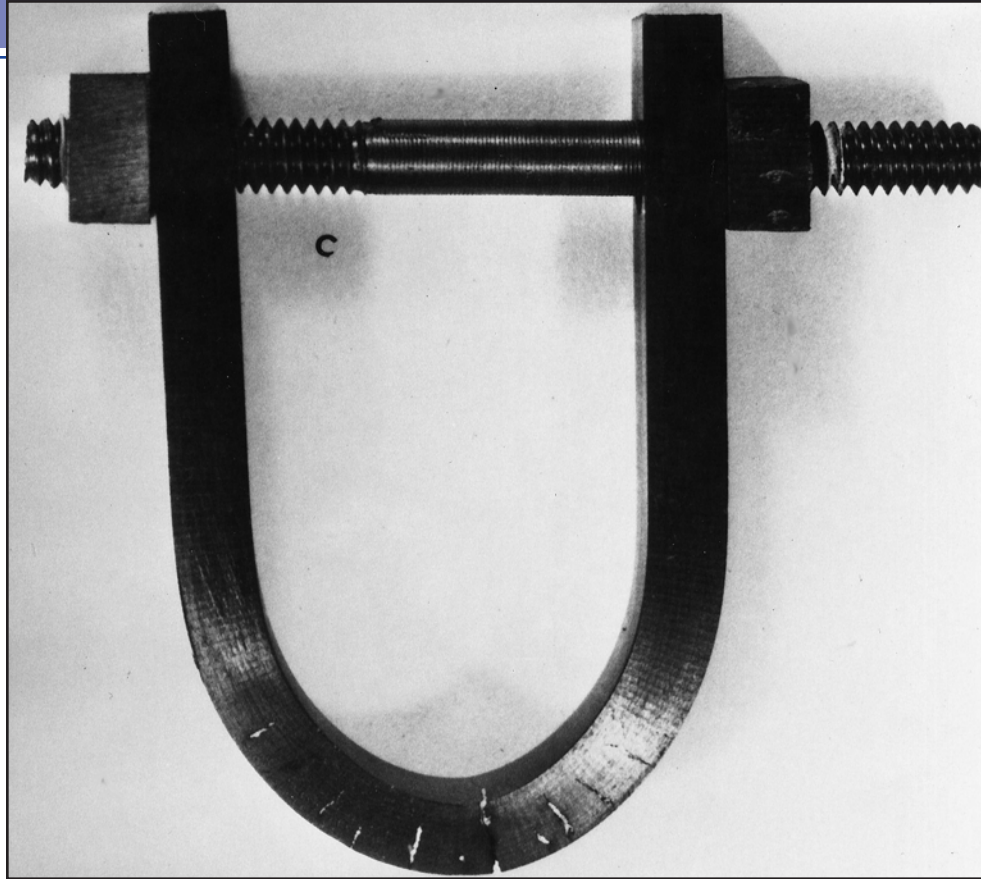


Chapter 17 Corrosion and Degradation of Materials



Photograph showing a bar of steel that has been bent into a "horseshoe" shape using a nut-and-bolt assembly. While immersed in seawater, stress corrosion cracks formed along the bend at those regions where the tensile stresses are the greatest. (Photograph courtesy of F. L. LaQue. From F. L. LaQue, *Marine Corrosion, Causes and Prevention*. Copyright © 1975 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)

WHY STUDY *Corrosion and Degradation of Materials*?

With a knowledge of the types of and an understanding of the mechanisms and causes of corrosion and degradation, it is possible to take measures to prevent them from occurring. For example, we may change

the nature of the environment, select a material that is relatively nonreactive, and/or protect the material from appreciable deterioration.

Learning Objectives

After careful study of this chapter you should be able to do the following:

1. Distinguish between oxidation and reduction electrochemical reactions.
2. Describe the following: galvanic couple, standard half-cell, and standard hydrogen electrode.
3. Compute the cell potential and write the spontaneous electrochemical reaction direction for two pure metals that are electrically connected and also submerged in solutions of their respective ions.
4. Determine metal oxidation rate given the reaction current density.
5. Name and briefly describe the two different types of polarization, and specify the conditions under which each is rate controlling.
6. For each of the eight forms of corrosion and hydrogen embrittlement, describe the nature of the deteriorative process, and then note the proposed mechanism.
7. List five measures that are commonly used to prevent corrosion.
8. Explain why ceramic materials are, in general, very resistant to corrosion.
9. For polymeric materials discuss (a) two degradation processes that occur when they are exposed to liquid solvents, and (b) the causes and consequences of molecular chain bond rupture.

17.1 INTRODUCTION

To one degree or another, most materials experience some type of interaction with a large number of diverse environments. Often, such interactions impair a material's usefulness as a result of the deterioration of its mechanical properties (e.g., ductility and strength), other physical properties, or appearance. Occasionally, to the chagrin of a design engineer, the degradation behavior of a material for some application is ignored, with adverse consequences.

corrosion

Deteriorative mechanisms are different for the three material types. In metals, there is actual material loss either by dissolution (**corrosion**) or by the formation of nonmetallic scale or film (*oxidation*). Ceramic materials are relatively resistant to deterioration, which usually occurs at elevated temperatures or in rather extreme environments; the process is frequently also called corrosion. For polymers, mechanisms and consequences differ from those for metals and ceramics, and the term **degradation** is most frequently used. Polymers may dissolve when exposed to a liquid solvent, or they may absorb the solvent and swell; also, electromagnetic radiation (primarily ultraviolet) and heat may cause alterations in their molecular structures.

degradation

The deterioration of each of these material types is discussed in this chapter, with special regard to mechanism, resistance to attack by various environments, and measures to prevent or reduce degradation.

Corrosion of Metals

Corrosion is defined as the destructive and unintentional attack of a metal; it is electrochemical and ordinarily begins at the surface. The problem of metallic corrosion is one of significant proportions; in economic terms, it has been estimated that approximately 5% of an industrialized nation's income is spent on corrosion prevention and the maintenance or replacement of products lost or contaminated as a result of corrosion reactions. The consequences of corrosion are all too common. Familiar examples include the rusting of automotive body panels and radiator and exhaust components.

17.2 Electrochemical Considerations • 623

Corrosion processes are occasionally used to advantage. For example, etching procedures, as discussed in Section 4.10, make use of the selective chemical reactivity of grain boundaries or various microstructural constituents.

17.2 ELECTROCHEMICAL CONSIDERATIONS

For metallic materials, the corrosion process is normally electrochemical, that is, a chemical reaction in which there is transfer of electrons from one chemical species to another. Metal atoms characteristically lose or give up electrons in what is called an **oxidation** reaction. For example, the hypothetical metal M that has a valence of n (or n valence electrons) may experience oxidation according to the reaction

oxidation

Oxidation reaction
for metal M

in which M becomes an $n+$ positively charged ion and in the process loses its n valence electrons; e^{-} is used to symbolize an electron. Examples in which metals oxidize are



anode

The site at which oxidation takes place is called the **anode**; oxidation is sometimes called an anodic reaction.

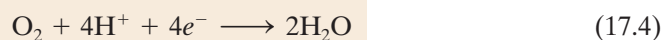
reduction

The electrons generated from each metal atom that is oxidized must be transferred to and become a part of another chemical species in what is termed a **reduction** reaction. For example, some metals undergo corrosion in acid solutions, which have a high concentration of hydrogen (H^{+}) ions; the H^{+} ions are reduced as follows:

Reduction of
hydrogen ions in
an acid solution

and hydrogen gas (H_2) is evolved.

Other reduction reactions are possible, depending on the nature of the solution to which the metal is exposed. For an acid solution having dissolved oxygen, reduction according to

Reduction reaction
in an acid solution
containing dissolved
oxygen

will probably occur. Or, for a neutral or basic aqueous solution in which oxygen is also dissolved,

Reduction reaction
in a neutral or basic
solution containing
dissolved oxygen

Any metal ions present in the solution may also be reduced; for ions that can exist in more than one valence state (multivalent ions), reduction may occur by

Reduction of a
multivalent metal
ion to a lower
valence state

in which the metal ion decreases its valence state by accepting an electron. Or a metal may be totally reduced from an ionic to a neutral metallic state according to

Reduction of a metal
ion to its electrically
neutral atom

624 • Chapter 17 / Corrosion and Degradation of Materials

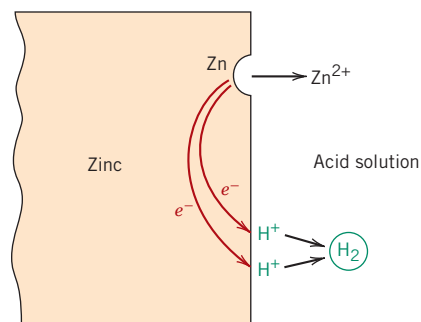


Figure 17.1 The electrochemical reactions associated with the corrosion of zinc in an acid solution. (From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

cathode

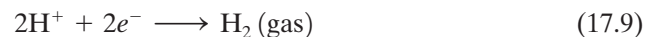
The location at which reduction occurs is called the **cathode**. Furthermore, it is possible for two or more of the reduction reactions above to occur simultaneously.

An overall electrochemical reaction must consist of at least one oxidation and one reduction reaction, and will be the sum of them; often the individual oxidation and reduction reactions are termed *half-reactions*. There can be no net electrical charge accumulation from the electrons and ions; that is, the total rate of oxidation must equal the total rate of reduction, or all electrons generated through oxidation must be consumed by reduction.

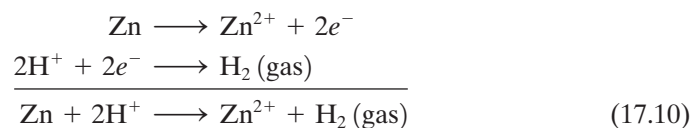
For example, consider zinc metal immersed in an acid solution containing H^+ ions. At some regions on the metal surface, zinc will experience oxidation or corrosion as illustrated in Figure 17.1, and according to the reaction



Since zinc is a metal, and therefore a good electrical conductor, these electrons may be transferred to an adjacent region at which the H^+ ions are reduced according to



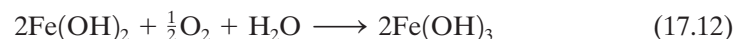
If no other oxidation or reduction reactions occur, the total electrochemical reaction is just the sum of reactions 17.8 and 17.9, or



Another example is the oxidation or rusting of iron in water, which contains dissolved oxygen. This process occurs in two steps; in the first, Fe is oxidized to Fe^{2+} [as $Fe(OH)_2$],



and, in the second stage, to Fe^{3+} [as $Fe(OH)_3$] according to



The compound $Fe(OH)_3$ is the all too familiar rust.

As a consequence of oxidation, the metal ions may either go into the corroding solution as ions (reaction 17.8), or they may form an insoluble compound with nonmetallic elements as in reaction 17.12.

17.2 Electrochemical Considerations • 625

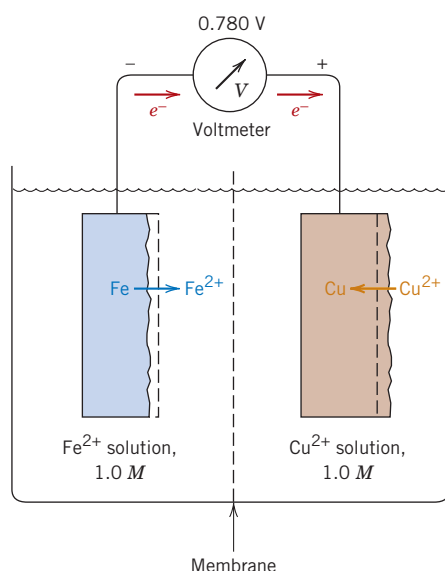


Figure 17.2 An electrochemical cell consisting of iron and copper electrodes, each of which is immersed in a 1M solution of its ion. Iron corrodes while copper electrodeposits.

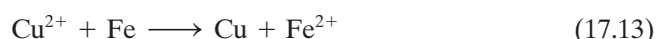
✓ Concept Check 17.1

Would you expect iron to corrode in water of high purity? Why or why not?

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

Electrode Potentials

Not all metallic materials oxidize to form ions with the same degree of ease. Consider the electrochemical cell shown in Figure 17.2. On the left-hand side is a piece of pure iron immersed in a solution containing Fe^{2+} ions of 1M concentration.¹ The other side of the cell consists of a pure copper electrode in a 1M solution of Cu^{2+} ions. The cell halves are separated by a membrane, which limits the mixing of the two solutions. If the iron and copper electrodes are connected electrically, reduction will occur for copper at the expense of the oxidation of iron, as follows:



or Cu^{2+} ions will deposit (electrodeposit) as metallic copper on the copper electrode, while iron dissolves (corrodes) on the other side of the cell and goes into solution as Fe^{2+} ions. Thus, the two half-cell reactions are represented by the relations



When a current passes through the external circuit, electrons generated from the oxidation of iron flow to the copper cell in order that Cu^{2+} be reduced. In addition, there

molarity

¹ Concentration of liquid solutions is often expressed in terms of **molarity**, M , the number of moles of solute per million cubic millimeters (10^6 mm^3 , or 1000 cm^3) of solution.

626 • Chapter 17 / Corrosion and Degradation of Materials

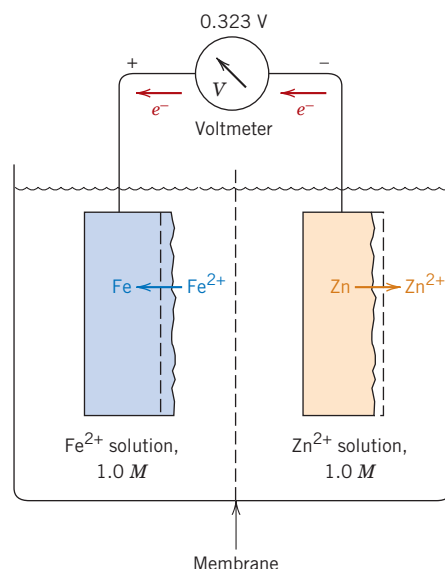


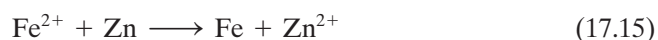
Figure 17.3 An electrochemical cell consisting of iron and zinc electrodes, each of which is immersed in a 1M solution of its ion. The iron electrode deposits while the zinc corrodes.

electrolyte

will be some net ion motion from each cell to the other across the membrane. This is called a *galvanic couple*—two metals electrically connected in a liquid **electrolyte** wherein one metal becomes an anode and corrodes, while the other acts as a cathode.

An electric potential or voltage will exist between the two cell halves, and its magnitude can be determined if a voltmeter is connected in the external circuit. A potential of 0.780 V results for a copper–iron galvanic cell when the temperature is 25°C (77°F).

Now consider another galvanic couple consisting of the same iron half-cell connected to a metal zinc electrode that is immersed in a 1M solution of Zn^{2+} ions (Figure 17.3). In this case the zinc is the anode and corrodes, whereas the Fe now becomes the cathode. The electrochemical reaction is thus



The potential associated with this cell reaction is 0.323 V.

Thus, various electrode pairs have different voltages; the magnitude of such a voltage may be thought of as representing the driving force for the electrochemical oxidation–reduction reaction. Consequently, metallic materials may be rated as to their tendency to experience oxidation when coupled to other metals in solutions of their respective ions. A half-cell similar to those described above [i.e., a pure metal electrode immersed in a 1M solution of its ions and at 25°C (77°F)] is termed a **standard half-cell**.

