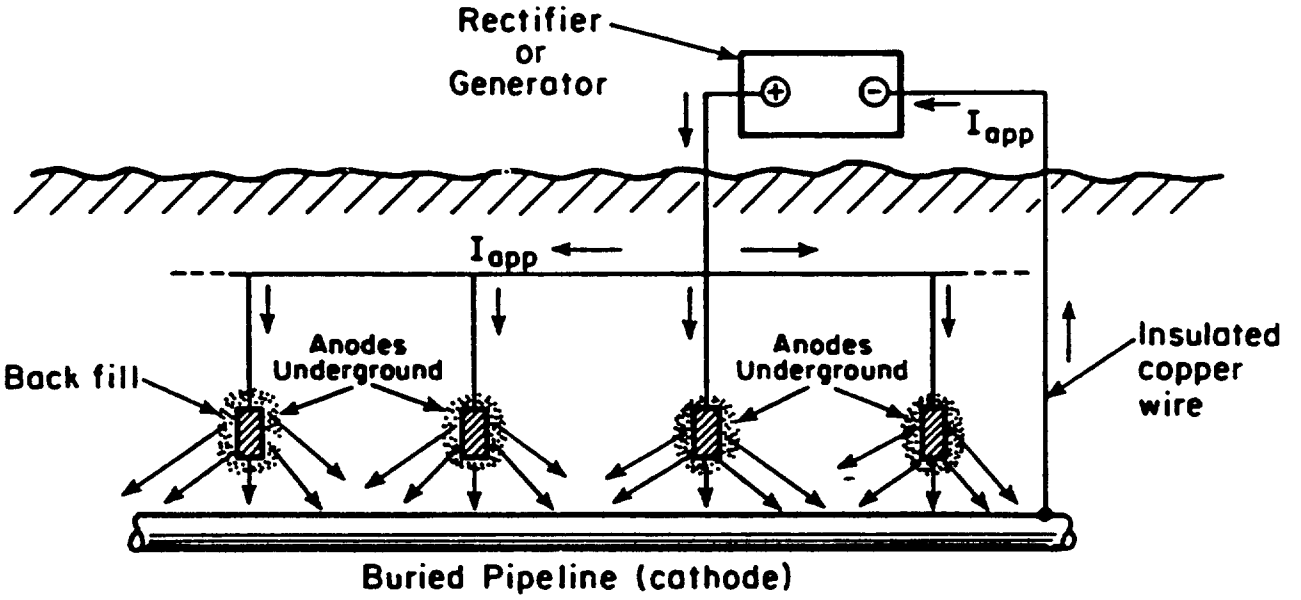


FIGURE 41. Cathodic protection of a buried pipeline by the impressed current (I_{app}) method.

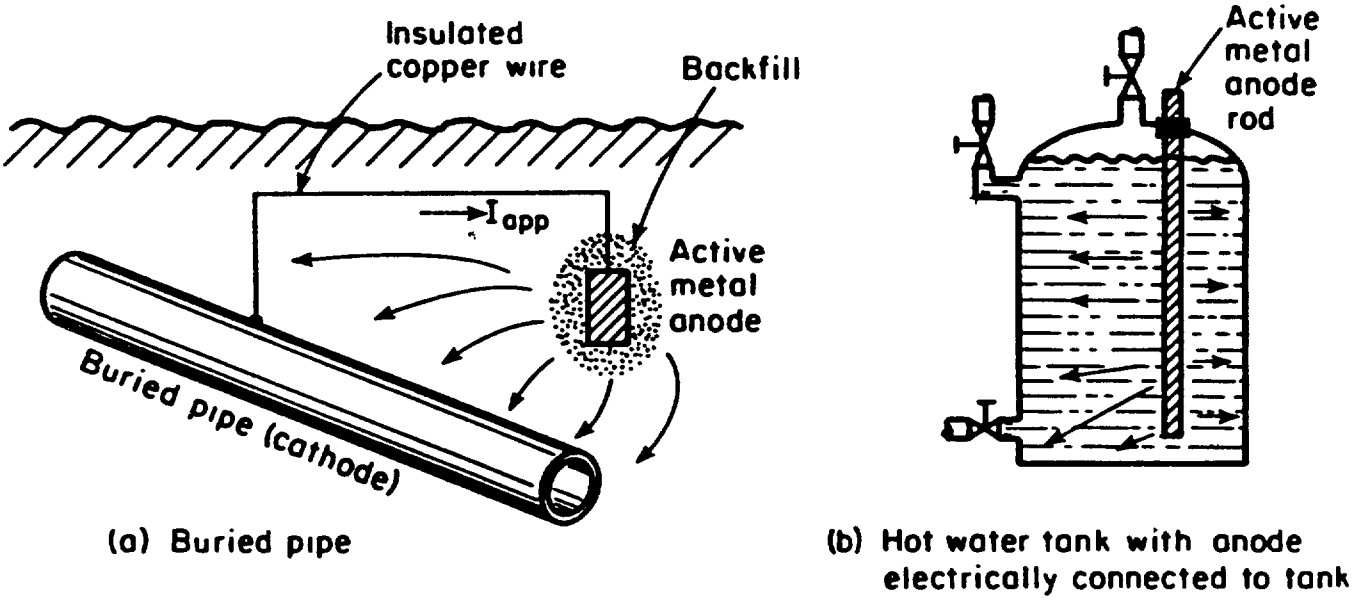


FIGURE 42. Cathodic protection of (a) a buried pipe and (b) a hot water tank by the galvanic (sacrificial anode) method.

The impressed current method described above is used where large structures or pieces of equipment are to be protected either underground or immersed where the resistivity of the soil or solution is high, and large currents are required to nullify the galvanic corrosion currents. For small structures or equipment, and where electrolyte resistivity is low, such that the impressed current need only be relatively small, a sacrificial anode having a potential more negative (more active in the galvanic series, table III) than the existing anode site can be coupled to the structure as shown in figure 42. This sacrificial anode (e.g., magnesium, zinc or aluminum alloys for ferrous materials) being more active than either the prior existing cathodic and anodic sites will preferentially corrode. Thus, this type of galvanic cathodic protection achieves the same result as the impressed current form of cathodic protection, namely making the system to be protected totally cathodic in the corrosive environment. The galvanic method is employed to protect hot water tanks, ships, ship hulls, buoys, some structures under water, and some buried pipelines and structures. The impressed current method is widely and efficiently used for underground gas, oil, and water pipelines and cable systems for cummunication and power distribution.

For underground applications, in both methods of protection (figures 41 and 42) the anodes are placed in a specially prepared "backfill". The purpose of this backfill is to provide a uniform environment around the purpose of this backfill is to provide a uniform environment around the anodes to promote uniform anode consumption and maximum protection efficiency. It also isolates the anodes from the soil which could contain aggressive chemicals, and which would attack the anodes and form passivating films on the surface, preventing them from functioning properly. Backfills are available from commercial suppliers. For magnesium galvanic anodes, the backfill could consist of 25 percent hydrated gypsium, 20 percent bentonite clay, and 5 percent sodium sulfate. Zinc anodes can be placed in a mixture of 50 percent plaster of paris and 50 percent bentonite clay.(69) With impressed current methods, coke or graphite backfill are commonly used(69) because of their low electrical resistivity.

In order to keep the I_{app} value as small as possible, cathodic protection is often used in conjunction with coatings or other chemical means of protection such as cathodic inhibitors. The impressed current is then only needed to protect the metal at bare spots. The size and choice of the sacrificial or auxiliary anodes will depend on the size of the structure being protected, the nature of the environment (e.g., electrolyte resistivity) and the availability and characteristics of the impressed current source, as well as the length of time desired before replacement is necessary.

Since cathodic protection requires an electrolyte to carry electrical current, in practice it is effective only for systems underground or under water; surfaces to be protected must be in contact with the electrolyte. Electrically shielded interiors such as interior surfaces of heat exchanger tubes will not receive protection, although the exchanger casing might be well protected. Cathodic protection of the interior surfaces of the tubes requires insertion of sacrificial or auxiliary anodes, and maintaining sufficient opposing current.

There are many laboratory experiments which show that stress-corrosion cracking can be prevented, or once started, stopped, by the application of cathodic protection. It has also been shown that the discharge of hydrogen on the surface of a high-strength steel during cathodic polarization can lead to hydrogen-stress cracking of the steel. Hence, cathodic protection should not be used on steels having a hardness greater than 22 Rockwell C.

In one instance, it was suggested that hydrogen diffusing through the steel wall of a pipeline from cathodic protection collected at a "hard spot" in the steel and triggered a failure by hydrogen-stress cracking. Generally, if there is no back pressure of hydrogen on the inside of a pipe, any hydrogen deposited on the outer surface is believed to diffuse through the pipe wall without causing trouble. However, it is recommended that to prevent excessive discharge of current and hydrogen, the potential of the pipeline be only high enough to protect the line.

Cathodic protection has been suggested for steel tanks containing hot hydroxides and for similar applications where there have been stress-corrosion failures.

The galvanizing of steel and the sandwiching of a high-strength aluminum alloy sheet between thin layers of aluminum or an aluminum-zinc alloy, are examples of cathodic protection of the base metal from general corrosion. Magnesium alloys have also been protected, using the Mg + 1 Mn alloy as the protective coating for the Mg + 3 Al + 1 Zn alloy. Where there is a break in a protective coating, if there is a continuous layer of moisture connecting the coating and the base metal, the coating layer will go into solution protecting the core material. If drops of mositure form on the core material alone as on a cut edge, it may corrode. The behavior of the clad layers, as long as no core metal is exposed, will depend on their reaction to the environment. Cladding will protect against the stress-corrosion cracking of any material to which it can be applied.

More comprehensive information on cathodic protection is to be found in the various texts and military publications given in the bibliography.

6.3.4 Anodic Protection. With cathodic protection, the goal is to provide immunity from corrosion by removing all anodic sites on the structure being protected. Other forms of corrosion protection rely on forming and maintaining stable films on anodic sites which impede further corrosion attack. Anodic protection is one of these forms of protection suitable for use with metals which exhibit an active-passive corrosion behavior, such as steels.

Active-passive behavior is best understood with the help of figure 43. With a passivating metal, as the potential of the anode is made more noble (or the solution oxidizing power is increased), a passivating film is formed on the surface which eventually protects the surface from further attack, and the corrosion current density falls to a very low value, I_{pass}, orders of magnitude lower than the maximum corrosion current density, I_{crit} which is observed in the active region (see figure 44). If the anode potential is further increased breakdown of the passivating film can occur, and the corrosion current (or rate of attack) can again increase to relatively high values. The metal is then said to be in a transpassive region. There is thus

a narrow range of anode potential (E_p' to E_p'', figure 44) over which the corrosion rate is very low. The object of anodic protection is to maintain the potential of the anode within this range, which preferably should be 50 to 100 mV, or more. To achieve this, the arrangement shown in figure 45 is necessary to monitor and hold the potential within the desired range. The device required to achieve this is called a potentiostat.

Anodic protection is usually applied to tanks and process vessels where the environment contains oxygen dissolved in an acid solution. Under these conditions, it is difficult to apply cathodic protection methods. Once an anodic film is built up, the impressed current required to maintain the potential in the desired range can be reduced, and even pulsing techniques can be applied.(69) Further details about anodic protection can be found in Reference (70).

6.4 Design Modification. The information presented in table XVI summarizes some general techniques and basic design considerations useful in protecting metals against corrosion in common design situations. Specific examples for different metals have already been presented in Paragraph 5 and other general approaches discussed in Paragraph 2.

6.4.1 Prevention of General Corrosion. The general approaches are recapitualted below. Shapes should be simple with rounded corners and contours wherever possible; sharp corners and recesses should be avoided so that mositure and solid matter cannot accumulate to initiate localized attack. Simple forms also facilitate coating, painting, and cleaning.

Constrution angles, channels, H and I beams, etc. should be placed so that catchment areas are eliminated. If this is not feasible, drainage holes should be provided (see figure 46). Piping systems should be accessible for inspection with no dead angles. Piping systems should be installed with expansion devices to absorb thermal expansion stresses. Tanks, containers or other structures should have all surfaces free of contact with the ground to avoid corrosive attack and to provide easy maintenance. This is often accomplished by supporting the structure on piers or legs at some convenient height from the ground.

The most corrosion-resistant metals within service and cost requirements should be used; in many cases, the use of thinner sections of a highly resistant metal will be more economical in the long run than largr sections of less resistant metal. Clad compostions can often be adapted with excellent results.

Joining or coupling of dissimilar metals which are widely separated in the galvanic series should be avoided, if possible. Frequently, however, in modern design of equipment, such couplings are not easily avoided. Therefore, dissimilar metals which must be joined should be adequately protected at the juncture surfaces to preclude galvanic and concentration cell corrosion (see figure 47).

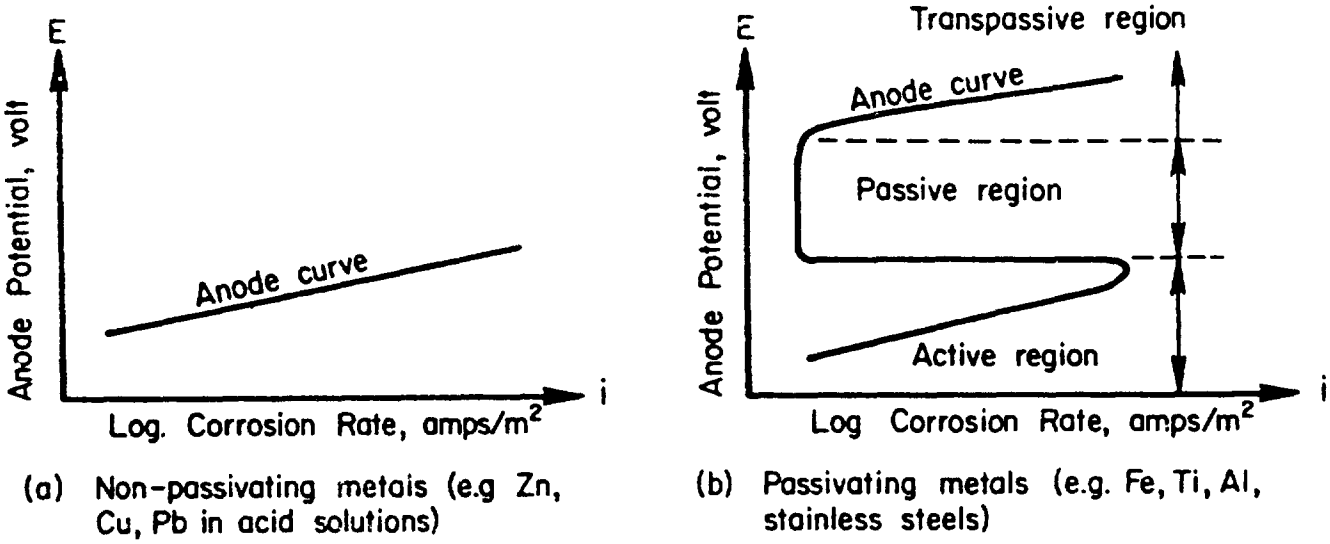


FIGURE 43. Corrosion characteristics of non-passivating and passivating metals.

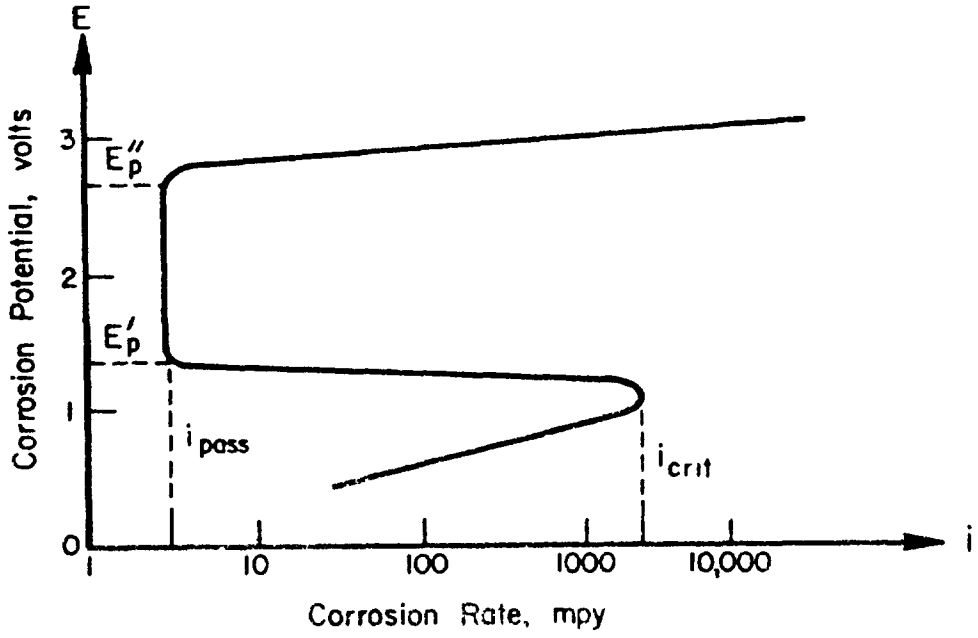


FIGURE 44. Relationship of passive to active corrosion current density.

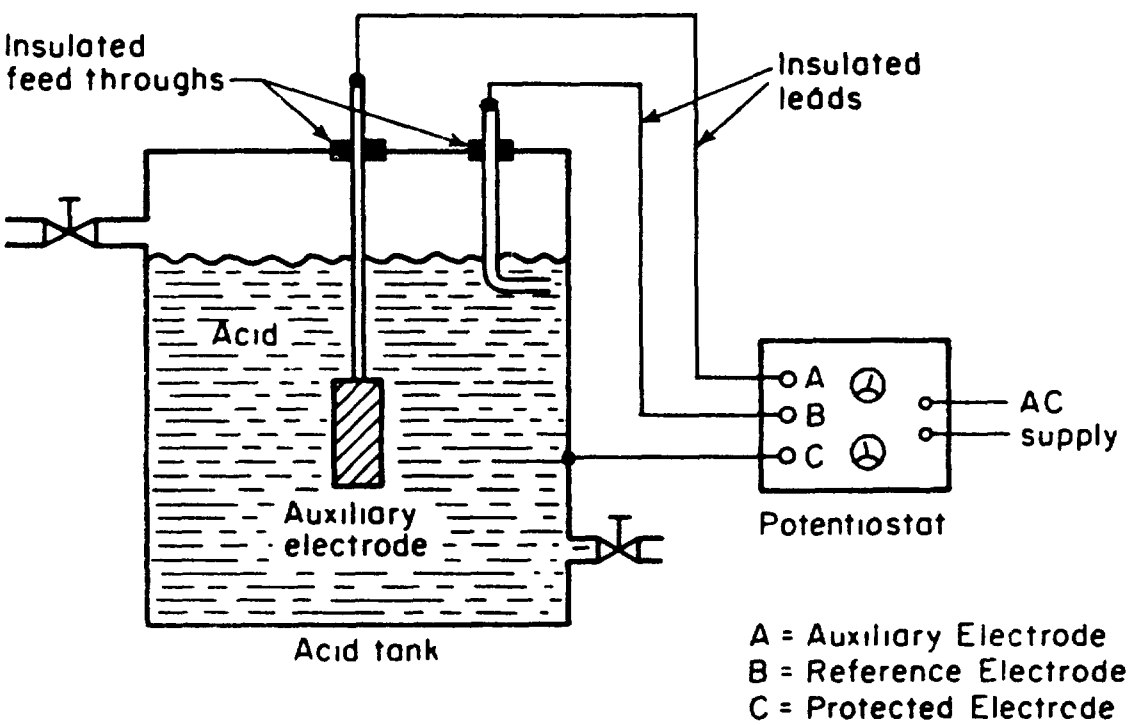
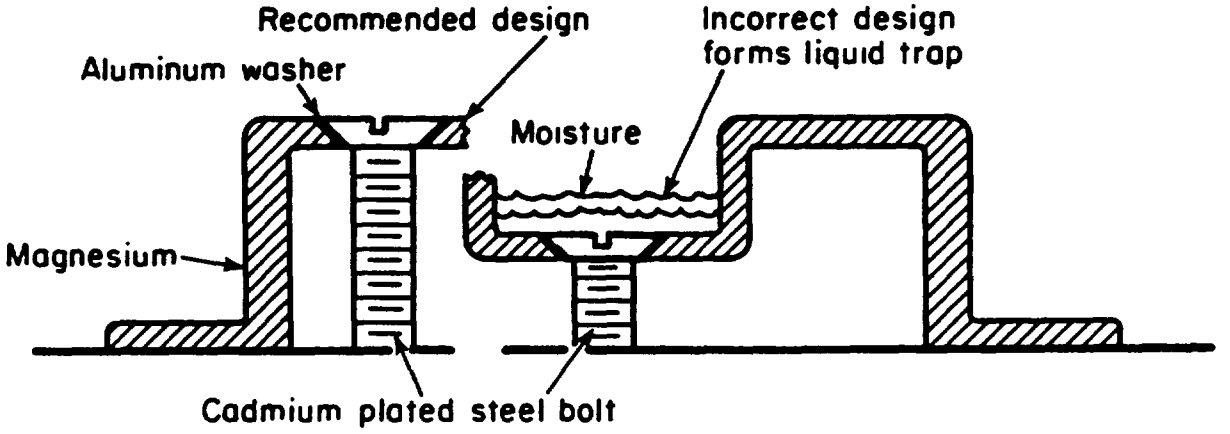


FIGURE 45. Anodic protection method applied to a storage vessel containing sulfuric acid.

