CORROSION AND CORROSION CONTROL

1. Introduction

Corrosion is the natural degradation of materials in the environment through electrochemical or chemical reaction. Traditionally, the definition of corrosion refers to the degradation of metals and has not included the degradation of nonmetals such as wood (rotting) or plastics (swelling or crazing), but increasingly, natural degradation of any engineering material is being regarded as corrosion. The vast majority of the technologically significant corrosion involves the deterioration of metallic materials, and only the corrosion of metallic materials is discussed here.

2. Electrochemical Nature of Corrosion

Ores are mined and are then refined in an energy intensive process to produce pure metals, which in turn are combined to make alloys (see METALLURGY; MINERALS RECOVERY AND PROCESSING). Corrosion occurs because of the tendency of these refined materials to return to a more thermodynamically stable state (1–3). The key reaction in corrosion is the oxidation or anodic dissolution of the metal to produce metal ions and electrons

$$\mathrm{M} \xrightarrow{k_1} \mathrm{M}^{n+} + n\,e^- \tag{1}$$

The ions, M^{n+}, formed by this reaction at a rate, k_1, may be carried into a bulk solution in contact with the metal, or may form insoluble salts or oxides. In order for this anodic reaction to proceed, a second reaction which uses the electrons produced, ie, a reduction reaction, must take place. This second reaction, the cathodic reaction, occurs at the same rate because the electrons produced by the anodic reaction must be consumed by the cathodic reaction to maintain electroneutrality. Therefore, $I_c = I_a$, where I_c and I_a are the cathodic and anodic currents, respectively. The cathodic reaction, in most cases, is hydrogen evolution or oxygen reduction.

The four elements necessary for corrosion are an aggressive environment, an anodic and a cathodic reaction, and an electron conducting path between the anode and the cathode. Other factors such as a mechanical stress also play a role. The thermodynamic and kinetic aspects of corrosion determine, respectively, if corrosion can occur, and the rate at which it does occur.

3. Manifestations of Corrosion

The most common form of corrosion is uniform corrosion, in which the entire metal surface degrades at a near uniform rate (1–4). Often the surface is covered by the corrosion products. The rusting of iron (qv) in a humid atmosphere or the tarnishing of copper (qv) or silver alloys in sulfur-containing environments are examples (see also SILVER AND SILVER ALLOYS). High temperature, or dry, oxidation, is also usually uniform in character. Uniform corrosion, the most visible form of corrosion, is the least insidious because the weight lost by metal dissolution can be monitored and predicted.

An especially insidious type of corrosion is localized corrosion (1–3,5,6), which occurs at distinct sites on the surface of a metal while the remainder of the metal is either not attacked or attacked much more slowly. Localized corrosion is usually seen on metals that are passivated, ie, protected from corrosion by oxide films, and occurs as a result of the breakdown of the oxide film. Generally the oxide film breakdown requires the presence of an aggressive anion, the most common of which is chloride. Localized corrosion can cause considerable damage to a metal structure without the metal exhibiting any appreciable loss in weight. Localized corrosion occurs on a number of technologically important materials such as stainless steels, nickel-base alloys, aluminum, titanium, and copper (see ALUMINUM AND ALUMINUM ALLOYS; NICKEL AND NICKEL ALLOYS; STEEL; and TITANIUM AND TITANIUM ALLOYS).

Two types of localized corrosion are pitting and crevice corrosion. Pitting corrosion occurs on exposed metal surfaces, whereas crevice corrosion occurs within occluded areas on the surfaces of metals such as the areas under rivets or gaskets, or beneath silt or dirt deposits. Crevice corrosion is usually associated with stagnant conditions within the crevices. A common example of pitting corrosion is evident on household storm window frames made from aluminum alloys.

Another type of corrosion is dealloying which has also been called parting or selective leaching. Dealloying (1–4) is the preferential removal of one of the alloying elements from an alloy resulting in the enrichment of the other alloying element(s). Common examples are the loss of zinc from brasses (dezincification) (see COPPER ALLOYS, CAST ALLOYS) and the loss of iron from cast irons (graphitization).

Corrosion may also appear in the form of intergranular attack, ie, preferential attack of the boundaries between the crystals (grains) in metals and alloys (1–5). Intergranular attack generally occurs because the grain boundary and the grain have different corrosion tendencies, ie, different potentials. Intergranular corrosion often leads to a loss in strength or ductility of the metal.

Corrosion also occurs as a result of the conjoint action of physical processes and chemical or electrochemical reactions (1–5). The specific manifestation of corrosion is determined by the physical processes involved. Environmentally induced cracking (EIC) is the failure of a metal in a corrosive environment and under a mechanical stress. The observed cracking and subsequent failure would not occur from either the mechanical stress or the corrosive environment alone. Specific chemical agents cause particular metals to undergo EIC, and mechanical failure occurs below the normal strength (yield stress) of the metal. Examples are the failure of brasses in ammonia environments and stainless steels in chloride or caustic environments.

When a stress is cyclic rather than constant, the failure is termed corrosion fatigue. Fretting corrosion results from the relative motion of two bodies in contact, one or both being a metal. The motion is small such as a vibration. Erosion corrosion results from the action of a high velocity fluid impinging on a metal surface. Metals and alloys can also experience cracking in liquid metal environments. This form of corrosion is referred to as liquid metal cracking (LMC) (1,2,7). For example, mercury (qv) promotes cracking in highly stressed copper alloys and high strength aluminum alloys, and liquid copper promotes cracking of steels and stainless steels. Titanium and nickel alloys are also susceptible to LMC in specific environments.

Galvanic corrosion (1–4) occurs as a result of the electrical contact of different metals in an aggressive environment. The driving force is the electrode potential difference between the two metals. One metal acts principally as a cathode and the other metal as the anode. Galvanic corrosion can result from the presence of a second phase in a metal. An example is manganese sulfide [18820-29-6], MnS, inclusions in steels. Galvanic corrosion is also an important consideration for the environmental stability of metal matrix composites (qv) such as graphite reinforced aluminum. Galvanic corrosion can accelerate many of the other types of corrosion.

Microbiologically influenced corrosion results from the interaction of microorganisms and a metal (3,8–11). The action of microorganisms is at least one of the reasons why natural seawater is more corrosive than either artificial seawater or sodium chloride solutions. Microorganisms attach to the surfaces of metals and can, for example, act as diffusion barriers; produce metabolites that enhance or initiate corrosion; act as sinks or sources for species involved in cathodic reactions, such as oxygen and hydrogen; increase the pH at the surface as a result of photosynthesis; or decrease the pH by production of acid metabolites. A more detailed discussion of the various forms of corrosion may be found in the literature (1–4).

4. Origin of Corrosion

In the presence of oxygen and water the oxides of most metals are more thermodynamically stable than the elemental form of the metal. Therefore, with the exception of gold, the only metal that is thermodynamically stable in the presence of oxygen, there is always a thermodynamic driving force for corrosion of metals. Most metals, however, exhibit some tendency to passivate, ie, to form a protective oxide film on the surface that retards further corrosion. Were it not for the passivation by oxide films, most metals and alloys would corrode rapidly.

The thermodynamics of electrochemical reactions can be understood by considering the standard electrode potential, E^0, the potential of a reaction under standard conditions of temperature and pressure where all reactants and products are at unit activity. Table 1 lists a variety of standard electrode potentials. The standard potential is expressed relative to the standard hydrogen reference electrode potential in units of volts. A given reaction tends to proceed in the anodic direction, ie, toward the oxidation reaction, if the potential of the reaction is positive with respect to the standard potential. Conversely, a movement of the potential in the negative direction away from the standard potential encourages a cathodic or reduction reaction.