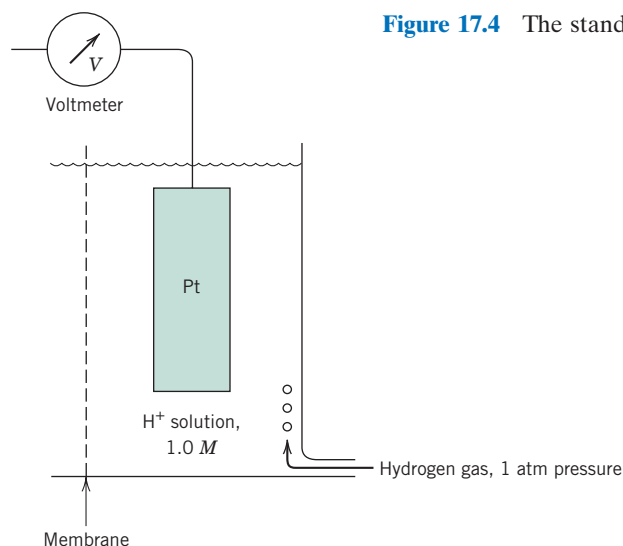
standard half-cell**The Standard emf Series**

These measured cell voltages represent only differences in electrical potential, and thus it is convenient to establish a reference point, or reference cell, to which other cell halves may be compared. This reference cell, arbitrarily chosen, is the standard hydrogen electrode (Figure 17.4). It consists of an inert platinum electrode in a 1M solution of H^+ ions, saturated with hydrogen gas that is bubbled through the solution at a pressure of 1 atm and a temperature of 25°C (77°F). The platinum itself does not take part in the electrochemical reaction; it acts only as a surface on which hydrogen atoms may be oxidized or hydrogen ions may be reduced. The **electromotive force (emf) series** (Table 17.1) is generated by coupling to the standard hydrogen electrode,

electromotive force (emf) series

17.2 Electrochemical Considerations • 627

Figure 17.4 The standard hydrogen reference half-cell.



standard half-cells for various metals and ranking them according to measured voltage. Table 17.1 represents the corrosion tendencies for the several metals; those at the top (i.e., gold and platinum) are noble, or chemically inert. Moving down the table, the metals become increasingly more active, that is, more susceptible to oxidation. Sodium and potassium have the highest reactivities.

The voltages in Table 17.1 are for the half-reactions as *reduction reactions*, with the electrons on the left-hand side of the chemical equation; for oxidation, the direction of the reaction is reversed and the sign of the voltage changed.

Table 17.1 The Standard emf Series

	Electrode Reaction	Standard Electrode Potential, V^0 (V)
	$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}$	+1.420
	$\text{O}_2 + 4\text{H}^+ + 4e^- \longrightarrow 2\text{H}_2\text{O}$	+1.229
	$\text{Pt}^{2+} + 2e^- \longrightarrow \text{Pt}$	$\sim +1.2$
	$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$	+0.800
	$\text{Fe}^{3+} + e^- \longrightarrow \text{Fe}^{2+}$	+0.771
	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \longrightarrow 4(\text{OH}^-)$	+0.401
	$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	+0.340
	$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.000
	$\text{Pb}^{2+} + 2e^- \longrightarrow \text{Pb}$	-0.126
	$\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$	-0.136
	$\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$	-0.250
	$\text{Co}^{2+} + 2e^- \longrightarrow \text{Co}$	-0.277
	$\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$	-0.403
	$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.440
	$\text{Cr}^{3+} + 3e^- \longrightarrow \text{Cr}$	-0.744
	$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	-0.763
	$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.662
	$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.363
	$\text{Na}^+ + e^- \longrightarrow \text{Na}$	-2.714
	$\text{K}^+ + e^- \longrightarrow \text{K}$	-2.924

Increasingly inert
(cathodic)

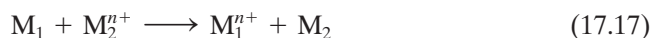
Increasingly active
(anodic)

628 • Chapter 17 / Corrosion and Degradation of Materials

Consider the generalized reactions involving the oxidation of metal M_1 and the reduction of metal M_2 as



where the V^0 's are the standard potentials as taken from the standard emf series. Since metal M_1 is oxidized, the sign of V_1^0 is opposite to that as it appears in Table 17.1. Addition of Equations 17.16a and 17.16b yields



and the overall cell potential ΔV^0 is

$$\Delta V^0 = V_2^0 - V_1^0 \quad (17.18)$$

Electrochemical cell potential for two standard half-cells that are electrically coupled

For this reaction to occur spontaneously, ΔV^0 must be positive; if it is negative, the spontaneous cell direction is just the reverse of Equation 17.17. When standard half-cells are coupled together, the metal that lies lower in Table 17.1 will experience oxidation (i.e., corrosion), whereas the higher one will be reduced.

Influence of Concentration and Temperature on Cell Potential

The emf series applies to highly idealized electrochemical cells (i.e., pure metals in 1M solutions of their ions, at 25°C). Altering temperature or solution concentration or using alloy electrodes instead of pure metals will change the cell potential, and, in some cases, the spontaneous reaction direction may be reversed.

Consider again the electrochemical reaction described by Equation 17.17. If M_1 and M_2 electrodes are pure metals, the cell potential depends on the absolute temperature T and the molar ion concentrations $[M_1^{n+}]$ and $[M_2^{n+}]$ according to the Nernst equation:

$$\Delta V = (V_2^0 - V_1^0) - \frac{RT}{n\mathcal{F}} \ln \frac{[M_1^{n+}]}{[M_2^{n+}]} \quad (17.19)$$

Nernst equation—electrochemical cell potential for two half-cells that are electrically coupled and for which solution ion concentrations are other than 1M

where R is the gas constant, n is the number of electrons participating in either of the half-cell reactions, and \mathcal{F} is the Faraday constant, 96,500 C/mol—the magnitude of charge per mole (6.023×10^{23}) of electrons. At 25°C (about room temperature),

$$\Delta V = (V_2^0 - V_1^0) - \frac{0.0592}{n} \log \frac{[M_1^{n+}]}{[M_2^{n+}]} \quad (17.20)$$

Simplified form of Equation 17.19 for $T = 25^\circ\text{C}$ (room temperature)

to give ΔV in volts. Again, for reaction spontaneity, ΔV must be positive. As expected, for 1M concentrations of both ion types (that is, $[M_1^{n+}] = [M_2^{n+}] = 1$), Equation 17.19 simplifies to Equation 17.18.



Concept Check 17.2

Modify Equation 17.19 for the case in which metals M_1 and M_2 are alloys.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

17.2 Electrochemical Considerations • 629

EXAMPLE PROBLEM 17.1

Determination of Electrochemical Cell Characteristics

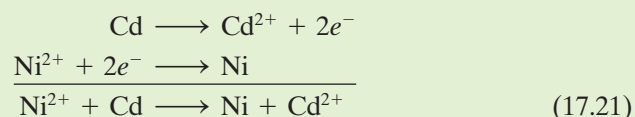
One-half of an electrochemical cell consists of a pure nickel electrode in a solution of Ni^{2+} ions; the other half is a cadmium electrode immersed in a Cd^{2+} solution.

(a) If the cell is a standard one, write the spontaneous overall reaction and calculate the voltage that is generated.

(b) Compute the cell potential at 25°C if the Cd^{2+} and Ni^{2+} concentrations are 0.5 and 10^{-3} M , respectively. Is the spontaneous reaction direction still the same as for the standard cell?

Solution

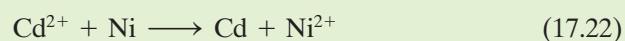
(a) The cadmium electrode will be oxidized and nickel reduced because cadmium is lower in the emf series; thus, the spontaneous reactions will be



From Table 17.1, the half-cell potentials for cadmium and nickel are, respectively, -0.403 and -0.250 V . Therefore, from Equation 17.18,

$$\Delta V = V_{\text{Ni}}^0 - V_{\text{Cd}}^0 = -0.250 \text{ V} - (-0.403 \text{ V}) = +0.153 \text{ V}$$

(b) For this portion of the problem, Equation 17.20 must be utilized, since the half-cell solution concentrations are no longer 1 M . At this point it is necessary to make a calculated guess as to which metal species is oxidized (or reduced). This choice will either be affirmed or refuted on the basis of the sign of ΔV at the conclusion of the computation. For the sake of argument, let us assume that in contrast to part (a), nickel is oxidized and cadmium reduced according to



Thus,

$$\begin{aligned} \Delta V &= (V_{\text{Cd}}^0 - V_{\text{Ni}}^0) - \frac{RT}{n\mathcal{F}} \ln \frac{[\text{Ni}^{2+}]}{[\text{Cd}^{2+}]} \\ &= -0.403 \text{ V} - (-0.250 \text{ V}) - \frac{0.0592}{2} \log \left(\frac{10^{-3}}{0.50} \right) \\ &= -0.073 \text{ V} \end{aligned}$$

Since ΔV is negative, the spontaneous reaction direction is the opposite to that of Equation 17.22, or



That is, cadmium is oxidized and nickel is reduced.

The Galvanic Series

Even though Table 17.1 was generated under highly idealized conditions and has limited utility, it nevertheless indicates the relative reactivities of the metals. A more realistic and practical ranking, however, is provided by the **galvanic series**, Table 17.2. This represents the relative reactivities of a number of metals and commercial alloys in seawater. The alloys near the top are cathodic and unreactive,

galvanic series

Table 17.2 The Galvanic Series

	Platinum
	Gold
	Graphite
	Titanium
	Silver
	[316 Stainless steel (passive)
	[304 Stainless steel (passive)
	[Inconel (80Ni–13Cr–7Fe) (passive)
	[Nickel (passive)
	[Monel (70Ni–30Cu)
	Copper–nickel alloys
	Bronzes (Cu–Sn alloys)
	Copper
	Brasses (Cu–Zn alloys)
	[Inconel (active)
	[Nickel (active)
	Tin
	Lead
	[316 Stainless steel (active)
	[304 Stainless steel (active)
	[Cast iron
	[Iron and steel
	Aluminum alloys
	Cadmium
	Commercially pure aluminum
	Zinc
	Magnesium and magnesium alloys

Source: M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright 1986 by McGraw-Hill Book Company. Reprinted with permission.

whereas those at the bottom are most anodic; no voltages are provided. Comparison of the standard emf and the galvanic series reveals a high degree of correspondence between the relative positions of the pure base metals.

Most metals and alloys are subject to oxidation or corrosion to one degree or another in a wide variety of environments; that is, they are more stable in an ionic state than as metals. In thermodynamic terms, there is a net decrease in free energy in going from metallic to oxidized states. Consequently, essentially all metals occur in nature as compounds—for example, oxides, hydroxides, carbonates, silicates, sulfides, and sulfates. Two notable exceptions are the noble metals gold and platinum. For them, oxidation in most environments is not favorable, and, therefore, they may exist in nature in the metallic state.

17.3 CORROSION RATES

The half-cell potentials listed in Table 17.1 are thermodynamic parameters that relate to systems at equilibrium. For example, for the discussions pertaining to Figures 17.2 and 17.3, it was tacitly assumed that there was no current flow through the external circuit. Real corroding systems are not at equilibrium; there will be a flow of electrons from anode to cathode (corresponding to the short-circuiting of the electrochemical cells in Figures 17.2 and 17.3), which means that the half-cell potential parameters (Table 17.1) cannot be applied.

Furthermore, these half-cell potentials represent the magnitude of a driving force, or the tendency for the occurrence of the particular half-cell reaction. However, it

17.4 Prediction of Corrosion Rates • 631

should be noted that although these potentials may be used to determine spontaneous reaction directions, they provide no information as to corrosion rates. That is, even though a ΔV potential computed for a specific corrosion situation using Equation 17.20 is a relatively large positive number, the reaction may occur at only an insignificantly slow rate. From an engineering perspective, we are interested in predicting the rates at which systems corrode; this requires the utilization of other parameters, as discussed below.

The corrosion rate, or the rate of material removal as a consequence of the chemical action, is an important corrosion parameter. This may be expressed as the **corrosion penetration rate (CPR)**, or the thickness loss of material per unit of time. The formula for this calculation is

corrosion
penetration rate—
(CPR)

Corrosion
penetration rate—
as a function of
specimen weight
loss, density, area,
and time of exposure

$$\text{CPR} = \frac{KW}{\rho At} \quad (17.23)$$

where W is the weight loss after exposure time t ; ρ and A represent the density and exposed specimen area, respectively, and K is a constant, its magnitude depending on the system of units used. The CPR is conveniently expressed in terms of either mils per year (mpy) or millimeters per year (mm/yr). In the first case, $K = 534$ to give CPR in mpy (where 1 mil = 0.001 in.), and W , ρ , A , and t are specified in units of milligrams, grams per cubic centimeter, square inches, and hours, respectively. In the second case, $K = 87.6$ for mm/yr, and units for the other parameters are the same as for mils per year, except that A is given in square centimeters. For most applications a corrosion penetration rate less than about 20 mpy (0.50 mm/yr) is acceptable.

Inasmuch as there is an electric current associated with electrochemical corrosion reactions, we can also express corrosion rate in terms of this current, or, more specifically, current density—that is, the current per unit surface area of material corroding—which is designated i . The rate r , in units of $\text{mol/m}^2\text{-s}$, is determined using the expression

Expression relating
corrosion rate and
current density

$$r = \frac{i}{n\mathcal{F}} \quad (17.24)$$

where, again, n is the number of electrons associated with the ionization of each metal atom, and \mathcal{F} is 96,500 C/mol.

17.4 PREDICTION OF CORROSION RATES

Polarization

polarization

Consider the standard Zn/H₂ electrochemical cell shown in Figure 17.5, which has been short-circuited such that oxidation of zinc and reduction of hydrogen will occur at their respective electrode surfaces. The potentials of the two electrodes will not be at the values determined from Table 17.1 because the system is now a nonequilibrium one. The displacement of each electrode potential from its equilibrium value is termed **polarization**, and the magnitude of this displacement is the *overvoltage*, normally represented by the symbol η . Overvoltage is expressed in terms of plus or minus volts (or millivolts) relative to the equilibrium potential. For example, suppose that the zinc electrode in Figure 17.5 has a potential of -0.621 V after it has been connected to the platinum electrode. The equilibrium potential is -0.763 V (Table 17.1), and, therefore,

$$\eta = -0.621 \text{ V} - (-0.763 \text{ V}) = +0.142 \text{ V}$$

There are two types of polarization—activation and concentration. We will now discuss their mechanisms since they control the rate of electrochemical reactions.

632 • Chapter 17 / Corrosion and Degradation of Materials

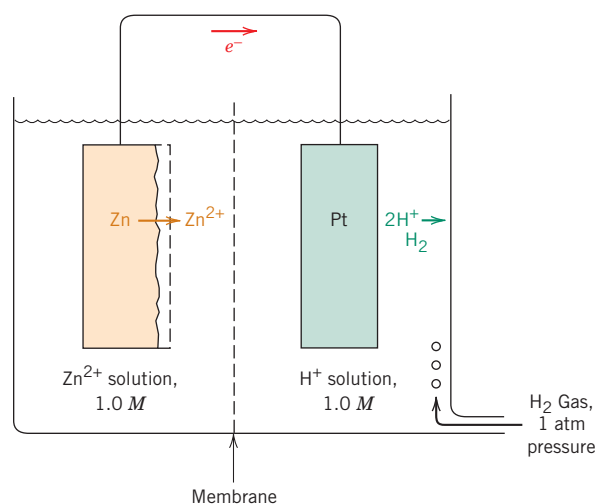


Figure 17.5 Electrochemical cell consisting of standard zinc and hydrogen electrodes that has been short-circuited.