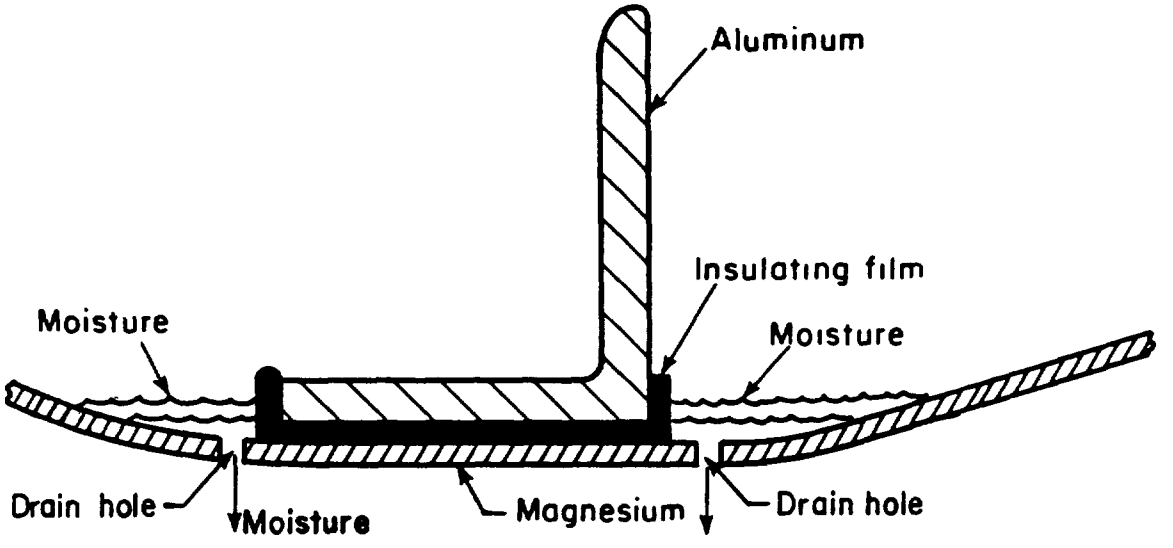
The reference electrode senses the potential of the steel tank liner surface, which if outside the preset range for protection, will signal the potentiostat to supply a current between the auxiliary electrode and the tank to bring the potential back into the range for protection.

TABLE XVI. General Techniques and Design Considerations for Protecting Metals Against Corrosion.

Item	Suggestions
1. Eliminate "sump" areas where trapped moisture is held in contact with metal.	a. Design them out in the first place by careful attention to design of structure details. b. Provide properly located drain holes. Minimum hole size 1/8 in. to prevent plugging
2. Choose non-absorbent, non-wicking materials.	a. Determine water absorption qualities of mateials to be used. (See text) b. Use epoxy and vinyl tapes and coatings, wax, latex, for protective barriers. c. Avoid, if possible, use of wood, paper, cardboard, open cell foams and sponge rubbers.
3. Protect all faying surfaces.	a. Use proper sealing materials (tapes, films, sealing compounds) on all faying surfaces. Use primers. b. Lengthen continuous liquid path to prevent forming an electrolytic cell
4. Use compatible metals.	a. For magnesium-aluminum couples, 5000 and 6000 series aluminum alloys are most compatible. b. For magnesium-steel couples, use tin or cadmium plated steel. c. For bimetallic couples use metals or alloys in the same group per table III or as close as possible. Use tapes or primers on faying surfaces to prevent metallic or electrical contact.
5. Select proper finishing systems.	a. Choose chemical treatments, paints, plating on basis of service requirements. b. Service test system before setting up protection run. c. Use past experience in similar applications as a guide to choice.



(a) Joint Design to Prevent Entrapment of Moisture



(b) Insulating Film and Drain Hole Used to Prevent Moisture From Bridging Between Magnesium and Aluminum

FIGURE 46. Elimination of moisture catchment areas and use of drain holes.

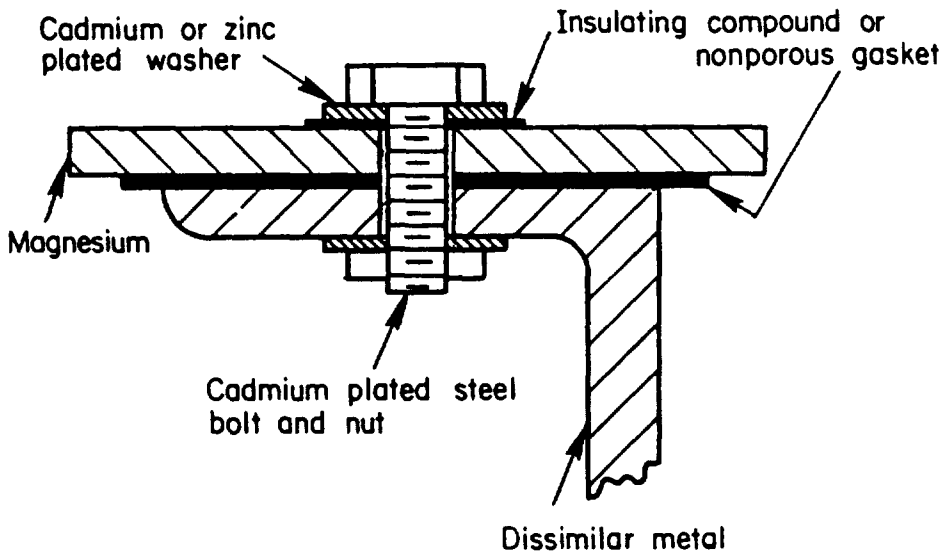


FIGURE 47. Protection at joined surfaces of dissimilar metals.

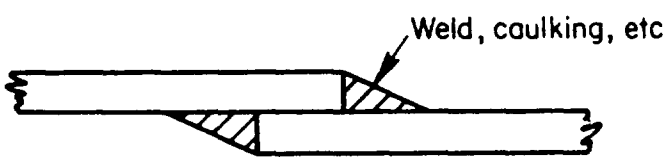


FIGURE 48. Sealing edges of lap joints to prevent crevice corrosion.

The appropriate protective measures should be utilized, such as chemical or anodic films, metallic coatings, and organic coatings. All surfaces should be painted or coated wherever possible. Cathodic protection should also be utilized where practicable.

During assembly, care must be taken to avoid damaging the metal surfaces or creating cracks or grooves where separate parts are being joined; surfaces should be kept smooth. Welding, riveting and bolting operations should follow the authorized procedures for the particular operation or handling of the metal involved.

Butt-welded joints should be used in preference to lap joints. If lap joints must be used, all exposed edges should be either filled with a non-absorbing caulking compound, or welded or soldered to prevent the entrance and retention of liquids in crevices (see figure 48).

Tack-welding of one component to another should also be avoided because of the crevices created due to mismatch and localized distrotion due to thermal stresses.(71) A continuous seam weld is preferred to remove crevices and equalize stresses.

6.4.2 Prevention of Stress-Corrosion Cracking. Stress-corrosion and hydrogen-stress cracking occur in material subjected to applied engineering stresses well below the yield strength of the material, or very frequently, under no applied stresses at all and in corrosive environments in which the metal suffers very little, if any, general corrosion. The effective tensile stresses causing the failure may be engineering stresses superimposed on residual stresses in the material, or residual stresses alone. If either the damaging tensile stresses or the corrosive environment could be eliminated, there would be no stress-corrosion or hydrogen-stress cracking failure.

The residual stress responsible for stress-corrosion cracking may result from such fabricating processes as welding, deep drawing, spinning, or punching. They may result from overtorqueing of threaded connections, from forced fitting of mismatched parts, or from the forcing of an oversized part (shaft, bushing, or bearing) into another part where there is too much interference.

Much can be done in the design and fabrication of structures so that they will be free from dangerous residual stresses. For example, the elimination of a tapered threaded joint by constructing a part in one piece helped prevent stress-corrosion failures in a hose connector.

Too much interference in oversized bushings or bearings can produce dangerous residual stresses in aluminum alloy fittings machined from extrusions. If the design is such that the applied stresses are normal to the short transverse direction of the extrusion, this tends to compound the problem.

If there is poor fit between two surfaces to be bolted together, shims to fill in space between the two surfaces (as shown in figure 49) may eliminate dangerous stresses in the short transverse direction of an extrusion that would result from simply pulling the surfaces together with bolts. Other

examples of poor design are shown in the same figure. Drainage holes should be located in channels so that water can drain away and permit the structure to dry.

Stress-corrosion cracking in austenitic stainless steels is usually initiated in areas where chlorides can concentrate. Crevices are particularly bad and should be avoided in the design of structures constructed of these steels. Other undesirable features can result in concentrations of chloride from drip of condensate, or hot spots on walls which the solution never really wets.

Methods used in assembling structures should be such as to prevent direct metallic contact between dissimilar metals where products of galvanic corrosion of one of these could, by the building up of corrosion products between the surfaces, exert sufficient pressure to produce stress-corrosion cracking. This can also develop with two parts of the same alloy. Water working its way along the threads of a 2024 bolt and nut combination produced sufficient buildup of corrosion product between the two to cause stress-corrosion cracking of the nut (see figure 32). It was recommended that the bolt be coated with a heavy paint containing zinc chromate before the nut was screwed into place and that the end of the bolt-nut exposed to the weather be sealed with a clear lacquer to keep out the moisture.

In one instance, the order in which condenser tubes were placed in a heat exchanger during retubing was blamed for high residual stresses and stress-corrosion cracking in some of the first installed.

6.5 Protective Coatings. Protective coatings may be classified into three groups: (1) chemical or anodic films, often referred to as inorganic or conversion coating; (2) metallic coatings; and (3) organic coating. The first type is produced by chemical or anodic treatment; the second group includes electroplates, hot-dip coating, cladding, and sprayed metal coatings; and the third group is composed of paints, varnishes, lacquers, enamels, oils, waxes, and similar rust preventive compounds. Each of these groups and types are discussed below. For details of pretreatments to be given metal surfaces prior to applying the coating, References (75) and (76) should be consulted.

6.5.1 Inorganic Coatings. Metals and alloys may be treated with suitable solutions of chemicals under controlled conditions to form protective surface coatings. These coatings are known as inorganic or chemical conversion coatings because during chemical treatment, the metal at the surface is converted to a nonmetallic compound. Thus, a surface layer is developed that is physically integral with the underlying metal. The surface coating serves as a barrier which is protective to the metal surface. The conversion coatings commonly formed by chemical treatments include oxides, phosphates, chromates, or complex compounds of the metal and the elements of the treatment solution.

Depending on circumstances, these coatings are generally resistant to corrosion and provide a measurable degree of protection. These serve as a base for paint or some other organic finishes, and improve the adhesion of

point or corrosion inhibiting oils and waxes applied to the coated metal products. Conversion coatings may be formed on iron and steel, aluminum, magnesium, cadmium, zinc, and other metals and alloys.

Chemical coatings. Black oxide coatings sometimes are applied to iron and steel parts. The coating is produced by immersion in an aqueous alkaline bath at a temperature from 100 to 150°C (212°F to 300°F). The resulting coating is usually less than 0.00025 cm (0.0001 inch) thick and will not powder off. The coating, however, provides limited corrosion protection. Consequently, it is seldom used bare unless the service involves indoor exposures where the corrosive conditions are not severe. The coating presents an attractive black color and provides a base for the application of rust inhibiting oils and waxes. The barrier layer of oil or wax is not used on optical instruments, since organic materials applied to the interior of optical instruments may increase light reflection and also cause condensation of volatile materials on the optical components.

Phosphate coating is a common method for chemically treating the surfaces of iron and steel and is sometimes used on zinc, cadmium, aluminum, and their alloys. During the process, a suitable dilute acid phosphate solution is partially saturated with one or more of these metals so that, upon immersion, the metal surface is coated with an insoluble crystalline phosphate coating. There are four main types of phosphate treatments; three are based on the use of zinc, manganese, and iron, while the fourth is produced in solutions of the dihydrogen phosphates of sodium, potassium, or ammonia. The zinc base phosphate is the most widely used. All of these methods are applicable to iron and steel, but zinc, cadmium and aluminum can be treated also by modification of the zinc base process.

Phosphate coatings are also classified by process or method of application. A heavy phoshate coating (MIL-P-16232) provides a good resistant coating that is ordinarily 0.0004 to 0.0018 cm (0.00015 to 0.00070 inch) thick and can be oiled, waxed, or colored to improve resistance. A light weight thin phosphate coating (TT-C-490) results in an excellent resistant coating on iron, steel, cadmium, and aluminum. It is especially useful because it provides an adherent base for paints and finishes. This coating produces from 0.4 to 4.0 grams of coating for every square meter (40 to 400 mg per square foot) of surface, depending on the details of treatment.

Small items are usually coated by immersion while large items, such as sheets and strips are sprayed. Sheets and strips may be immersed, sprayed, or passed through a conveyor-type device that expedites the coating.

Chromate conversion coatings are applied to zinc, cadmium, aluminum, magnesium, and other metals. When applied to magnesium,, this treatment provides a thin coating that is resistant to atmospheric exposures. The resistance imparted by the coating depends on the metal on which it is applied. In general, chromate coatings will provide a base for paints and other organic finishes. In some cases where conditions of exposure are mild, the unpainted coating may provide adequate protection.

Of the two principal chromate treatments used for magnesium alloy (chrome pickle, and dichromatic treatment), the dichromate process produces no

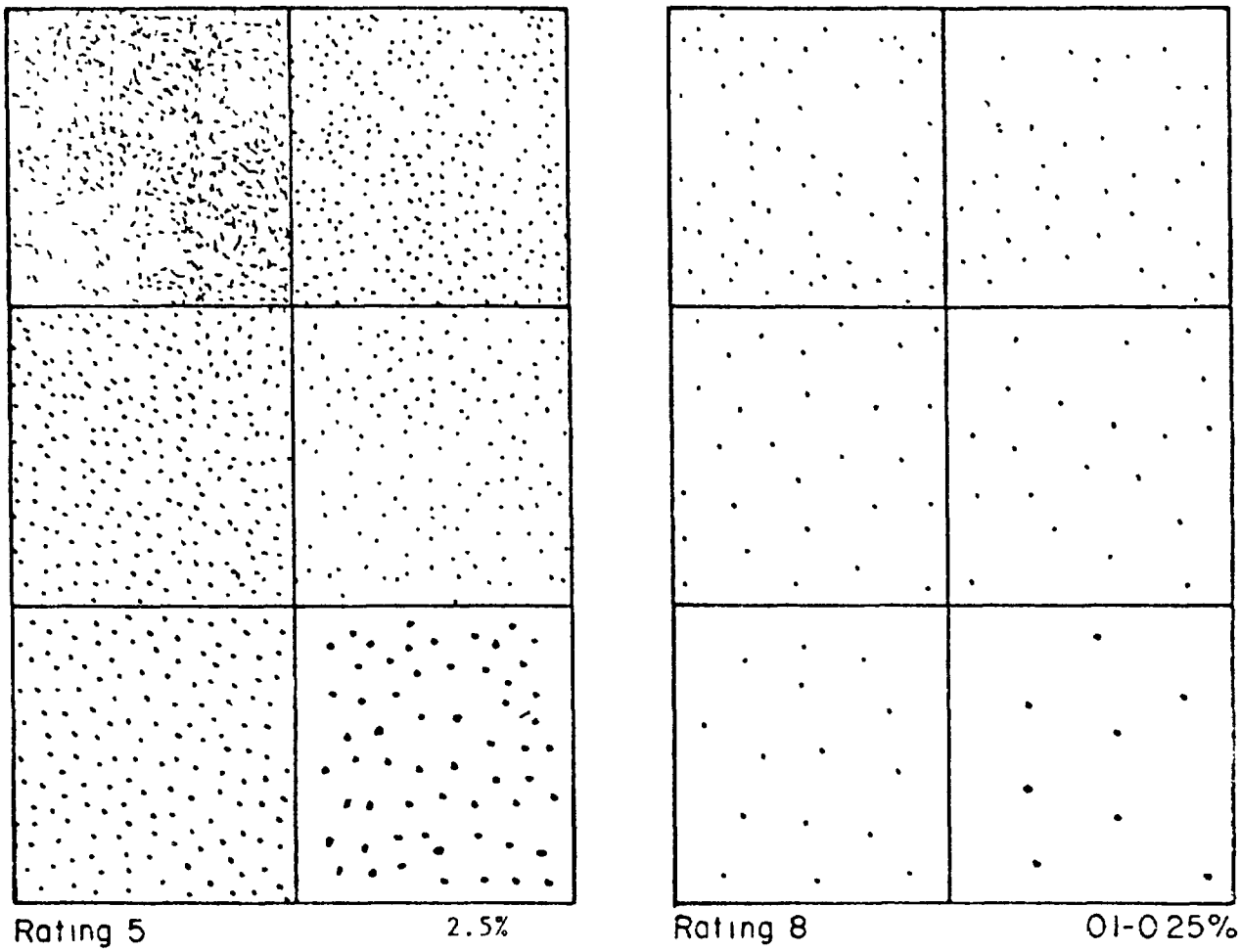


FIGURE 50. Examples of rating charts for assessing the extent of corrosion attack by pitting.

Each rating number corresponds to a narrow range of percentage surface coverage by the pits, e.g. Rating 5 is equivalent to between 1.0 and 2.5% of the surface covered by pits.

dimensional change. The chrome pickle offers a better paint base, but produces a dimensional change. Consequently, it should not be used on parts of close tolerance.

Although zinc or cadmium are often used as coatings to prevent the rusting of steel, in certain environments the metal coatings are attacked with the formation of corrosion products (see paragraph 5.4). This attack on zinc and cadmium can be prevented or minimized by chromate treatments. Zinc products, galvanized sheet, and zinc alloy die castings can be treated in this manner. Chromate treatments are also applied to aluminum in certain cases where anodizing is impracticable. In one such process, coatings are produced by treatment of the aluminum product with a hot carbonate-chromate solution, followed by sealing in a dichromate solution to eliminate porosity.

Anodic Films. Films or coatings formed by electrolytic oxidation can be produced on several types of metals and alloys to increase protection against atmospheric attack. These coatings are generally known as anodic films and the production method is referred to as anodizing. Anodic films are superior to the oxide films formed by chemical treatment. Moremover, the thickness and characteristics of anodic films can be regulated by suitable variations in the electrolytic processing.

Films that are produced by electrolytic oxidation are usually thicker, harder, and more corrosion-resistant, more abrasion-resistant and more satisfactorily dyed than films and coatings formed by chemical treatment. Electrolytic films also provide increased adhesion and longer life to applied paint finishes. Anodic films are frequently given some post-treatment that includes sealing of pores in the film to enhance its efficacy. Anodic coatings are also sometimes used to prevent galling, to hold a lubricant in drawing, and in the case of aluminum and magnesium, to hold colored pigments and dyes. Anodic oxide coatings are used mainly on aluminum and magnesium metals and alloys, but can also be formed on many other metals such as copper, tin, titanium, zirconium, tantalum, and niobium. For copper, for instance, there is the copper oxide, optical black coating which is also a base for paint.

The anodic oxidation of aluminum and its alloys is ordinarily carried out in acid solutions. In a common process, sulphuric acid is used as the electrolyte to impart a colorless and transparent film. Other processes use chromic, oxalic, oxalic-sulphuric, or phosphoric acids for particular purposes. Aluminum anodic coatings are sub-microscopically porous and must be sealed by various methods. Sealing without coloring is usually accomplished by treatment with hot or boiling water. This produces little change in the appearance of the film but renders it nonadsorptive. Chromate solutions are sometimes used for sealing of pores. The anodic coatings essentially consist of aluminum oxide, but may contain sulfate or other substances absorbed from the electrolyte. Anodic films on aluminum may range from 0.00025 to 0.025 cm (0.0001 to 0.010 inch) thick. Satisfactory corrosion resistance is commonly achieved with films 0.0013 cm (0.0005 inch thick). Thick coatings are generally not recommended because they lower fatigue strength, except in specific applications where hard, abrasion resistant coatings are required.

During anodic tratment of aluminum and its alloys, the behavior of alloying constituents may modify the resistance characteristics of the coatings. Certain constituents may be anodically dissolved and hence not interfere with the formation of the coating, while others which are either removed, unattacked or partially oxidized, may remain as occlusions. The removal of constituents and the development of occlusions may alter the continuity of the coating and affect its endurance and appearance. Correct procedures must be firmly adhered to as improper practices of use or incompatible compositions and processes will result in unsatisfactory coatings.

Anodic coatings may be colored or serve as a base for paints and finishes. The usual method of coloring the coating is to impregnate the pores with a suitable solution of dye. Dyeing must precede sealing; sealing after dyeing renders the surface resistant to smudging and staining. The dye becomes firmly absorbed and colors the compound throughout its depth. A variety of colors can be produced with an attractive semimettallic luster. Depending on the light fastness of the dye, the color of dyed anodic coatings may fade in sunlight after several years, although they are virtually permanent indoors.

The pores of aluminum anodic coatings are too small to admit the comparatively solid particles of paints and finishes, but after the coatings are properly impregnated and treated, mineral pigments can be applied. Anodic coatings may also be oiled or waxed.

Anodic films have been applied extensively to both nonclad and clad aluminum products. If not damaged mechanically, properly applied anodic coatings may serve to protect aluminum structures for many years against ordinary outdoor atmospheres. Waxed anodic coatings may maintain good appearance for more than 10 years in such atmospheres.

Magnesium and magnesium alloys may be anodized by several methods. Some of the coatings that are produced, especially in strongly alkaline solutions, are more resistant to corrosion in the atmosphere or in aqueous solutions than are chemically formed coatings. The coating methods which have proved successful include: the Dow-9 process, the Dow-17 process, and the HAE process. Each of these processes and their variations result in films with different characteristics and thicknesses.

The HAE process produces a coating that is about 0.0025 cm (0.001 inch) thick. It is characteristically very hard, corrosion-resistant, and abraison-resistant. In variations of the HAE process, coatings are formed having thicknesses in the range of 010004 to 0.006 cm (0.00015 to 0.0025 inch). The surface coloration of the standard HAE coating is medium brown.

The Dow-17 process results in a green coating and normally is applicable to all magnesium alloys. With regard to corrosion resistance offered when applied to magnesium for approximatley equal thickness, the Dow-17 anodic coating is as proctective as the HAE coating. The Dow-9 galvanic anodize treatment is primarily a proctective and paint base treatment, but because of the consistently good black surface that results, it is sometimes classed as a blackening treatment. The treatment causes no dimensional change and may be applied after machining operations.

HAE anodic coatings on magnesium components should be sealed by treatment with ammonium difluoride-sodium dichromate solution, whether or not to be followed by paint or other organic finishes. Varnishes or heat reactive resins should be used to fill voids in castings of magnesium before or after anodizing--preferably before. Sealing the anodic coatings with high molecular weight waxes or lubricating resins is recommended if the anodized magnesium component is to serve as a bearing surface.