Table 1. **Standard Electrode (Reduction) Potentials, 25°C**[a]

Electrode	E^0, V[b]
$Li^+ + e^- \rightarrow Li$	−3.045
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.763
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.440
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.403
$Co^{2+} + 2e^- \rightarrow Co$	−0.277
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.250
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.140
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.126
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.15
$Cu^{2+} + e^- \rightarrow Cu^+$	0.158
$Cu^{2+} + 2e^- \rightarrow Cu$	0.337
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771
$Ag^+ + e^- \rightarrow Ag$	0.799
$Br_2(l) + 2e^- \rightarrow 2Br^-$	1.065
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.358

[a] Ref. 3.

[b] Against standard hydrogen electrode (SHE) set at $E^0 = 0.000$V

A piece of zinc placed in an aqueous 1 *M* Zn^{2+} solution attains a potential of approximately − 0.763 V vs standard hydrogen. If Cu^{2+} ions are then introduced into the solution, the zinc begins to corrode because the zinc surface exists at a potential which encourages the cathodic reaction for copper, ie, the standard potential of the zinc reaction is negative to that of the copper and the Cu ions electroplate onto the zinc via the reaction $Cu^{2+} + 2\,e^- \rightarrow Cu$. This coupling causes the zinc potential to shift, ie, to be polarized, in the positive direction and the reaction $Zn \rightarrow Zn^{2+} + 2\,e^-$ then proceeds. The potentials of the two reactions are polarized toward each other, away from the respective standard potentials. The rates of these two reactions must be the same to preserve electroneutrality, and additionally, some of the zinc surface must be exposed to the solution. That is, if a continuous coating of copper were to be electroplated on the zinc surface such that none of the zinc were exposed, further oxidation would be prevented.

Corrosion occurs even if the two reactants involved are not at standard conditions. In this case, the nonstandard equilibrium potential for each reaction, often referred to as the reversible potential, can be calculated from the Nernst equation. Additional information on thermodynamic aspects of corrosion can be found in the literature (1–4,12,13).

The larger the potential difference between the equilibrium potentials of the anodic and cathodic reactions involved in corrosion, the greater the driving force which is more traditionally represented as the change in Gibbs free energy, ΔG. The free-energy change for a reaction is related to the difference in the equilibrium potentials of the two reactions, cathodic minus anodic by

$$\Delta G = -nFE \tag{2}$$

where n is the number of electrons involved in the overall reaction, F is the Faraday constant, and E, the cell voltage or the difference in the equilibrium potential values of the cathode and the anode, respectively, given in volts.

The standard reduction potential of oxygen (taken at pH = 0)

$$O_2 + 4\,H^+ + 4\,e^- \longrightarrow 2\,H_2O \qquad (3)$$

is 1.229 V, a much more positive number than the metal reactions given in Table 1. Therefore, the free-energy change for a coupling of any of the metal reactions, considered as the anode, and the oxygen reaction, considered as the cathode, would be a large negative number; ie, the reaction is thermodynamically highly favored to proceed. Reduction of oxygen is the most common cathodic reaction in the corrosion of metals in neutral and alkaline media. In acidic media the common cathodic reaction is hydrogen evolution

$$2\,H^+ + 2\,e^- \longrightarrow H_2 \qquad (4)$$

The standard potential for this reaction is 0.000 V. Most of the metal reactions have standard potentials below this value.

5. Electrochemical Equilibrium Diagrams

The thermodynamic data pertinent to the corrosion of metals in aqueous media have been systematically assembled in a form that has become known as Pourbaix diagrams (13). The data include the potential and pH dependence of metal, metal oxide, and metal hydroxide reactions and, in some cases, complex ions. The potential and pH dependence of the hydrogen and oxygen reactions are also supplied because these are the common corrosion cathodic reactions as discussed above. The Pourbaix diagram for the iron–water system is given as Figure 1.

If the potential of a metal surface is moved below line A, the hydrogen reaction line, cathodic hydrogen evolution is favored on the surface. Similarly a potential below line B, the oxygen reaction line, favors the cathodic oxygen reduction reaction. A potential above the oxygen reaction line favors oxygen evolution by the anodic oxidation of water. In between these two lines is the region where water is thermodynamically stable.

The Pourbaix diagram is constructed from data for a variety of reactions. The expressions for these reactions can be (*1*) potential dependent and pH independent, (*2*) pH dependent and potential independent, (*3*) both pH and potential dependent, or (*4*) both pH and potential independent. The dependence is determined by whether the reaction of interest is electrochemical or chemical and whether or not it involves the components of water. From this diagram it is possible to determine if there is a driving force for corrosion at any given potential–pH combination and what the corresponding cathodic reaction is likely to be. Regions where insoluble corrosion products form are indicated. These are regions where passivity is possible. Passivity generally results from the formation of an oxide film on a metal surface. The film can dramatically reduce further corrosion of the metal. Regions of immunity, where there is no thermodynamic driving

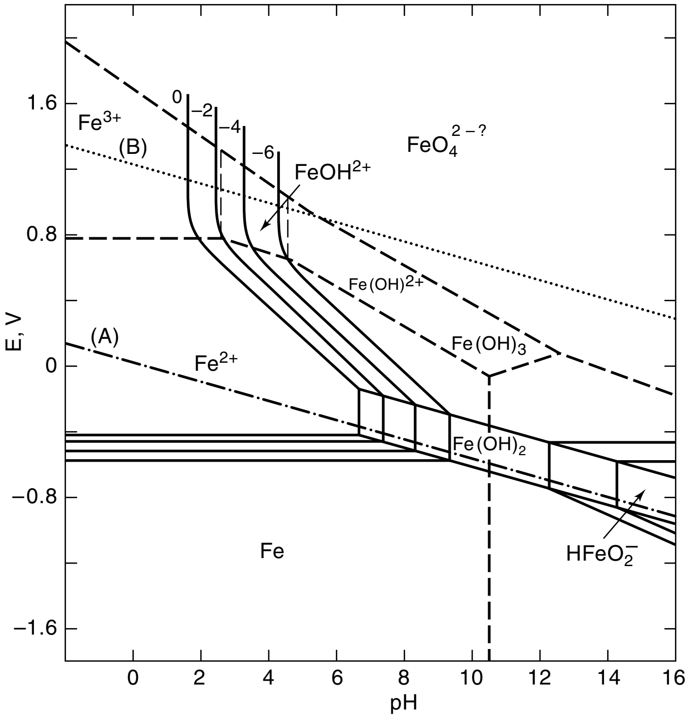

Fig. 1. Pourbaix diagram for the iron−water system at 25°C, considering as solid substances only Fe, $Fe(OH)_2$, and $Fe(OH)_3$, where (—·—·), line A, represents the hydrogen reaction line; (···), line B, the oxygen line(13). The values 0,−2, −4, −6 are molar concentrations of the ions involved in each reaction.

force for the metal to corrode, can also be determined. Figure 2 presents a simplified picture of the Pourbaix diagram of Figure 1 showing the regions of immunity, possible corrosion, and possible passivation. A complete collection of electrochemical equilibrium diagrams can be ordered from NACE International (13).

Pourbaix diagrams are only thermodynamic predictions and yield no information about the kinetics of the reactions involved nor are the influences of other ionic species which may be present in the solution included. Complexing ions, particularly halides, can interfere with passivation and can influence the position of the lines in a Pourbaix diagram. Further, in real corrosion situations the local chemistry in pits, crevices, and cracks differs from that of the bulk concentration and influences the actual electrochemical reactions at those sites. More comprehensive information on Pourbaix diagrams and the use of them in corrosion is available (1−3,12,13).