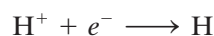
Activation Polarization

activation polarization

All electrochemical reactions consist of a sequence of steps that occur in series at the interface between the metal electrode and the electrolyte solution. **Activation polarization** refers to the condition wherein the reaction rate is controlled by the one step in the series that occurs at the slowest rate. The term “activation” is applied to this type of polarization because an activation energy barrier is associated with this slowest, rate-limiting step.

To illustrate, let us consider the reduction of hydrogen ions to form bubbles of hydrogen gas on the surface of a zinc electrode (Figure 17.6). It is conceivable that this reaction could proceed by the following step sequence:

1. Adsorption of H^+ ions from the solution onto the zinc surface
2. Electron transfer from the zinc to form a hydrogen atom,



3. Combining of two hydrogen atoms to form a molecule of hydrogen,

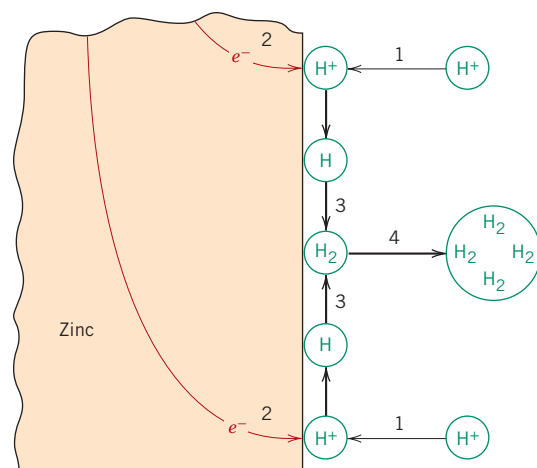
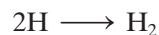


Figure 17.6 Schematic representation of possible steps in the hydrogen reduction reaction, the rate of which is controlled by activation polarization. (From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

17.4 Prediction of Corrosion Rates • 633

4. The coalescence of many hydrogen molecules to form a bubble

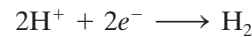
The slowest of these steps determines the rate of the overall reaction.

For activation polarization, the relationship between overvoltage η_a and current density i is

For activation polarization, relationship between overvoltage and current density

$$\eta_a = \pm \beta \log \frac{i}{i_0} \quad (17.25)$$

where β and i_0 are constants for the particular half-cell. The parameter i_0 is termed the *exchange current density*, which deserves a brief explanation. Equilibrium for some particular half-cell reaction is really a dynamic state on the atomic level. That is, oxidation and reduction processes are occurring, but both at the same rate, so that there is no net reaction. For example, for the standard hydrogen cell (Figure 17.4) reduction of hydrogen ions in solution will take place at the surface of the platinum electrode according to



with a corresponding rate r_{red} . Similarly, hydrogen gas in the solution will experience oxidation as



at rate r_{oxid} . Equilibrium exists when

$$r_{\text{red}} = r_{\text{oxid}}$$

This exchange current density is just the current density from Equation 17.24 at equilibrium, or

At equilibrium, equality of rates of oxidation and reduction, and their relationship to the exchange current density

$$r_{\text{red}} = r_{\text{oxid}} = \frac{i_0}{n\mathcal{F}} \quad (17.26)$$

Use of the term “current density” for i_0 is a little misleading inasmuch as there is no net current. Furthermore, the value for i_0 is determined experimentally and will vary from system to system.

According to Equation 17.25, when overvoltage is plotted as a function of the logarithm of current density, straight-line segments result; these are shown in Figure 17.7

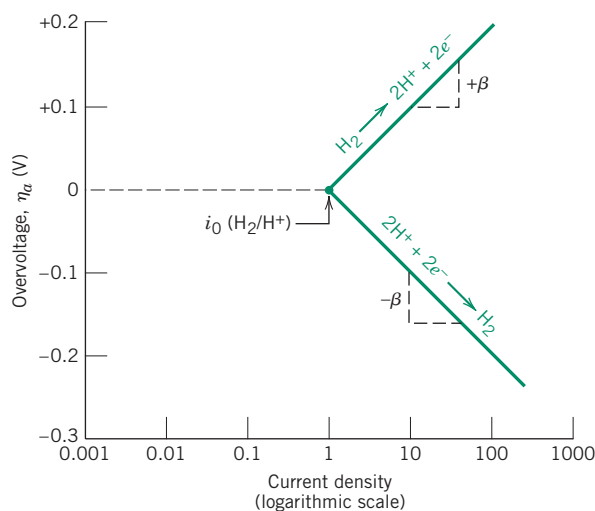


Figure 17.7 For a hydrogen electrode, plot of activation polarization overvoltage versus logarithm of current density for both oxidation and reduction reactions. (Adapted from M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

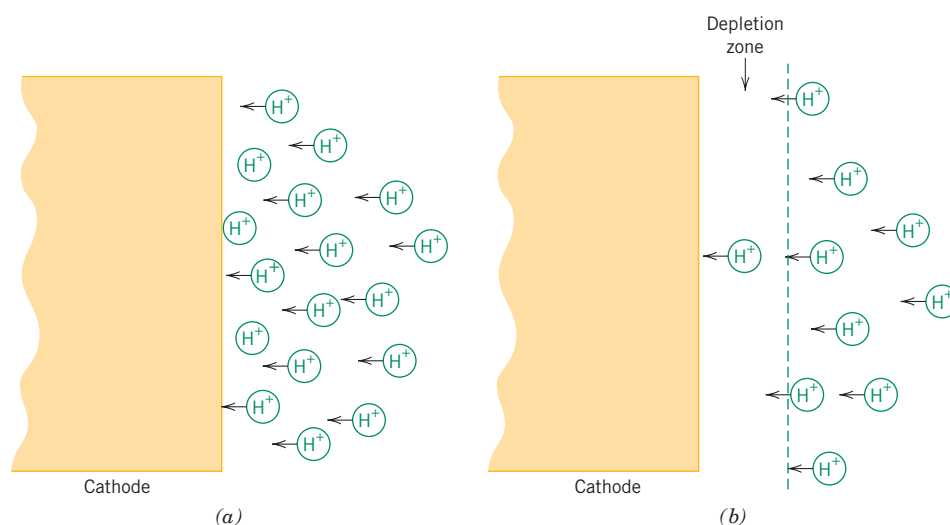


Figure 17.8 For hydrogen reduction, schematic representations of the H^+ distribution in the vicinity of the cathode for (a) low reaction rates and/or high concentrations, and (b) high reaction rates and/or low concentrations wherein a depletion zone is formed that gives rise to concentration polarization. (Adapted from M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

for the hydrogen electrode. The line segment with a slope of $+\beta$ corresponds to the oxidation half-reaction, whereas the line with a $-\beta$ slope is for reduction. Also worth noting is that both line segments originate at i_0 (H_2/H^+), the exchange current density, and at zero overvoltage, since at this point the system is at equilibrium and there is no net reaction.

Concentration Polarization

concentration polarization

Concentration polarization exists when the reaction rate is limited by diffusion in the solution. For example, consider again the hydrogen evolution reduction reaction. When the reaction rate is low and/or the concentration of H^+ is high, there is always an adequate supply of hydrogen ions available in the solution at the region near the electrode interface (Figure 17.8a). On the other hand, at high rates and/or low H^+ concentrations, a depletion zone may be formed in the vicinity of the interface, inasmuch as the H^+ ions are not replenished at a rate sufficient to keep up with the reaction (Figure 17.8b). Thus, diffusion of H^+ to the interface is rate controlling, and the system is said to be concentration polarized.

Concentration polarization data are also normally plotted as overvoltage versus the logarithm of current density; such a plot is represented schematically in Figure 17.9a.² It may be noted from this figure that overvoltage is independent

² The mathematical expression relating concentration polarization overvoltage η_c and current density i is

$$\eta_c = \frac{2.3RT}{n\mathcal{F}} \log \left(1 - \frac{i}{i_L} \right) \quad (17.27)$$

where R and T are the gas constant and absolute temperature, respectively, n and \mathcal{F} have the same meanings as above, and i_L is the limiting diffusion current density.

For concentration polarization, relationship between overvoltage and current density

17.4 Prediction of Corrosion Rates • 635

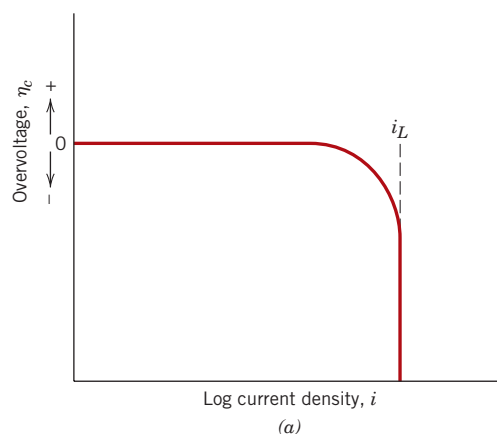
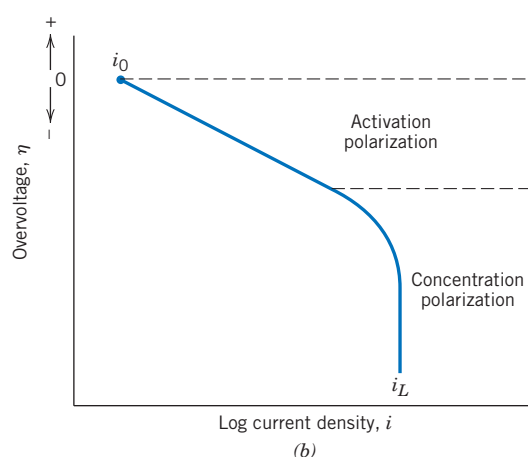


Figure 17.9 For reduction reactions, schematic plots of overvoltage versus logarithm of current density for (a) concentration polarization, and (b) combined activation–concentration polarization.



of current density until i approaches i_L ; at this point, η_c decreases abruptly in magnitude.

Both concentration and activation polarization are possible for reduction reactions. Under these circumstances, the total overvoltage is just the sum of both overvoltage contributions. Figure 17.9b shows such a schematic η -versus- $\log i$ plot.

✓ Concept Check 17.3

Briefly explain why concentration polarization is not normally rate controlling for oxidation reactions.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

Corrosion Rates from Polarization Data

Let us now apply the concepts developed above to the determination of corrosion rates. Two types of systems will be discussed. In the first case, both oxidation and reduction reactions are rate limited by activation polarization. In the second case, both concentration and activation polarization control the reduction reaction, whereas only activation polarization is important for oxidation. Case one will be illustrated by considering the corrosion of zinc immersed in an acid solution (see Figure 17.1).

636 • Chapter 17 / Corrosion and Degradation of Materials

The reduction of H^+ ions to form H_2 gas bubbles occurs at the surface of the zinc according to



and the zinc oxidizes as



No net charge accumulation may result from these two reactions; that is, all electrons generated by reaction 17.8 must be consumed by reaction 17.3, which is to say that rates of oxidation and reduction must be equal.

Activation polarization for both reactions is expressed graphically in Figure 17.10 as cell potential referenced to the standard hydrogen electrode (not overvoltage) versus the logarithm of current density. The potentials of the uncoupled hydrogen and zinc half-cells, $V(H^+/H_2)$ and $V(Zn/Zn^{2+})$, respectively, are indicated, along with their respective exchange current densities, $i_0(H^+/H_2)$ and $i_0(Zn/Zn^{2+})$. Straight line segments are shown for hydrogen reduction and zinc oxidation. Upon immersion, both hydrogen and zinc experience activation polarization along their respective lines. Also, oxidation and reduction rates must be equal as explained above, which is only possible at the intersection of the two line segments; this intersection occurs at the corrosion potential, designated V_C , and the corrosion current density i_C . The corrosion rate of zinc (which also corresponds to the rate of hydrogen evolution) may thus be computed by insertion of this i_C value into Equation 17.24.

The second corrosion case (combined activation and concentration polarization for hydrogen reduction and activation polarization for oxidation of metal M) is treated in a like manner. Figure 17.11 shows both polarization curves; as above, corrosion potential and corrosion current density correspond to the point at which the oxidation and reduction lines intersect.

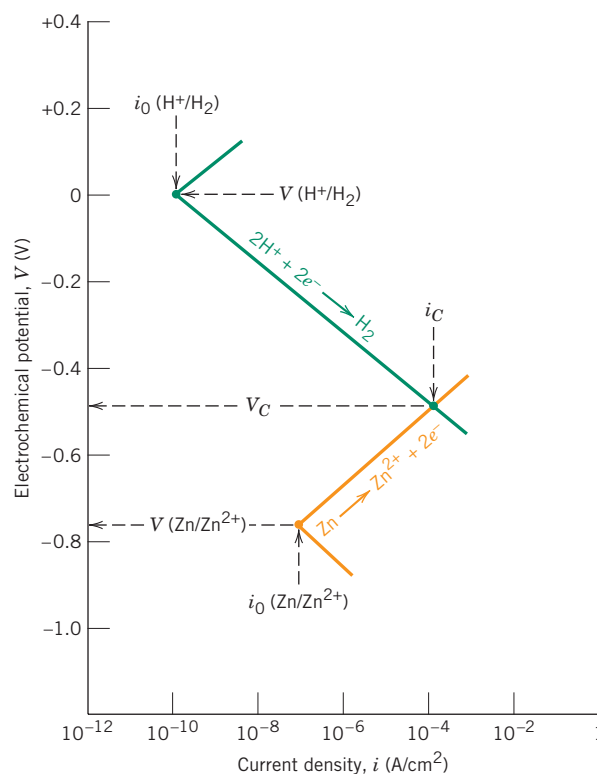


Figure 17.10 Electrode kinetic behavior of zinc in an acid solution; both oxidation and reduction reactions are rate limited by activation polarization. (Adapted from M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

17.4 Prediction of Corrosion Rates • 637

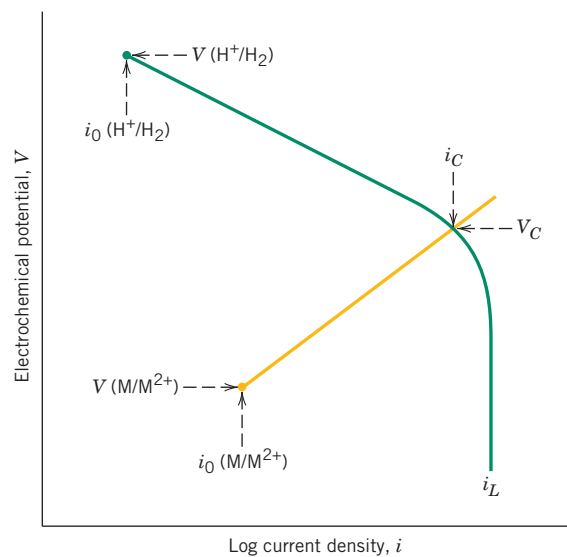
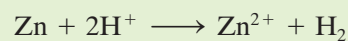


Figure 17.11 Schematic electrode kinetic behavior for metal M; the reduction reaction is under combined activation–concentration polarization control.