6.5.2 Metallic Coatings. Plated coatings are commonly utilized to protect metals against corrosion. In the process of electroplating, the metal product to be coated is made the cathode in a bath composed of a salt solution of the metal to be deposited. The anode is usually the metal to be deposited. The plating is accomplished by passing a direct current through the work for a period of time calculated according to the thickness of the plating desired.

The quality of electroplated coatings, including appearance, adhesion, porosity, and resistance depends upon several factors. These include the characteristics of the basis metal, the type and extent of pretreatment, the characteristics of the metal that is to be plated out, and the technique of electrodeposition.

The characteristics of the coating are the most significant factors in determining the effectiveness of the electroplating. A continuous coating serves as a barrier until it is corroded or otherwise damaged. It may develop discontinuities as a result of abrasion or corrosion. Under such circumstances, the coated metal could be exposed and the galvanic relationship between the two metals would determine the degree of protection subsequently provided by the coating. Coatings anodic to the exposed metal will protect it by sacrificial action; cathodic coatings will accelerate the corrosion of the basis metal wherever it is exposed. Accodingly, electrodeposited coatings are generally considered for use based on their inherent corrosion resistance and as to whether they are anodic or cathodic to the coated metal.

In some cases, it is important to know whether the coating is anodic or cathodic to the metal it is to protect, especially if the coating is very thin and porous. In some applications, such considerations are not of concern. Iron, for example, may be protected by either type. The two anodic metals used on iron are zinc and cadmium. Coatings of both these metals will protect ferrous alloys in mild or even in marine atmospheres, but not in industrial atmospheres. On the other hand, almost all the other electrodeposited coatings used on ferrous alloys are cathodic to the basis metal and can be expected to be protective, particularly in highly corrosive environments only if they are free of pores or discontinuities. With coatings of sufficient thicknesses of copper, nickel, tin, lead, chromium, gold, and silver, surface corrosion resistance is improved, but if any pores exist or if discontinuities develop in the plate, corrosion of the metal underneath is usually severe. A thicker coating may be used to insure adequate imperviousness and protective service. In general, the number of pores per unit area decreases with increasing coat thickness. For example, a nickel plate 0.00075 cm (0.0003 inch) thick may contain numerous pores, while the number of pores in a plate 0.0025 cm (0.001 inch) thick might be one-half as many and decrease to almost none with a 0.005 cm (0.002 inch) thick coat.

Despite the possibilities of penetration and attack, many electrodeposited coatings are cathodic to the base metal. For example, all metal platings which might be applied to magnesium are cathodic to it. According to the galvanic series and excepting zinc, all other metal platings are cathodic to aluminum. As mentioned above, they are applied to ferrous alloys and also to copper alloys when they are used in contact with steel, magnesium, and aluminum to narrow potential differences of the couples. It should be recognized that in certain situations there are exceptions to the electrochemical action apparently predicted by positions in the Electromotive Series (see table 1). For example, cadmium appears to be more noble than iron according to the Series, but a cadmium coating will protect iron exposed through small pores (see Galvanic Series, table III). Chromium, on the other hand, is anodic to iron under equilibrium conditions, but when chromium becomes passive in the air, it accelerates the corrosion of exposed iron.

The thickness of an electrodeposited coating represents a condition on which is dependent the protective value of the coating. The design engineer must specify the desired thickness depending on end-use requirements. To assist the design engineer, coatings are classified into thickness levels in Government specifications and ASTM Standards, and the notes in specifications of electroplated coatings is quite extensive, including thickness and composition of even multi-layer forms. For example, a specification (ASTM B-142) for a three layer copper-nickel-chromium plating, type K-Z for zinc alloys, calls for the following minimun thicknesses: copper 0.00050 cm (0.00020 inch); copper plus nickel 0.0019 cm (0.00075 inch); and chromium 0.000025 cm (0.000010 inch).

Each of the metals commonly considered as electroplates offer certain advantages and characteristics. Cadmium, chromium, copper, lead, nickel, tin, gold, and silver are selected for particular reasons. The following discussion briefly analyzes the uses of these metals.

Cadmium and zinc may be considered together because they are the only anodic metals used for electroplating. Zinc electroplated to steel or iron articles produces a product sometimes known as electro-galvanized steel or iron. (See also hot-dipped galvanized coatings describes below.) Zinc is used on ferrous products for three reasons. First, zinc has considerably better corrosion resistance than ferrous alloys in most environments. Second, under most conditions, zinc coatings will protect (sacrificially) exposed steel at discontinuities, pores, breaks, and cut edges. Finally, zinc is relatively inexpensive in comparison with almost all other metallic coatings. It should not be used on critical, high-temperature steel parts under tension because diffusion of minute amounts of zinc into grain boundaries of steel to form a brittle alpha alloy occurs at temperatures above 150°C (300°F). A number of serious accidents have been traced to this phenomenon. Zinc coatings in marine or tropical atmospheres produce bulky white corrosion products, and must be treated with chromate treatments to retard this action. Cadmium electroplated to steel and other alloys has much the same general effect as zinc but it is more expensive. Cadmium is also very toxic and should not be used in contact with food or drinking water containers. Fumes from cadmium welding operations are likewise toxic.

Chromium electroplated coatings are among the most extensively used protective coatings to combat strong chemical corrosives. Chromium coatings are usually thin; the typical specified thickness is 0.00025 cm (0.0001 inch) minimum. Such coatings are highly corrosion resistant if they remain impervious. Unfortunately, chromium plates are often discontinuous and if applied to ferrous alloys, would probably afford less protection than the bare iron or steel since any pores or discontinuities would initiate severe galvanic corrosion. The usual practice is to apply chromium over a relatively thick coat of copper plus nickel. In this way, the nickel provides corrosion resistance for the steel and the chromium prevents tarnishing of the nickel. Chromium is also used extensively for wear resistance. Gages, dies, molds, printing plates, and certain cutting tools are coated with chromium for this purpose.

Copper is not ordinarily recommended as a general protective coating. It is used for particular applications, such as plating of aluminum to permit soldering, or to steel articles to prevent certain parts from absorbing carbon during case hardening. Copper electroplates of substantial thickness will provide a fairly durable coating on steel. But, copper is used more extensively as an undercoat for nickel and chromium plates on steel and zinc alloy. One reason for this is that the copper can be polished and treted more cheaply than the underlying steel or the superimposed nickel. Copper plates are sometimes used for appearance, as for color or luster, but they are tarnished quickly by oxygen and sulfur. Chemical (electroless) deposition of copper is used widely for plating printed circuit boards. The advantages of this process are the same as those given under electroless nickel plating.

The precious metals, gold and silver, have special applications as plates on articles for military purposes. Their primary use in providing surfaces with specific electrical or electromagnetic characteristics; e.g., surface conductivity, r-f shielding, specific emissivity or reflectivity. They are also used for tarnish resistance. Silver plating is applied to steel, brasses, and other alloys for decorative and corrosion-resistance purposes. In the case of steel, silver may be plated on an underlayer of copper or nickel. Silver is cathodic to most metals, and its principal uses in military applications are in the plating of electrical contacts, wave guides, reflectors, and as a base for gold-plated low-voltage electrical conductors. Silver tarnishes readily in atmospheres containing sulphur compounds, but this has little effect on its electrical conductivity.

Electrodeposited lead coatings are not extensively used as general corrosion resistant coatings. They are applied to steel to provide protection from atmospheric attack, although they tarnish easily. Lead coatings may be plated directly on steel or on a copper layer. They are used to protect copper, brass, or steel from sulfuric acid. Battery cable terminals, diesel engine valve springs, and many other parts are lead plated for such corrosion resistance. To insure a pore free coating, a thickness of 0.0025 cm (0.001 inch) or more is usually specified. Lead alloys with 0.5 to 50 percent tin have been used as electroplates for solderability or as chemical contain liners.

Tin electroplated coatings are used primarily on steel sheet formed into containers for food and beverages. Formerly, almost all the tin plate was produced by the hot-dip method, but development of the electroplate process

has made it possible to produce "tin cans" and containers over a wide range of coat thicknesses. Tin coatings are also occasionally applied to small steel articles and special fittings. Tin has been electroplated also on copper and aluminum to reduce friction. Tin coatings are applied in the following thicknesses: 0.00004 to 0.00015 cm (0.000015 to 0.00006 inch) for electroplated tin; and 0.00015 to 0.0025 cm (0.00006 to 0.001 inch) for hot-dip tin.

Nickel is extensively used in electroplating. About 10 percent of the annual output of nickel is used for electroplating processes. Nickel electroplates have good resistance to corrosion, although they discolor on exposure to the atmosphere. Except for special applications or where decorative effect is the main purpose, commercial nickel platings are overplated with chromium. The thin layer of chromium increases tarnish resistance markedly. Nickel is the most commonly used resistant metal to protect steel against corrosion. It is also used on aluminum, brass, copper, zinc, Inconel, and zinc-base die castings. Nickel has also been occasionally used to build up the dimensions of worn parts of parts made accidently undersized. Nickel plated steel is used in alkaline storage batteries and in the manufacture of films and plastics, because of resistance to many compounds. In the plating applied to iron and steel parts, the layer of nickel ranges from 0.004 to 0.008 cm (0.0015 to 0.003 inch) thick. As previously mentioned, a preliminary coating of copper is often applied and the nickel coat overlaid with a plate of chromium as thin as one percent of the nickel plate.

Nickel can also be applied over steel, copper, brass, aluminum, nickel, cobalt and precious metals without the use of electricity. This electroless nickel process plates nickel on surfaces by chemical reduction of a nickel salt. The process is used where a nickel coat of uniform thickness is desirable but has been either impractical or impossible to obtain by electroplating. The nickel deposit is semi-bright and smooth, varying somewhat according to the conditions of deposition and the surface of the underlying metal. It is not pure metal but contains about 93 to 95 percent nickel with the remainder being largely phosphorus as finely dispersed phosphides.

The electroless nickel bath may be either acid or alkaline. The acid bath, which is more common, is used for steel parts; the alkaline bath for parts made of nonferrous metals. As indicated above, electroless nickel can be applied over steel, copper, brass, aluminum, nickel, cobalt and precious metals. On the other hand, it cannot be applied to zinc, cadmium, lead, tin, manganese or surfaces contaminated with them. In some instances, this inability may be overcome by a copper flash. It cannot be applied on parts soldered or braxed with tin or lead alloys. Good adhesion cannot be obtained on casting alloys of steel or aluminum with a high silicon content. With proper cleaning, assemblies of different metals (steel and aluminum, steel and copper, etc.) can be plated after welding. It can also be plated on sintered metal parts. Electroless nickel can also be plated on a variety of non-metallic surfaces such as glass and certain thermosetting plastics. In these cases, the surface must be sensitized with various agents such as palladium, etc., and may also require roughening to provide adequate adhesion.

The corrosion resistance of electroless nickel is about the same as that of electroplated nickel. In some environments, such as high humidity or conditions leading to fretting corrosion, it is better than electroplated nickel; in other, such as severe marine or outdoor weathering exposures, it is inferior.

Probably the most important advantage of the process is that the coating is deposited evenly over irregular shapes, crevices, blind holes, recesses and both internal and external surfaces where these are in the design. The throwing power has been described as "infinite". Electroless nickel will coat the contours of an item where a conforming anode for electroplating is impossible, such as the insides of fine tubes, valve stems, etc. It plates uniformly over the roots and tips of threads, worms and fine gears such as are found in watch and instrument assemblies. Another advantage is that there is no build-up of points or edges. Electroless nickel is harder (about 500 Vickers) and more wear resistant than electroplated nickel. This hardness can be further increased by proper heat treatment. However, the coating is also brittle and may crack when flexed. The brittleness remains after hardening. If heated to still higher temperatures, the coating becomes somewhat more ductile but hardness is lowered.

Electroless nickel is more costly than electroplated nickel. However, overplating, to obtain a minimum thickness in recesses, is obviated.

Hot dipped metallic coatings are applied to some metals to provide corrosion protection. In common practice, this process is confined largely to the coating of ferrous alloys with metals and alloys of relatively low melting points. The typical hot-dip coating materials are zinc, tin, and lead alloys, including terne metal. Aluminum is also used as a hot-dip coating for steel in certain applications. Tinned steel and zinc-coated or galvanized iron and steel articles are the important hot-dipped products.

The hot-dipping process consists essentially of immersing the article to be coated in a bath of liquid (molten) metal for a short time and then withdrawing it. Strip and wire may be continuously coated by this method. Suitable pretreatment of the work is necessary, but the coated surface is usually not treated afterwards. Fairly thick coatings are obtained by hot dipping; coatings produced by this process are thicker than electroplates of the same metals. Moreover, hot-dipped coatings are not porous. In terms of galvanic relationship, hot-dipped coatings behave as do the corresponding electroplated coatings. But hot-dipped coatings, primarily because of greater thickness, generally provide better corrosion resistance than electroplates of the same metals. Hot dipping is applicable to a variety of products including sheet, wire, castings, wrought fabrications, and parts for structural purposes.

One action necessary for successful hot dipping is that the two metals must alloy with each other, at least to some degree. A coating produced by hot dipping is not a mere film of the composition applied. In microstructure, a hot-dipped coating always exhibits at least two layers, more or less distinct. There is an inner or alloy diffusion layer, and an outer or coating layer. The outer layer has basically the same characteristics as the composition would have if not used as coating. The inner layer, although diffused, is often quite brittle, and as a result, the coating may flake or

crack when bent. Consequently, such coated articles cannot be deformed extensively. In most cases, a hot-dipped sheet or wire has much less flexibility and less resistance to cracking caused by deformation than the uncoated material.

Hot dipping is one of the important methods for coating iron and steel parts with zinc to produce galvanized iron or steel. Low-carbon and alloy steels, gray cast iron, and malleable iron are commonly hot dipped with zinc. Coatings may vary in weight between 150 to 750 grams per square meter (0.5 to 2.5 ounces per square foot) (approximately 0.0025 to 0.0075 cm per side). The variety of products that are protected by this process include flat sheet, strip and wire, corrugated sheet, structural parts, fabricated articles, nuts, bolts, pails, cans, pipes and nails. The specific techniques have been modified and refined to develop or improve coating properties.

Hot-dipped tin coatings are applied principally to low-carbon steel sheet and strip. Some fabricated steel articles are also tinned by hot dipping. As in the case of zinc coating, there is an outer layer and an inner diffusion layer formed by liquid tin in contact with the steel. Coating thicknesses are in the order of 0.0002 to 0.0005 cm (0.0001 to 0.0002 inch) per side.

There are several aspects of the tinning of steel which are carefully controlled to obtain the desired product. For instance, the composition of the steel base for tinned containers is controlled to produce the proper balance of strength and corrosion resistance for a particular application. Most constituents will not affect the resistance or utility of tinned steel but phosphorus, silicon, and the heavy residual metal constituents may affect resistance to specific substances.

A number of lead alloy coatings are applied to steel and other alloys by hot dipping. These coatings include lead compositions and several lead-tin alloys used mainly for protecting steel. Lead-tin alloys are necessary where lead-coated ferrous products are desirable because lead does not form diffusion alloys with cast iron, steel, or copper compositions. Straight lead coatings may be applied over galvanized coatings by hot dipping. The most widely used steel product coated with a lead-tin (terne) alloy is flat-rolled stock. This stock is composed of sheet of different sizes and weights and has approximately the same resistance to atmospheric corrosion as a galvanized product. Coating thickness ranges from 0.00015 to 0.0005 cm (0.00006 to 0.0002 inch) per side. The terne coating may contain 10 to 25 percent tin and the remainder lead. Painting is often necessary because lead coatings have inferior resistance to wear or mild abrasion. Moreover, lead coatings tend to exhibit minute holes unless manufactured precisely, and, when bare, develop a surface coating of oxide or sulfate upon exposure to certain types of atmospheres.

Ferrous alloys are also coated with aluminum by hot dipping. This is a comparatively new process continually being improved to develop a relatively light-weight and low-priced, heat-resistant, corrosion-resistant, coated steel sheet. So-called aluminized steel is available in one standard coating weight for all gages and grades. The coating weight is approximately 150 grams per square meter (0.5 ounce per square foot) of sheet and corresponds to a coating

thickness of about 0.0025 cm (0.001 inch) on each surface. The thickness of hot-dipped aluminum is comparable to that of ordinary zinc coatings, but heavier than that of terne or tin coatings.

As developed to date, the hot-dipped aluminum coating can be applied to sheet, strip, and wire. It offers several advantages. First, the coating provides the excellent corrosion resistance, heat resistance, reflectivity, and appearance of aluminum. Secondly, in environments where it does not passivate readily or does not form a protective oxide film on its surface, the aluminum coating can provide sacrificial protection to the underlying iron or steel. Finally, aluminized steel maintains the strength and other mechanical properties of the steel and can be joined and fabricated with relative ease.

Cladding is a process for covering one metal with another metal to utilize the superior corrosion resistance properties of the exposed metal. The term "clad metal" is generally used to denote relatively thick coatings which are metallurgically bonded to a basis metal. Thus, a clad product is a duplex or composite metal combination consisting of the core (the basis metal) and a surface (the clad metal). Cladding is usually applied to sheet and strip, but some clad materials are available in bars, tubing, and wire. The cladding may be applied or affixed by working, co-rolling, pressure welding (rolling or drawing), spot welding, and diffusion welding.

The use of cladding makes is possible to provide a corrosion-resistant coating that is much thicker than the coating applied by hot dipping or electroplating. Cladding overcomes the practical or economical limitations of these latter methods while providing an impervious coating free from pores. Since the resistance characteristics of the coating are most important, the galvanic relationship between the two metals in a clad product is not a prime consideration; the cladding may be cathodic to the base metal but the composite will nevertheless serve satisfactorily under most conditions. However, the galvanic relationship must be considered where there are cut edges, as in sheet, or where it is likely that the coating may be abraded and penetrated.

Cladding may be applied to one or both sides of flat-rolled products. The thickness may be adjusted as desired, ranging from about 5 percent to 50 percent of the thickness of the stock. Ten to 20 percent is commonly specified. For example, a composite plate 1.25 cm (0.5 inch) thick with a cladding of 0.125 cm (0.05 inch) on one side is designated as 10 percent cladding.

The principal clad composites produced for industrial purposes are: high-purity aluminum or aluminum alloys on less resistant aluminum alloys: stainless steel on steel; and several nonferrous metals including copper, brass, lead, nickel, and nickel alloys on steel. Cladding with some of the more precious metals such as gold, silver, platinum, and palladium is also practiced, but these composites are used only in unusual circumstances that warrant the high cost. The following discussion highlights the important aspects of the common clad composites.

Aluminum clad sheets are one of the most important clad products and consist of an aluminum alloy core sheathed on each side with a thin sheet of high purity aluminum or of another corrosion resistant alloy. The core

material generally is heat treatable, so that the composite usually exhibits high strength as well as corrosion resistance. The coating composition is applied to the ingot when practicable, and becomes alloyed with the core composition during hot working and fabrication. The thickness of aluminum clad layers may range from 2 to 15 percent of the composite thickness.

Aluminum clad sheets utilize cathodic protection as well as surface barrier protection. The composition that forms the coating is selected so as to be anodic to the basis alloy. This electrolytic protection insures that sheared edges and metal exposed by scratching or penetration of the coating layer will not be vulnerable to galvanic action. In fact, rivets and small fasteners or stiffeners of non-aluminum clad materials that are in contact with the aluminum clad surface are similarly given added protection.

Aluminum clad specimens have withstood industrial and marine environments for many years with no significant changes of physical properties.

Plates and sheets of mild steels, faced on one or both side with stainless steel, have been developed largely to reduce the cost of fabrication with stainless plates and to obtain the advantage of improved properties. Such clad sheets are particularly useful for the many applications where only one side of the steel plate needs to be stainless. The layer of stainless steel is usually about 10 to 20 percent of the thickness of the plate or sheet. It is especially important that the bond between the basis metal and the cladding be strong enough to withstand the stress of fabrication and the effects of differing rates of thermal expansion. Various steel alloys may be used to form clad composites, but the use of austenitic steels such as 18/8 must be considered carefully. These types will lend excellent resistance characteristics to the composite, but at elevated temperatures, the effects of the difference in coeffients of expansion will be marked. For instance, the use of 18/8 cladding on mild steel for vessels in chemical food processing is common. However, if the fabrication of the vessel requires fusion welding and there is a possibility of intergranular corrosion, an 18/8 stabilized alloy should be used. This will avoid warping of the composite which would occur because of the differences of coefficients of expansion between the mild steel and the stainless steel, if the stabilizing treatment was to be performed following the cladding.

Copper cladding is also applied to steel sheet, and to steel wire and tubing. Copper-covered steel wire is a particularly useful product that combines high electrical conductivity, good resistance to corrosion, and tensile strengths considerably above those attainable with hard-drawn copper and bronze wires. When properly clad, it is possible to guarantee a minimum thickness of copper at any point around the circumference of the wire. The finished wire may be bent, twisted or deformed, without causing a break or separation of the two metals.

Nickel-clad steels consist of a core of open-hearth steel and a coating of pure nickel or a nickel-chromium alloy. The nickel is bonded to one or both sides of the steel plate and provides the corrosion resistance of the nickel at a lower cost than that of solid wrought nickel. It is the usual practice to clad both sides of the steel with equal thickness of nickel, although it is possible to obtain composites with different thicknesses of nickel on each side or with nickel on one side and a nickel alloy on the other side. The

modulus of elasticity and the coefficient of expansion of the two metals are close; the composite material, therefore, exhibits equal distribution of stress across the section of the plate with no problems of warping at the nickel-steel interface. Steel plates and sheets of various grades are also clad with brass, Monel, and Inconel. They can be fabricated and welded easily if certain precautions are heeded, to provide composite structures of great strength and corrosion resistance.

The bonding of gold, silver, platinum, and palladium, and their alloys, to base metals is accomplished for some unusual applications. The precious metals provide an attractive appearance that is highly reflective as well as resistant to corrosion and oxidation. Clad composites of these types are used in special electronic and chemical equipment that justifies the higher cost of the precious metal cladding.