6. Kinetics of Electrochemical Reactions

Even in uniform corrosion, a corroding metal surface has numerous local anodes and cathodes. The sites of these local reactions may be fixed by microstructural

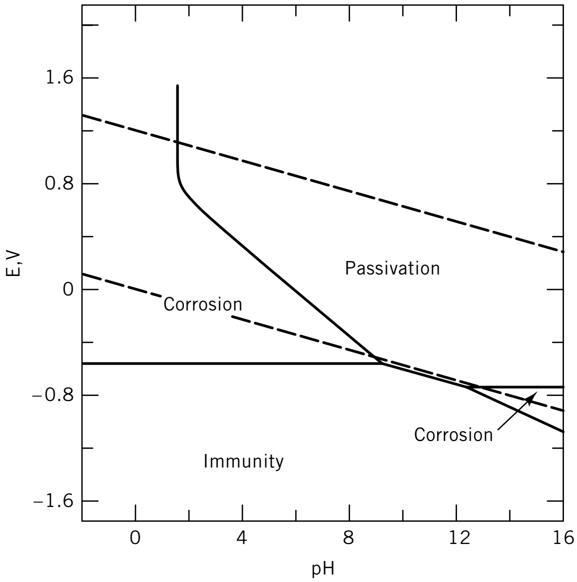

Fig. 2. The thermodynamic regions of corrosion, immunity, and passivation of iron in an iron–water system assuming passivation by a film of Fe_2O_3(13).

features or may change as corrosion proceeds. The oxidation reaction at anodic sites on the metal surface can be represented as in equation 1. A corresponding reduction reaction must be occurring at cathodic sites. In acidic solutions this would likely be hydrogen evolution as shown in equation 4. The potentials of these two reactions would be moved toward each other, away from the respective equilibrium potentials, and the metal surface would assume an overall uniform potential. The dotted lines in Figure 3 illustrate the relationships of the individual electrochemical reaction kinetics as influenced by electrochemical potential. These lines also illustrate the interaction of the two reactions on the metal surface. Diagrams of this sort are referred to as Evans or mixed potential diagrams. The terms are used interchangeable in the corrosion community.

The two dashed lines in the upper left hand corner of the Evans diagram represent the electrochemical potential vs electrochemical reaction rate (expressed as current density, ie, current divided by surface area) for the oxidation and the reduction forms of the hydrogen reaction. At point A the two are equal, ie, at equilibrium, and the potential is therefore the equilibrium potential, E^0, for the hydrogen reaction for the specific conditions involved. Note that the reaction kinetics are linear on these axes. The change in potential for each decade of log current density is referred to as the Tafel slope (14). The Tafel slope is related to the activation energy for the reaction. A more detailed treatment of Tafel slopes can be found elsewhere (1–4,14,15).

The value of the current density where the oxidation and reduction forms of a reaction cross, ie, at point A or point B in Figure 3, is referred to as the exchange current density, i_0. For any equilibrium point, the exchange current density is the rate of the two forms of the reaction, ie, cathodic and anodic, occur-

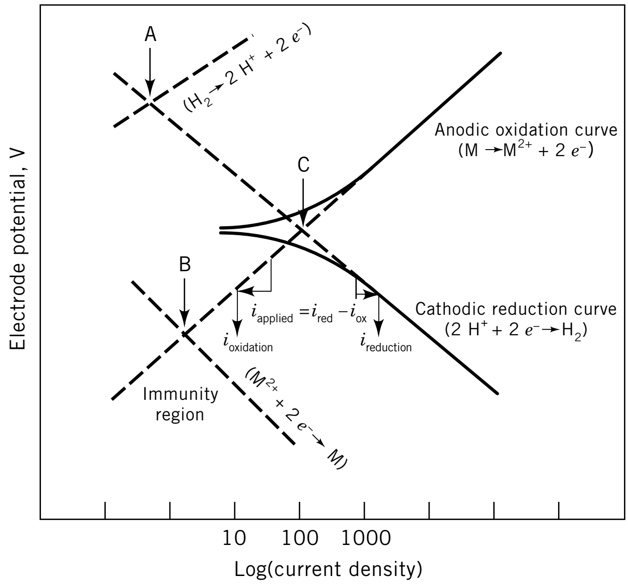

Fig. 3. Hypothetical Evans diagram and polarization curve for a metal corroding in an acidic solution, where point A represents the exchange current density, i_0, for the hydrogen electrode at equilibrium; point B, the exchange current density at the reversible or equilibrium potential, E_{rev}, for $M \rightleftarrows M^{2+} + 2e^-$; and point C, the corrosion current density, i_{corr}, at the open-circuit corrosion potential, E_{corr}. See also discussion in text.

ring at equilibrium. The greater the exchange current density the more kinetically favored is the reaction. The exchange current density for the reduction of hydrogen on platinized platinum is 10^{-3}A/cm^2, whereas on mercury it is 10^{-13}A/cm^2, indicating that platinum is a good catalyst for hydrogen evolution. The exchange current densities for most electrochemical reactions fall in between these two values. Exchange current density and Tafel slope values for a variety of other electrochemical reactions of interest to corrosion can be found in the literature (2,3,16). The example in Figure 3 involves hydrogen evolution on a corroding surface and the exchange current density value for the hydrogen reaction on that surface must then be applied.

In the lower left part of the Evans diagram, the oxidation and reduction forms of metal dissolution reactions are given. Assuming the data of this diagram are accurate, a prediction of corrosion rate and the potential of the corroding metal surface can be made. The potentials of the hydrogen and the metal reactions are pulled toward one another following the dashed lines, or Tafel slope, appropriate for the particular polarization; ie, the anodic line is followed for the metal dissolution reaction, the cathodic line followed for the hydrogen reaction. Point C where the two cross is the only potential where the rates of the anodic and the cathodic reactions are equal. This defines the corrosion potential, E_{corr}, and the corrosion current density, i_{corr}, from which the corrosion rate can be calculated by Faraday's law. The other dotted lines were not considered because the rates at the corrosion potential are so low as to be insignificant.

The solid line in Figure 3 represents the potential vs the measured (or the applied) current density. Measured or applied current is the current actually measured in an external circuit; ie, the amount of external current that must be applied to the electrode in order to move the potential to each desired point. The corrosion potential and corrosion current density can also be determined from the potential versus measured current behavior, which is referred to as polarization curve rather than an Evans' diagram, by extrapolation of either or both the anodic or cathodic portion of the curve. This latter procedure does not require specific knowledge of the equilibrium potentials, exchange current densities, and Tafel slope values of the specific reactions involved. Thus Evans diagrams, constructed from information contained in the literature, and polarization curves, generated by experimentation, can be used to predict and analyze uniform and other forms of corrosion. Further treatment of these subjects can be found elsewhere (1–4,17).

7. Galvanic Corrosion and Cathodic Protection

Galvanic corrosion results when two or more dissimilar metals or alloys immersed in the same electrolyte are in electrical contact (1–4). This form of corrosion is one of the most common and most preventable. The metal or alloy in a galvanic couple having the lower corrosion potential has its potential pulled in the positive direction by the coupling with the metal or alloy that has the higher corrosion potential, generally causing the one with the lower potential to experience accelerated corrosion. Conversely, the metal with the higher corrosion potential experiences a negative shift in potential as a result of the coupling causing it to corrode less and to support additional cathodic reaction. Figure 4 is a galvanic series for a variety of metals and alloys listing the corrosion potentials of these materials in seawater. Free corrosion potentials, not coupled or equilibrium potentials, are given and these allow a determination of which metal has the lower potential in a galvanic couple. Generally, the larger the potential difference between components in a galvanic couple the faster will be the corrosion of the one having the lower potential. However, the kinetics of the particular reactions involved must be evaluated for an accurate determination of corrosion rate.