EXAMPLE PROBLEM 17.2**Rate of Oxidation Computation**

Zinc experiences corrosion in an acid solution according to the reaction



The rates of both oxidation and reduction half-reactions are controlled by activation polarization.

(a) Compute the rate of oxidation of Zn (in mol/cm²-s) given the following activation polarization data:

For Zn	For Hydrogen
$V_{(\text{Zn}/\text{Zn}^{2+})} = -0.763 \text{ V}$	$V_{(\text{H}^+/\text{H}_2)} = 0 \text{ V}$
$i_0 = 10^{-7} \text{ A/cm}^2$	$i_0 = 10^{-10} \text{ A/cm}^2$
$\beta = +0.09$	$\beta = -0.08$

(b) Compute the value of the corrosion potential.

Solution

(a) To compute the rate of oxidation for Zn, it is first necessary to establish relationships in the form of Equation 17.25 for the potential of both oxidation and reduction reactions. Next, these two expressions are set equal to one another, and then we solve for the value of i that is the corrosion current density, i_C . Finally, the corrosion rate may be calculated using Equation 17.24. The two potential expressions are as follows: For hydrogen reduction,

$$V_{\text{H}} = V_{(\text{H}^+/\text{H}_2)} + \beta_{\text{H}} \log \left(\frac{i}{i_{0_{\text{H}}}} \right)$$

638 • Chapter 17 / Corrosion and Degradation of Materials

and for Zn oxidation,

$$V_{\text{Zn}} = V_{(\text{Zn}/\text{Zn}^{2+})} + \beta_{\text{Zn}} \log \left(\frac{i}{i_{0\text{Zn}}} \right)$$

Now, setting $V_{\text{H}} = V_{\text{Zn}}$ leads to

$$V_{(\text{H}^+/\text{H}_2)} + \beta_{\text{H}} \log \left(\frac{i}{i_{0\text{H}}} \right) = V_{(\text{Zn}/\text{Zn}^{2+})} + \beta_{\text{Zn}} \log \left(\frac{i}{i_{0\text{Zn}}} \right)$$

And solving for $\log i$ (i.e., $\log i_{\text{C}}$) leads to

$$\begin{aligned} \log i_{\text{C}} &= \left(\frac{1}{\beta_{\text{Zn}} - \beta_{\text{H}}} \right) [V_{(\text{H}^+/\text{H}_2)} - V_{(\text{Zn}/\text{Zn}^{2+})} - \beta_{\text{H}} \log i_{0\text{H}} + \beta_{\text{Zn}} \log i_{0\text{Zn}}] \\ &= \left[\frac{1}{0.09 - (-0.08)} \right] [0 - (-0.763) - (-0.08)(\log 10^{-10}) \\ &\quad + (0.09)(\log 10^{-7})] \\ &= -3.924 \end{aligned}$$

or

$$i_{\text{C}} = 10^{-3.924} = 1.19 \times 10^{-4} \text{ A/cm}^2$$

And, from Equation 17.24,

$$\begin{aligned} r &= \frac{i_{\text{C}}}{n\mathcal{F}} \\ &= \frac{1.19 \times 10^{-4} \text{ C/s}\cdot\text{cm}^2}{(2)(96,500 \text{ C/mol})} = 6.17 \times 10^{-10} \text{ mol/cm}^2\cdot\text{s} \end{aligned}$$

(b) Now it becomes necessary to compute the value of the corrosion potential V_{C} . This is possible by using either of the above equations for V_{H} or V_{Zn} and substituting for i the value determined above for i_{C} . Thus, using the V_{H} expression yields

$$\begin{aligned} V_{\text{C}} &= V_{(\text{H}^+/\text{H}_2)} + \beta_{\text{H}} \log \left(\frac{i_{\text{C}}}{i_{0\text{H}}} \right) \\ &= 0 + (-0.08 \text{ V}) \log \left(\frac{1.19 \times 10^{-4} \text{ A/cm}^2}{10^{-10} \text{ A/cm}^2} \right) = -0.486 \text{ V} \end{aligned}$$

This is the same problem that is represented and solved graphically in the voltage-versus-logarithm current density plot of Figure 17.10. It is worth noting that the i_{C} and V_{C} we have obtained by this analytical treatment are in agreement with those values occurring at the intersection of the two line segments on the plot.

17.5 PASSIVITY

passivity

Some normally active metals and alloys, under particular environmental conditions, lose their chemical reactivity and become extremely inert. This phenomenon, termed **passivity**, is displayed by chromium, iron, nickel, titanium, and many of their alloys. It is felt that this passive behavior results from the formation of a highly adherent and very thin oxide film on the metal surface, which serves as a protective barrier

17.5 Passivity • 639

to further corrosion. Stainless steels are highly resistant to corrosion in a rather wide variety of atmospheres as a result of passivation. They contain at least 11% chromium that, as a solid-solution alloying element in iron, minimizes the formation of rust; instead, a protective surface film forms in oxidizing atmospheres. (Stainless steels are susceptible to corrosion in some environments, and therefore are not always “stainless.”) Aluminum is highly corrosion resistant in many environments because it also passivates. If damaged, the protective film normally reforms very rapidly. However, a change in the character of the environment (e.g., alteration in the concentration of the active corrosive species) may cause a passivated material to revert to an active state. Subsequent damage to a preexisting passive film could result in a substantial increase in corrosion rate, by as much as 100,000 times.

This passivation phenomenon may be explained in terms of polarization potential–log current density curves discussed in the preceding section. The polarization curve for a metal that passivates will have the general shape shown in Figure 17.12. At relatively low potential values, within the “active” region the behavior is linear as it is for normal metals. With increasing potential, the current density suddenly decreases to a very low value that remains independent of potential; this is termed the “passive” region. Finally, at even higher potential values, the current density again increases with potential in the “transpassive” region.

Figure 17.13 illustrates how a metal can experience both active and passive behavior depending on the corrosion environment. Included in this figure is the S-shaped oxidation polarization curve for an active–passive metal M and, in addition, reduction polarization curves for two different solutions, which are labeled 1 and 2. Curve 1 intersects the oxidation polarization curve in the active region at point A, yielding a corrosion current density $i_c(A)$. The intersection of curve 2 at point B is in the passive region and at current density $i_c(B)$. The corrosion rate of metal M in solution 1 is greater than in solution 2 since $i_c(A)$ is greater than $i_c(B)$ and rate is proportional to current density according to Equation 17.24. This difference in corrosion rate between the two solutions may be significant—several orders of magnitude—when one considers that the current density scale in Figure 17.13 is scaled logarithmically.

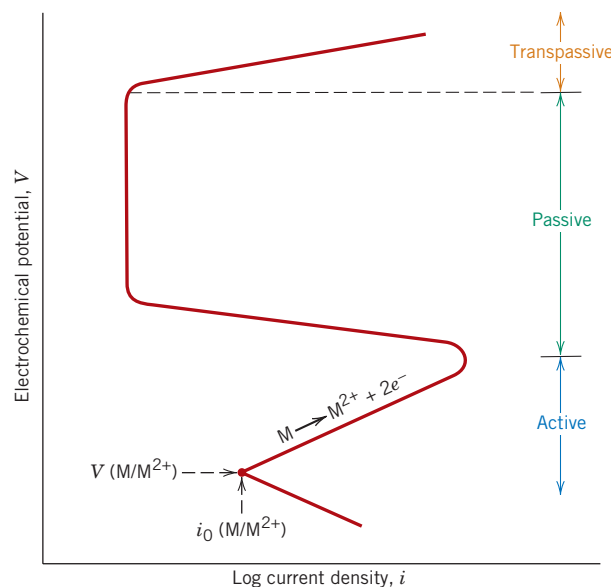


Figure 17.12 Schematic polarization curve for a metal that displays an active-passive transition.

640 • Chapter 17 / Corrosion and Degradation of Materials

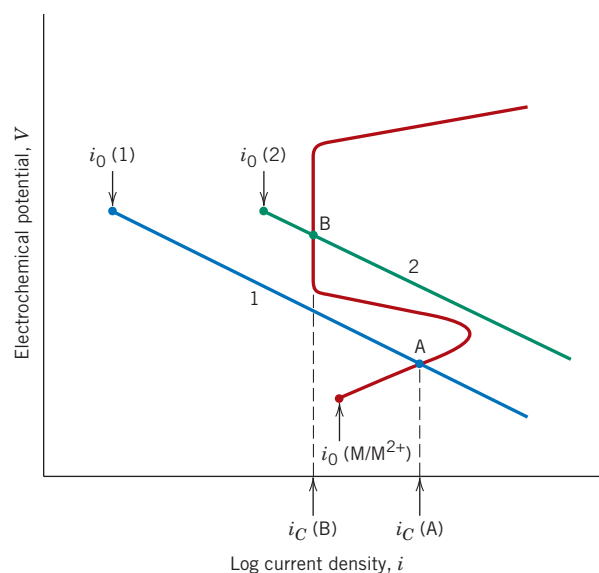


Figure 17.13 Demonstration of how an active-passive metal can exhibit both active and passive corrosion behaviors.

17.6 ENVIRONMENTAL EFFECTS

The variables in the corrosion environment, which include fluid velocity, temperature, and composition, can have a decided influence on the corrosion properties of the materials that are in contact with it. In most instances, increasing fluid velocity enhances the rate of corrosion due to erosive effects, as discussed later in the chapter. The rates of most chemical reactions rise with increasing temperature; this also holds for the great majority of corrosion situations. Increasing the concentration of the corrosive species (e.g., H^+ ions in acids) in many situations produces a more rapid rate of corrosion. However, for materials capable of passivation, raising the corrosive content may result in an active-to-passive transition, with a considerable reduction in corrosion.

Cold working or plastically deforming ductile metals is used to increase their strength; however, a cold-worked metal is more susceptible to corrosion than the same material in an annealed state. For example, deformation processes are used to shape the head and point of a nail; consequently, these positions are anodic with respect to the shank region. Thus, differential cold working on a structure should be a consideration when a corrosive environment may be encountered during service.

17.7 FORMS OF CORROSION

It is convenient to classify corrosion according to the manner in which it is manifest. Metallic corrosion is sometimes classified into eight forms: uniform, galvanic, crevice, pitting, intergranular, selective leaching, erosion-corrosion, and stress corrosion. The causes and means of prevention of each of these forms are discussed briefly. In addition, we have elected to discuss the topic of hydrogen embrittlement in this section. Hydrogen embrittlement is, in a strict sense, a type of failure rather than a form of corrosion; however, it is often produced by hydrogen that is generated from corrosion reactions.

Uniform Attack

Uniform attack is a form of electrochemical corrosion that occurs with equivalent intensity over the entire exposed surface and often leaves behind a scale or deposit. In a microscopic sense, the oxidation and reduction reactions occur randomly over the

17.7 Forms of Corrosion • 641

surface. Some familiar examples include general rusting of steel and iron and the tarnishing of silverware. This is probably the most common form of corrosion. It is also the least objectionable because it can be predicted and designed for with relative ease.

Galvanic Corrosion**galvanic corrosion**

Galvanic corrosion occurs when two metals or alloys having different compositions are electrically coupled while exposed to an electrolyte. This is the type of corrosion or dissolution that was described in Section 17.2. The less noble or more reactive metal in the particular environment will experience corrosion; the more inert metal, the cathode, will be protected from corrosion. For example, steel screws corrode when in contact with brass in a marine environment; or if copper and steel tubing are joined in a domestic water heater, the steel will corrode in the vicinity of the junction. Depending on the nature of the solution, one or more of the reduction reactions, Equations 17.3 through 17.7, will occur at the surface of the cathode material. Figure 17.14 shows galvanic corrosion.

Again, the galvanic series (Table 17.2) indicates the relative reactivities, in seawater, of a number of metals and alloys. When two alloys are coupled in seawater, the one lower in the series will experience corrosion. Some of the alloys in the table are grouped in brackets. Generally the base metal is the same for these bracketed alloys, and there is little danger of corrosion if alloys within a single bracket are coupled. It is also worth noting from this series that some alloys are listed twice (e.g., nickel and the stainless steels), in both active and passive states.

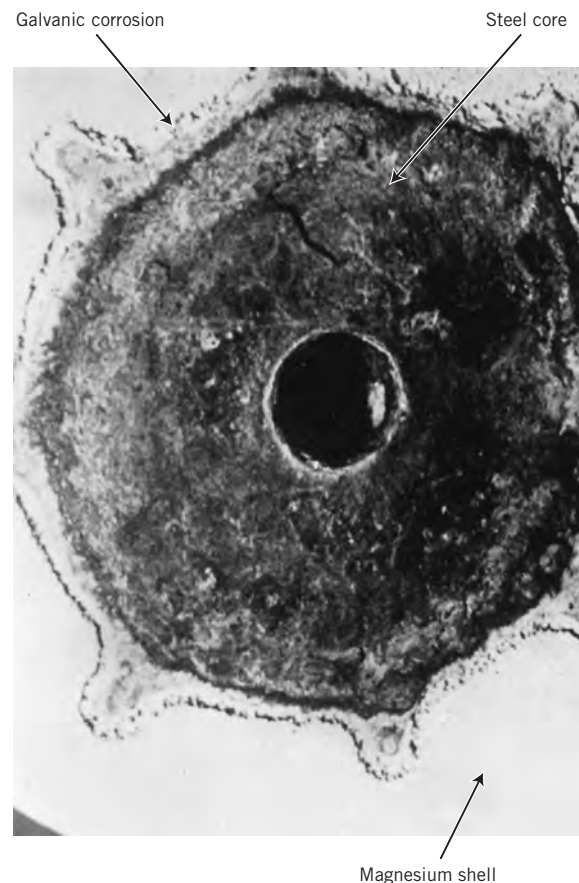


Figure 17.14 Photograph showing galvanic corrosion around the inlet of a single-cycle bilge pump that is found on fishing vessels. Corrosion occurred between a magnesium shell that was cast around a steel core. (Photograph courtesy of LaQue Center for Corrosion Technology, Inc.)

642 • Chapter 17 / Corrosion and Degradation of Materials

The rate of galvanic attack depends on the relative anode-to-cathode surface areas that are exposed to the electrolyte, and the rate is related directly to the cathode–anode area ratio; that is, for a given cathode area, a smaller anode will corrode more rapidly than a larger one. The reason for this is that corrosion rate depends on current density (Equation 17.24), the current per unit area of corroding surface, and not simply the current. Thus, a high current density results for the anode when its area is small relative to that of the cathode.