Sprayed Metal Coatings. Metallizing or metal spraying is process of applying metal coatings by blowing finely-divided molten particles against a metallic surface. The air blast and impingement of the particles results in the flattening and welding of the particles on the coated surface. Sprayed metal coatings are porous, but they provide protection from corrosion primarily because of their greater thickness. They can be used to coat large articles rapidly and easily. Because these coatings are porous, they must be applied thickly. They require sealing or impregnation with a resin solution, followed by painting.

Sprayed metal coatings may be anodic or cathodic to the basis metal. Zinc or aluminum applied to steel will sacrificially protect the more cathodic steel. With sprayed coatings which are anodic to the basis metal, porosity is no great handicap. On the other hand, coatings of stainless steel, copper, tin, and lead must be relatively impermeable when used over metals such as iron and steel; otherwise, the underlying metal would corrode anodically through the pores of the coating. An anodic metal, which is exposed at pore sites in a coating of a nobler metal, will undergo rapid attack in the region of the pore because of the large cathode, small anode situation. In this instance, perforation of the basic anodic metal becomes highly probable.

Zinc, cadmium, and aluminum sprayed coatings on ferrous alloys range in thickness from 0.01 to 0.03 cm (0.004 to 0.012 inch) thick. Sprayed zinc and cadmium coatings as thin as 0.003 cm (0.0012 inch) will enhance the corrosion resistance of ferrous alloys to seawater. Under such conditions, however, sealing or impregnation is usually recommended and practical to prolong the life of the sprayed sacrificial coating, hence extending the life of the system.

The adhesion of sprayed metal coatings to the basis metal is not as good as that obtained by plating, hot dipping or cladding. The metallic surface must be properly prepared, and desirably the atmosphere must be reasonably controlled during the spraying. If they are properly applied, sprayed coatings provide excellent corrosion resistance for specific applications. For example, coatings of aluminum and steel applied in the proper manner improve resistance to hydrogen sulfide gas. Certain spring-steel parts are sprayed to avoid hydrogen embrittlement associated with electrodeposition. Steels, lead, Monel, and red brass used in the petroleum industry are also sprayed for prevention of corrosion. Iron and steel parts that are exposed to

high temperatures, such as grate fingers, stacks, and certain parts of bridges and ship superstructures, are often sprayed with aluminum to improve their resistance. Metal spraying is also used to reclaim worn or undersized parts, and for providing light metal members with a hard-surfaced coating that combines light weight and corrosion resistance.

6.5.3 Organic Coatings. Organic coatings are used to protect metal parts, equipment and structures primarily against atmospheric corrosion. They are applied as liquids and act chiefly as a barrier between the metal to be protected and the environment. As a class, organic coatings include paints, varnishes, enamels, and lacquers.

Organic coatings are generally composed of volatile and nonvolatile ingredients. The volatile components act as a thinner and consist of solvents and diluents; while the nonvolatile constituents are the film-forming materials, such as resin, oil or wax, and may include both pigments and plasticizers. The value of the organic coating as a protective barrier depends upon its ability to provide: (1) complete and uniform coverage, (2) a good degree of impermeability, (3) good adhesion, (4) cohesion, (5) resistance to mechanical damage, and (6) good chemical inertness.

It is the function of the pigments in the composition to either retard any moisture penetration of the film, or to reduce the corrosiveness of penetrating moistures. Pigments reduce the damage by sunlight to film-forming component (the vehicle), and add body to the formulation for easier application. They supply color to the organic coating for identification, decoration, or to meet the particular color requirements of service, e.g., camouflage. Plasticizers frequently are contained in the formulation to prevent the coating from becoming brittle during application or service.

The successful service life of an organic coating varies widely according to the characteristics of the basis metal, the type and formulation of finish, the surface preparation, and the nature of the service environment. There is no universal protective coating which is serviceable under all environments or usable on all metals. The coating is chosen on the basis of the service conditions, the metal to be protected, and the degree of protection or endurance desired. In general, the useful life of a coating depends on two major factors: the durability of the organic coating itself, and the adherence of the film to the surface it is to protect. Excellent adhesion is an important requisite for improving protective performance.

The proper application of an organic coating is essential for obtaining permanent adhesion and optimum protection. Too frequently the composition of the coating is blamed for failure to give the required service, while the true cause may be improper or inadequate treatment of the metallic surface prior to application of the coating. Proper surface treatments will insure the maintenance of a stable and non-reactive coating that will retard corrosion and provide greater adhesion. To achieve this effective coating, the metal surface to be coated should be free of dirt, oil, grease, mill scale, and any initial corrosion products. Furthermore, the method of preparing the metal should reduce the activity of the metallic surface to prevent corrosion between the coating and the metal at the interface. The ideal in surface

cleanliness and treatment may not always be fulfilled. But if treatment is de-emphasized for savings in time or cost, corrosion very probably will develop prematurely while the system is in service.

In certain situations, a correct analysis of the circumstances of service will determine the coating procedure. For instance, in providing protection for a metal that is corroding rapidly as a result of being coupled with a more noble metal, the tendency would be to coat the more vulnerable surface. However, coating only the anodic or less noble metal may actually accelerate the attack at discontinuities and established pits. In such a case, coatings should be applied to the surfaces of both metals or possibly to the nobler or cathodic metal only, to effect a small-cathodic-large anodic situation.

As a means of providing corrosion protection, organic coatings offer some advantages over metallic coatings. They are less expensive and can be applied over metallic and conversion coatings. They can also be produced in various colors and with a variety of physical characteristics. On the other hand, organic coatings are less resistant to mechanical damage such as abrasion and scratching. Another disadvantage is that they provide no anodic protection in areas that are scratched or penetrated.

In actual use, there are certain differentiations made between the various types of materials included in the class of organic coatings. The following terms and definitions are commonly used:

Paint - A pigmented composition of liquid consistency which after application as a thin layer is converted to solid, adherent, tough film.

Oil Paint - A paint that contains drying oil or oil varnish as the basic film-forming vehicle.

Water Paint - A paint that contains a water emulsion or dispersion as the basic ingredient.

Enamel - A paint that is characterized by an especially smooth surface film.

Varnish - 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, air-drying by oxidation of the oil.

Lacquer - A film-forming liquid composition containing polymeric esters or ethers and plasticizers as the basic film-forming ingredients in a solvent, and which dries by evaporation of the solvent. Lacquer may be constituted with or without resins.

Baking Finish - A paint or varnish that requires baking above 66°C (150°F) for the development of the desired properties.

Paint and other organic coating systems ordinarily consist of more than one coat. The number and type of coats are important factors in the development of satisfactory corrosion protection. Clear lacquer may be applied as a single coat in cases where it is used to protect against simple

tarnishing and to show the color of the metal for decorative purposes. Generally, though, more than one organic coating is applied to attain a certain minimum thickness and insure the formation of a pore-free film. The thickness that may be required depends upon the physical characteristics of the film and of the particular environment in which it will be used. A minimum thickness of approximately 0.01 cm (0.004 inch) is generally recommended for moderately severe environments.

In a paint system, the primer deserves great consideration. The primer provides the basic adhesion to the metal and usually comprises the largest part of the entire coating system; two coats of corrosion-inhibiting primer may be applied and covered by a single finished top coat. In order to improve adhesion, it is common practice to apply the primer to a surface coating formed by chemical or anodic treatment of the metallic surface. With some priming materials, it is quite possible that electrochemical action may be initiated between the pigments in the primer and the metal to which it is to be applied. Pertinent technical reports and manufacturers' recommendations should be consulted to avoid such difficulties.

Only a relatively small number of paint pigments have been extensively used in corrosion-resistant paints, either in primers or top coats. Typical pigments commonly used in metal priming paints include red lead, lead silico-chromate, zinc chromate, strontium chromate and zinc dust. They are particularly effective inhibitors on steel. But all the constituents of the paint (the driers, the vehicles, and the pigments) must be inert to steel, otherwise corrosion will ensue. Carbon pigments, for instance, sometimes stimulate increased attack when used on steel. Likewise, caution should also be exercised in using lead pigments with aluminum, magnesium, or zinc since they may accelerate corrosion on some alloys. Thus, zinc chromate and strontium chromate are commonly used as inhibitive pigments in priming coats for these metals, and generally provide satisfactory resistance. In addition, zinc oxide, metallic zinc dust and iron oxide are used as pigments in primers. The iron oxide pigments are primarily barriers and neither inhibit corrosion, as the chromates do, nor promote attack on active metals.

The composition of the top or finishing coat is usually different from that of primers since they are designed to provide initial surface protection rather than adhesion to the metal, color for identification, decoration or to meet particular requirements of service such as camouflage. Such pigments as titanium dioxide, red and yellow iron oxide, lead chromates, molybdates, aluminum, graphite, and other carbon pigments are used primarily in top coats rather than in primers. The aluminum powder, as a paint pigment, is in the shape of flat flakes. When the paint is applied, the flakes "leaf" or overlap each other as the film dries. This action results in a film of high impermeability.

Slushing compounds are organic materials employed as temporary corrosion-protection compounds for the protection of metal parts and equipment during manufacture, assembly, shipment, or storage. These compounds are nondrying substances consisting usually of a petroleum derivative base combined with additives.

The general specification for the corrosion protection of Army material by painting and finishing is MIL-STD-171. It includes the methods, materials, pretreatment, and other details about the application of such coatings to particular parts and equipment. It also contains a list of the applicable specifications for paints, varnishes, lacquers, and enamels. MIL-HDBK-132 "Protective Finishes" gives a more detailed description of the various organic finishes and finishing systems applicable to Army material.

Rubber is a special example of an organic coating. Rubber coatings or linings are widely used for pipes and tanks, and resistance to water is excellent. Rubber has also been used to coat ships' propellers as protection against cavitation. Another special example of a coating is concrete, which also is used to line large diameter pipes and tanks not subject to thermal and mechanical stresses.

6.5.4 Rust-Preventive Compounds. Rust-preventive compounds are a type of organic protection applied to metal products to improve resistance to attack through barrier action. These compounds do not remove corrosion products on the metallic surface, and to be effective they are usually applied directly to surfaces that have been thoroughly cleaned and dried. For purposes of comparison, such compounds may be subdivided into two groups: flexible non-drying, and hard-drying. The characteristics of these groups and the typical uses of rust-preventive compounds in general are discussed as follows:

The flexible non-drying types do not dry to a hard film or coating; they are the more common of the compounds. They have a petroleum base and can thus be removed easily by petroleum solvents. Because of this petroleum base, they may serve as lubricants where necessary. These compounds normally contain inhibitors which provide more protection of metal against corrosion than do the old type, uninhibited "slushing compounds" of petrolatum and oil. The viscous type has the heaviest consistency and provides the best resistance to the atmosphere among compounds that can be removed. This plastic type can be applied or removed easily, and maintains a self-healing, resistance surface.

A fluid type is available for applications where the heavy viscous type would be impractical or undesirable, such as in oil-lubricated machinery, hydraulic systems, turbines, and similar equipment. Other forms are designed for use in inactivated internal-combustion engines.

A flexible non-drying solvent form is available for application to a wet surface. This product displaces the water and leaves a thin, transparent film that is flexible and tacky over a long period of time. It is primarily for indoor use and permits inspection and handling of the coated article.

The hard-drying compounds are usually of the lacquer type that provide a hard film, resistant to mild abrasion as well as to cracking, that might result from normal expansion and contraction of the metal. These types are transparent, permitting examination or identification of the coated articles. Their films can either be removed by machining, left to wear off naturally, or covered by painting. One special version is an aluminum-base coating that is resistant to hot oil, hot water, or a combination of the two.

Rust-preventive compounds my be used advantageously in several areas of application. They are extremely valuable in protecting machinery or equipment kept in stand-by storage without disassembly. These relatively inexpensive compounds can be used to preserve military equipment and thus avoid replacement problems, the loss of valuable time, or prevent subsequent breakdown in service. Rust-preventive compounds are used to protect dies, molds, gages, fabricating equipment, gears, armatures, bearings, tools of all kinds, spare parts, and machinery in temporary storage. The solvent type that displaces water and neutralizes fingerprints is especially useful. For finished products such as sheets, strips, and bar stock, the solvent type provides protection during transportation, storage or exposure. Products such as piping, rods, wire, contoured parts and plates, can be protected during handling, shipment, and storage by application of these compounds.

6.6 Protection Against Specific Types of Corrosion. In this section, some general guidelines are presented for providing protection against various common types of corrosion attack.

6.6.1 Minimizing Atmospheric Corrosion.

(1) Designs and materials used should reflect careful study of the type of corrosive agents to be encountered.

(2) Organic coatings and metallic coatings should be used to reduce corrosion wherever possible.

(3) Butt-welded joints should be used in preference to lap joints. If lap joints must be used, all exposed edges should be either filled with a nonabsorbing caulking compound, or welded or soldered to prevent the entrance and retention of liquids in crevices (see figure 48).

6.6.2 Minimizing Underwater Corrosion.

(1) Designs and material used should reflect the study of the acidity, temperature, rate of motion, and the amount of free oxygen, soluble salts, and organisms present.

(2) Bottoms of tanks should be rounded or sloped with rounded corners; baffles and stiffeners inside tanks should permit free drainage. Drain-out valves and plugs should be flush with the tank bottom.

(3) When possible, special underwater paints should be used. Cathodic protection should be utilized where practicable.

(4) Authorized assembly standards and procedures should be followed; in welds, the weld metal should be slightly more noble (cathodic) than the base metal; where lap joints are used, special precautions should be instituted to insure tightness.

(5) In some cases it is practical and possible to prevent internal corrosion in piping systems by deactivating and/or deaerating the water. Oxygen removal may be accomplished by mechanical deaeration using necessary apparatus, or by chemical treatment involving the use of some material such as scrap iron or sodium sulfite. The two methods may be used in combination. Free carbon dioxide may be removed by identical means.

(6) Where practical, water systems should be given a chemical treatment to reduce corrosiveness. This may be accomplished through pH control, precipitation of corrosive salts, use of inhibitors, etc.

(7) Protection from anaerobic bacteria in piping systems may be obtained by certain reinforced tar coatings and cathodic protection, or by keeping the pH of the water over 9.

6.6.3 Minimizing Corrosion in Soil.

(1) Designs and materials used should reflect study of the type of soil, temperature, and other local characteristics. Soil surveys are recommended.

(2) When possible, all metal surfaces should be painted or coated. Certain bituminous coal tar and asphalt dip coatings are especially useful for underground protection of pipe systems.

(3) Cathodic protection should be utilized.

(4) Pipes laid in corrosive soils may be protected by being imbedded in a mixture of Portland cement which is free from cracks and voids; the mixture is usually applied in a wooden box surrounding the pipe. Rich cement mixtures may also be used for protecting steel and cast-iron pipe. Pipe systems laid under electric railroad tracks or similar equipment must be completely electrically insulated; such piping can be coated with hot asphalt and then boxed in cement.

6.6.4 Controlling Galvanic Corrosion.

(1) Metals and alloys widely separated in the Galvanic Series must be protected if they are to be coupled. If they must be joined, appropriate measures should be taken to prevent contact. Insulate all surfaces adequately. One way this can be accomplished is by applying to the cathodic member a sacrificial metal coating having a potential similar to or near that of the anodic member; by sealing to insure that faying surfaces are watertight; by painting or coating all surfaces to increase the resistance of a galvanic circuit.

(2) Small anodic areas (relative to cathodic areas) should be avoided. The same metal or more noble metals should be utilized for small fastenings, bolts, and rivets.

(3) Whenever feasible, cathodic protection should be employed. In lieu of the sacrificial or cathodic protection, corrosion inhibitors may be used in the electrolyte. The combined use of sacrificial protection and inhibitors usually is not practical unless the inhibitor has no passivating action on the sacrificial anode.

(4) Welded joints should be used in preference to brazed or soldered joints, which in turn are better than threaded joints.

(5) Where other methods are not practical, design anodic components for easy replacement, or make them thicker for longer life.

6.6.5 Controlling Pitting Corrosion.

(1) Substitute a metal which is less susceptible in the given environment.

(2) Use inhibitors, but ensure that protection is complete, otherwise attack will be exacerbated.

6.6.6 Preventing Crevice Corrosion.

(1) Sharp corners, re-entrant angles, pockets, or other conditions where solids or liquids could collect should be eliminated. Design vessels for complete drainage.

(2) Equipment for liquid transport should be designed so that turbulent flow and gas or air entrainment is held to a minimum.

(3) Wood, insulating materials or other substances which absorb or retain water should not be in contact with metallic surfaces. Use nonabsorbent, solid gasket materials.

(4) Butt-welded joints should be used rather than riveted or spot-welded lap joints. All lap joints that are used should be sealed with solder, weld metal, or caulking compound to prevent trapping of corrosive agents.

(5) Inspect and clean equipment regularly. Remove all deposits. Filter out suspended solids.

(6) Lower relative humidity of an environment to reduce occurrence of filiform (underfilm) corrosion.

6.6.7 Controlling Intergranular Corrosion.

(1) Employ a high-temperature solution heat treatment to keep chromium (carbides) in solution in stainless steels.

(2) Add stabilizing elements to stainless steels to preferentially form carbides with excess carbon.

(3) Lower the carbon content to prevent formation of significant amounts of chromium carbide in stainless steels.

(4) Keep impurity levels to a minimum, and choose heat treatments carefully to minimize precipitation at grain boundaries.

6.6.8 Controlling Selective Leaching.

(1) Reduce the aggressiveness of the environment or apply cathodic protection.

(2) Select metals which are less susceptible to this form of corrosion attack. Resistance can often be improved by alloying (e.g., dezincification) or controlling composition (e.g., carbon content in gray cast iron).

6.6.9 Preventing Fretting Corrosion.

(1) Cold working of surfaces could be used to harden them and thus minimize fretting corrosion.

(2) Steps should be taken to reduce relative motion of surfaces subject to fretting corrosion: surfaces could be built up to provide an interference fit or temporary coatings can increase friction and prevent movement during shipping.

(3) Any sliding surfaces should be well lubricated to prevent fretting corrosion.

(4) Select materials with a better resistance to erosion corrosion.

(5) Modify the environment by removing entrained gases and suspended particles, for example to reduce impingement, cavitation and erosion corrosion attack. Lower temperature of the environment.

(6) Apply coatings to provide a resilient barrier between the metal and the aggressive environment. Hard facings or welded overlays may sometimes be used. Alternatively use resilient gaskets to lessen fretting corrosion.

(7) Consider using cathodic protection for reducing erosion corrosion attack.

(8) Change the designs of equipment (structures) to reduce fretting, impingement and cavitation attack.

(9) If relative motion cannot be totally stopped, even by increasing the load, fretting corrosion attack can sometimes be lessened by increasing the relative motion between the surfaces.

6.6.10 Avoiding Stress-Corrosion Failures.

(1) Annealing should be used to relieve internal residual stresses which result from deep-drawing, spinning and welding used in the fabrication process.

(2) Compressive surface stresses should be substituted for tensile stresses whenever possible by shot-peening, rolling or swagging during fabrication. Rolling of the shanks adjacent to the head of high-strength cap screws and also rolling of the threads has materially increased the life of these cap screws in a corrosive environment.(72)

The process of peening or rolling of the metal surface results in a compressive layer of metal on the surface and a tension layer below it. Pits extending through the compression layer may in some instances expose a tension layer to the environment; cracking will then develop more rapidly than in the untreated surface. This will depend on whether there are components in the environment that will pit the metal as well as those that produce stress-corrosion cracking. Pits in themselves act as regions of stress concentration.

The shot peening of high-strength aluminum alloys is believed to delay stress-corrosion cracking, in that it destroys the continuity of the grain boundaries at the metal surface. This delays the propagation of intergranular or intercrystalline stress-corrosion cracks into the metal.

(3) Alloys should be heat-treated to relieve tensile stresses and to make the microstructures more homogeneous to minimize the effect of intergranular attack.

(4) Cathodic protection should be adopted where practical.

(5) The appropriate protective coatings should be utilized to protect the structure from corrosive agents. Conversion coatings, electrodeposited metal coatings, claddings, or organic coating systems should be used in accordance with the purpose and use of the equipment or structure. Some guidelines are given below.

Any coatings that will act as a barrier between the corrosive environment and the metal will prevent stress-corrosion cracking as long as it is intact. Proprietary coatings have been developed particularly for aluminum and magnesium alloys. These may in themselves help to protect the metal from stress-corrosion cracking and they may also offer excellent bases for a good paint schedule.

Epoxy paints, polyurethane coatings, silicons, etc., have been used as protective coatings to prevent stress-corrosion cracking, particularly of high-strength steels. Protective greases have also been tried. An inhibited epoxy coating (containing a chromate compound as an inhibitor) protected both the H11 die steel and the 18% Ni maraging steel in a 3% NaCl solution. The polyurethane proved to be less effective in protecting the H-1 steel than the maraging steel in the same solution.(73)

In an investigation to determine the effectiveness of several treatments on the resistance to failure of the vascojet-1000 high-strength steel, a zinc phosphate pretreatment and organic coatings, MIL-P-52192, were reported best. Generally, organic coatings prevent corrosion and delay failures by stress-corrosion or hydrogen-stress cracking only insofar as they prevent contact between the corrosive environment and the base material.

The stress-corrosion cracking of insulated stainless steel pipes carrying hot liquids has been a problem. Early investigators suggested that if the insulation became wet, chlorides would leach out onto the pipe surface, causing cracking; hence metal jackets to cover the insulation were suggested. Others are of the opinion that chlorides cannot be kept out of insulation used on pipes and tanks in chemical plants, particularly those located near the seacoast. To solve this problem, it has been recommended that the stainless steel tanks and piping be painted with a zinc-free high temperature silicon paint, or protected with a heavy duty epoxy phenolic coating with a rapid catalyst cure, before they are insulated.(74)

Metallic coatings have been suggested as a means of protecting the base metal from the corrosive environment. These may function either as a barrier coating or to protect the base metal cathodically.

There are only limited data on some of these coatings. Electrodeposited cadmium or cadmium-titanium coatings were reported to be ineffective in protecting high-strength steels. Vapor deposited cadmium offered about the same protection to an H11 steel as a zinc chromate primer. However, in separate investigations, nickel and nickel-cadmium (diffused) electroplates were stated to give good protection to high-strength steels. An aluminum sprayed coating applied after the austenitizing of a high-strength 5.0% Cr steel afforded good protection to this steel, both in a semi-industrial and a marine atmosphere. A zinc dibutyl titanate coating also proved effective in these environments.(44)

6.6.11 Preventing Corrosion Fatigue.

(1) Reduce the stress(es) acting on the component by changing the design, by applying stress-relieving heat treatments, or by shot-peening to induce surface compressive stresses.