Galvanic corrosion can be used to a corrosion advantage. If, eg, a metal such as zinc or magnesium, having a low corrosion potential in most environments, is coupled with a steel component, the zinc or magnesium pulls the potential of the steel down causing the steel to corrode less. When a sacrificial metal or alloy, called a sacrificial anode, is attached to a structure having a higher corrosion potential to intentionally pull the potential of the higher potential metal down and thus decrease the corrosion rate, it is called cathodic protection. This method of corrosion mitigation is common for underground pipelines (qv), residential hot water heaters, and hulls and tanks (qv) of ships. The lowering of potential can also be achieved by the application of external electrical current, ie, impressed current cathodic protection. Electrons are pumped into the structure to lower the potential and thus discourage anodic (corrosion) reactions. A second electrode (anode) is needed for this procedure and this electrode is often a highly inert

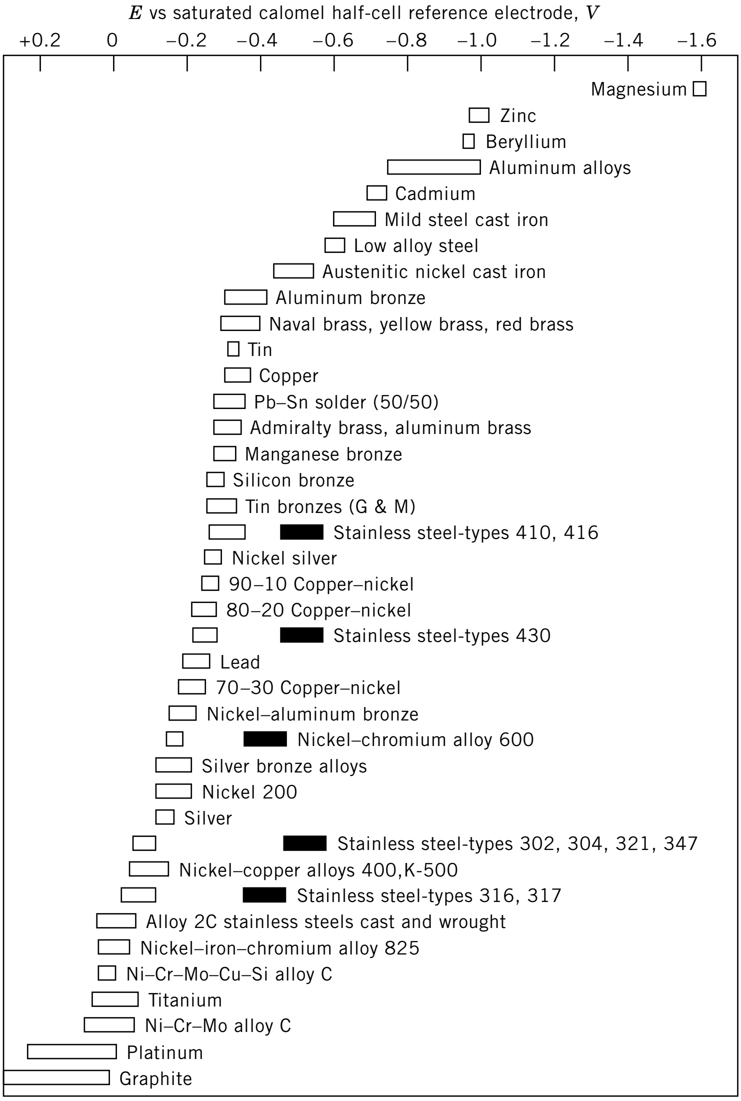

Fig. 4. Galvanic series in flowing seawater. Certain alloys may become more active in low velocity or poorly aerated seawater and the potentials exhibited under these conditions are indicated as darkened potential ranges (1).

material such as platinum to prevent it from being corroded away. However, scrap iron or steel is sometimes used as the impressed current anode. This approach remains functional until the scrap metal anode corrodes away.

The lower potential metal in a galvanic couple does not always have its corrosion rate accelerated. For metals that form a passive film, coupling with another metal of higher potential can cause the film-forming metal's potential to shift from a value at which it corrodes to one at which it passivates and therefore corrodes less. When this is done intentionally the procedure is referred to as anodic protection, ie, achieving protection by intentionally shifting the potential in the positive direction. Anodic protection is generally achieved by adding oxidizers to the electrolyte or by an external electrical circuit.

The higher potential metal in a galvanic couple is not always rendered less corrodible. A passive metal can sometimes be pulled out of its passive region and into a more corrosive region. A metal can also have its potential pulled down to the point where hydrogen reaction is possible and this can lead to one of the forms of EIC called hydrogen induced cracking (HIC). Another example involves organic coatings (qv) on metal structures. These coatings can be damaged by having the potential of the structure shifted too far in the negative direction. This is one of the consequences of excessive cathodic protection.

8. Environmental Effects

The environment plays several roles in corrosion. It acts to complete the electrical circuit, ie, supplies the ionic conduction path; provides reactants for the cathodic process; removes soluble reaction products from the metal surface; and/or destabilizes or breaks down protective reaction products such as oxide films that are formed on the metal. Some important environmental factors include: the oxygen concentration; the pH of the electrolyte; the temperature; and the concentration of anions.

Reduction of oxygen is one of the predominant cathodic reactions contributing to corrosion. Awareness of the importance of the role of oxygen was developed in the 1920s (18). In classical liquid drop experiments, the corrosion of iron or steel by drops of electrolytes was shown to depend on electrochemical action between the central relatively unaerated area, which becomes anodic and suffers attack, and the peripheral aerated portion, which becomes cathodic and remains unattacked. In 1945, the linear relationship between rate of iron corrosion and oxygen pressure from 0 to 2.5 MPa (0–25 atm) was shown (19).

The concentration dependence of iron corrosion in potassium chloride [7447-40-7], sodium chloride [7647-14-5], andlithium chloride [7447-44-8] solutions is shown in Figure 5 (20). In all three cases there is a maximum in corrosion rate. For NaCl this maximum is at $\sim 0.5\ N$ ($\sim$3 wt%). Oxygen solubility decreases with increasing salt concentration, thus the lower corrosion rate at higher salt concentrations. The initial increase in the iron corrosion rate is related to the action of the chloride ion in concert with oxygen. The corrosion rate of iron reaches a maximum at $\sim 70^\circ$C. As for salt concentration, the increased rate of chemical reaction achieved with increased temperature is balanced by a decrease in oxygen solubility.

The corrosion rate of iron in aerated water is also a function of pH and generally follows the pattern in Figure 6 (21). At pH 4–10 , the rate is controlled by the availability of oxygen. In more acidic solutions (lower pH) the corrosion rate is accelerated, and the reduction of hydrogen ion replaces the reduction of oxygen as the rate controlling cathodic reaction. Many metals follow approximately the same behavior with the exception of those metals that dissolve to form amphoteric ions. Zinc forms the zincate ion, ZnO_2^{2-}, which causes zinc to corrode excessively above a pH 12 (see ZINC COMPOUNDS); whereas Al forms the aluminate ion

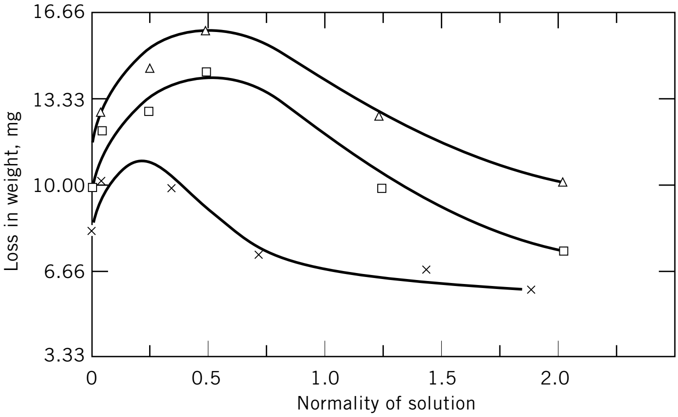

Fig. 5. Corrosion–concentration curves for alkali chlorides where × denotes LiCl; □, NaCl; and △, KCl (20).

[11098-82-1],, AlO_2^-, which increases the dissolution rate above a pH of ~8 (see Aluminum compounds, aluminates).