A number of measures may be taken to significantly reduce the effects of galvanic corrosion. These include the following:

1. If coupling of dissimilar metals is necessary, choose two that are close together in the galvanic series.
2. Avoid an unfavorable anode-to-cathode surface area ratio; use an anode area as large as possible.
3. Electrically insulate dissimilar metals from each other.
4. Electrically connect a third, anodic metal to the other two; this is a form of **cathodic protection**, discussed presently.

cathodic protection

**Concept Check 17.4**

- (a) From the galvanic series (Table 17.2), cite three metals or alloys that may be used to galvanically protect nickel in the active state.
- (b) Sometimes galvanic corrosion is prevented by making an electrical contact between both metals in the couple and a third metal that is anodic to these other two. Using the galvanic series, name one metal that could be used to protect a copper-aluminum galvanic couple.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

**Concept Check 17.5**

Cite two examples of the beneficial use of galvanic corrosion. *Hint:* One example is cited later in this chapter.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

Crevice Corrosion

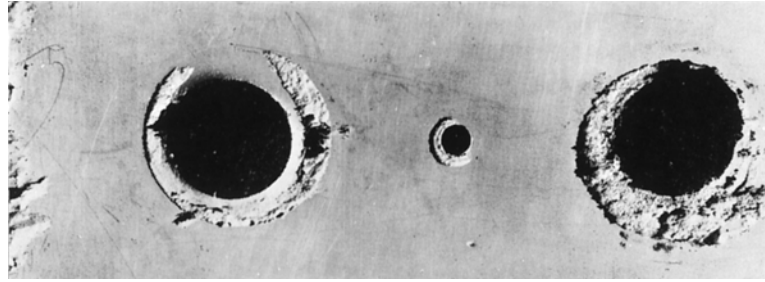
Electrochemical corrosion may also occur as a consequence of concentration differences of ions or dissolved gases in the electrolyte solution, and between two regions of the same metal piece. For such a *concentration cell*, corrosion occurs in the locale that has the lower concentration. A good example of this type of corrosion occurs in crevices and recesses or under deposits of dirt or corrosion products where the solution becomes stagnant and there is localized depletion of dissolved oxygen. Corrosion preferentially occurring at these positions is called **crevice corrosion** (Figure 17.15). The crevice must be wide enough for the solution to penetrate, yet narrow enough for stagnancy; usually the width is several thousandths of an inch.

crevice corrosion

The proposed mechanism for crevice corrosion is illustrated in Figure 17.16. After oxygen has been depleted within the crevice, oxidation of the metal occurs at

17.7 Forms of Corrosion • 643

Figure 17.15 On this plate, which was immersed in seawater, crevice corrosion has occurred at the regions that were covered by washers. (Photograph courtesy of LaQue Center for Corrosion Technology, Inc.)



this position according to Equation 17.1. Electrons from this electrochemical reaction are conducted through the metal to adjacent external regions, where they are consumed by reduction—most probably reaction 17.5. In many aqueous environments, the solution within the crevice has been found to develop high concentrations of H^+ and Cl^- ions, which are especially corrosive. Many alloys that passivate are susceptible to crevice corrosion because protective films are often destroyed by the H^+ and Cl^- ions.

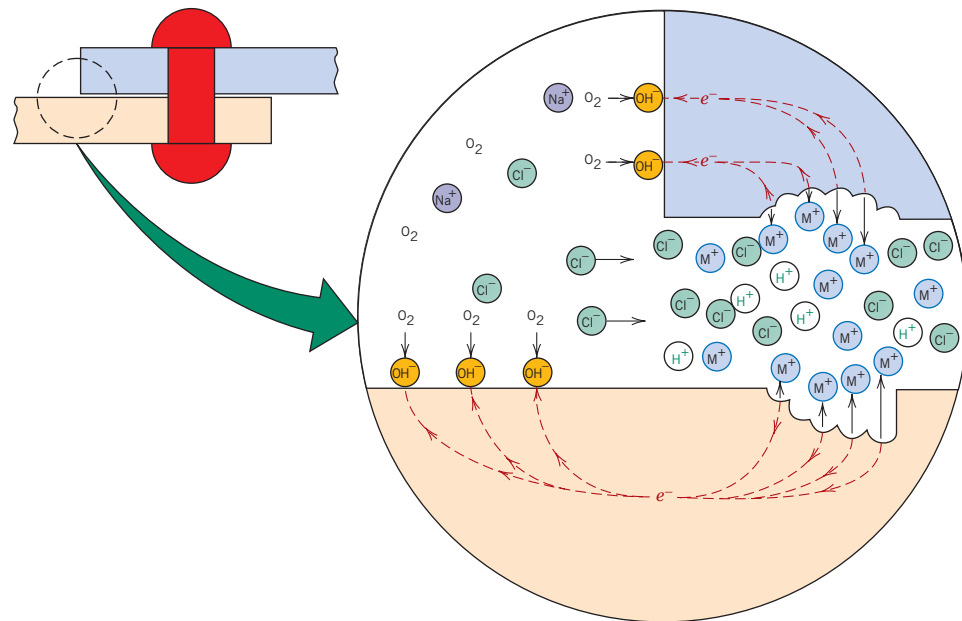
Crevice corrosion may be prevented by using welded instead of riveted or bolted joints, using nonabsorbing gaskets when possible, removing accumulated deposits frequently, and designing containment vessels to avoid stagnant areas and ensure complete drainage.

Pitting

pitting

Pitting is another form of very localized corrosion attack in which small pits or holes form. They ordinarily penetrate from the top of a horizontal surface downward in a nearly vertical direction. It is an extremely insidious type of corrosion, often going

Figure 17.16 Schematic illustration of the mechanism of crevice corrosion between two riveted sheets. (From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)



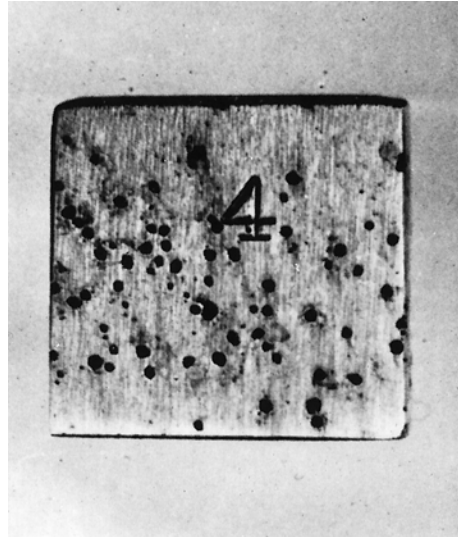


Figure 17.17 The pitting of a 304 stainless steel plate by an acid-chloride solution. (Photograph courtesy of Mars G. Fontana. From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

undetected and with very little material loss until failure occurs. An example of pitting corrosion is shown in Figure 17.17.

The mechanism for pitting is probably the same as for crevice corrosion in that oxidation occurs within the pit itself, with complementary reduction at the surface. It is supposed that gravity causes the pits to grow downward, the solution at the pit tip becoming more concentrated and dense as pit growth progresses. A pit may be initiated by a localized surface defect such as a scratch or a slight variation in composition. In fact, it has been observed that specimens having polished surfaces display a greater resistance to pitting corrosion. Stainless steels are somewhat susceptible to this form of corrosion; however, alloying with about 2% molybdenum enhances their resistance significantly.



Concept Check 17.6

Is Equation 17.23 equally valid for uniform corrosion and pitting? Why or why not? [The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

intergranular corrosion

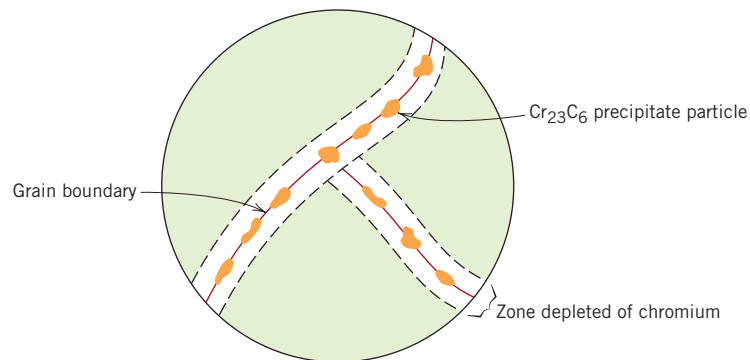
Intergranular Corrosion

As the name suggests, **intergranular corrosion** occurs preferentially along grain boundaries for some alloys and in specific environments. The net result is that a macroscopic specimen disintegrates along its grain boundaries. This type of corrosion is especially prevalent in some stainless steels. When heated to temperatures between 500 and 800°C (950 and 1450°F) for sufficiently long time periods, these alloys become sensitized to intergranular attack. It is believed that this heat treatment permits the formation of small precipitate particles of chromium carbide (Cr_{23}C_6) by reaction between the chromium and carbon in the stainless steel. These particles form along the grain boundaries, as illustrated in Figure 17.18. Both the chromium and the carbon must diffuse to the grain boundaries to form the precipitates, which leaves a chromium-depleted zone adjacent to the grain boundary. Consequently, this grain boundary region is now highly susceptible to corrosion.

17.7 Forms of Corrosion • 645

Figure 17.18

Schematic illustration of chromium carbide particles that have precipitated along grain boundaries in stainless steel, and the attendant zones of chromium depletion.

**weld decay**

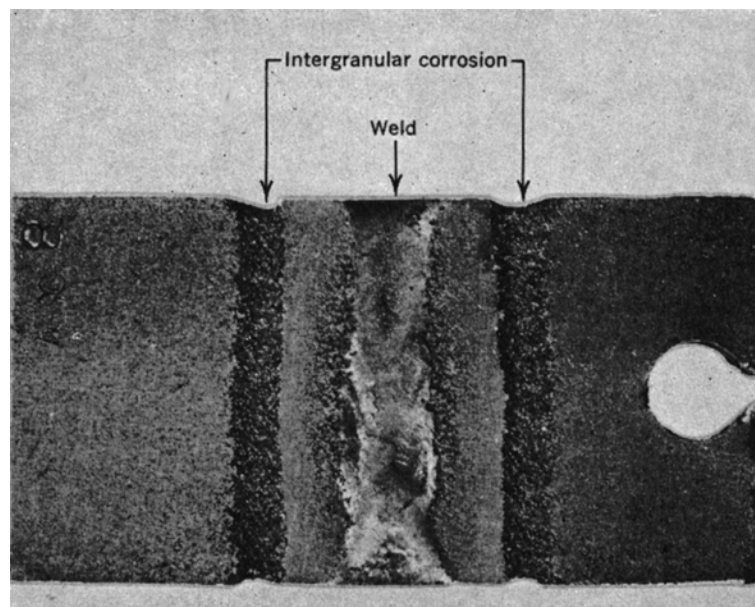
Intergranular corrosion is an especially severe problem in the welding of stainless steels, when it is often termed **weld decay**. Figure 17.19 shows this type of intergranular corrosion.

Stainless steels may be protected from intergranular corrosion by the following measures: (1) subjecting the sensitized material to a high-temperature heat treatment in which all the chromium carbide particles are redissolved, (2) lowering the carbon content below 0.03 wt% C so that carbide formation is minimal, and (3) alloying the stainless steel with another metal such as niobium or titanium, which has a greater tendency to form carbides than does chromium so that the Cr remains in solid solution.

selective leaching**Selective Leaching**

Selective leaching is found in solid solution alloys and occurs when one element or constituent is preferentially removed as a consequence of corrosion processes. The most common example is the dezincification of brass, in which zinc is selectively leached from a copper–zinc brass alloy. The mechanical properties of the alloy are

Figure 17.19 Weld decay in a stainless steel. The regions along which the grooves have formed were sensitized as the weld cooled. (From H. H. Uhlig and R. W. Revie, *Corrosion and Corrosion Control*, 3rd edition, Fig. 2, p. 307. Copyright © 1985 by John Wiley & Sons, Inc. Reprinted by permission of John Wiley & Sons, Inc.)



646 • Chapter 17 / Corrosion and Degradation of Materials

significantly impaired, since only a porous mass of copper remains in the region that has been dezincified. In addition, the material changes from yellow to a red or copper color. Selective leaching may also occur with other alloy systems in which aluminum, iron, cobalt, chromium, and other elements are vulnerable to preferential removal.

Erosion–Corrosion**erosion–corrosion**

Erosion–corrosion arises from the combined action of chemical attack and mechanical abrasion or wear as a consequence of fluid motion. Virtually all metal alloys, to one degree or another, are susceptible to erosion–corrosion. It is especially harmful to alloys that passivate by forming a protective surface film; the abrasive action may erode away the film, leaving exposed a bare metal surface. If the coating is not capable of continuously and rapidly reforming as a protective barrier, corrosion may be severe. Relatively soft metals such as copper and lead are also sensitive to this form of attack. Usually it can be identified by surface grooves and waves having contours that are characteristic of the flow of the fluid.

The nature of the fluid can have a dramatic influence on the corrosion behavior. Increasing fluid velocity normally enhances the rate of corrosion. Also, a solution is more erosive when bubbles and suspended particulate solids are present.

Erosion–corrosion is commonly found in piping, especially at bends, elbows, and abrupt changes in pipe diameter—positions where the fluid changes direction or flow suddenly becomes turbulent. Propellers, turbine blades, valves, and pumps are also susceptible to this form of corrosion. Figure 17.20 illustrates the impingement failure of an elbow fitting.

One of the best ways to reduce erosion–corrosion is to change the design to eliminate fluid turbulence and impingement effects. Other materials may also be utilized that inherently resist erosion. Furthermore, removal of particulates and bubbles from the solution will lessen its ability to erode.

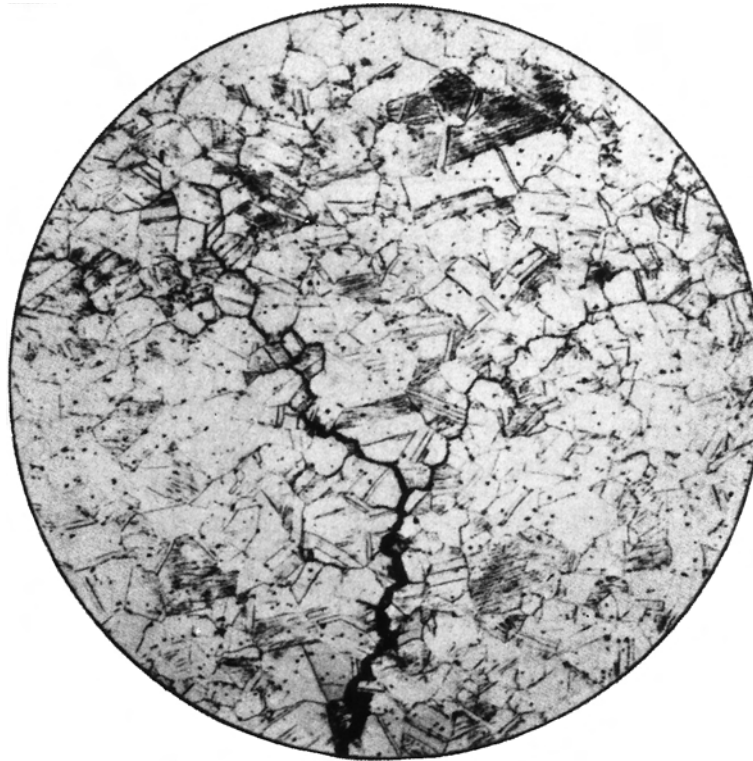
Stress Corrosion**stress corrosion**

Stress corrosion, sometimes termed stress corrosion cracking, results from the combined action of an applied tensile stress and a corrosive environment; both influences are necessary. In fact, some materials that are virtually inert in a particular corrosive medium become susceptible to this form of corrosion when a stress is



Figure 17.20 Impingement failure of an elbow that was part of a steam condensate line. (Photograph courtesy of Mars G. Fontana. From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

Figure 17.21
Photomicrograph
showing
intergranular stress
corrosion cracking in
brass. (From H. H.
Uhlig and R. W.
Revie, *Corrosion
and Corrosion
Control*, 3rd edition,
Fig. 5, p. 335.
Copyright 1985 by
John Wiley & Sons,
Inc. Reprinted by
permission of John
Wiley & Sons, Inc.)



applied. Small cracks form and then propagate in a direction perpendicular to the stress (see the chapter-opening photograph for this chapter), with the result that failure may eventually occur. Failure behavior is characteristic of that for a brittle material, even though the metal alloy is intrinsically ductile. Furthermore, cracks may form at relatively low stress levels, significantly below the tensile strength. Most alloys are susceptible to stress corrosion in specific environments, especially at moderate stress levels. For example, most stainless steels stress corrode in solutions containing chloride ions, whereas brasses are especially vulnerable when exposed to ammonia. Figure 17.21 is a photomicrograph in which an example of intergranular stress corrosion cracking in brass is shown.