(2) Use corrosion inhibitors to prevent corrosion attack, and the initiation of surface cracks, pits or other detrimental defects.

(3) Apply protective coatings such as electrodeposited zinc, chromium, nickel or copper, but ensure that hydrogen is not charged into the metal substrate.

6.6.12 Preventing Hydrogen-Induced Cracking.

The approaches for preventing hydrogen embrittlement and hydrogen-stress cracking are similar to those outlined for stress-corrosion cracking, and include (1) substitution of materials, (2) using coatings as barriers, (3) using inhibitors, (4) removing poisons from the environment, (5) applying heat treatments to degas or reduce residual stresses, (6) redesign to minimize applied stresses, and (7) use low-hydrogen welding rods when fabricating structures.

6.6.13 Preventing Biological Attack.

(1) Metals to be buried in soils should be coated with asphalt or wrapped with polyvinyl tape to prevent contact of biological and chemical agents with the metal surfaces.

6.6.14 Preventing Corrosion at Joints and Faying Surfaces. Special consideration must be given to the prevention of corrosion at joints and faying surfaces in metal parts and assemblies. At these points there may be contact between similar metals, dissimilar metals, or nonmetallic materials such as wood. Corrosion may be easily initiated in these areas. Riveted and bolted joints, spot and other welds, brazed and soldered joints, and threaded fittings are also typical contacting surfaces in parts and equipment where corrosion can develop. The use of gaskets, shims, washers, clips, springs, inserts, and bushings may also create areas susceptible to corrosion. In welded structures, contact between dissimilar metals may give rise to galvanic action. Moreover, similar metals may be welded with a rod of the same or different composition, while the rods used in welding dissimilar metals may be the same as either one of the metals or a completely different composition.

It is evident that the principal types of attack associated with joints and similar contacts are galvanic and crevice corrosion. Galvanic corrosion may be expected when dissimilar metals are joined, especially when these metals are listed well apart in the Galvanic Series (see table III). Crevice action may occur at washers, under applied protective coatings, at threaded joints, and at surface defects in welds. The form of concentration-cell action initiated by liquid trapped in crevices may also occur. In many instances the vulnerable features are due to faulty design, and the susceptibility is aggravated by typical outdoor exposure or more severe environments. Where adverse conditions are expected, suitable protection of joints and faying surfaces depends upon the intended service, the type of metals joined, and the presence of dissimilar metals or nonmetallic materials. If it were possible to keep contacts completely dry or joints absolutely tight, corrosion could be eliminated or minimized. Most conditions of service, however, require that contact areas be given some protection. Where practicable, dissimilar metals should be insulated at contact faces by paint, sealing tape, plastic coatings, or similar materials. Other precautions are summarized in Paragraph 6.4.1, which lists general protective measures for various types of exposures and forms of attack.

The protective measures that are applicable for light metals such as aluminum and magnesium are well developed. The following discussion presents methods of corrosion protection adopted for use with these metals.

The faying surfaces of riveted aluminum and aluminum alloy joints should be painted before riveting. Before being painted, the surfaces should be chemically treated (with a phosphoric acid solution or a chromating solution) and then thoroughly rinsed and dried. After treatment, a coat of zinc chromate primer is applied to the faying surfaces. The paint should be dry before riveting. After riveting, a sealing compound containing zinc chromate may be applied to the exposed ends. Another acceptable procedure is accomplished as follows: a suitable joint compound is applied to the faying surfaces, a primer is applied to all of the structure including rivet heads, and then the top coat is added. For spot-welding joints, corrosion resistance may be improved by performing the welding through a primer. Where aluminum parts are machined to close tolerances, the use of anodic coatings before assembly may virtually eliminate the need for painting. The alternative method is also recommended for other light metals (see Paragraph 6.5.1).

The special methods devised for the protection of magnesium joints and contacts include techniques applicable under relatively severe conditions of service, such as continuous exposure in industrial atmospheres. For magnesium-to-magnesium contacts, such as riveted and bolted assemblies, the faying surfaces should be given a chemical treatment or a conversion coating, then one or more coats of a primer having an alkali resistance vehicle such as epoxy or vinyl resin. For fastening in general, 5056 aluminum rivets, 6061 aluminum bolts, and zinc or cadmium plated steel bolts are recommended for use with magnesium.

For riveted joints involving magnesium and dissimilar metals, the contact faces should be suitably painted or insulated with organic tape or sealing compound before assembly. When joining magnesium to nonmetallic materials such as wood, similar precautions are necessary. When wood is joined to magnesium, the wood should be sealed with paint or varnish to prevent absorption of water. In this type of union, the faying surface of the metal should be primed with zinc chromate. The process of assembly is the same as that for the bolting of magnesium and dissimilar metals, as described below.

When magnesium is joined to dissimilar metals by bolting, the surfaces should be well insulated and only the proper materials used for fastening. One recommended method of assembly is performed as follows: (1) cadmium-plated steel bolts and nuts are used, (2) a 5052 aluminum washer is inserted between the bolt head and the magnesium (3) sealing compound, organic tape, or alkali resistant paint is applied between the dissimilar metal and the nut. Inserts used in magnesium structures should also be plated with cadmium or zinc.

Only 5056, 6061, and 6053 aluminum alloy bolts and screws can be used bare in magnesium assemblies. Bolts and screws of other aluminum alloys, and of brass, steel, and nickel, as well as rivets of steel, and copper, should not be used in a bare condition against magnesium because there is no way of insulating them from the magnesium. If they must be used, a zinc or cadmium should be given a chemical treatment for the purpose of improving the adhesion of the paint coating.

Cadmium and/or zinc plated parts should not be used in unventilated areas where they may come in contact with organic vapors from phenolics, amines, etc. (see Paragraph 5.9).

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SECTION 7. CORROSION TESTING

7.1 Types of Corrosion Test. The scope of this handbook precludes a detailed discussion of corrosion testing principles and procedures. A general, but comprehensive coverage may be obtained by reading References (77) through (81). The purpose of this paragraph is to outline the types of tests available, the nature of the data collected, and its interpretation and use for diagnostic or preventive measures in combatting corrosion. Table XVIII lists some of the more common, approved corrosion tests for a wide variety of materials and environments. Other tests and recommended procedures are given in Table XXII in Paragraph 8.2.

Corrosion tests may be classified according to various criteria, however, it is convenient to think of (a) laboratory tests, and (b) field tests. Laboratory corrosion tests are useful for (1) studying the mechanisms and chemistry of corrosion processes (2) determining the types of environment in which a metal will function adequately (3) studying the effects of changes in composition, heat treatment or fabrication on corrosion performance in given environments (4) serving as a control for the comparison between metals, or for different batches of the same metal (5) determining the effect of changes in the environment, in a controlled manner, on corrosion for a specific metal, and (6) determining whether a metal, coating, structure or piece of equipment will meet the relevant specifications pertaining to its use. Field tests, carried out in natural environments, or in actual service in the plant, field, or as part of a preventive maintenance program, are useful for (1) confirming that a specific metal, coating or structure is impervious to a given environment (2) yielding data permitting the useful life to be estimated, and (3) studying the effectiveness of the chosen means of corrosion protection. Some aspects of corrosion testing will be common to both types of tests, some procedures used in the laboratory will not be suitable for use in the field. For optimum results, both types of testing should be used to complement each other, and provide the corrosion engineer with the maximum amount of qualitative and quantitative data possible, and a thorough understanding of the corrosion processes involved.

TABLE XVII. Some Approved Corrosion Tests Commonly Used

Test Number	Organization and Test Description
	(1) Federal Test Method 151
812	Synthetic Seawater Spray Test
822	Intergranular Corrosion Test for Aluminum Alloys
	(2) National Association of Corrosion Engineers
TM-01-69	Laboratory Corrosion Testing of Metals for the Process Industries
TM-02-70	Test Method for Conducting Controlled Velocity Laboratory Corrosion Tests
TM-01-71	Test Method for Autoclave Corrosion Testing of Metals in High Temperature Water
TM-01-72	Test Method for Antirust Properties of Petroleum Products Pipeline Cargoes
TM-01-73	Test Methods for Determining Water Quality for Subsurface Injection Using Membrane Filters
TM-01-74	Laboratory Methods for the Evaluation of Protective Coatings Used as Lining Materials in Immersion Service
TM-02-74	Dynamic Corrosion Testing of Metals in High Temperature Water
TM-03-74	Laboratory Screening Tests to Determine the Ability of Scale Inhibitors to Prevent the Precipitation of Calcium Sulfate and Calcium Carbonate from Solution
TM-02-75	Performance Testing of Sucker Rods by the Mixed String, Alternate Rod Method
TM-03-75	Test Method for the Abrasion Resistance Testing of Thin Film Baked Coatings and Linings Using the Falling Sand Method
	(3) American Society for Testing and Materials
A262	Detecting Susceptibility to Intergranular Attack in Stainless Steels
A279	Total Immersion Corrosion Test of Stainless Steels
B117	Salt Spray (Fog) Testing
B287	Acetic Acid-Salt Spray (Fog) Testing
B368	Copper-Accelerated Acetic Acid Salt Spray (Fog) Test (CASS Test)
B380	Corrosion Testing of Decorative Chromium Plating by the Corrodkote Procedure
B538	Method of FACT (Ford Anodized Aluminum Corrosion Test) Testing
D543	Test for Resistance of Plastics to Chemical Reagents
D807	Corrosivity Test of Industrial Water (U.S. Bureau of Mines Embrittlement Detector Method)

TABLE XVII. (Continued)

Test Number	Organization and Test Description
D870	Water Immersion Test of Organic Coatings on Steel
D1384	Corrosion Test for Engine Antifreeze in Glassware
D1735	Water For Gesting of Organic Coatings
D1748	Test for Rust Protection by Metal Preservatives in the Humidity Cabinet
D2247	Testing of Coated Metal Specimens at 100 Percent Relative Humidity
D2570	Simulated Service Corrosion Testing of Engine Coolants
D2803	Test for Filiform Corrosion Resistance of Organic Coatings on Metals
D2966	Test for Cavitation-Erosion Characteristics of Aluminum in Engine Antifreeze Solutions Using Ultrasonic Energy
G1	Preparing, Cleaning and Evaluating Corrosion Test Specimens
G4	Conducting Plant Corrosion Tests
G5	Standard Reference Method for Making Potentiostatic and Potentiodynamic Measurements
G7	Atmospheric Environmental Exposure Testing of Nonmetallic Materials
G11	Test for Effects of Outdoor Weathering on Pipeline Coatings
G28	Detecting Susceptibility to Intergranular Attack in Wrought Nickel-Rich, Chromium-Bearing Alloys
G31	Laboratory Immersion Corrosion Testing of Metals
G32	Vibratory Cavitation Erosion Test
G34	Test for Exfoliation Corrosion Susceptibility in 7XXX Series Copper-Containing Aluminum Alloys (EXCO Test)
G35	Determining the Susceptibility of Stainless Steels and Related Nickel-Chromium-Iron Alloys to Stress-Corrosion Cracking in Polythionic Acids
G36	Performing Stress-Corrosion Cracking Tests in a Boiling Magnesium Chloride Solution
G37	Use of Mattson's Solution of pH 7.2 to Evaluate the Stress-Corrosion Cracking Susceptibility of Copper-Zinc Alloys
G41	Determining Cracking Susceptibility of Titanium Alloys Exposed Under Stress to a Hot Salt Environment
G43	Acidified Synthetic Seawater (Fog) Testing
G44	Alternate Immersion Stress-Corrosion Testing in 3.5 Percent Sodium Chloride Solution.

Note: A more detailed listing of specifications, standards, and recommended practices is given in Paragraph 8, and specifically in Table XXII.

7.2 Laboratory Tests. The distinguishing feature of laboratory tests, as opposed to field tests, is that the tests are made with pure chemicals under carefully controlled conditions to assure reproducibility of the data. Ideally, in each series of tests only one variable should be changed so that the cause of improved or decreased corrosion resistance can be determined unequivocally. When the most important variables influencing corrosion are not known, or properly understood, then it is helpful to first perform a series of factorial experiments. As a result of such tests the important variables may often be easily identified, and used to design subsequent tests.

Laboratory tests are usually conducted with small metal specimens, often of a prescribed size and shape, either for convenience, or for offering the opportunity of performing additional mechanical tests (e.g., bending, tensile testing) or using in special equipment such as stress-corrosion cracking test apparatus. With such an approach the specimens are reproducible, and because of their small size, they are relatively inexpensive. Discs, flat panels, or coupons and flat tensile test specimens can be cut or stamped from sheet stock. Round tensile specimens, parts of wrought or fabricated structures are often cut then machined to the required dimensions. For the evaluation of protective coatings, the panels generally have rounded edges to promote an even coating thickness during the coating process (especially if electroplating is used). Sometimes coated panels are intentionally damaged to try and reproduce service conditions and failures. Scribing, the countersinking of drilled holes, hammering to produce crazing, or the removal of part of the coating are some of the methods used to produce intentional damage. When laboratory tests are performed using this type of specimen, undamaged control specimens should be evaluated at the same time.

Sometimes small fabricated articles are also corrosion tested in the laboratory, primarily to determine if test results on small specimens can be correlated with the finished product. Where galvanic corrosion attack is a possibility, either because of the use of dissimilar metals, or the presence of brazed, soldered or welded joints, it is often desirable to test the article because relative position and size of the anode and cathode sites play important roles in determining the extent and rate of attack.

The surface finish and metallurgical treatment of the test specimens can be important variables in corrosion tests. They can be controlled to either help ensure reproducibility of the test data, or reproduce service conditions. In any event the surfaces should be clean and free of grease (including fingerprints). Mechanical (e.g., abrasives) or chemical (e.g., pickling) or even electrochemical (e.g., anodic cleaning) cleaning methods can be used. The latter do not introduce any cold work in the metal, but could under some circumstances introduce hydrogen into the metal, causing an embrittlement problem.

The corrodents can be gases, liquids, or both, varying widely in composition, toxicity, aggressiveness, viscosity, and so on, according to the applications for which test data are being generated. Temperature, pressure, and pH are important variables and should be closely controlled and monitored. Control of aeration and velocity of liquid corrodents is more difficult. To help the rapid solution of oxygen from the air being bubbled through an electrolyte solution, it is important that the bubble size be kept small. A porous disc or cup connected to the end of the supply tube is useful

for this purpose. Bubbles should not be allowed to directly impinge on the test specimens. Control of the amount of dissolved oxygen is best achieved by controlling the proportion of oxygen in the saturating gas, rather than trying to alter the rate of bubbling. A completely inert gas, such as argon or nitrogen, can be used for stirring purposes. Often it is easier to move the test specimen through the corrodent (by rotation or reciprocating movements) than to flow the corrodent past the specimen. With the latter approach a much larger volume of corrodent is needed as well as a separate reservoir, and pumping and metering/control equipment. However, in studying certain types of corrosion attack (e.g., erosion-corrosion or cavitation) flowing solutions more closely resemble actual service conditions. It may be possible to scale down the test apparatus and yet still obtain data which correlates well with service failures and other corrosion data.

The specimens may be totally or partially immersed in a liquid, or alternatively dipped in the liquid. In gaseous environments, with controlled humidity and temperature (fixed or cyclically varied) the specimens can be oriented horizontally, vertically, or at an angle, and one of the surfaces can be made to point upwards or downwards, or varied according to some preprogrammed schedule. From time to time the specimens can be sprayed with a specific corrodent to simulate service conditions.

Special attention should be given to the volume of corrodent and the method used to hold the specimen during the tests. If one of the constituents in the corrodent is consumed, and this constituent is responsible for the corrosion attack, if the test volume is limited, corrosion can stop during the course of the test. Similarly, if one of the constituents contributes to the formation of a protective film, it is important that a sufficient quantity is available, compatible to what may be present in actual service. Crevices can be set up when specimens are held in holders, particularly if the holders are not properly designed. Such crevices can cause concentration cell corrosion such as that resulting from differential aeration cells (see Paragraph 4.3.4). Surfaces should be shielded as little as possible, and not permit gas bubbles to be trapped for the same reason.

Various pieces of electronic equipment are avaialbe for measuring corrosion current, potentials, solution pH, temperature, and so on. Equipment is available for performing galvanostatic, potentiostatic, potentiodynamic, and linear polarization experiments. The current is held constant in the first method, and changes in electrode potential are measured versus a reference electrode (e.g., saturated calomel electrode). In the potentiostatic method the electrode potential is held constant, while the change in corrosion current is measured. The potential of an electrode is varied in a controlled manner and the corresponding corrosion current response is measured in the potentiodynamic method. Finally, in the linear polarization method the electrode potential is changed by a few (<10) millivolts about the open-circuit potential, and the corrosion current measured after each incremental change. Each of the above method yields data about the type of corrosion reaction occurring or the kinetics of such a reaction. However, experienced corrosion technologists are required to interpret the information generated. Further description about these experimental methods, and schematic circuit arrangements are given in References (78) and (80). The above discussion was given only to indicate that a variety of simple and sophisticated test methods are available to the corrosion engineer.

7.3 Field Tests. These types of tests are useful because they form the bridge between laboratory tests and service failures. Field tests last from sometimes a few days or months, to tens of years, depending on the type of information being generated.

A common field test is an exposure test to determine the corrosion resistance towards atmospheric, water or soil environments. Usually test specimens are cut to standardized dimensions, and mounted appropriately with insulating fasteners. General considerations for the mounting of specimens are (a) the specimens should be isolated from each other, and from the rack or test fixture, (b) the specimens should be arranged on the fixture such that the corrosion products (solids or dissolved species) from one does not contaminate any of the others, and (c) the corrodent should be equally accessible to all the specimens.

Many replicates of a given material, coating type or metal combination, whatever, are mounted on the test fixture, and carefully marked with identifying numbers, letters, or codes. In this manner it is possible to remove a specimen at prescribed intervals (say, 1, 2, 5, 7, and 10 years) and measure the rate of progress of corrosion attack. Three data points are the minimum needed to illustrate a trend, while five data points are helpful in showing if a change in trend occurs. Of course, the more data points obtained, the more accurate will be the interpretation of the results.

With atmospheric exposure the variables include the type of atmosphere (rural, industrial, and marine), the angle of exposure (horizontal, tilted, vertical), the direction of exposure (amount of incident sunlight, prevailing winds; and whether the test surface is exposed towards or away from the ground (amount of shelter, frequency of washing by rain, collection of condensation). With marine exposures there are the choices between total immersion (below low tide level), non-immersion (above high tide level) but subjected to salt spray, and partial immersion (between high and low tide levels). Testing at considerable depths in the ocean or in lakes is often referred to as the "hydrospace" environment. With offshore oil drilling platforms, underwater cables, and underwater salvage and habitat equipment becoming more common, testing in such an environment is becoming more necessary. Other variables with water exposure include temperature, pH, salinity (constant changing near an estuary), dissolved gases and solids (hardness), suspended particulates and velocity (stagnant or flowing; laminar or turbulent flow). Similar variables may be listed for soil corrosion tests, the more common being water content, conductivity (or its inverse, resistivity) pH, temperature, and presence of aggressive chemicals.

Having progressed from laboratory through field tests with test specimens, the next stage is to conduct tests with partial structures or pieces of equipment, or simulated structures, the validity of gathered data can thus be checked, and any influence of scale-up detected. Final testing involves pilot plant or experimental model testing under simulated operating conditions. If the material or structure behaves satisfactorily in such tests, then from a corrosion standpoint at least, the material or structure may be put into service.

7.4 Reporting of Test Data. There is no need to emphasize that careful written documentation is necessary for all corrosion tests. Certain test

data, for example when evaluating a new alloy, are best kept in a laboratory notebook, with each page dated and witnessed by someone knowledgeable about the nature of the tests. Patent attorneys prefer this type of record when trying to establish or defend a patent position. Such records should be carefully protected against loss or damage.

With laboratory and field tests especially, there are various ways of assessing corrosion damage, both qualitative and quantitative in nature. Visual examinations are usually made of all test specimens before and after suitable cleaning. Where the metal or coating is to be used for decorative purposes such a visual examination is important, and the area of the test specimen used should be large enough so that any nonuniform effects are visible. Corrosion attack will be evidenced by such defects as pitting, blistering, exfoliation, discoloration, loss of luster, crazing, and the presence of corrosion products, for example. Sketches or photographs of the test specimen before and after testing may serve for useful future reference provided they carry proper identification. A record should be made of any regularity in the distributuon of corrosion attack (e.g. along grain boundaries, around the edge of the specimen). With a structure or piece of equipment, in addition the visual examination should include evidence of galvanic corrosion, or concentration cell corrosion, and record its extent.

It is always advisable to record the total amount of data collected. Subsequently, when the final record is made, or report is written, the most pertinent data can be selected. Sometimes, however, it is the chance observations, or recording of unexpected results, that lead to a breakthrough in materials development or form the basis for a new type of corrosion test. Many inventions are the result of serendipity and acute powers of observation coupled with an alert mind to understand the significance of the results.

A few tools exist to assist in interpreting the test data and making its recording easier.[78] For example, pitting is a common form of corrosion attack, but it is tedious to have to count the number of pits per unit area, or to determine the average diameter, when the number of pits is large. Rating diagrams, such as those shown in figure 50, are available (see table XXII) to make relative rating of pitting attack easier. Such diagrams are often used to evaluate the attack on electroplated coatings.

Depth of attack and weight loss or gain are other frequently used parameters to measure quantitatively the extent of corrosion attack. When depth of attack is measured, the test specimens should be thick enough so that perforation does not occur. The average depth may be determined by using a micrometer gage, or a commercial surface profile-indicating device (e.g. Talysurf machine). Units of measurement are millimeters per year, mpy (or inches per year, ipy).

However, average depth of attack can be readily calculated from a weight loss measurement, which can be quickly performed after suitable cleaning procedures have been followed. Table XVIII lists some approved methods for cleaning common metals, while Chapter 7 of Reference (78) gives further details. ASTM G1 contains standard recommended practices for preparing, cleaning, and evaluating corrosion test specimens. Reference (82) briefly discusses non-chemical techniques, particularly pertinent for organic coatings

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TABLE XVIII. Some Approved Methods For Removing Corrosion Products From Test Specimens Prior To Inspection.