Chlorides, which are ubiquitous in nature, play an important role in the corrosion of metals. Chlorides and other anions also play an important role in localized corrosion, ie, the breakdown of the insoluble protective reaction product films, eg, passive films, that prevent corrosion of the underlying metal. A variety of mechanisms attempting to explain the role of chloride in general and in localized corrosion have been proposed (6,22–25).

Very often the environment is reflected in the composition of corrosion products, eg, the composition of the green patina formed on copper roofs over a

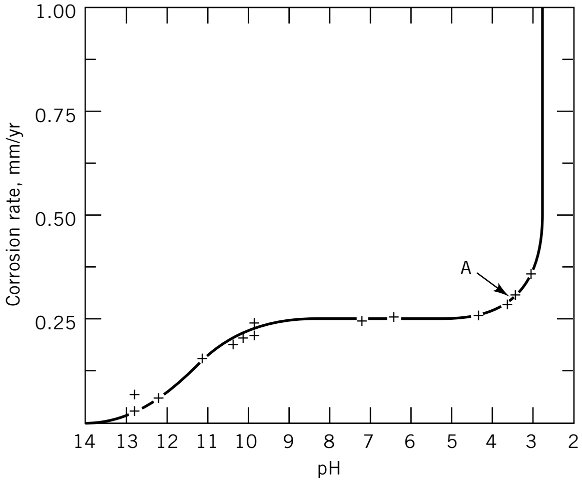

Fig. 6. Effect of pH on corrosion of iron in aerated water at room temperature (21). Point A is where H_2 evolution begins. To convert mm/yr to mils per year (mpy), multiply by 39.37.

Table 2. **Composition of Green Patina on Copper from Different Locations**[a]

Location of structure	Age of structure, year	Composition of green patina, %			
		$CuCO_3$	$CuCl_2$	$Cu(OH)_2$	$CuSO_4$
urban	30	14.6		9.6	49.8
rural	300	1.4		58.5	25.6
marine	13	12.8	26.7	52.5	2.5
urban–marine	38		4.6	61.5	29.7

[a] Refs. 26 and 27.

period of years. The determination of the chemical composition of this green patina was one of the first systematic corrosion studies ever made (see COPPER). The composition varied considerably depending on the location of the structure as shown in Table 2 (26,27).

9. Alloy Composition and Metallurgical Factors

A primary factor in determining corrosion behavior of metals and alloys is their chemical composition. Alloys having varying degrees of corrosion resistance have been developed in response to environmental needs. A good example of how corrosion resistance can be successfully changed by altering the composition can be seen in the alloying of steels. At the lower end of the alloying scale are the less costly and less corrosion resistant low alloy steels. These are iron-base alloys containing from 0.5–3.0 wt% Ni, Cr, Mo, or Cu and generally small amounts of P, N, and S. At the higher end of the alloying scale are the more costly and significantly more corrosion resistant stainless steels. These latter alloys contain a minimum of 10.5 weight percent Cr and, depending on the grade, other alloying elements such as Ni, Mo, and N. The corrosion resistance of these alloys is based on the protective nature of the surface film, which in turn is based on the physical and chemical properties of the oxide film.

In addition to alloying there are other metallurgical factors, such as crystallography, grain size and shape, grain heterogeneity, second phases, impurity inclusions, and residual stress, that influence corrosion. The technologically important structural materials are polycrystalline aggregates. Each individual crystal is referred to as a grain. Grain orientation can affect corrosion resistance as evidenced by metallographic etching rates and pitting behavior (22). Grain shape may likewise vary greatly depending on the alloy and processing history. Alloys, particularly in the as-cast condition, generally exhibit chemical inhomogeneity such that there is segregation of alloying elements and impurities to the grain boundary regions. These heterogeneities, which can also develop during subsequent processing such as welding (qv) or heat treatment, can produce different electrochemical characteristics at the grain boundary relative to the grain interior and can lead to intergranular corrosion. This problem can be of great practical importance, especially to wrought stainless steels and nickel alloys. Second phases, such as ferrite grains in an otherwise austenitic stainless steel and beta grains in an otherwise alpha brass, can be of considerable importance in some alloy systems and some forms of corrosion. Residual stresses from cold-working or other sources can lead to increased corrosion rates (22,24,28), and are also important in stress–corrosion cracking.

The following sections briefly discusses some of the alloying and metallurgical factors in a three technologically important alloy systems. A more complete discussion of the corrosion behavior of these and other alloy systems and the influence of metallurgical factors on each is available (4).

9.1. Stainless Steels. The stainless steels, by virtue of the alloying additions and processing, can be categorized as ferritic (body-centered cubic structure), austenitic (face-centered cubic structure), duplex (a combination of ferritic and austenitic), martensitic (body-centered tetragonal or cubic structure), and precipitation hardened. There are some 180 different alloys that can be recognized as stainless steels. These alloys contain a minimum of 10.5 wt% Cr and, depending on the grade, other alloying elements such as Ni, Mo, and N (5,29). The concentration of particular alloying elements are based on the desired properties of the stainless steel. Figure 7 shows the compositional and property linkages for the stainless steels (29).

Figure 7 Compositional and property linkages for the stainless steels (29).

The corrosion resistance of stainless steels results from the formation of a passive film and, for this reason these materials are susceptible to pitting corrosion and to crevice corrosion. The resistance to pitting or crevice corrosion is improved by additional alloying with Cr, Mo, and N for the austenitic and duplex

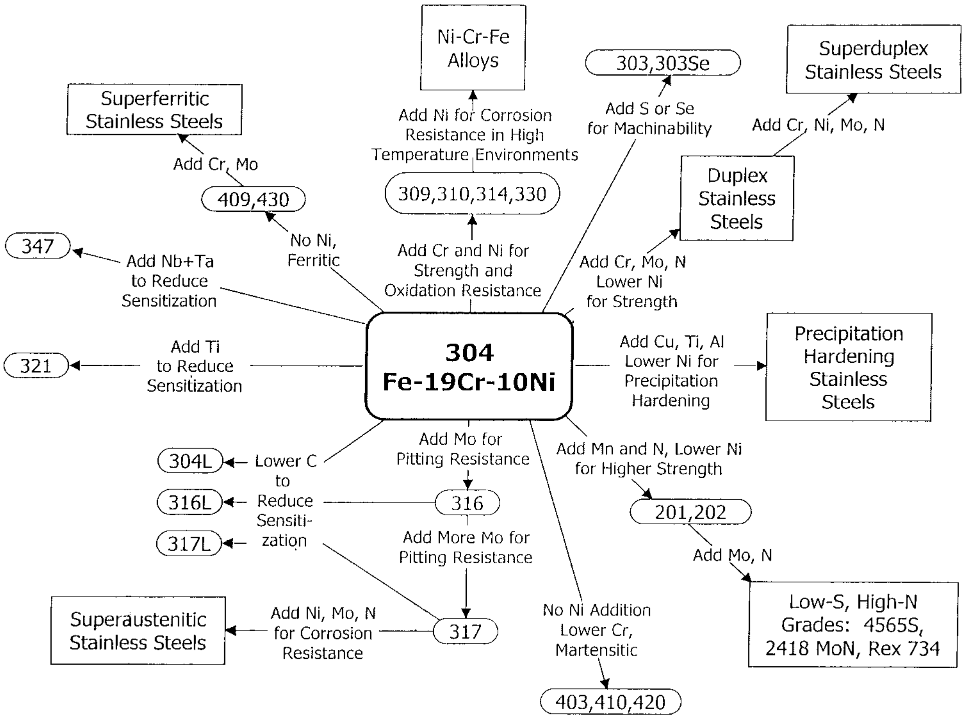

Fig. 7. Compositional and property linkages for the stainless steels (29).

stainless steels and alloying the ferritic stainless steels with additional Cr and Mo. The manufacturers of stainless steels have developed indexes for resistance to pitting and crevice corrosion based on the composition of the alloy. The index is known as the pitting resistance equivalent number (PREN). PREN is given by $\text{PREN} = \%\text{Cr} + 3.3\ (\%\text{Mo}) + 16\ (\%\text{N}) + 1.65\ (\%\text{W})$. In general, the higher the value of PREN, the greater the resistance to crevice and pitting corrosion. The major problem with using a PREN is that it is based solely on composition and ignores the detrimental effects of microstructure, such as Cr depleted zones and alloy segregation (29).