The stress that produces stress corrosion cracking need not be externally applied; it may be a residual one that results from rapid temperature changes and uneven contraction, or for two-phase alloys in which each phase has a different coefficient of expansion. Also, gaseous and solid corrosion products that are entrapped internally can give rise to internal stresses.

Probably the best measure to take in reducing or totally eliminating stress corrosion is to lower the magnitude of the stress. This may be accomplished by reducing the external load or increasing the cross-sectional area perpendicular to the applied stress. Furthermore, an appropriate heat treatment may be used to anneal out any residual thermal stresses.

Hydrogen Embrittlement

Various metal alloys, specifically some steels, experience a significant reduction in ductility and tensile strength when atomic hydrogen (H) penetrates into the material. This phenomenon is aptly referred to as **hydrogen embrittlement**; the terms

**hydrogen
embrittlement**

648 • Chapter 17 / Corrosion and Degradation of Materials

hydrogen-induced cracking and *hydrogen stress cracking* are sometimes also used. Strictly speaking, hydrogen embrittlement is a type of failure; in response to applied or residual tensile stresses, brittle fracture occurs catastrophically as cracks grow and rapidly propagate. Hydrogen in its atomic form (H as opposed to the molecular form, H_2) diffuses interstitially through the crystal lattice, and concentrations as low as several parts per million can lead to cracking. Furthermore, hydrogen-induced cracks are most often transgranular, although intergranular fracture is observed for some alloy systems. A number of mechanisms have been proposed to explain hydrogen embrittlement; most of them are based on the interference of dislocation motion by the dissolved hydrogen.

Hydrogen embrittlement is similar to stress corrosion (as discussed in the preceding section) in that a normally ductile metal experiences brittle fracture when exposed to both a tensile stress and a corrosive atmosphere. However, these two phenomena may be distinguished on the basis of their interactions with applied electric currents. Whereas cathodic protection (Section 17.9) reduces or causes a cessation of stress corrosion, it may, on the other hand, lead to the initiation or enhancement of hydrogen embrittlement.

For hydrogen embrittlement to occur, some source of hydrogen must be present, and, in addition, the possibility for the formation of its atomic species. Situations wherein these conditions are met include the following: pickling³ of steels in sulfuric acid; electroplating; and the presence of hydrogen-bearing atmospheres (including water vapor) at elevated temperatures such as during welding and heat treatments. Also, the presence of what are termed “poisons” such as sulfur (i.e., H_2S) and arsenic compounds accelerates hydrogen embrittlement; these substances retard the formation of molecular hydrogen and thereby increase the residence time of atomic hydrogen on the metal surface. Hydrogen sulfide, probably the most aggressive poison, is found in petroleum fluids, natural gas, oil-well brines, and geothermal fluids.

High-strength steels are susceptible to hydrogen embrittlement, and increasing strength tends to enhance the material's susceptibility. Martensitic steels are especially vulnerable to this type of failure; bainitic, ferritic, and spheroiditic steels are more resilient. Furthermore, FCC alloys (austenitic stainless steels, and alloys of copper, aluminum, and nickel) are relatively resistant to hydrogen embrittlement, mainly because of their inherently high ductilities. However, strain hardening these alloys will enhance their susceptibility to embrittlement.

Some of the techniques commonly used to reduce the likelihood of hydrogen embrittlement include reducing the tensile strength of the alloy via a heat treatment, removal of the source of hydrogen, “baking” the alloy at an elevated temperature to drive out any dissolved hydrogen, and substitution of a more embrittlement-resistant alloy.

17.8 CORROSION ENVIRONMENTS

Corrosive environments include the atmosphere, aqueous solutions, soils, acids, bases, inorganic solvents, molten salts, liquid metals, and, last but not least, the human body. On a tonnage basis, atmospheric corrosion accounts for the greatest losses. Moisture containing dissolved oxygen is the primary corrosive agent, but other substances, including sulfur compounds and sodium chloride, may also contribute. This is especially true of marine atmospheres, which are highly corrosive because of the presence of

³ *Pickling* is a procedure used to remove surface oxide scale from steel pieces by dipping them in a vat of hot, dilute sulfuric or hydrochloric acid.

17.9 Corrosion Prevention • 649

sodium chloride. Dilute sulfuric acid solutions (acid rain) in industrial environments can also cause corrosion problems. Metals commonly used for atmospheric applications include alloys of aluminum and copper, and galvanized steel.

Water environments can also have a variety of compositions and corrosion characteristics. Freshwater normally contains dissolved oxygen, as well as other minerals several of which account for hardness. Seawater contains approximately 3.5% salt (predominantly sodium chloride), as well as some minerals and organic matter. Seawater is generally more corrosive than freshwater, frequently producing pitting and crevice corrosion. Cast iron, steel, aluminum, copper, brass, and some stainless steels are generally suitable for freshwater use, whereas titanium, brass, some bronzes, copper–nickel alloys, and nickel–chromium–molybdenum alloys are highly corrosion resistant in seawater.

Soils have a wide range of compositions and susceptibilities to corrosion. Compositional variables include moisture, oxygen, salt content, alkalinity, and acidity, as well as the presence of various forms of bacteria. Cast iron and plain carbon steels, both with and without protective surface coatings, are found most economical for underground structures.

Because there are so many acids, bases, and organic solvents, no attempt is made to discuss these solutions in this text. Good references are available that treat these topics in detail.

17.9 CORROSION PREVENTION

Some corrosion prevention methods were treated relative to the eight forms of corrosion; however, only the measures specific to each of the various corrosion types were discussed. Now, some more general techniques are presented; these include material selection, environmental alteration, design, coatings, and cathodic protection.

Perhaps the most common and easiest way of preventing corrosion is through the judicious selection of materials once the corrosion environment has been characterized. Standard corrosion references are helpful in this respect. Here, cost may be a significant factor. It is not always economically feasible to employ the material that provides the optimum corrosion resistance; sometimes, either another alloy and/or some other measure must be used.

Changing the character of the environment, if possible, may also significantly influence corrosion. Lowering the fluid temperature and/or velocity usually produces a reduction in the rate at which corrosion occurs. Many times increasing or decreasing the concentration of some species in the solution will have a positive effect; for example, the metal may experience passivation.

inhibitor

Inhibitors are substances that, when added in relatively low concentrations to the environment, decrease its corrosiveness. Of course, the specific inhibitor depends both on the alloy and on the corrosive environment. There are several mechanisms that may account for the effectiveness of inhibitors. Some react with and virtually eliminate a chemically active species in the solution (such as dissolved oxygen). Other inhibitor molecules attach themselves to the corroding surface and interfere with either the oxidation or the reduction reaction, or form a very thin protective coating. Inhibitors are normally used in closed systems such as automobile radiators and steam boilers.

Several aspects of design consideration have already been discussed, especially with regard to galvanic and crevice corrosion and erosion–corrosion. In addition, the design should allow for complete drainage in the case of a shutdown, and easy washing. Since dissolved oxygen may enhance the corrosivity of many solutions, the design should, if possible, include provision for the exclusion of air.

650 • Chapter 17 / Corrosion and Degradation of Materials

Physical barriers to corrosion are applied on surfaces in the form of films and coatings. A large diversity of metallic and nonmetallic coating materials are available. It is essential that the coating maintain a high degree of surface adhesion, which undoubtedly requires some preapplication surface treatment. In most cases, the coating must be virtually nonreactive in the corrosive environment and resistant to mechanical damage that exposes the bare metal to the corrosive environment. All three material types—metals, ceramics, and polymers—are used as coatings for metals.

Cathodic Protection

cathodic protection

One of the most effective means of corrosion prevention is **cathodic protection**; it can be used for all eight different forms of corrosion as discussed above, and may, in some situations, completely stop corrosion. Again, oxidation or corrosion of a metal M occurs by the generalized reaction

Oxidation reaction
for metal M



Cathodic protection simply involves supplying, from an external source, electrons to the metal to be protected, making it a cathode; the reaction above is thus forced in the reverse (or reduction) direction.

sacrificial anode

One cathodic protection technique employs a galvanic couple: the metal to be protected is electrically connected to another metal that is more reactive in the particular environment. The latter experiences oxidation, and, upon giving up electrons, protects the first metal from corrosion. The oxidized metal is often called a **sacrificial anode**, and magnesium and zinc are commonly used as such because they lie at the anodic end of the galvanic series. This form of galvanic protection, for structures buried in the ground, is illustrated in Figure 17.22a.

The process of *galvanizing* is simply one in which a layer of zinc is applied to the surface of steel by hot dipping. In the atmosphere and most aqueous environments, zinc is anodic to and will thus cathodically protect the steel if there is any surface damage (Figure 17.23). Any corrosion of the zinc coating will proceed at an extremely slow rate because the ratio of the anode-to-cathode surface area is quite large.

For another method of cathodic protection, the source of electrons is an impressed current from an external dc power source, as represented in Figure 17.22b for an underground tank. The negative terminal of the power source is connected to the structure to be protected. The other terminal is joined to an inert anode (often graphite), which is, in this case, buried in the soil; high-conductivity backfill material provides good electrical contact between the anode and surrounding soil. A current

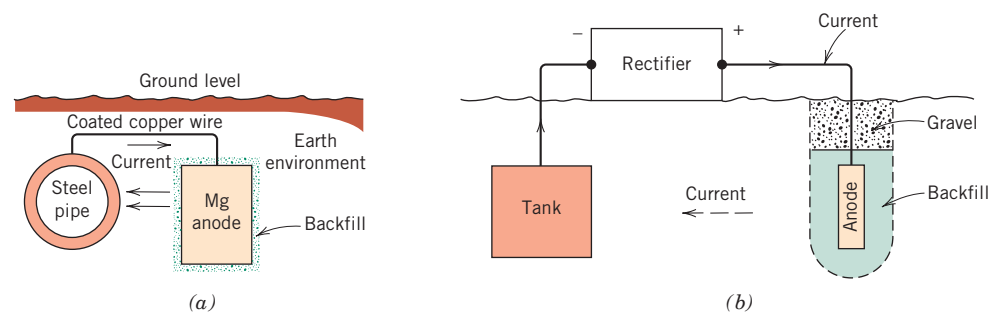


Figure 17.22 Cathodic protection of (a) an underground pipeline using a magnesium sacrificial anode, and (b) an underground tank using an impressed current. (From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

17.10 Oxidation • 651

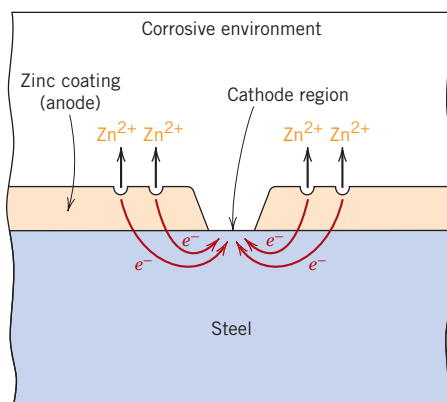


Figure 17.23 Galvanic protection of steel as provided by a coating of zinc.

path exists between the cathode and anode through the intervening soil, completing the electrical circuit. Cathodic protection is especially useful in preventing corrosion of water heaters, underground tanks and pipes, and marine equipment.

✓ Concept Check 17.7

Tin cans are made of a steel the inside of which is coated with a thin layer of tin. The tin protects the steel from corrosion by food products in the same manner as zinc protects steel from atmospheric corrosion. Briefly explain how this cathodic protection of tin cans is possible, given that tin is electrochemically less active than steel in the galvanic series (Table 17.2).

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

17.10 OXIDATION

The discussion of Section 17.2 treated the corrosion of metallic materials in terms of electrochemical reactions that take place in aqueous solutions. In addition, oxidation of metal alloys is also possible in gaseous atmospheres, normally air, wherein an oxide layer or scale forms on the surface of the metal. This phenomenon is frequently termed *scaling*, *tarnishing*, or *dry corrosion*. In this section we will discuss possible mechanisms for this type of corrosion, the types of oxide layers that can form, and the kinetics of oxide formation.

Mechanisms

As with aqueous corrosion, the process of oxide layer formation is an electrochemical one, which may be expressed, for divalent metal M, by the following reaction:⁴



Furthermore, the above reaction consists of oxidation and reduction half-reactions. The former, with the formation of metal ions,



⁴ For other than divalent metals, this reaction may be expressed as



652 • Chapter 17 / Corrosion and Degradation of Materials

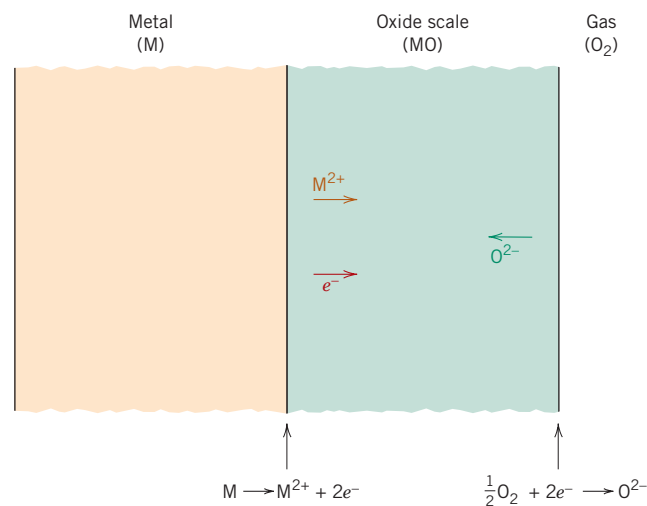


Figure 17.24 Schematic representation of processes that are involved in gaseous oxidation at a metal surface.

occurs at the metal–scale interface. The reduction half-reaction produces oxygen ions as follows:



and takes place at the scale–gas interface. A schematic representation of this metal–scale–gas system is shown in Figure 17.24.

For the oxide layer to increase in thickness via Equation 17.28, it is necessary that electrons be conducted to the scale–gas interface, at which point the reduction reaction occurs; in addition, M^{2+} ions must diffuse away from the metal–scale interface, and/or O^{2-} ions must diffuse toward this same interface (Figure 17.24).⁵ Thus, the oxide scale serves both as an electrolyte through which ions diffuse and as an electrical circuit for the passage of electrons. Furthermore, the scale may protect the metal from rapid oxidation when it acts as a barrier to ionic diffusion and/or electrical conduction; most metal oxides are highly electrically insulative.