(1) Aluminum Alloys [a]
(a) Chromic acid (20 g/l) plus phosphoric acid (85%) (40 g/l) at 93°C,
or (b) Nitric acid (s.G. = 1.42) at 25°C maximum. Periodically remove and scrub with a bristle brush under running water. Dry before immersing again.
(2) Copper
(a) Hydrochloric acid (50% at 10 to 15°C. Dip for 2 or 3 minutes only,
or (b) Sulfuric acid (10% at ≤ 25°C. Dip for 2 or 3 minutes. Scrub with a bristle brush under running water. Dry before immersing again, if this is necessary.
or (c) Hydrochloric acid (10%) plus Rodine No. 50 [b] (1%) at ≤ 25°C for 3 minutes.
(3) Magnesium Alloys
(a) Chromic acid (20%) plus silver nitrate (1%) at ≥ 25°C. for 1 minute. Rinse and dry,
or (b) Ammonium chromate (10%) at 25°C, with air bubbling through, for 24 hours.
(4) Nickel Alloys
(a) Hydrochloric acid (50%) at ≤ 25°C for less than 5 minutes,
or (b) Sulfuric acid (10%) at ≤ 25°C for less than 5 minutes.

TABLE XVIII (Continued)

(5) Steels
(a) Hydrochloric acid (10%) plus Rodine No. 50[b] (1%) for 1 hour. Scrub and rinse under running water,
or (b) Hydrochloric acid (.s.g. = 1.16) (100 ml) plus antimonious oxide (2 g) plus stannous chloride (2 g) at $\geq$ 20°C for up to 30 minutes.
(6) Stainless Steels
(a) Nitric acid (30%) at $\sim$ 25°C, or nitric acid (10%) free from chlorides at 60°C.
(7) Zinc Alloys
(a) Ammonium chloride (10%) at 60 to 80°C for less than 5 minutes. Rinse and scrub with soft brush. Immerse 15 to 20 seconds in boiling chromic acid (5%) plus silver nitrate (1%). Rinse in hot water and dry,
or (b) Saturated ammonium acetate solution at 20 to 25°C.

(a) Additional methods and metals are discussed in ASTM G1, "Preparing, Cleaning, and Evaluating Corrosion Test Specimens".

(b) Amchem Products Company, Inc., Andover, PA.

on metals. When cleaning before determining weight changes, it is important to run controls to ensure that the uncorroded metal is not being unduly attacked itself.

Specimens of large area to volume ratio are preferred for weight change determinations, with relatively small overall dimensions, and easily convenient (see table XXII), and ASTM, for example, use panels measuring about 10 x 22.5 x 0.15 cm (4 x 9 x 1/16 in.) for atmospheric exposures of rolled stock. After cleaning and drying (and storage, if necessary) the specimens are weighed to a predetermined accuracy. The smaller the initial specimen weight, the more decimal figures are required. Thus for a specimen initially weighing less than 100 g (0.22 lb), three or four decimals (tenths of a milligram) may be needed to ensure suitable sensitivity. For specimens weighing in excess of 100 g two decimal places (centigrams) may give sufficient sensitivity.

After the weight change data have been obtained it is convenient to convert the raw data into suitable units which are unambiguous and simple to understand. The data may be expressed as a precentage weight change, as follows:

$$\text{Percentage Weight Change} = \frac{\text{Original Weight-Final Weight}}{\text{Original Weight}} \times 100,$$

or as a corrosion rate. In metric units the rate is usually expressed as milligrams per square decimeter per day, and abbreviated as mdd, as follows:

$$\text{Corrosion Rate (mdd)} = \frac{\text{Weight Change in mg}}{\text{Exposed Area } (dm^2) \times \text{Time of Exposure (days)}}.$$

Table XIX lists some common conversion factors for changing metric units into Imperial (U.S.) units, and vice-versa, while table XX lists the densities of some common metals and corresponding corrosion rates are listed in Reference (77). Note that ipy values are really cubic inches of metal removed per square inch of specimen exposed per year. Also in table XIX the symbol D refers to the density of the metal, measured in grams per cubic centimeter (g/cc).

Under circumstances where the corrosion current is being monitored (or preferably the amount of charge, It, transferred is measured) the theoretical weight loss can be calculated, and used either for predicting experimental results, or for comparison with the experimental results. Such comparisons are only valid when there are no current-consuming side reactions, such as the evolution of hydrogen gas. From Faraday's Law of Electrolysis:

$$\Delta W = I.t.e.$$

Where I is the current in amperes; t the time in seconds; e the electrochemical equivalent of the metal, and ΔW the change of weight in grams. The electrochemical equivalent is given by dividing the equivalent weight of the metal by the Faraday Constant (96,487). The equivalent weight is obtained by dividing the atomic weight by the valence (the number of electrons exchanged per unit reaction). Thus for iron:

TABLE XIX. Conversion Factors for Obtaining Units of mdd or mpy.

To Get mmd		To Get mpy	
Multiply	By	Multiply	By
Gms per sq in per hr	372,000	Gms per sq in per hr	536,300/D
Gms per sq in per day	15,000	Gms per sq in per day	22,270/D
Gms per sq in per yr	42.5	Gms per sq in per yr	61/D
Gms per sq cm per hr	2,400,000	Gms per sq cm per hr	3,460,000/D
Gms per sq cm per day	100,000	Gms per sq cm per day	143,700/D
Gms per sq cm per yr	274	Gms per sq cm per yr	394/D
Gms per sq meter per hr	240	Gms per sq meter per hr	364/D
Gms per sq meter per day	10	Gms per sq meter per day	14.37/D
Gms per sq meter per yr	0.0274	Gms per sq meter per yr	0.0394/D
Oz per sq in per day	439,200	Oz per sq in per day	632,160/D
Oz per sq ft per day	3,050	Oz per sq ft per day	4,390/D
Cm per yr.	274 x D(a)	Cm per yr.	394
Mm per yr.	27.4 x D	Mn per yr.	39.4
ıpy.	696.0 x D	In per yr (ipy).	1000
mpy.	0.696 x D	mdd	1.437/D

(a) D is density in grams per cubic centimeter.

TABLE XX. Density of Common Metals and Alloys, and Corrision Rates Equivalent to 1 mdd.

Material	Density, g/cc	Penetration Equivalent to a Corrosion Rate of 1 mdd	
		ipy	cm/year
Aluminum 2S	2.72	0.000 528	0.001 346
Brass (admiralty)	8.54	0.000 168	0.000 427
Brass (red)	8.75	0.000 164	0.000 416
Brass (yellow)	8.47	0.000 170	0.000 432
Bronze, phosphor (5% Sn)	8.86	0.000 162	0.000 412
Bronze, (silicon)	8.54	0.000 168	0.000 427
Bronze, Cast (85-5-5-5)	8.70	0.000 165	0.000 419
Cast iron	7.20	0.000 200	0 000 508
Copper	8.92	0.000 161	0.000 409
Copper/nickel alloy (70/30)	8.95	0.000 161	0.000 409
Hastelloy A	8.80	0.000 163	0.000 414
Hastelloy B	9.24	0.000 155	0.000 394
Hastelloy C	8.94	0.000 161	0.000 409
Inconel	8.51	0.000 169	0.000 429
Iron/silicon alloy	7.0	0.000 205	0.000 521
Lead (chemical)	11.35	0.000 127	0.000 323
Magnesium	1.74	0.000 828	0.002 096
Monel	8.84	0.000 163	0.000 414
Nickel	8.89	0.000 162	0.000 412
Nickel silver (18% Ni)	8.75	0.000 164	0.000 417
Ni-resist	7.48	0.000 192	0.000 488
Silver	10.50	0.000 137	0.000 348
Stainless steel Type 304	7.92	0.000 181	0.000 462
Stainless steel Type 430	7.61	0.000 189	0.000 480
Steel (mild)	7.86	0.000 183	0.000 465
Tin	7.29	0.000 197	0.000 500
Titanium	4.50	0.000 320	0.000 811
Zinc	7.15	0.000 201	0.000 510

$$e = \frac{(55.85/2)}{96.487} = 0.000289$$

and for a current of 1 ampere, flowing for 1 hour over an area of 1 m^2, the weight change could be:

$$\Delta W = 1 \times (60 \times 60) \times 0.000289 \text{ g},$$
$$= 3600 \times 0.000289 \text{ g},$$
$$= 1.04 \text{ g},$$

for an exposed area of 1 square meter, or from table XIX this would be equivalent to about 250 mdd.

Other parameters for measuring the extent of corrosion attack are related to the mechanical properties of the metal. Thus the loss in ultimate tensile strength or ductility (elongation) can be used to compare corrosion effects. If tensile strength changes are to be the quantitative measure for corrosion, then the test specimens can be in the form of tensile specimens, preferably to ASTM Standards. For sheet metal up to 1.25 cm (0.5 in.) thick the specimen can be cut directly from the sheet. For other forms of metal round tensile test specimens can be machined from the stock, noting the position from which the blank was cut because grain orientation can have a marked effect on corrosion rates. If the specimens are cut or machined to shape before corrosion testing, there is always the possibility that localized attack will give notch effects during tensile testing, and failure can occur at unrealistically low values. Thus, it may be desirable to machine the tensile test specimens from the metal after the corrosion tests.

7.5 Accelerated Corrosion Tests. Accelerated corrosion tests were originally devised to hasten the evaluation of atmospheric corrosion test specimens. The premise behind such tests was that because of the electrochemical nature of corrosion, if the corrodent was made more aggressive, or the electrode potentials displaced further from the open-circuit potentials, an increased corrosion rate would be observed proportional to such perturbations. In general, this is not found, and often such changes alter the normal corrosion behavior sufficiently to provide no consistent relationship for the basis of prediction. Nonetheless, some types of accelerated tests have persisted, and are used despite their shortcomings, often for the purposes of materials procurement. These tests include exposure to sprays, increased humidity, and more aggressive atmospheric and liquid environments.

Various forms of spray or fog tests are used to evaluate coatings, whether organic (paints, varnishes) or inorganic (anodic films, conversion coating). In some tests the specimens are continuously exposed to the spray, in others the spray is intermittent. Common spray solutions are (1) distilled water, (2) salt solutions containing 3.5, 5, or 20 percent sodium chloride, and (3) salt solutions acidified to a chosen pH, or with metal cations added which will plate out during the test and accelerate local corrosion. Operating temperatures vary, but are often in the range of 35 to 50°C (95 to 120°F). The spray should never impinge directly on the specimen, but should be allowed to settle. To permit drainage of this corrodent the specimens are often tilted at angles to 15, 30, or 45 degrees from vertical. The tests can

be shortened by purposely introducing defects into the coatings such as scribe marks. The data obtained in such a way are useful for comparing different materials, but are not quantitative in the sense that they can be directly applied to service uses.

Modifications of the salt-spray test exist, and proprietary versions exist such as "the CASS test". The acetic acid/salt spray test developed for producing blistering on chromium-plated zinc die castings has been modified in the CASS test by the addition of cupric chloride for testing nickel/chromium coatings on both steel and zinc. Accelerated galvanic corrosion of the nickel occurs at any discontinuities in the chromium layer, which itself is virtually unattacked.

High relative humidity coupled with elevated temperatures form the essential features of another type of accelerated corrosion test, particularly used for evaluating the behavior of temporary coatings on aluminum, or in structures where metal components are in contact with absorbent non-metallic components such as wood, paper, or insulation. For small specimens a simple test is to store the specimens above water in a closed container (in a temperature-controlled environment, if necessary). For large specimens, multi-specimen tests, or structures, commercial test equipment is available. The tests can be modified to include cyclic condensation on the specimens, or by the addition of trace contaminants such as gases, in which case the environment can resemble a simulated atmosphere.

Recently, because of changing technology in power generation, waste incineration, space travel, and various other industries, many tests have sought to duplicate the aggressive environments encountered. These simulated atmospheres, for example, may involve the presence of gases or particulate matter in a controlled pressure chamber held at elevated temperatures. Ultraviolet light can be used to simulate photochemical effects in such atmospheres. Usually such chambers are tailor-made; however, a few are available commercially, for example for performing the "Kesternich Test". This test involves injection of CO_2, SO_2, and water vapor into the specially designed equipment.

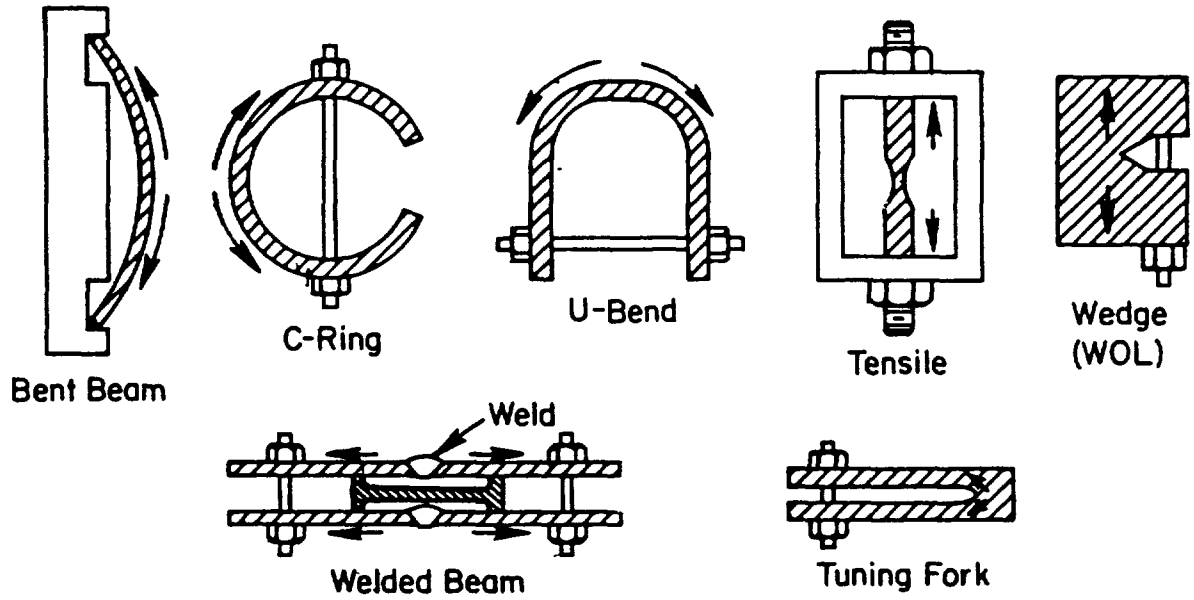
A wide range of immersion tests can be designed for full, partial, or intermittent immersion. The results obtained often cannot be correlated with service applications; however, these tests serve as a quick screening procedure for determining susceptibility to various environments. A special type of combined immersion and humidity test is the "Corrodkote test" in which a slurry, representing melted street slush in winter, is paddled onto the specimen, then the specimen is exposed to a warm humid atmosphere. Good success has been obtained with this method of simulating winter driving conditions in the U.S. when the automobile is infrequently washed, but kept in a garage. The slurry contains cupric nitrate, ferric chloride, and ammonium chloride mixed into Kaolin powder. After coating the specimen it is allowed to dry for an hour, then exposed to a relative humidity (non-condensing) of 90 to 95 percent RH at 38°C (100°F). The specimen is removed after 20 hours, cleaned, and inspected (for zinc alloys) or inspected and cleaned (for iron alloys). One of the test cycles is typically equivalent to one winter's exposure in a city which uses salt for de-icing.

7.6 Stress-Corrosion Testing. Detailed discussions of the procedures for evaluating stress-corrosion cracking susceptibility are given in References (78), (81), and (83) through (86); and for evaluating hydrogen-stress cracking of high-strength steels in Reference (87). Only the general principles and procedures will be given here.

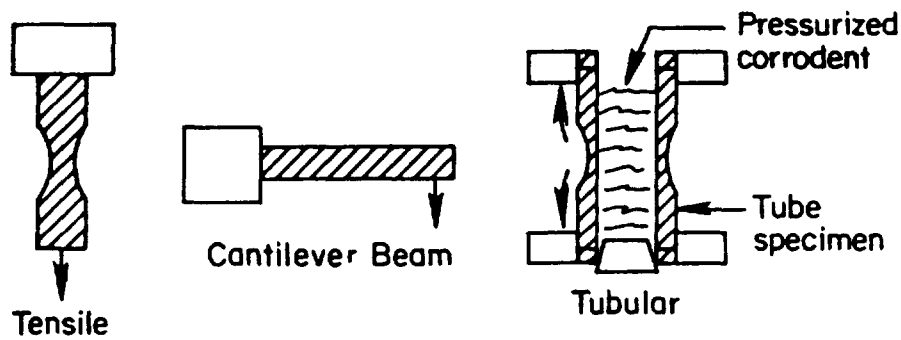
At the present time there is no single, universally accepted stress-corrosion test. The procedures are usually designed for specific materials and environments. Until recently most test specimens were smooth and uncracked (tensile, U-bend and bent beam configurations, see figure 51), and tests tended to be lengthy and not easily reproduced, although easy to perform. However, with the advent of applying fracture mechanics principles to stress-corrosion tests and the interpretation of the data, notched and precracked specimens in a variety of shapes are being used more frequently. Some materials are susceptible to cracking in certain environments, only if cracks are present (e.g. some high-strength steels in humid air or water, and some titanium alloys in aqueous chloride solutions). Because cracks or other surface flaws can be present in structures and equipment, the use of precracked specimens could lead to a better correlation with service failures. The notch serves to concentrate the applied stress in a known area of the specimen, and makes visual or metallographic inspection for cracking easier to accomplish. Fatigue cycling is usually applied to initiate a small crack at the tip of the notch in some specimens (see figure 51). The presence of the crack in the test specimens further localizes the stresses, and the tendency for the crack to propagate in a specific environment can be measured. Subcommittee G01.06 of the ASTM is currently drafting recommended practices for the use of precracked specimens for stress-corrosion testing.

Test specimens and test fixtures can be further characterized according to how the stress is applied to the specimen. Thus, there are (a) constant strain, (b) constant load and (c) constant stress tests. In a constant strain test the applied stress decreases as the crack grows. In the constant load test the applied stress effectively increases as the crack grows, while in tests where constant stress conditions are approximated the applied stress remains fairly constant for the duration of the test. Specimens and fixtures to achieve these conditions are shown in figure 51. The nature of the material to be tested (whether sheet, tube, bar, or wire) will place some restrictions on the type of test specimen which can be fabricated. With bar or thick sheet stock, if specimens cannot be cut from each direction, it is important to at least test in the short, transverse direction (see Paragraph 5.1.3).

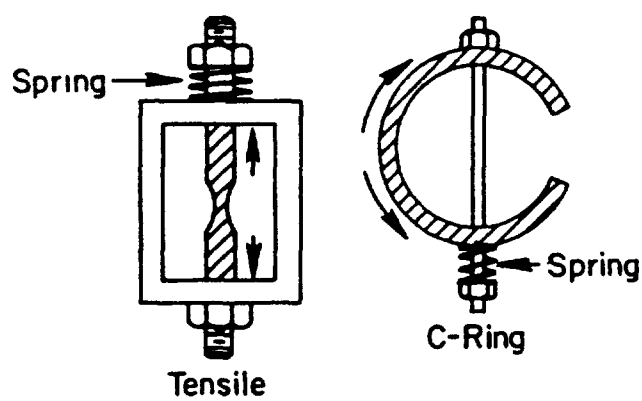
If a test program calls for very many specimens to be evaluated, the test specimens should be self-loading, and not require equipment such as tensile test machines to impress the strain/stress. This is particularly important when the duration of a test is very long, and the machine could be used in the meantime for other testing programs. Also, if the purpose of a test is to determine K_{Iscc}, the threshold stress intensity, this can be done with a single specimen if it is of the "crack-arrest" type. That is, as the crack propagates the load decreases, until eventually the crack will stop. The stress than has a value equivalent to K_{Iscc}. Conventionally, as figure 52 shows, for a given set of conditions, and for a material in which the stress intensity factor, K_I, decreases with crack propagation.



(a) Constant Strain Test Specimens



(b) Constant Load Test Specimens



(c) Constant Stress Test Specimen

FIGURE 51. Various types of specimens used for stress-corrosion cracking tests Smooth specimens are shown although many may be used in the notched or notched and precarcked condition.

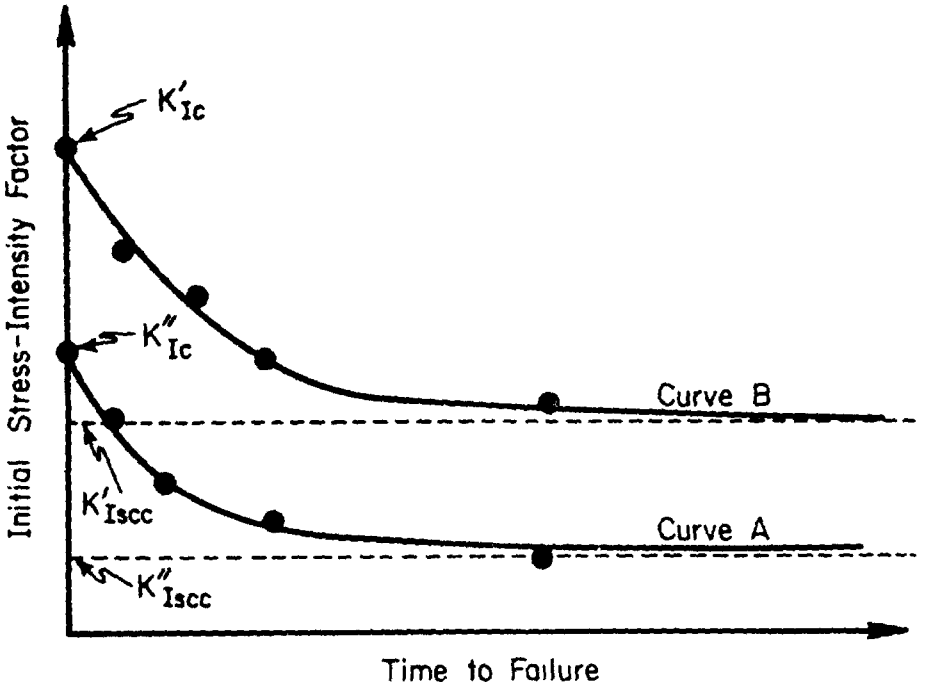


FIGURE 52. Stress-corrosion characterization of a material with low resistance (curve A) and high resistance (curve B) to cracking.