The most common and serious metallurgical factor affecting the corrosion resistance of stainless steels is termed sensitization. This condition is caused by the precipitation of chromium-rich carbides (qv) at the grain boundaries, giving rise to chromium depleted grain boundary areas. For example, heating a type 304 stainless steel containing 0.039% carbon for 10 h at 700°C will reduce the chromium level from 19% to <13% in the region next to the carbide precipitate (29). The depleted areas are anodic to the grain interior and tend to dissolve thereby causing intergranular corrosion. Sensitization can also make stainless steel more prone to stress–corrosion cracking (SCC). There are several measures available to mitigate sensitization. Low carbon grades such as AISI 304L and 316L are available that have much less tendency toward sensitization. Also, alloying additions of titanium or niobium and tantalum can be used to tie up carbon. Another area of concern with stainless steel alloys is EIC and this topic is treated in more detail later in this article for stainless steels as well as for other selected alloys. A more detailed discussion of stainless steels may be found in the literature (5,29).

9.2. Copper Alloys. Copper and its alloys have good corrosion resistance in many nonoxidizing aqueous environments and atmospheric conditions. Several copper alloys are exceptionally resistant to certain atmospheres. The copper–nickel alloys are the most corrosion resistant of the commercial copper alloys (3). The two most common Cu–Ni alloys are 90% Cu–10% Ni and 70% Cu–30% Ni. They have good resistance to corrosion in both fresh and salt water (4).

The most known of the copper alloys is brass, which is produced by the addition of zinc. The zinc improves the mechanical properties by solid solution strengthening. However, the zinc reduces the corrosion resistance. A variety of names are associated with brasses with a particular zinc content: 40% Zn–Cu alloys are referred to as Muntz metal; 30% Zn–Cu alloys are referred to as yellow brass; and 15% Zn–Cu alloys are termed red brass (2). Brasses are susceptible to dealloying in the form of dezincification, ie, the preferential loss of zinc from the alloy. Brasses having zinc concentrations of 15% or greater are prone to dezincification and dezincification is generally more severe in brasses that have two metallurgical phases. For the two-phase alloys, greater than ~38 wt% Zn, dezincification usually starts in the high zinc content β-phase and is followed by dezincification of the lower zinc α-phase (4). Naval brass and admiralty brass are similar in composition to Muntz metal and yellow brass, respectively, but have 1 wt% tin added for improved resistance to dezincification. Red brass is relatively resistant to dezincification but is more susceptible to impingement attack than, for example, yellow brass (2).

Conditions that favor dezincification include stagnant solutions, especially acidic ones, high temperatures, and porous scale formation (2). Tin tends to inhibit dealloying especially in cast alloys (4). Additions of small amounts of arsenic, antimony, or phosphorus can increase the resistance to dezincification. These elements are, however, not entirely effective in preventing the dezincification of the two-phase (α-β) brasses because dezincification of the β-phase is not prevented (4). Another area of corrosion concern involves applied or residual stresses from fabrication that can lead to EIC of brasses in the form of SCC.

9.3. Aluminum Alloys. The corrosion resistance of aluminum, like stainless steels, is provided by a passive film that protects the surface from degradation by the environment. However, in environments that contain aggressive anions such as chloride, the passive film can be degraded locally causing film breakdown and, depending on the geometry of the sample, pitting or crevice corrosion.

Copper, silicon, magnesium , zinc, and manganese are some common alloying additions to aluminum. Most of the alloying elements are added to aluminum to produce alloys having improved mechanical properties. However, the strengthening phases that result from the alloying can disrupt the passive oxide layer on aluminum and lead to localized corrosion. Also, the second phase constituents can produce local galvanic cells as discussed below. Common alloying elements that are added to steels and many other metals to improve corrosion resistance, such as Cr and Mo, have a very low solubility in aluminum and result in second phase precipitates. The presence of the second phase constituents, in turn, lowers the corrosion resistance. A number of surface modification techniques that produce single phase, metastable aluminum alloys have been shown to increase the localized corrosion resistance as compared to pure aluminum (30–34). These techniques include ion implantation, laser alloying, and magnatron sputtering. However, due to capital costs and the sizes of the sample that can be treated, these techniques have not gained widespread use.

Aluminum alloys are susceptible to intergranular corrosion when precipitates form. Intergranular corrosion in aluminum alloys is caused by a potential difference, ie, galvanic couple. The formation of the anodic and cathodic areas in the couple varies depending on the alloying additions (3). Reference (35) is a compilation of potentials reported for intermetalic phases in aluminum alloys. Stress–corrosion cracking is characteristically intergranular for aluminum alloys. Wrought high strength aluminum alloys, whether the products are rolled, forged, or extruded, tend to be highly textured because of the manner in which the secondary phases or inclusions are strung out. Exfoliation corrosion, a type of intergranular corrosion, proceeds along subsurface paths. The corrosion products have a greater volume than the alloy and produce a layer type attack. Selection of alloys with proper tempers can provide resistance to exfoliation corrosion (4). The texture is also is important to the SCC of high strength aluminum alloys (see ALUMINUM AND ALUMINUM ALLOYS).

10. Environmentally Induced Cracking

Environmentally induced cracking is a brittle fracture process caused by the conjoint action of a mechanical stress and a corrosive environment. There are several different types of EIC: stress–corrosion cracking (SCC), corrosion fatigue cracking (CFC), and hydrogen induced cracking (HIC). In SCC and HIC the stress may be normal stress experienced in operation or residual stress from welding, heat treatment, and/or cold work. CFC results from cyclic stresses. In any of these, the corrosion rates are generally very low and the stress level required for the cracking is generally well below the normal yield stress of the particular alloy involved. The concentration of the chemical species responsible for the cracking need not be high. EIC failures are often catastrophic such as the Pt. Pleasant, West Virginia, bridge collapse that killed 46 people in 1967 (3). Cracking in steam pipes, underground pipelines, and aircraft have also been attributed to EIC.

The chemical species that can lead to EIC in each alloy system are fairly well known although the exact mechanisms of crack initiation and propagation are not thoroughly understood. The species that promote EIC in one alloy system do not necessarily promote EIC in others. A discussion of EIC and the chemical species that promote it can be found in the literature (3).

The cracking in EIC can proceed either intergranularly, ie, between the grains, or transgranularly, ie, across the grains. Small changes in the environment can cause a shift from one type to the other as can relatively small changes in the composition of the alloy. Likewise the crack may be single and unbranched or have multiple origins and also be branched. Thus neither intergranular or transgranular cracking is indicative of or excludes EIC as the cause of a service crack. More detailed information regarding EIC is available (1,3,4,36).

10.1. Copper Alloys. Copper alloys under an applied or residual stress are susceptible to SCC in environments containing ammonia (qv) or ammonium compounds (qv). In addition to ammonia, water and oxygen, or another cathodic reactant, are required to cause SCC. Ammonia and ammonium compounds are sometimes found in the atmosphere, in cleaning compounds, in fertilizers (qv), or in chemicals used for water treatment. Brasses containing $<15\%$ zinc are highly resistant to SCC, whereas brasses containing 20–40% zinc are highly susceptible and this susceptibility increases only slightly as zinc concentration increases from 20 to 40% (4). SCC is usually intergranular but can occur transgranular under certain conditions (2,4).