Scale Types

Rate of oxidation (i.e., the rate of film thickness increase) and the tendency of the film to protect the metal from further oxidation are related to the relative volumes of the oxide and metal. The ratio of these volumes, termed the **Pilling–Bedworth ratio**, may be determined from the following expression:⁶

$$\text{P-B ratio} = \frac{A_{\text{O}}\rho_{\text{M}}}{A_{\text{M}}\rho_{\text{O}}} \quad (17.32)$$

Pilling–Bedworth ratio

Pilling–Bedworth ratio for a divalent metal—dependence on the densities and atomic/formula weights of the metal and its oxide

Pilling–Bedworth ratio for a metal that is not divalent

⁵ Alternatively, electron holes (Section 18.10) and vacancies may diffuse instead of electrons and ions.

⁶ For other than divalent metals, Equation 17.32 becomes

$$\text{P-B ratio} = \frac{A_{\text{O}}\rho_{\text{M}}}{aA_{\text{M}}\rho_{\text{O}}} \quad (17.33)$$

where a is the coefficient of the metal species for the overall oxidation reaction described by Equation 17.30.

Table 17.3 Pilling–Bedworth Ratios for a Number of Metals

<i>Protective</i>		<i>Nonprotective</i>	
Ce	1.16	K	0.45
Al	1.28	Li	0.57
Pb	1.40	Na	0.57
Ni	1.52	Cd	1.21
Be	1.59	Ag	1.59
Pd	1.60	Ti	1.95
Cu	1.68	Ta	2.33
Fe	1.77	Sb	2.35
Mn	1.79	Nb	2.61
Co	1.99	U	3.05
Cr	1.99	Mo	3.40
Si	2.27	W	3.40

Source: B. Chalmers, *Physical Metallurgy*. Copyright © 1959 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.

where A_O is the molecular (or formula) weight of the oxide, A_M is the atomic weight of the metal, and ρ_O and ρ_M are the oxide and metal densities, respectively. For metals having P–B ratios less than unity, the oxide film tends to be porous and unprotective because it is insufficient to fully cover the metal surface. If the ratio is greater than unity, compressive stresses result in the film as it forms. For a ratio greater than 2–3, the oxide coating may crack and flake off, continually exposing a fresh and unprotected metal surface. The ideal P–B ratio for the formation of a protective oxide film is unity. Table 17.3 presents P–B ratios for metals that form protective coatings and for those that do not. Note from these data that protective coatings normally form for metals having P–B ratios between 1 and 2, whereas nonprotective ones usually result when this ratio is less than 1 or greater than about 2. In addition to the P–B ratio, other factors also influence the oxidation resistance imparted by the film; these include a high degree of adherence between film and metal, comparable coefficients of thermal expansion for metal and oxide, and, for the oxide, a relatively high melting point and good high-temperature plasticity.

Several techniques are available for improving the oxidation resistance of a metal. One involves application of a protective surface coating of another material that adheres well to the metal and also is itself resistant to oxidation. In some instances, the addition of alloying elements will form a more adherent and protective oxide scale by virtue of producing a more favorable Pilling–Bedworth ratio and/or improving other scale characteristics.

Kinetics

One of the primary concerns relative to metal oxidation is the rate at which the reaction progresses. Inasmuch as the oxide scale reaction product normally remains on the surface, the rate of reaction may be determined by measuring the weight gain per unit area as a function of time.

When the oxide that forms is nonporous and adheres to the metal surface, the rate of layer growth is controlled by ionic diffusion. A *parabolic* relationship exists

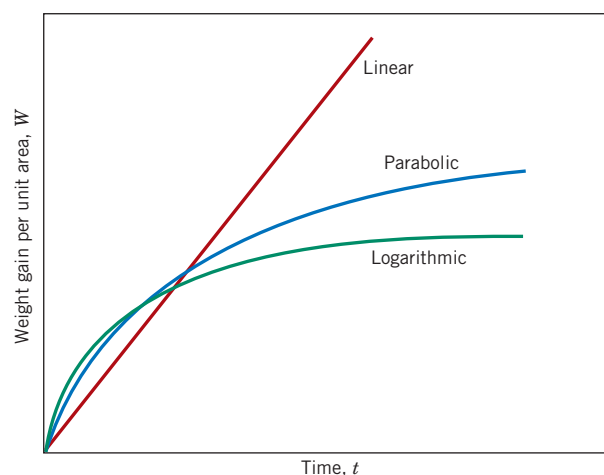


Figure 17.25 Oxidation film growth curves for linear, parabolic, and logarithmic rate laws.

between the weight gain per unit area W and the time t as follows:

$$W^2 = K_1 t + K_2 \quad (17.34)$$

where K_1 and K_2 are time-independent constants at a given temperature. This weight gain–time behavior is plotted schematically in Figure 17.25. The oxidation of iron, copper, and cobalt follows this rate expression.

In the oxidation of metals for which the scale is porous or flakes off (i.e., for P–B ratios less than about 1 or greater than about 2), the oxidation rate expression is *linear*; that is,

$$W = K_3 t \quad (17.35)$$

where K_3 is a constant. Under these circumstances oxygen is always available for reaction with an unprotected metal surface because the oxide does not act as a reaction barrier. Sodium, potassium, and tantalum oxidize according to this rate expression and, incidentally, have P–B ratios significantly different from unity (Table 17.3). Linear growth rate kinetics is also represented in Figure 17.25.

Still a third reaction rate law has been observed for very thin oxide layers (generally less than 100 nm) that form at relatively low temperatures. The dependence of weight gain on time is *logarithmic* and takes the form

$$W = K_4 \log(K_5 t + K_6) \quad (17.36)$$

Again, the K 's are constants. This oxidation behavior, also shown in Figure 17.25, has been observed for aluminum, iron, and copper at near-ambient temperatures.

Corrosion of Ceramic Materials

Ceramic materials, being compounds between metallic and nonmetallic elements, may be thought of as having already been corroded. Thus, they are exceedingly immune to corrosion by almost all environments, especially at room temperature. Corrosion of ceramic materials generally involves simple chemical dissolution, in contrast to the electrochemical processes found in metals, as described above.

17.11 Swelling and Dissolution • 655

Ceramic materials are frequently utilized because of their resistance to corrosion. Glass is often used to contain liquids for this reason. Refractory ceramics must not only withstand high temperatures and provide thermal insulation but, in many instances, must also resist high-temperature attack by molten metals, salts, slags, and glasses. Some of the new technology schemes for converting energy from one form to another that is more useful require relatively high temperatures, corrosive atmospheres, and pressures above the ambient. Ceramic materials are much better suited to withstand most of these environments for reasonable time periods than are metals.

Degradation of Polymers

Polymeric materials also experience deterioration by means of environmental interactions. However, an undesirable interaction is specified as degradation rather than corrosion because the processes are basically dissimilar. Whereas most metallic corrosion reactions are electrochemical, by contrast, polymeric degradation is physiochemical; that is, it involves physical as well as chemical phenomena. Furthermore, a wide variety of reactions and adverse consequences are possible for polymer degradation. Polymers may deteriorate by swelling and dissolution. Covalent bond rupture, as a result of heat energy, chemical reactions, and radiation is also possible, ordinarily with an attendant reduction in mechanical integrity. It should also be mentioned that because of the chemical complexity of polymers, their degradation mechanisms are not well understood.

To briefly cite a couple of examples of polymer degradation, polyethylene, if exposed to high temperatures in an oxygen atmosphere, suffers an impairment of its mechanical properties by becoming brittle. Also, the utility of poly(vinyl chloride) may be limited because this material may become colored when exposed to high temperatures, although such environments do not affect its mechanical characteristics.

17.11 SWELLING AND DISSOLUTION

When polymers are exposed to liquids, the main forms of degradation are swelling and dissolution. With swelling, the liquid or solute diffuses into and is absorbed within the polymer; the small solute molecules fit into and occupy positions among the polymer molecules. Thus the macromolecules are forced apart such that the specimen expands or swells. Furthermore, this increase in chain separation results in a reduction of the secondary intermolecular bonding forces; as a consequence, the material becomes softer and more ductile. The liquid solute also lowers the glass transition temperature and, if depressed below the ambient temperature, will cause a once strong material to become rubbery and weak.

Swelling may be considered to be a partial dissolution process in which there is only limited solubility of the polymer in the solvent. Dissolution, which occurs when the polymer is completely soluble, may be thought of as just a continuation of swelling. As a rule of thumb, the greater the similarity of chemical structure between the solvent and polymer, the greater is the likelihood of swelling and/or dissolution. For example, many hydrocarbon rubbers readily absorb hydrocarbon liquids such as gasoline. The responses of selected polymeric materials to organic solvents are contained in Tables 17.4 and 17.5.

Swelling and dissolution traits also are affected by temperature as well as characteristics of the molecular structure. In general, increasing molecular weight, increasing degree of crosslinking and crystallinity, and decreasing temperature result in a reduction of these deteriorative processes.

656 • Chapter 17 / Corrosion and Degradation of Materials

Table 17.4 Resistance to Degradation by Various Environments for Selected Plastic Materials^a

<i>Material</i>	<i>Nonoxidizing Acids (20% H₂SO₄)</i>	<i>Oxidizing Acids (10% HNO₃)</i>	<i>Aqueous Salt Solutions (NaCl)</i>	<i>Aqueous Alkalis (NaOH)</i>	<i>Polar Solvents (C₂H₅OH)</i>	<i>Nonpolar Solvents (C₆H₆)</i>	<i>Water</i>
Polytetrafluoro-ethylene	S	S	S	S	S	S	S
Nylon 6,6	U	U	S	S	Q	S	S
Polycarbonate	Q	U	S	U	S	U	S
Polyester	Q	Q	S	Q	Q	U	S
Polyetheretherketone	S	S	S	S	S	S	S
Low-density polyethylene	S	Q	S	—	S	Q	S
High-density polyethylene	S	Q	S	—	S	Q	S
Poly(ethylene terephthalate)	S	Q	S	S	S	S	S
Poly(phenylene oxide)	S	Q	S	S	S	U	S
Polypropylene	S	Q	S	S	S	Q	S
Polystyrene	S	Q	S	S	S	U	S
Polyurethane	Q	U	S	Q	U	Q	S
Epoxy	S	U	S	S	S	S	S
Silicone	Q	U	S	S	S	Q	S

^a S = satisfactory; Q = questionable; U = unsatisfactory.**Source:** Adapted from R. B. Seymour, *Polymers for Engineering Applications*, ASM International, Materials Park, OH, 1987.

In general, polymers are much more resistant to attack by acidic and alkaline solutions than are metals. For example, hydrofluoric acid (HF) will corrode many metals as well as etch and dissolve glass, so it is stored in plastic bottles. A qualitative comparison of the behavior of various polymers in these solutions is also presented in Tables 17.4 and 17.5. Materials that exhibit outstanding resistance to attack by both solution types include polytetrafluoroethylene (and other fluorocarbons) and polyetheretherketone.

Table 17.5 Resistance to Degradation by Various Environments for Selected Elastomeric Materials^a

<i>Material</i>	<i>Weather Sunlight Aging</i>	<i>Oxidation</i>	<i>Ozone Cracking</i>	<i>Alkali Dilute/ Concentrated</i>	<i>Acid Dilute/ Concentrated</i>	<i>Chlorinated Hydrocarbons, Degreasers</i>	<i>Aliphatic Hydrocarbons, Kerosene, Etc.</i>	<i>Animal, Vegetable Oils</i>
Polyisoprene (natural)	D	B	NR	A/C-B	A/C-B	NR	NR	D-B
Polyisoprene (synthetic)	NR	B	NR	C-B/C-B	C-B/C-B	NR	NR	D-B
Butadiene	D	B	NR	C-B/C-B	C-B/C-B	NR	NR	D-B
Styrene-butadiene	D	C	NR	C-B/C-B	C-B/C-B	NR	NR	D-B
Neoprene	B	A	A	A/A	A/A	D	C	B
Nitrile (high)	D	B	C	B/B	B/B	C-B	A	B
Silicone (polysiloxane)	A	A	A	A/A	B/C	NR	D-C	A

^a A = excellent, B = good, C = fair, D = use with caution, NR = not recommended.**Source:** *Compound Selection and Service Guide*, Seals Eastern, Inc., Red Bank, NJ, 1977.

17.12 Bond Rupture • 657

**Concept Check 17.8**

From a molecular perspective, explain why increasing crosslinking and crystallinity of a polymeric material will enhance its resistance to swelling and dissolution. Would you expect crosslinking or crystallinity to have the greater influence? Justify your choice. *Hint:* you may want to consult Sections 14.7 and 14.11.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

17.12 BOND RUPTURE**scission**

Polymers may also experience degradation by a process termed **scission**—the severance or rupture of molecular chain bonds. This causes a separation of chain segments at the point of scission and a reduction in the molecular weight. As previously discussed (Chapter 15), several properties of polymeric materials, including mechanical strength and resistance to chemical attack, depend on molecular weight. Consequently, some of the physical and chemical properties of polymers may be adversely affected by this form of degradation. Bond rupture may result from exposure to radiation or to heat, and from chemical reaction.

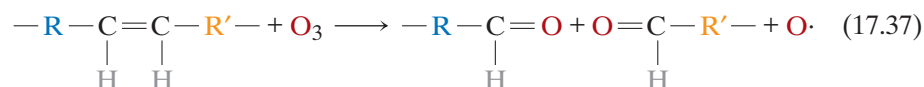
Radiation Effects

Certain types of radiation [electron beams, x-rays, β - and γ -rays, and ultraviolet (UV) radiation] possess sufficient energy to penetrate a polymer specimen and interact with the constituent atoms or their electrons. One such reaction is *ionization*, in which the radiation removes an orbital electron from a specific atom, converting that atom into a positively charged ion. As a consequence, one of the covalent bonds associated with the specific atom is broken, and there is a rearrangement of atoms or groups of atoms at that point. This bond breaking leads to either scission or crosslinking at the ionization site, depending on the chemical structure of the polymer and also on the dose of radiation. Stabilizers (Section 15.21) may be added to protect polymers from radiation damage. In day-to-day use, the greatest radiation damage to polymers is caused by UV irradiation. After prolonged exposure, most polymer films become brittle, discolor, crack, and fail. For example, camping tents begin to tear, dashboards develop cracks, and plastic windows become cloudy. Radiation problems are more severe for some applications. Polymers on space vehicles must resist degradation after prolonged exposures to cosmic radiation. Similarly, polymers used in nuclear reactors must withstand high levels of nuclear radiation. Developing polymeric materials that can withstand these extreme environments is a continuing challenge.

Not all consequences of radiation exposure are deleterious. Crosslinking may be induced by irradiation to improve the mechanical behavior and degradation characteristics. For example, γ -radiation is used commercially to crosslink polyethylene to enhance its resistance to softening and flow at elevated temperatures; indeed, this process may be carried out on products that have already been fabricated.