K_{Ic} = Initial Stress Intensity Factor

K_{Iscc} = Threshold Stress Intensity

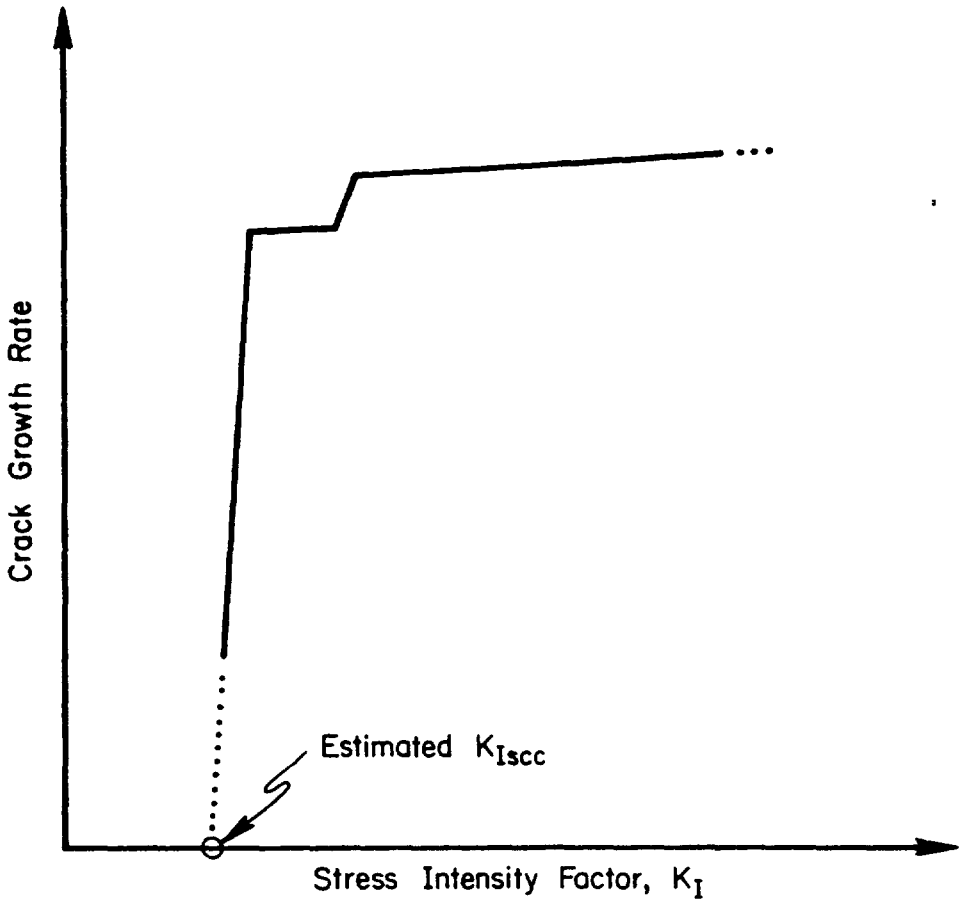


FIGURE 53. Relationship between stress intensity and crack growth rate for a commercial aluminum alloy.

With reference to figure 52, the plane strain fracture toughness, K_{Ic}, of a material is determined from tests (e.g. 3 or 4-point bending) performed in air. Various stress intensity levels, K_{Isc}, below K_{Ic} are selected for performing the stress-corrosion tests in a suitable environment. The time for failure at each K_{Isc} level is recorded, and graphically plotted to yield an estimate of K_{Iscc}. Below this value stress-corrosion crack growth does not occur for the arbitrary time period investigated. At least 6 hours for titanium alloys; 100 hours for low-alloy steels; and 1,000 hours for high-alloy (maraging) steels and aluminum alloys should be allowed before looking for evidence of cracking.(86) With some aluminum alloys, and short transverse direction test specimens, the tendency to crack in this direction is so strong that a planar crack is obtained which allows accurate fracture mechanics analyses to be made.(86) With such materials the stress-corrosion crack growth rate can be determined, and plotted as a function of K_I as shown in figure 53. Two regions of differing behavior are usually observed. At low stress intensities the crack growth rate is strongly dependent on K_I. At higher stress intensities the crack growth rate is independent of K_I, although up to three plateaus may be observed with high-purity aluminum alloys.

Recently, the constant strain-rate test has received more attention. This test has been used extensively to determine conditions necessary to promote stress-corrosion cracking in structural alloys. A tensile specimen is pulled at a slow, constant rate of strain to failure while immersed in the environment of interest. The strain rates are typically in the range of 10^{-8} to 10^{-3} sec^{-1}, and the solution potential of a specimen can be controlled during a test by using a potentiostatic method. The advantage of this method is that failure always occurs within a reasonable time frame. However, care should be taken to distinguish between three possible forms of failure: (1) straightforward, brittle (mechanical) failure, (2) mechanical failure due to a reduction in cross-sectional area as a result of corrosion attack, and (3) true stress-corrosion cracking as a result of a conjoint action between corrosion and residual and/or applied stresses.

As mentioned earlier, there is not standard test environment, and often conditions simulate service environments. However, an effort has been made to design accelerated laboratory tests because of the long times often necessary before cracking becomes apparent. Such tests are only useful if calibration against controls has been performed (i.e., accelerated tests compared with service tests for each individual material). Of the accelerated tests the most popular are (a) sodium chloride alternate immersion, (b) boiling magnesium chloride, and (c) polythionic acid tests, as listed in Table XXII. Test (a) has been used for aluminum alloys, while test (b) has been used for austenitic and ferritic stainless steels, and related alloys. Test (c) has been developed for stainless steels and other Ni/Cr/Fe alloys for use in sulfur containing environments. In addition, ammoniacal solutions are often used to test copper alloys. Further typical environments are given in Reference (86).

SECTION 8. QUALITY ASSURANCE

8.1 Quality Control. Quality control and standardization of material and procedures by which quality is assessed are important aspects of corrosion prevention. Once a material has been selected for a given application, the quality of the material received should be as specified. Quality control corrosion tests, such as the Huey and the Strauss Tests[79], supplement the conventional mechanical property tests that can be performed. They are usually brief and simple to perform, but often do not give data representative of end use behavior. However, they do show if the metal received has similar corrosion resistance to the metal on which development or screening tests were made. Similar tests must be performed for coated materials and for fabricated materials. With some metals the presence of residual stresses leads to stress-corrosion failures, therefore, it must be proven that specified heat treatments or tempers have been adhered to by the supplier, particularly annealing treatments after fabrication. Adequate supervision during construction will help to ensure the fabricated item will meet its design and performance objectives.

Tests for surface and subsurface defects in the finished structure may include visual examinations, penetrant dyes, fluorescent magnetic particle (for ferromagnetic materials), ultrasonic, eddy-current and X-ray inspections. In some materials subcritical defects that may grow to a critical size are so small as to be difficult to detect by the methods listed above. With materials of increasingly higher tensile strengths, the notch toughness characteristics are decreased, and undetected flaws can cause failure in service when subjected to nominal stresses in a relatively noncorrosive environment. Pressure vessels for critical service are thus frequently proof-tested. The proof-test pressure selected is above the expected service pressure, and is applied for as short a period as is consistent with a meaningful test. Preferably such a test should be performed with an inert medium, and any effect of the material to be contained in service on the fracture toughness of the material used to construct the vessel should be taken into consideration.

In addition to the usual chemical analysis and determination of mechanical properties of raw materials, there are two specific tests to determine susceptibility to stress-corrosion cracking. The first is a specific test for 7075-T73 high-strength aluminum alloy to determine whether it is resistant to stress-corrosion cracking as purchased. This test is described in Federal Specification QQ-A-250/12, Section 4.2. Unfortunately the test is of 30 days duration. Efforts are in progress to develop a satisfactory test of shorter duration.

The second specific test applies to copper alloys and is the mercurous nitrate test of ASTM Designation B154-73 (see table XXII). This test is used to detect the presence of residual (internal) stresses in wrought and cast copper alloy products (that might cause failure of the material in service or storage through stress-corrosion cracking).

If the raw materials as received meet the requirements of the applicable specification, there is much information available to insure that "in house" heat treatments are correct. Specification MIL-H-6088 for the heat treatment of aluminum alloys indicates heating time at temperature for solution heat treating, aging, and annealing of the various commercial alloys. It also describes a technique for determining whether certain alloys are susceptible, after heat treatment, to intercrystalline corrosion.

MIL-S-8955(ASG), MIL-S-8840B(ASG), and MIL-S-25043C give recommended heat-treating practices for the precipitation-hardening steels PH 15-7Mo; the AM350 and AM355; and the 17-7PH steels, respectively. Specification MIL-S-8840B(ASG) includes recommended heat treatments for steels to be exposed to conditions conducive to stress-corrosion cracking.

The American Society for Metals Handbook, Vol. 2, 8th Edition, on "Properties and Selection of Metals", gives annealing procedures for both steels and nonferrous materials that may contain high-residual stresses because of welding or cold work.

Electrodeposited cadmium, nickel, and zinc coatings have been used to protect other metals from corrosive attack. During the plating process, some hydrogen is codeposited on the base metal with the electrodeposited coating. If the base metal is a high-strength steel alloy, there is danger of hydrogen embrittlement, which may lead to hydrogen-stress cracking. Federal Specification QQ-N-290, Amendment 1, provides a baking treatment for nickel-plated, hardened steel parts which is designed to remove any codeposited hydrogen in the nickel. The amendment also describes a sustained load testing technique to determine if the plated parts are free from damaging hydrogen.

8.2 Standardization. There is a considerable effort, both by the Department of Defense and the American Society for Testing and Materials, in conjunction with the National Association of Corrosion Engineers, to standardize corrosion terminology, and those aspects of corrosion science and technology which can be quantified. There is no need to elaborate on the benefits of any program which results in the publication of various specifications and standards.

Specifications covering corrosion resistant metals and alloys, and specifications for the various methods and procedures used in providing corrosion protection for metallic items are included in "Department of Defense Index of Specifications and Standards" and its supplements. Since the existing specifications for the metals, alloys, and paints used in the military services are so numerous, no listing of them is included in this handbook. However, a listing of specifications of protective finishes, processes and materials is presented in table XXI. Listing of specifications for paints used in corrosion prevention are contained in MIL-STD-171 and MIL-STD-186, and also in MIL-STD-193 and MIL-STD-194. The listings in these documents do not include all paints used by the military services. Some services or agencies use paints which, in their experience, have been proven satisfactory in meeting their requirements for corrosion protection of material. Listings of specifications for individual metals and alloys are to be found in the series of Military Standardization Handbooks which include:

MIL-HDBK-694(MR)	Aluminum and Aluminum Alloys
MIL-HDBK-698(MR)	Copper and Copper Alloys
MIL-HDBK-693(MR)	Magnesium and Magnesium Alloys
MIL-HDBK-697(MR)	Titanium and Titanium Alloys

An additional useful source of reference to specifications is ASTM E-527, "Unified Numbering System for Metals and Alloys."

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TABLE XXI. Specifications and Recommended Practices for Some Protective Finishes, Materials, and Processes

Specification[a]	Title
MIL-STD-171	Finishing of Metal and Wood Surfaces (for aluminum)
MIL-STD-186	Protective Finishing Systems for Rockets, Guided Missiles, Support Equipment and Related Materials
MIL-STD-193	Painting Procedures, Tactical Vehicles (Tracked and Wheeled)
MIL-STD-194	Painting and Finishing Systems for Fire Control Instruments
MIL-STD-276	Impregnation of Porous Nonferrous Metal Castings
MIL-A-8625	Anodic Coatings for Aluminum and Aluminum Alloys
MIL-A-21380	Abrasive Materials for Blasting
MIL-C-5541	Chemical Films and Chemical Film Materials for Aluminum and Aluminum Alloys
MIL-C-8837	Coating, Cadmium (Vacuum Deposited)
MIL-C-11796	Corrosion Preventive, Petrolatum, Hot Application
MIL-C-14550	Copper Plating (Electrodeposited)
MIL-C-26074	Coating, Nickel-Phosphorus, Electroless Nickel, Requirements for
MIL-C-46079	Coating, Epoxy, Baking Type, for Magnesium Castings
MIL-C-60536	Coating, Hard, Anodized (for Aluminum)
MIL-C-60539	Coatings, Anodic, for Aluminum
MIL-F-495	Finish, Chemical, Black, for Copper Alloys
MIL-F-7179	Finishes and Coatings; General Specifications for Protection of Aircraft and Aircraft Parts
MIL-F-13924	Coating, Oxide, Black, for Ferrous Metals
MIL-F-14072	Finishes, for Ground Signal Equipment
MIL-G-45204	Gold Plating (Electrodeposited)
MIL-I-13857	Impregnation of Metal Castings
MIL-L-13762	Lead Alloy Coating, Hot Dip (for iron and steel parts)
MIL-L-13808	Lead Plating (Electrodeposited)
MIL-M-3171	Magnesium Alloy, Processes for Corrosion Protection of
MIL-M-45202	Magnesium Alloys, Anodic Treatment of
MIL-P-8116	Putty, Zinc Chromate, General Purpose
MIL-P-14458	Paint, Rubber, Red Fuming Nitric Acid Resistant
MIL-P-15184	Primer, Zinc Chromate, Anticorrosive
MIL-P-15328	Primer, Pretreatment, Formula 117 for Metals
MIL-P-15929	Primer Coating, Shipboard, and Anticorrosive Paint, Vinyl-Red Lead for Hot Spray

TABLE XXI. (Continued)

Specification[a]	Title
MIL-P-15930	Primer Coating, Shipboard, Vinyl-Zinc Chromate for Hot Spray
MIL-P-16232	Phosphate Coatings, Heavy, Manganese or Zinc Base (for Ferrous Metals)
MIL-P-19451	Plastic, Cold, Antifouling
MIL-P-23408	Plating, Tin-Cadmium (Electrodeposited)
MIL-P-45209	Palladium Plating (Electrodeposited)
MIL-S-7124	Sealing Compound, Pressure Cabin
MIL-S-11031	Sealing Compound, Noncuring, Polysulfide Base
MIL-S-22262	Sand Blasting, Abrasive Materials for
MIL-T-152	Treatment, Moisture- and Fungus-Resistant, of Communication, Electronic, and Associated Electrical Equipment
MIL-T-10727	Tin Plating, Electrodeposited or Hot Dipped, for Ferrous and Nonferrous Metals
MIL-V-173	Varnish, Moisture- and Fungus-Resistant (for the Treatment of Communications, Electronic, and Associated Electrical Equipment)
QQ-C-320	Chromium Plating (Electrodeposited)
QQ-N-290	Nickel Plating (Electrodeposited)
QQ-P-35	Passivation Treatments for Austenitic, Ferritic and Martensitic Corrosion-Resisting Steel (Fastening Devices)
QQ-S-365	Silver Plating, Electrodeposited, General Requirements for
TT-C-490	Cleaning Methods and Pretreatment of Ferrous Surfaces for Organic Coatings
TT-C-520	Coating, Underbody (for Motor Vehicles
TT-P-645	Primer, Alkyd-Zinc Chromate Type
ASTM-A164[b]	Specifications for Electrodeposited Coatings of Zinc on Steel
ASTM-A165[b]	Specifications for Electrodeposited Coatings of Cadmium on Steel
ASTM-B449[b]	Recommended Practice for Chromate Treatments on Aluminum

TABLE XXI. (Continued)

Specification(a)	Title
ASTM-D823(b)	Producing Films of Uniform Thickness of Paint, Varnish, Lacquer and Related Products on Test Panels
ASTM-D870(b)	Water Immersion Test of Organic Coatings on Steel
ASTM-D2200(b)	Pictorial Surface Preparation Standards for Painting Steel Surfaces
ASTM-D2454(b)	Recommended Practice for Determining the Effect of Overbaking on Organic Coating
ASTM-G12(b)	Nondestructive Measurement of Film Thickness of Pipeline Coatings on Steel
RP-01-72(c)	Surface Preparation of Steel and Other Hard Materials by Water Blasting Prior to Coating or Recoating
RP-03-72(c)	Method for Lining Lease Production Tanks with Coal Tar Epoxy

Notes:

(a) Specifications for paints are not listed. See DOD Index of Specifications and Standards, MIL-STD-171 and MIL-STD-186, also MIL-STD-193, MIL-STD-194. Specifications for metals and alloys are not listed. See DOD Index of Specifications and Standards, MIL-HDBK-694(Al), MIL-HDBK-698(Cu), MIL-HDBK-693(Mg) and MIL-HDBK-697(Ti).

(b) American Society for Testing and Materials, Philadelphia, PA.

(c) National Association of Corrosion Engineers, Houston, TX.

TABLE XXII. Recommended Procedures and Methods for Corrosion Testing

Test Number	Title
	(1) American Society for Testing and Materials
A143(a)	Recommended Practice for Safeguarding Against Embrittlement of Hot Dip Galvanized Structural Steel Products and Procedure for Detecting Embrittlement
A239	Test for Locating the Thinnest Spot in a Zinc (Galvanized) Coating on Iron or Steel Articles by the Preece Test (Copper Sulfate Dip)
A262	Recommended Practices for Detecting Susceptibility to Intergranular Attack in Stainless Steels (Including Huey Test)
A380	Recommended Practice for Descaling Stainless Steel Parts, Equipment and Systems
A708	Recommended Practice for Detection of Susceptibility to Intergranular Corrosion in Severely Sensitized Austenitic Stainless Steels
B117(a)	Salt Spray (Fog) Testing
B136(a)	Test for Resistance of Anodically Coated Aluminum to Staining by Dyes
B154	Mercurous Nitrate Test for Copper and Copper Alloys
B287(a)	Acetic Acid-Salt Spray (Fog) Testing
B368(a)	Copper-Accelerated Acetic Acid Salt Spray (Fog) Test (CASS Test)
B380(a)	Corrosion Testing of Decorative Chromium Plating by the Corrodkote Procedure
B537(a)	Recommended Practice for Rating of Electroplated Panels Subjected to Atmospheric Exposure
B538	Method of FACT (Ford Anodized Aluminum Corrosion Test) Testing
B602	Sampling Procedures for Inspection of Electrodeposited Metallic Coatings and Related Finishes
C464(a)	Test for Corrosion Effect of Thermal Insulating Cements on Base Metal
C703(a)	Test for Spalling Resistance of Porcelain Enameled Aluminum
D5(a)	Test for Penetration of Bituminous Materials
D130(a)	Test for Detection of Copper from Petroleum Products by the Copper Strip Tarnish Test
D427	Test for Shrinkage Factors of Soils
D543	Test for Resistance of Plastics to Chemical Reagents

TABLE XXII. (Continued)

Test Number	Title
D609	Preparation of Steel Panels for Testing Paint, Varnish, Lacquer and Related Products
D610(a)	Evaluating Degree of Rusting on Painted Steel Surfaces
D659	Evaluating Degree of Resistance to Chalking of Exterior Paints
D660	Evaluating Degree of Checking of Exterior Paints
D661	Evaluating Degree of Cracking of Exterior Paints
D665(a)	Test for Rust-Preventing Characteristics of Steam Turbine Oils in the Presence of Water
D714	Evaluating Degree of Blistering of Paints
D801	Dipentene Sampling and Testing
D807(a)	Corrosivity Test of Industrial Water (U.S. Bureau of Mines Embrittlement Detector Method)
D823	Producing Films of Uniform Thickness of Paint, Varnish, Lacquer and Related Products on Test Panels
D849(a)	Test for Copper Corrosion of Industrial Aromatic Hydrocarbons
D870	Water Immersion Test of Organic Coatings on Steel
D930	Total Immersion Corrosion Test of Water-Soluble Aluminum Cleaners
D1141(a)	Specification for Substitute Ocean Water
D1261(a)	Test for Effect of Grease on Copper
D1275(a)	Test for Corrosive Sulfur in Electrical Insulating Oils
D1280	Total Immersion Corrosion Test for Soak Tank Metal Cleaners
D1374	Aerated Total Immersion Corrosion Test for Metal Cleaners
D1384(a)	Corrosion Test for Engine Antifreeze in Glassware
D1611	Test for Corrosion Produced by Leather in Contact with Metal
D1616	Test for Copper Corrosion by Mineral Spirits (Copper Strip Test)
D1654	Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments
D1735	Water Fog Testing of Organic Coatings
D1743	Test for Rust Preventative Properties of Lubricating Greases
D1748(a)	Test for Rust Protection by Metal Preservatives in the Humidity Cabinet
D2043	Test for Silver Tarnishing by Paper
D2200(a)	Pictorial Surface Preparation Standards for Painting Steel Surfaces

TABLE XXII. (Continued)

Test Number	Title
D2246	Testing Finishes on Primed Metallic Substrates for Resistance to Humidity-Thermal Cycle Cracking
D2247	Test of Coated Metal Specimens at 100 Percent Relative Humidity
D2251	Test for Metal Corrosion by Halogenated Organic Solvents and Their Admixtures
D2454	Recommended Practice for Determining the Effect of Overbaking an Organic Coating
D2570	Simulated Service Corrosion Testing of Engine Coolants
D2649(a)	Determining Corrosion Characteristics of Dry Solid Film Lubricants
D2688(a)	Test for Corrosivity of Water in the Absence of Heat Transfer (Weight Loss Methods)
D2803	Test for Filiform Corrosion Resistance of Organic Coatings on Metals
D2809	Test for Cavitation-Erosion Corrosion Characteristics of Aluminum Automotive Water Pumps with Coolants
D2966	Test for Cavitation-Erosion Characteristics of Aluminum in Engine Antifreeze Solutions Using Ultrasonic Energy
E104	Recommended Practice for Maintaining Constant Relative Humidity by Means of Aqueous Solutions
F64(a)	Test for Corrosive and Adhesive Effects of Gasket Materials on Metal Surfaces
G1(a)	Recommended Practice for Preparing, Cleaning and Evaluating Corrosion Test Specimens
G2(a)	Recommended Practice for Aqueous Corrosion Testing of Samples of Zirconium and Zirconium Alloys
G3	Recommended Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing
G4	Recommended Practice for Conducting Plant Corrosion Tests
G5	Recommended Practice for Standard Reference Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements
G6	Test for Abrasion Resistance of Pipeline Coatings
G7	Recommended Practice for Atmospheric Environmental Exposure Testing of Nonmetallic Materials
G8	Test for Cathodic Disbonding of Pipeline Coatings
G9	Test for Water Penetration into Pipeline Coatings
G10	Test for Bendability of Pipeline Coatings
G11	Test for Effects of Outdoor Weathering on Pipeline Coatings
G12	Nondestructive Measurement of Film Thickness of Pipeline Coatings on Steel