Trace quantities of nitrogen oxides may also cause SCC. These failures are probably the result of the nitrogen oxides being converted to ammonium salts on the brass surface. The premature failure of yellow brass brackets in the humidifier chamber of an air-conditioning system was traced to this latter cause (2). In another case, SCC of 12% Ni–23% Zn–Cu alloy, known as nickel brass, parts of the Central Office Telephone equipment in Los Angeles occurred within 2 years of installation for similar reasons. The source of nitrogen was the air in the Los Angeles area which has high concentrations of nitrogen oxides and suspended nitrates (see AIR POLLUTION). The nitrates settle as dust on the brass parts (2). The susceptibility to SCC can be minimized by (*1*) proper alloy selection; (*2*) thermal stress relief; (*3*) avoiding contact with ammonia and ammonia compounds; and (*4*) using an inhibitor (2,4).

10.2. Aluminum Alloys. Both the 2000 and the 7000 series aluminum alloys have experienced significant SCC in service. These high strength alloys in the wrought form are highly textured, the grains are flattened and elongated into specific crystallographic directions due to the processing. SCC behavior differs greatly according to the direction of tensile stress with respect to the texture directions. The alloys are most vulnerable to SCC if stressed parallel to the short transverse grain direction, ie, parallel to the thinnest dimension of the grain and most resistant if stressed only parallel to the longest grain dimension. In practice, it is the short transverse-direction stresses that cause SCC problems. Hence prudent practice is to avoid designs in which high sustained stresses are imposed across the short transverse direction. For example, one avoids an interference-fit fastener, or a taper pin fastener oriented to stress a part across the vulnerable texture unless the alloy is inherently of low susceptibility to SCC. Table 3 summarizes alloys and tempers in various categories of susceptibility as judged from specimens having short transverse, ie, most vulnerable, orientations.

In addition to the possibility of selecting alloys having minimum SCC susceptibility while retaining other properties as needed, there are other steps possible to reduce the SCC probability: (*1*) avoid designs that permit water to accumulate; (*2*) avoid conditions in which salts, especially chlorides, can concentrate; and (*3*) where available and otherwise acceptable, use a clad alloy (2) (see METAL SURFACE TREATMENTS).

10.3. High Strength Steels. Steels that owe their strength to heat treatment, whether martensitic, precipitation hardened, or maraging, and whether stainless or not, are susceptible to SCC in aqueous environments, including

Table 3. **Susceptibility Classification of Commercial Wrought Aluminum Alloys in Plate Form—Short Transverse Orientation**[a]

Aqueous susceptibility	Aluminum alloy	Temper[b]
very low	1100	all
	3003, 3004, 3005	all
	5000, 5050, 5052, 5154	all
	5454, 6063	
	5086	O, H32, H34
	6061, 6262	O, T6
	Alclad: 2014, 2219, 6061, 7075	all
low	2219	T6, T8
	5086	H36
	5083, 5456	controlled
	6061	T4
	6161, 5351	all
	6066, 6070, 6071	T6
	2021	T8
	7049, 7050, 7075	T73
moderate	2024, 2124	T8
	7050, 7175	T736
	7049, 7075, 7178	T6
appreciable	2024, 2219	T3, T4
	2014, 7075, 7079, 7178	T6
	5083, 5086, 5456	sensitized
	7005, 7039	T5, T6

[a] Ref. 37.

[b] Standard mill designation.

water vapor. The primary factor in determining the degree of SCC susceptibility of a given steel is its strength. There is no sharply defined threshold strength that defines a threshold susceptibility, but above 1200 MPa (174,000 psi) yield strength the problem becomes of increasing concern, until at 1400 MPa (~200,000 psi) susceptibility is generally very high. This does not mean that steels cannot be used at such strength levels or even higher, but for steels to be used at these strengths, great care must be exercised in design such that any tensile or bending stresses are small, or that moisture is excluded from the surface of the steel.

High strength steels are also susceptible to HIC. Cadmium electroplating is a useful protection measure for steels, but hydrogen either must not be codeposited with cadmium, or if it is codeposited, as in the cyanide plating bath, hydrogen must be safely redistributed by thermal treatment before the high strength steel component is stressed. Otherwise the steel may experience HIC.

10.4. Stainless Steels. Austenitic stainless steels undergo SCC when stressed in hot aqueous environments containing chloride ion. The oxygen level of the environment can be important, probably through its effect in establishing the electrode potential of the steel. The total matrix of combinations of stress level, chloride ion and oxygen concentrations, and temperature that cause SCC has not been worked out. At about the yield strength stress and ca 290°C, 1 ppm chloride and 1 ppm dissolved oxygen are about the minimum levels that initiate SCC. At room temperature, SCC by chloride seldom occurs in austenitic stainless steels except when the steels are heavily sensitized. When these steels are not heavily sensitized, there is not usually SCC except at elevated temperatures. Whereas there is no well-defined threshold temperature for vulnerability to SCC in stainless steels, above ~60°C, it becomes of increasing concern.

The relative susceptibilities of the common grades of austenitic stainless steel to SCC in chloride do not differ greatly, although the steels that can and do become sensitized are decidedly inferior in this condition. The high purity ferritic grades of stainless steel offer appreciable improvement in SCC resistance as compared to the austenitic grades, but they are not immune to cracking. Care must also be exercised to avoid the ductile-to-brittle transition that most steels undergo as the temperature is decreased and potential embrittlement by σ-phase formation in elevated temperature service. The standard methods for avoiding chloride SCC in austenitic stainless steels include: avoidance of fabrication stresses; minimizing chloride ion level; and minimizing oxygen concentration in the environment. Additionally, where feasible, it is possible to mitigate against SCC in these alloys by cathodic protection, but excessive cathodic protection can lead to HIC.

11. Inhibitors

Corrosion inhibitors are substances that slow or prevent corrosion when added to an environment in which a metal usually corrodes. Corrosion inhibitors are usually added to a system in small amounts either continuously or intermittently. The effectiveness of corrosion inhibitors is partly dependent on the metals or alloys to be protected as well as the severity of the environment. The main factors, which must be considered before application of a corrosion inhibitor to an aqueous system, are the compatibility of the inhibitor and the metal(s), the salt concentration, the pH, the dissolved oxygen concentration, and the concentration of interfering species such as chlorides or metal cations. In addition, many inhibitors, most notably chromates, are toxic and environmental regulations limit use. (38).

Inhibitors act and are classified in a variety of ways (1,3,38,39). The classifications used herein closely follow the discussion in (38). Types of inhibitors discussed below include (*1*) anodic, (*2*) cathodic, (*3*) organic, (*4*) precipitation, and (*5*) vapor-phase inhibitors.

11.1. Anodic Inhibitors. Passivating or anodic inhibitors produce a large positive shift in the corrosion potential of a metal. There are two classes of anodic inhibitors which are used for metals and alloys where the anodic shift in potential promotes passivation, ie, anodic protection. The first class includes oxidizing anions that can passivate a metal in the absence of oxygen. Chromate is a classical example of an oxidizing anodic inhibitor for the passivation of steels. The second class of anodic inhibitors contains ions which need oxygen to passivate a metal. Tungstate and molybdate, eg, require the presence of oxygen to passivate a steel. The concentration of the anodic inhibitor is critical for corrosion protection. Insufficient concentrations can lead to pitting corrosion or an increase in the corrosion rate. The use of anodic inhibitors is more difficult at higher salt concentrations, higher temperatures, lower pH values, and in some cases, at lower oxygen concentrations (38).