TABLE XXII. (Continued)

Test Number	Title
G13	Test for Impact Resistance of Pipeline Coatings (Limestone Drop Test)
G14	Test for Impact Resistance of Pipeline Coatings (Falling Weight Test)
G15	Definition of Terms Relating to Corrosion and Corrosion Testing
G16	Practice for Applying Statistics to Analysis of Corrosion Data
G17	Test for Penetration Resistance of Pipeline Coatings
G18	Test for Joints, Fitting and Patches in Coated Pipelines
G19	Test for Disbonding Characteristics of Pipeline Coatings by Direct Soil Burial
G20	Test for Chemical Resistance of Pipeline Coatings
G21	Recommended Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi
G22	Recommended Practice for Determining Resistance of Plastics to Bacteria
G23	Recommended Practice for Operating Light- and Water-Exposure Apparatus (Carbon-Arc Type) for Exposure of Nonmetallic Materials
G24	Recommended Practice for Conducting Natural Light Exposures Under Glass
G25	Recommended Practice for Operating Enclosed Carbon-Arc Type Apparatus for Light Exposure of Nonmetallic Materials
G26	Recommended Practice for Operating Light- and Water-Exposure Apparatus (Xenon-Arc Type) for Exposure of Nonmetallic Materials
G27	Recommended Practice for Operating Xenon-Arc Type Apparatus for Light Exposure of Nonmetallic Materials
G28	Detecting Susceptibility to Intergranular Attack in Wrought Nickel-Rich, Chromium-Bearing Alloys
G29	Test for Algal Resistance of Plastic Films
G30	Recommended Practice for Making and Using U-Bend Stress Corrosion Test Specimens
G31	Recommended Practice for Laboratory Immersion Corrosion Testing of Metals
G32	Vibratory Cavitation Erosion Test
G33	Recommended Practice for Recording Data from Atmospheric Corrosion Tests of Metallic-Coated Steel Specimens

TABLE XXII. (Continued)

Test Number	Title
G34	Test for Exfoliation Corrosion Susceptibility in 7XXX Series Copper-Containing Aluminum Alloys (EXCO Test)
G35	Recommended Practice for Determining the Susceptibility of Stainless Steels and Related Nickel-Chromium-Iron Alloys to Stress Corrosion Cracking in Polythionic Acids
G36	Recommended Practice for Performing Stress Corrosion Cracking Tests in a Boiling Magnesium Chloride Solution
G37	Recommended Practice for Use of Mattson's Solution of pH 7.2 Evaluate the Stress-Corrosion Cracking Susceptibility of Copper-Zinc Alloys
G38	Recommended Practices for Making and Using the C-Ring Stress-Corrosion Cracking Test Specimen
G39	Preparation and Use of Bent-Beam Stress-Corrosion Specimens
G40	Definition of Terms Relating to Erosion by Cavitation and Impingement
G41	Recommended Practice for Determining Cracking Susceptibility of Titanium Alloys Exposed Under Stress to a Hot Salt Environment
G42	Cathodic Disbonding of Pipeline Coatings Subjected to Elevated of Cyclic Temperatures
G43	Acidified Synthetic Seawater (Fog) Testing
G44	Recommended Practice for Alternate Immersion Stress Corrosion Testing in 3.5 Sodium Chloride Solution
G45	Recommended Practice for Specifying Limits for Fading and Discoloration of Nonmetallic Materials
G46	Recommended Practice for Examination, Evaluation of Pitting Corrosion
G47	Recommended Practice for Determining Susceptibility to Stress-Corrosion Cracking of High-Strength 7XXX Aluminum Alloy Products
G48	Test Method for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by the Use of Ferric Chloride Solution
G49	Standard Recommended Practice for Preparation and Use of Direct Tension Stress Corrosion Test Specimens

TABLE XXII. (Continued)

Test Number	Title
	(2) National Association of Corrosion Engineers
RP-01-73	Collection and Identification of Corrosion Products
TM-01-69	Laboratory Corrosion Testing of Metals for the Process Industries
TM-01-70	Visual Standards for Surfaces of New Steel Air-Blast Cleaned with Sand Abrasive
TM-02-70	Method of Conducting Controlled Velocity Laboratory Corrosion Tests
TM-01-71	Method for Autoclave Corrosion Testing of Metals in High Temperature Water
TM-01-72	Test Method for Measuring the Antirust Properties of Petroleum Products Pipeline Cargoes
TM-01-73	Test Methods for Determining Water Quality for Subsurface Injection Using Membrane Filters

Test Number	Title
	(3) Federal Test Method 151
812	Synthetic Seawater Spray Test
822	Intergranular Corrosion Test for Aluminum Alloys

Notes:

(a) Approved as an American National Standard by the American National Standards Institute (ANSI).

TABLE XXIII. Federal Test Methods and Recommended Practices for the Control of Corrosion Issued by the National Association of Corrosion Engineers

Number	Title
	(1) National Association of Corrosion Engineers
RP-01-69	Control of External Corrosion on Underground or Submerged Metallic Piping Systems
RP-01-70	Protection of Austenitic Stainless Steel in Refineries Against Stress-Corrosion Cracking by the Use of Neutralizing Solutions During Shutdown
RP-03-72	Method for Lining Lease Production Tanks with Coal Tar Epoxy
RP-04-72	Methods and Controls to Prevent In-Service Cracking of Carbon Steel (P-1) Welds in Corrosive Petroleum Refining Environments
RP-05-72	Design, Installation, Operation and Maintenance of Impressed Current Deep Groundbeds
RP-01-74	Corrosion Control of Electric Underground Residential Distribution Systems
RP-01-75	Control of Internal Corrosion in Steel Pipelines and Piping Systems
RP-02-75	Application of Organic Coatings to the External Surface of Steel Pipe for Underground Service
RP-03-75	Application and Handling of Wax-Type Protective Coatings and Wrapper Systems for Underground Pipelines
RP-05-75	Design, Installation, Operation and Maintenance of Internal Cathodic Protection Systems in Oil Treating Vessels
RP-06-75	Control of Corrosion on Offshore Steel Pipelines
RP-01-76	Control of Corrosion on Steel, Fixed Offshore Platforms Associated with Petroleum Production
RP-02-76	Extruded Asphalt Mastic Type Protective Coatings for Underground Pipelines
	(2) Federal Test Methods
MIL-M-3171	Magnesium Alloy, Processes for Corrosion, Protection of

Note: Other Federal Test Methods describing protective coatings and treatments are listed in table XXI. Military Specifications for corrosion inhibitors are listed in table XV.

Specific examples of failure analysis procedures are given in Reference (88). In the section dealing with failures from various mechanisms and related environmental factors, there are discussions of (1) liquid-erosion failures, (2) corrosion failures, (3) stress-corrosion, (4) liquid-metal embrittlement, (5) hydrogen-damage failures, and (6) corrosion-fatigue failures. In the section dealing with the analysis and prevention of service failures of manufactured components and assemblies there are discussions of (1) the corrosion of shafts, (2) the failure of rolling-element bearings by corrosion, (3) the corrosion of seals and seal components, (4) corrosion in threaded fasteners, (5) corrosion protection by plating of threaded fasteners, (6) corrosion failures of springs, (7) the corrosive wear of gears, (8) failures by corrosion of boilers and related steam power-plant equipment, (9) failures by corrosion in heat exchangers; and (10) the stress-corrosion and hydrogen-stress cracking of pressure vessels. Because of this extensive and recent coverage of specific failure investigations, the material will not be repeated here. Reference should be made to specific sections in this handbook when the need arises.

As a result of the information gained from failure analysis investigations, and other laboratory and field work, several Federal Test Methods and Recommended Practices of the National Association of Corrosion Engineers have been formulated to control corrosion processes. These methods are listed in table XXIII. Other Federal Test Methods, ASTM and NACE Standards, Test Methods and Recommended Practices describing protective coatings and treatments are listed in tables XXI and XXII. Military Specifications for corrosion inhibitors are listed in table XV.

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SECTION 10. GLOSSARY

Active - referring to the negative direction of electrode potential (opposite of noble).

Alpha-Phase - a solid solution of one or more alloying elements in the base metal.

Anerobic - an absence of oxygen in the uncombined state.

Anion - An ion having a negative charge which is attracted to the anode (opposite of cation).

Anode - an electrode at which oxidation of the anode surface or some component of the solution is occurring (opposite of cathode).

Anodic Inhibitor - a chemical substance or combination of substances that prevent or reduce the rate of the anodic or oxidation reaction by a physical, physico-chemical or chemical action.

Anodic Polarization - a polarization of the anode: the anode potential becomes more noble (positive) because of the nonreversible conditions resulting when a corrosion current flows.

Anodic Protection - a technique to reduce corrosion of a metal surface under some conditions by passing sufficient anodic current to it to cause its electrode potential to enter and remain in the passive region.

Anolyte - the electrolyte of an electrolytic cell adjacent to the anode.

Anti-Fouling - a chemical control of a surface to prevent the attachment or growth of marine organisms when submerged: the toxicity can be invoked by careful selection of the metal itself, by chemical treatments, or by suitable coatings.

Aqueous - pertaining to water: an aqueous solution is made by using water as a solvent.

Austenitic - an adjective describing a face-centered cubic crystal structure found in ferrous materials, usually at elevated temperatures; however, certain stainless steels (300 series) can exhibit this structure at ambient temperatures.

Auxiliary Electrode - an electrode commonly used in polarization studies to pass current to or from a test electrode. It is usually made from a noncorroding material.

Beta-Phase - a phase containing more of the alloying elements than the alpha-phase, and differing markedly from it in one or more properties and/or crystallagraphic structure.

Carbine Precipitate - a precipitate composed of a compound of carbon with one or more metallic elements often found in ferrous materials, but also in aluminum and titanium.

Cathode - the electrode of an electrolytic cell at which reduction occurs, (opposite of anode).

Cathodic Polarization - a polarization of the cathode: the cathode potential becomes more active (negative) because of the non-reversible conditions resulting when a corrosion current flow.

Cathodic Protection - a technique to reduce corrosion of a metal surface by passing sufficient cathodic current to it to cause its anodic dissolution rate to become negligible.

Cation - an ion having a positive charge which is attracted to the cathode (opposite of anion).

Caustic Embrittlement - a form of stress-corrosion cracking occurring in steel exposed to alkaline solutions.

Cavitation - a formation and sudden collapse of vapor bubbles in a liquid which momentarily can cause localized regions of high pressure.

Cavitation Corrosion - damage of a material associated with the collapse of cavities in the liquid at a solid-liquid interface.

Cell - an electrochemical system consisting of a cathode and anode immersed in an electrolyte. The anode and cathode may be separate metals or dissimilar areas on the same metal.

Chalking - a development of a loose, removable powder at or just beneath an organic coating surface.

Chemical Conversion Coating - a protective or decorative coating produced in situ by a chemical reaction of a metal with a chosen environment.

Chemisorption - a chemical bonding of an adsorbed species to the surface of a different material.

Concentration Cell - a cell in which potential differences at the anode and cathode are the result of differences in chemistry (concentration of reactants or products) of the environment adjacent to the electrodes.

Corrosion - a deterioration of a material usually a metal because of a reaction with its environment.

Corrosion-Erosion - an accelerated corrosion process because of the abrasive action of a moving liquid, especially one which contains suspended particles.

Corrosion Fatigue - a failure of a metal resulting from the combined action of corrosion and fatigue (cyclic stressing).

Corrosion Potential - a potential of a corroding surface in an electrolyte relative to a reference electrode (also known as rest potential, open-circuit potential or freely-corroding potential).

Corrosion Rate - a measure of the speed (usually averaged) at which corrosion proceeds and expressed as a weight loss per unit area, or thickness change per unit time: alternatively the corrosion current density (in amps per unit area) gives a measure of the instantaneous rate of corrosion for specified conditions of the environment at a given time.

Crevice Corrosion - a localized corrosive attack resulting from the formation of a concentration cell in a crevice between two metal surfaces or a metal and nonmetal surface.

Critical Flaw Size - a size of flaw in a structure that will cause failure of the structure at the expected operational stress level.

Current Density - a current expressed as a function of the area of the metal through which it flows: expressed as amps per square meter, milliamps per square decimeter, and so on.

Dealuminimization - See "parting".

Depolarization - a removal of factors resisting the flow of current in a cell.

Deposit - a foreign substance, which comes from the environment, adhering to a surface of a material.

Dezincification - See "parting".

Differential Aeration Cell - a special type of concentration cell in which potential differences are established due to local differences in dissolved oxygen content.

Electrochemical Solution Potential - a potential of a metal measured with respect to a standard (reference) half-cell such as a saturated calomel electrode (also known as electrode potential).

Electrode - an electrical conductor in contact with an electrolyte which serves as an electron acceptor or donor (see anode and cathode as specific examples).

Electrolyte - a chemical substance or mixture, usually liquid, containing ions which migrate in an electric field.

Electromotive Force Series - a listing of elements according to their standard electrode potentials with the value for hydrogen arbitrarily taken as 0.0 volt (also called Emf series).

Electron Flow - a movement of electrons in an external circuit connecting an anode and cathode in a corrosion cell: the current flow is arbitrarily considered to be in an opposite direction to the electron flow.

Embrittlement - a loss of load carrying capacity of a metal or alloy.

Endurance Limit - a maximum cyclic stress level a metal can withstand without a fatigue failure.

Environment - a description of the surroundings or conditions (physical chemical, mechanical) in which a material exists.

Erosion Corrosion - a corrosion reaction accelerated by velocity and air abrasion.

Exfoliation - a thick, layered growth of loose corrosion products often separating from the metal surface.

Ferritic - an adjective describing a body-centered cubic crystal structure found in ferrous materials.

Filiform Corrosion - a form of attack that occurs under films on metals and which appears as randomly distributed hairlines (also called Underfilm Corrosion).

Fogging - a reduction in the luster of a metal surface as the result of the formation of a thin film of corrosion products.

Fracture Toughness - a mechanical property characteristic of a metal that determines its resistance to brittle fracture: fracture toughness may be expressed in terms of stress intensity factors K_C of K_{IC}.

Free Caustic - an amount of alkalinity of a solution measured in terms of pH values in excess of 7 (pH = 7 is neutral, e.g., water).

Fretting Corrosion - a form of deterioration caused by repetitive friction between two sliding surfaces and accelerated by a conjoint corrosive action.

Galvanic Cell - a corrosion cell consisting of two dissimilar metals in contact, or in a narrower context consisting of adjacent anodic and cathodic sites: the former definition is on a macro-scale, the latter on a micro-scale.

Galvanic Corrosion - a type of corrosion associated with the current resulting from the coupling of dissimilar electrodes in an electrolyte.

Galvanic Series - a listing of metals arranged according to their relative corrosion potentials in a specific environment (such as sea water.)

Galvanostat - an electronic device which maintains a constant current flow at an electrode surface.

General Corrosion - a type of corrosion attack uniformly distributed over a metal surface.

Grain Boundary - a narrow zone in a metal corresponding to the transition from one crystallographic orientation to another, thus separating one grain from another: the atoms in each grain are arranged in an orderly pattern.

Graphitic Corrosion - a type of attack in gray cast irons in which the metallic constituents are converted to corrosion products leaving the graphite flakes (cathodes) intact (also called graphitization).

Heat-Affected Zone - an area adjacent to a weld where heat has caused microstructural changes which affect the corrosion behavior of the metal.

Hot Salt Cracking - a type of stress-corrosion cracking of titanium alloys whn in contact with chloride salts at temperatures in the range of 288°C (550°F) to 538°C (1000°F).

Hydrogen Embrittlement - a reduction of the load carrying capability by entrance of hydrogen into the metal (e.g., during pickling or cathodic polarization).

Hydrogen-Stress Corrosion - a premature failure of a metal resulting from the combined action of tensile stresses and the penetration of hydrogen into the metal.

Immunity - a state of resistance to corrosion or anodic dissolution caused by the fact that the electrode potential of the surface in question is below the equilibrium potential of anodic dissolution.

Impingement Attack - a form of localized corrosion-erosion caused by turbulance or impinging flow.

Incubation Period - a period prior to the detection of stress-corrosion cracking while the metal is in contact with a corrodent.

Industrial Atmosphere - an atmosphere in an area of heavy industry with soot, fly ash and sulfur compounds as the principal constituents.

Inhibitor - a chemical substance or combination of substances which, when present in the proper concentration and forms in the environment, prevents or reduces corrosion by a physical, physico-chemical or chemical action.

Intergranular Corrosion - a type of corrosion attack which occurs preferentially at grain boundaries (also called intercrystalline corrosion).

Internal Oxidation - a formation of isolated particles of corrosion products beneath the surface of a metal resulting from inward diffusion of oxygen, nitrogen, sulfur, etc. (also known as subsurface corrosion).

$K_C K_{IC}$ - a limiting value of K or K_I, the stress intensity factor of the stress field in the vicinity of the crack front, at which the crack front will propagate in an inert environment (I indicates opening mode of crack extension).

K_{ISCC} - a limiting (threshold) value of K_I for a metal exposed in an aggressive environment at which the crack front will propagate.

Knife Line Attack - a form of weld decay sometimes observed on stablilized stainless steel in which the zone of attack is very narrow and close to the weld.

Local Action - a form of corrosion resulting from the action of local cells.

Local Cell - a galvanic cell caused by small differences in composition on a metal surface or in the electrolyte.

Maraging Steel - a steel containing neckel as the principal alloying addition (with lesser amounts of Co and Mo) that can be heat treated to a tensile strength of 200,000 psi or more by aging between 455 and 510°C.

Marine Environment - an environment immediately adjacent to the sea coast affected by prevailing winds, fog and other factors.

Martensitic Steel - a stainless steel containing more than 12 percent chromium (and up to 2.5% Ni) that can be hardened by quenching and tempering.

Metal - in the context of this handbook a metal, metallic alloy or material or combinations of these, which exhibit metal-like properties (are electronic conductors) and are subject to corrosive attack.

Noble - refers to the positive direction of electrode potential, thus resembling the noble metals (such as gold).

Open Circuit Potential - a measured cell potential when no corrosion current flows.

Parting - a selective attack of one or more components of a solid solution alloy e.g., dealuminization, dezincification (sometimes known as dealloying, or selective corrosion).

Passive - a condition in which the behavior of a metal is more noble (less active) than its position in the Emf Series would predict: a surface film protects the underlying metal from corrosion (oppositve of active).

Passivity - a phenomenon by which an active metal becomes passive.

Patina - a green coating of corrosion products that grows on copper and some of its alloys after long exposure to the atmosphere.

pH - s measure of acidity of alkalinity of a solution: at 25°C a neutral solution has a pH of 7; acid solutions have a pH 7; and alkaline solutions have a pH 7.

Pitting - a very localized type of corrosion attack resulting in deep penetration at only a few sites (opposite of general corrosion).

Polarization - a shift in electrode potential from the open-circuit value as a result of current flow (also know as overvoltage).

Potentiostat - an electronic device which maintains an electrode at a constant potential: used in anodic protection devices.

Precracked Specimen - a specimen that is notched and subjected to alternating stresses until a fatigue crack has developed at the root of the notch.

Relative Humidity - a (percentage) ratio of the amount of moisture in the air compared to what it could hold if saturated at a given temperature.

Residual Stress - a stress present in a metal that is free of external forces or temperature gradients: usually the result of fabrication processes, and can be tensile or compressive in nature.

Rest Potential - See corrosion potential.

Rusting - a type of corrosion attack limited to ferrous materials which results in reddish-brown corrosion products.

Sacrificial Protection - a reduction or prevention of corrosion of metal by galvanically coupling it to a more anodic metal.

Scaling - a formation at high temperature of thick corrosion product layers on a metal surface; or the deposition of water insoluble constituents on a metal surface.

Season Cracking - a cracking caused by the conjoint action of corrosion and internal tensile stress usually applied to the stress-corrosion cracking of brass.

Stabilized Steel - a stainless steel that has been alloyed with a carbide forming metal (e.g., Ti) to reduce or remove susceptibility to weld decay.

Standard Electdrode Potential - a reversible potential of an electrode process (when all reactants and products are at unit activity) on a scale in which the potential for such a standard hydrogen process is zero volt.

Stray Current Corrosion - a type of corrosion attack resulting from direct current flow through paths other than the intended circuit (e.g., extraneous currents in soil).

Stress Accelerated Corrosion - a form of intergranular attack that can occur in the absence of stress but is accelerated by the application of a tensile stress ;which opens up any cracks permitting the corrodent to attack the metal at the crack tips.

Stress-Corrosion Cracking - a premature failure of a metal as the result of the combined action of tensile stresses and a corrosive environment. The surface tensile stresses may be residual or applied.

Stress Relief Anneal - a procedure in which a metal is heated to a sufficiently high temperature for a given period of time to eliminate residual stresses; slow cooling afterwards is necessary to prevent stresses redeveloping.

Tarnish - a surface discoloration of a metal caused by the formation of a thin film of corrosion product.

Thermogalvanic Corrosion - a type of galvanic corrosion resulting from temperature differences at different points on a metal surface.

Threshold Stress - a limiting stress at which stress-corrosion or hydrogen-stress cracking will develop in a metal in a given exposure period.

Transpassive - a noble region of potential where an electrode exhibits a higher than passive current density.

Weld Decay - a localized corrosion of weld metal.

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Custodians:

Army - MR
Navy - SH
Air Force - 11

Military Coordinating Activity:

Army - MR

Project No. MFFP-0166

Review activities:

Army - AL, AR, AT, AV, CR, ME, MI
Navy - SH, YD
Air Force - 99

User activity:

Navy - OS