11.2. Cathodic Inhibitors. Cathodic inhibitors act to retard or poison the cathodic reaction or selectively precipitate onto cathodic areas producing diffusion barriers to cathodic reactants, thereby reducing the rate of the cathodic reaction. There are three types of cathodic inhibitors: (*1*) hydrogen poisons, (*2*) oxygen scavengers, and (*3*) cathodic precipitates. Hydrogen poisons are chemical species such as arsenic or antimony that retard the hydrogen reduction reaction. Because the hydrogen poison slows the cathodic reaction, and because the cathodic and anodic reactions must proceed at the same rate, the whole of the corrosion process is slowed. A potentially serious drawback upon use of hydrogen poisons is that the hydrogen on the surface can be more easily absorbed into the metal or alloy and can lead to HIC in susceptible materials. Oxygen scavengers prevent corrosion by tying up the oxygen in solution, thereby making it unavailable for the cathodic reaction. The most common oxygen scavengers used in water at ambient temperatures are sulfur dioxide [7446-09-5] and sodium sulfate [7757-82-6]. Cathodic precipitate inhibitors such as calcium carbonate [471-34-1] or magnesium carbonate [546-93-0] precipitate onto the cathodic areas producing a film that reduces the cathodic activity (38).

11.3. Organic Inhibitors. Generally, organic inhibitors adsorb on the entire metal surface and impede corrosion reactions (38). Organic inhibitors consist of broad classes of organic compounds. For example, aliphatic organic amines (qv) adsorb by the surface-active NH_2 group that forms a chemisorptive bond with the metal surface. The hydrocarbon tails orient away from the interface toward the solution, so that further protection is provided by the formation of a hydrophobic network that excludes water and aggressive ions from the metal surface (39). Organic inhibitors influence both anodic and cathodic reactions to varying degrees depending on the potential, the chemical structure of the inhibitor, and the size of the inhibitor molecule. Soluble organic inhibitors produce a protective layer that is only a few molecules thick, whereas insoluble inhibitors added as dispersions can build a film to a thickness of several hundredths of a centimeter (38).

11.4. Precipitation and Vapor-Phase Inhibitors. Precipitation inhibitors are film-forming compounds that produce barrier films over the entire surface. Phosphates and silicates, which are the most common, do not provide the degree of protection afforded by chromate inhibitors, but are useful in situations where nontoxic additives are required. Two main drawbacks to the use of phosphates and silicates are the dependence on the water composition and the control required to achieve maximum inhibition (38,39).

Vapor-phase inhibitors are volatile compounds that adsorb onto metal surfaces, and retard or prevent corrosion by a variety of mechanisms (38). Inhibitors such as dicyclohexamine nitrate [3882-06-02] can protect a variety of metals including steel, aluminum, and tinplate. A number of vapor-phase inhibitors are commercially available as powders or tablets. However, vapor-phase inhibitors attack nonferrous metals to varying degrees, thus the manufacturers' recommendations should be checked before application. The system to be protected must be closed to maintain the volatile compound, but objects as large as the interior of an ocean-going tanker have been treated by this technique.

11.5. Environmentally Compatible Inhibitors. The recent and expected environmental regulations concerning the release of hazardous materials and the growing list of materials considered as hazardous are impacting the use of many effective inhibitors such as chromate. Thus, new research and development on environmentally acceptable inhibitors is proceeding. This is a great challenge as inhibitor and coating users and manufacturers have to replace commercial products that have decades of acceptable field performance in regard to corrosion (40,41).

12. Coatings for Corrosion Prevention

Coatings (qv) are applied to metal substrates to prevent corrosion. Generally, the coating protects the metal by imposing a physical barrier between the metal substrate and the environment. However, the coating can also act to provide cathodic protection or by serving as holding reservoirs for inhibitors. Coatings may be divided into organic, inorganic, and metallic coatings (1–3,42). For a more in-depth coverage of this topic see (1–3) (see also COATINGS, MARINE; METAL SURFACE TREATMENTS).

12.1. Coating Types. Organic coatings afford protection by providing a physical barrier and are often used as holding reservoirs for corrosion inhibitors. Organic coatings include paints, resins, lacquers, and varnishes (see also BARRIER POLYMERS; PAINT). These coatings usually comprise four basic constituents: binder, pigments and fillers, additives and solvents. The properties of the coating strongly depend on the formulation of the coating (43). The effective application of an organic coating requires (*1*) proper surface preparation of the metal substrate, (*2*) selection of the proper primer or priming coat, and (*3*) selection of the appropriate top coat(s). Poor performance of organic coatings most often results from improper surface preparation or poor application (1). Maintenance programs involving periodic inspection and repair are necessary for reliable corrosion protection by organic coatings. Organic coatings probably protect more metal on a tonnage basis than any other means of corrosion protection. As a rule, however, organic coatings should not be used in environments that would rapidly corrode the metal if the coating were compromised. For example, paint would not be used to protect the inside of a tank car used for shipping hydrochloric acid because one small coating defect would result in the rapid perforation of the tank car wall.

Inorganic coatings are also used to provide a barrier between the environment and the metal (1,2,42). Inorganic coatings include chemical conversion coatings, glass (qv) linings, enamels (see ENAMELS, PORCELAIN OR VITREOUS), and cement (qv). Chemical conversion coatings are produced by intentionally corroding the metal surface in a controlled manner. This is done so as to produce an adherent corrosion product that protects the metal from further corrosion. Anodization of aluminum, one of the more commonly used conversion coatings techniques, produces a protective aluminum oxide film on the aluminum metal. Another example of a chemical conversion coating is phosphatizing for the protection of automobile bodies. Porcelain enamel coatings, that are inert in water and resistant to most weather are routinely applied to steel, cast iron, and aluminum (4). They are commonly seen on appliances and plumbing fixtures. Glass-lined metals are used in process industries where there is concern over corrosion or contamination of the product. For example, glass-lined metals are used in the pharmaceutical industry (4). Portland cement coatings have been used to protect steel and cast-iron water pipes (2).

Often metallic coatings, in addition to providing a barrier between the metal substrate and the environment, provide cathodic protection when the coating is compromised (2,3). Metallic coatings (qv) and other inorganic coatings are produced using a variety of techniques including hot dipping, electroplating, cladding, thermal spray techniques, chemical vapor deposition, or by surface modification using directed energy (laser or ion) beams. Two classic metallic coating techniques and a relatively recent technique are described below.

13. Coating Methods

Hot dipping is one of the oldest methods used for coating metals. In hot dipping, coatings are applied by dipping the metal in a molten bath commonly of zinc, tin, lead, or aluminum (2,4). The best known hot dipping procedure is that of coating steel with zinc to produce galvanized steel. In addition to providing a barrier between the steel substrate and the environment, the zinc acts as a sacrificial anode and provides cathodic protection to the underlying steel when the coating is breached.

Electroplating (qv) consists of immersing a metal in a plating bath and electrochemically plating the solution species onto the metal substrate (1,4). Electroplating is used to provide coatings for a variety of reasons including corrosion protection, wear resistance, decoration, and to build up the dimensions of a substrate. Additives to the plating bath can improve coating properties such as grain size, strength, uniformity, and brightness. The electroplate can be a single metal, an alloy, or a sequence of layers of different composition. Coating thicknesses can range from on the order of thousandths of a mil to 20 mils (1). Zinc, nickel, tin, and cadmium are the most commonly plated materials on a tonnage basis. Electroplated tin is used as a protective coating for food cans (see FOOD PACKAGING). The electroplated tin provides a physical barrier and galvanic protection (in most food products) if the coating is compromised. However, the tin coating cannot provide galvanic protection in the presence of dissolved oxygen so that food should not remain in tin plated cans after opening (3).

The ability to modify metal surfaces using directed energy beams is a new approach being used to improve the corrosion resistance of metals (31,44). Techniques such as ion implantation (qv), ion beam mixing, and ion beam assisted deposition (IBAD), as well as laser-surface alloying and processing have been shown to improve the corrosion behavior of metals (see LASERS). These techniques are versatile and have been used to modify the cathodic or anodic reactions, improve the nature of passive films, and produce barrier coatings (31). Ion implantation has been used to improve the corrosion resistance of titanium in hot acids and aluminum and steels in aqueous chloride environments (44). However, due to capital costs and the sizes of the sample that can be treated, these techniques have not yet gained wide spread use.

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