Chemical Reaction Effects

Oxygen, ozone, and other substances can cause or accelerate chain scission as a result of chemical reaction. This effect is especially prevalent in vulcanized rubbers that have doubly bonded carbon atoms along the backbone molecular chains, and that are exposed to ozone (O_3), an atmospheric pollutant. One such scission reaction may be represented by



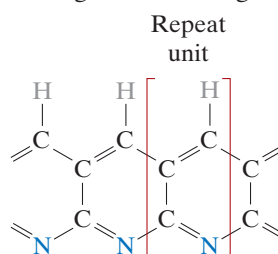
658 • Chapter 17 / Corrosion and Degradation of Materials

where the chain is severed at the point of the double bond; R and R' represent groups of atoms that are unaffected during the reaction. Ordinarily, if the rubber is in an unstressed state, a film will form on the surface, protecting the bulk material from any further reaction. However, when these materials are subjected to tensile stresses, cracks and crevices form and grow in a direction perpendicular to the stress; eventually, rupture of the material may occur. This is why the sidewalls on rubber bicycle tires develop cracks as they age. Apparently these cracks result from large numbers of ozone-induced scissions. Chemical degradation is a particular problem for polymers used in areas with high levels of air pollutants such as smog and ozone. The elastomers in Table 17.5 are rated as to their resistance to degradation by exposure to ozone. Many of these chain scission reactions involve reactive groups termed *free radicals*. Stabilizers (Section 15.21) may be added to protect polymers from oxidation. The stabilizers either sacrificially react with the ozone to consume it, or they react with and eliminate the free radicals before they (the free radicals) can inflict more damage.

Thermal Effects

Thermal degradation corresponds to the scission of molecular chains at elevated temperatures; as a consequence, some polymers undergo chemical reactions in which gaseous species are produced. These reactions are evidenced by a weight loss of material; a polymer's thermal stability is a measure of its resilience to this decomposition. Thermal stability is related primarily to the magnitude of the bonding energies between the various atomic constituents of the polymer: higher bonding energies result in more thermally stable materials. For example, the magnitude of the C—F bond is greater than that of the C—H bond, which in turn is greater than that of the C—Cl bond. The fluorocarbons, having C—F bonds, are among the most thermally resistant polymeric materials and may be utilized at relatively high temperatures. However, due to the weak C—Cl bond, when poly(vinyl chloride) is heated to 200°C for even a few minutes it will discolor and give off large amounts of HCl that accelerates continued decomposition. Stabilizers (Section 15.21) such as ZnO can react with the HCl, providing increased thermal stability for poly(vinyl chloride).

Some of the most thermally stable polymers are the ladder polymers.⁷ For example, the ladder polymer having the following structure



is so thermally stable that a woven cloth of this material can be heated directly in an open flame with no degradation. Polymers of this type are used in place of asbestos for high-temperature gloves.

17.13 WEATHERING

Many polymeric materials serve in applications that require exposure to outdoor conditions. Any resultant degradation is termed *weathering*, which may, in fact, be a combination of several different processes. Under these conditions deterioration

⁷ The chain structure of a “ladder polymer” consists of two sets of covalent bonds throughout its length that are crosslinked.

Case Study:
“Artificial Total Hip
Replacement,” Chap-
ter 22, which may be
found at www.wiley.com/college/callister
(Student Companion
Site)

is primarily a result of oxidation, which is initiated by ultraviolet radiation from the sun. Some polymers such as nylon and cellulose are also susceptible to water absorption, which produces a reduction in their hardness and stiffness. Resistance to weathering among the various polymers is quite diverse. The fluorocarbons are virtually inert under these conditions; but some materials, including poly(vinyl chloride) and polystyrene, are susceptible to weathering.



Concept Check 17.9

List three differences between the corrosion of metals and

- (a) the corrosion of ceramics, and
- (b) the degradation of polymers.

[The answer may be found at www.wiley.com/college/callister (Student Companion Site).]

SUMMARY

Electrochemical Considerations

Metallic corrosion is ordinarily electrochemical, involving both oxidation and reduction reactions. Oxidation is the loss of the metal atom's valence electrons; the resulting metal ions may either go into the corroding solution or form an insoluble compound. During reduction, these electrons are transferred to at least one other chemical species. The character of the corrosion environment dictates which of several possible reduction reactions will occur.

Not all metals oxidize with the same degree of ease, which is demonstrated with a galvanic couple; when in an electrolyte, one metal (the anode) will corrode, whereas a reduction reaction will occur at the other metal (the cathode). The magnitude of the electric potential that is established between anode and cathode is indicative of the driving force for the corrosion reaction.

The standard emf and galvanic series are simply rankings of metallic materials on the basis of their tendency to corrode when coupled to other metals. For the standard emf series, ranking is based on the magnitude of the voltage generated when the standard cell of a metal is coupled to the standard hydrogen electrode at 25°C (77°F). The galvanic series consists of the relative reactivities of metals and alloys in seawater.

The half-cell potentials in the standard emf series are thermodynamic parameters that are valid only at equilibrium; corroding systems are not in equilibrium. Furthermore, the magnitudes of these potentials provide no indication as to the rates at which corrosion reactions occur.

Corrosion Rates

The rate of corrosion may be expressed as corrosion penetration rate, that is, the thickness loss of material per unit of time. Mils per year and millimeters per year are the common units for this parameter. Alternatively, rate is proportional to the current density associated with the electrochemical reaction.

Prediction of Corrosion Rates

Corroding systems will experience polarization, which is the displacement of each electrode potential from its equilibrium value; the magnitude of the displacement is termed the overvoltage. The corrosion rate of a reaction is limited by polarization, of which there are two types—activation and concentration. Polarization data

660 • Chapter 17 / Corrosion and Degradation of Materials

are plotted as potential versus the logarithm of current density. The corrosion rate for a particular reaction may be computed using the current density associated with the intersection point of oxidation and reduction polarization curves.

Passivity

A number of metals and alloys passivate, or lose their chemical reactivity, under some environmental circumstances. This phenomenon is thought to involve the formation of a thin protective oxide film. Stainless steels and aluminum alloys exhibit this type of behavior. The active-to-passive behavior may be explained by the alloy's S-shaped electrochemical potential-versus-log current density curve. Intersections with reduction polarization curves in active and passive regions correspond, respectively, to high and low corrosion rates.

Forms of Corrosion

Metallic corrosion is sometimes classified into eight different forms: uniform attack, galvanic corrosion, crevice corrosion, pitting, intergranular corrosion, selective leaching, erosion–corrosion, and stress corrosion. Hydrogen embrittlement, a type of failure sometimes observed in corrosion environments, was also discussed.

Corrosion Prevention

The measures that may be taken to prevent, or at least reduce, corrosion include material selection, environmental alteration, the use of inhibitors, design changes, application of coatings, and cathodic protection.

Oxidation

Oxidation of metallic materials by electrochemical action is also possible in dry, gaseous atmospheres. An oxide film forms on the surface which may act as a barrier to further oxidation if the volumes of metal and oxide film are similar, that is, if the Pilling–Bedworth ratio is near unity. The kinetics of film formation may follow parabolic, linear, or logarithmic rate laws.

Corrosion of Ceramic Materials

Ceramic materials, being inherently corrosion resistant, are frequently utilized at elevated temperatures and/or in extremely corrosive environments.

Swelling and Dissolution**Bond Rupture****Weathering**

Polymeric materials deteriorate by noncorrosive processes. Upon exposure to liquids, they may experience degradation by swelling or dissolution. With swelling, solute molecules actually fit into the molecular structure. Scission, or the severance of molecular chain bonds, may be induced by radiation, chemical reactions, or heat. This results in a reduction of molecular weight and a deterioration of the physical and chemical properties of the polymer.

IMPORTANT TERMS AND CONCEPTS

Activation polarization	Concentration polarization	Degradation
Anode	Corrosion	Electrolyte
Cathode	Corrosion penetration rate	Electromotive force (emf) series
Cathodic protection	Crevice corrosion	Erosion–corrosion

Questions and Problems • 661

Galvanic corrosion	Oxidation	Sacrificial anode
Galvanic series	Passivity	Scission
Hydrogen embrittlement	Pilling–Bedworth ratio	Selective leaching
Inhibitor	Pitting	Standard half-cell
Intergranular corrosion	Polarization	Stress corrosion
Molarity	Reduction	Weld decay

REFERENCES

- ASM Handbook, Vol. 13, *Corrosion*, ASM International, Materials Park, OH, 1987.
- ASM Handbook, Vol. 13A, *Corrosion: Fundamentals, Testing, and Protection*, ASM International, Materials Park, OH, 2003.
- Craig, B. D. and D. Anderson, (Editors), *Handbook of Corrosion Data*, 2nd edition, ASM International, Materials Park, OH, 1995.
- Fontana, M. G., *Corrosion Engineering*, 3rd edition, McGraw-Hill, New York, 1986.
- Gibala, R. and R. F. Hehemann, *Hydrogen Embrittlement and Stress Corrosion Cracking*, ASM International, Materials Park, OH, 1984.
- Jones, D. A., *Principles and Prevention of Corrosion*, 2nd edition, Pearson Education, Upper Saddle River, NJ, 1996.
- Marcus, P. and J. Oudar (Editors), *Corrosion Mechanisms in Theory and Practice*, Marcel Dekker, New York, 1995.
- Revie, R. W. (Editor), *Uhlig's Corrosion Handbook*, 2nd edition, John Wiley & Sons, New York, 2000.
- Schweitzer, P. A., *Atmospheric Degradation and Corrosion Control*, Marcel Dekker, New York, 1999.
- Schweitzer, P. A. (Editor), *Corrosion and Corrosion Protection Handbook*, 2nd edition, Marcel Dekker, New York, 1989.
- Talbot, D. and J. Talbot, *Corrosion Science and Technology*, CRC Press, Boca Raton, FL, 1998.
- Uhlig, H. H. and R. W. Revie, *Corrosion and Corrosion Control*, 3rd edition, John Wiley & Sons, New York, 1985.

QUESTIONS AND PROBLEMS

Electrochemical Considerations

- 17.1 (a)** Briefly explain the difference between oxidation and reduction electrochemical reactions.
- (b)** Which reaction occurs at the anode and which at the cathode?
- 17.2 (a)** Write the possible oxidation and reduction half-reactions that occur when magnesium is immersed in each of the following solutions: (i) HCl, (ii) an HCl solution containing dissolved oxygen, (iii) an HCl solution containing dissolved oxygen and, in addition, Fe^{2+} ions.
- (b)** In which of these solutions would you expect the magnesium to oxidize most rapidly? Why?
- 17.3** Demonstrate that **(a)** the value of \mathcal{F} in Equation 17.19 is 96,500 C/mol, and **(b)** at 25°C (298 K),

$$\frac{RT}{n\mathcal{F}} \ln x = \frac{0.0592}{n} \log x$$

- 17.4 (a)** Compute the voltage at 25°C of an electrochemical cell consisting of pure lead immersed in a $5 \times 10^{-2} M$ solution of Pb^{2+} ions, and pure tin in a 0.25 M solution of Sn^{2+} ions.
- (b)** Write the spontaneous electrochemical reaction.
- 17.5** An Fe/Fe^{2+} concentration cell is constructed in which both electrodes are pure iron. The Fe^{2+} concentration for one cell half is 0.5 M, for the other, $2 \times 10^{-2} M$. Is a voltage generated between the two cell halves? If so, what is its magnitude and which electrode will be oxidized? If no voltage is produced, explain this result.
- 17.6** An electrochemical cell is composed of pure copper and pure cadmium electrodes immersed in solutions of their respective divalent ions. For a $6.5 \times 10^{-2} M$ concentration of Cd^{2+} , the cadmium electrode is oxidized yielding a cell potential of 0.775 V. Calculate the concentration of Cu^{2+} ions if the temperature is 25°C.

662 • Chapter 17 / Corrosion and Degradation of Materials

- 17.7** An electrochemical cell is constructed such that on one side a pure Zn electrode is in contact with a solution containing Zn^{2+} ions at a concentration of $10^{-2} M$. The other cell half consists of a pure Pb electrode immersed in a solution of Pb^{2+} ions that has a concentration of $10^{-4} M$. At what temperature will the potential between the two electrodes be $+0.568 V$?
- 17.8** For the following pairs of alloys that are coupled in seawater, predict the possibility of corrosion; if corrosion is probable, note which metal/alloy will corrode.
- (a) Aluminum and cast iron
 - (b) Inconel and nickel
 - (c) Cadmium and zinc
 - (d) Brass and titanium
 - (e) Low-carbon steel and copper
- 17.9** (a) From the galvanic series (Table 17.2), cite three metals/alloys that may be used to galvanically protect cast iron.
- (b) As Concept Check 17.4(b) notes, galvanic corrosion is prevented by making an electrical contact between the two metals in the couple and a third metal that is anodic to the other two. Using the galvanic series, name one metal that could be used to protect a nickel-steel galvanic couple.

Corrosion Rates

- 17.10** Demonstrate that the constant K in Equation 17.23 will have values of 534 and 87.6 for the CPR in units of mpy and mm/yr, respectively.
- 17.11** A piece of corroded metal alloy plate was found in a submerged ocean vessel. It was estimated that the original area of the plate was 800 cm^2 and that approximately 7.6 kg had corroded away during the submersion. Assuming a corrosion penetration rate of 4 mm/yr for this alloy in seawater, estimate the time of submersion in years. The density of the alloy is 4.5 g/cm^3 .
- 17.12** A thick steel sheet of area 100 in.^2 is exposed to air near the ocean. After a one-year period it was found to experience a weight loss of 485 g due to corrosion. To what rate of corrosion, in both mpy and mm/yr, does this correspond?

- 17.13** (a) Demonstrate that the CPR is related to the corrosion current density i (A/cm^2) through the expression

$$\text{CPR} = \frac{KAi}{n\rho} \quad (17.38)$$

where K is a constant, A is the atomic weight of the metal experiencing corrosion, n is the number of electrons associated with the ionization of each metal atom, and ρ is the density of the metal.

(b) Calculate the value of the constant K for the CPR in mpy and i in $\mu\text{A/cm}^2$ (10^{-6} A/cm^2).

- 17.14** Using the results of Problem 17.13, compute the corrosion penetration rate, in mpy, for the corrosion of iron in HCl (to form Fe^{2+} ions) if the corrosion current density is $8 \times 10^{-5} \text{ A/cm}^2$.

Prediction of Corrosion Rates

- 17.15** (a) Cite the major differences between activation and concentration polarizations.
- (b) Under what conditions is activation polarization rate controlling?
- (c) Under what conditions is concentration polarization rate controlling?
- 17.16** (a) Describe the phenomenon of dynamic equilibrium as it applies to oxidation and reduction electrochemical reactions.
- (b) What is the exchange current density?
- 17.17** Nickel experiences corrosion in an acid solution according to the reaction



The rates of both oxidation and reduction half-reactions are controlled by activation polarization.

(a) Compute the rate of oxidation of Ni (in $\text{mol/cm}^2\text{-s}$) given the following activation polarization data:

For Nickel	For Hydrogen
$V_{(\text{Ni}/\text{Ni}^{2+})} = -0.25 \text{ V}$	$V_{(\text{H}^+/\text{H}_2)} = 0 \text{ V}$
$i_0 = 10^{-8} \text{ A/cm}^2$	$i_0 = 6 \times 10^{-7} \text{ A/cm}^2$
$\beta = +0.12$	$\beta = -0.10$

- (b) Compute the value of the corrosion potential.

Questions and Problems • 663

- 17.18** The corrosion rate is to be determined for some divalent metal M in a solution containing hydrogen ions. The following corrosion data are known about the metal and solution:

For Metal M	For Hydrogen
$V_{(M/M^{2+})} = -0.90 \text{ V}$	$V_{(H^+/H_2)} = 0 \text{ V}$
$i_0 = 10^{-12} \text{ A/cm}^2$	$i_0 = 10^{-10} \text{ A/cm}^2$
$\beta = +0.10$	$\beta = -0.15$

- (a) Assuming that activation polarization controls both oxidation and reduction reactions, determine the rate of corrosion of metal M (in $\text{mol/cm}^2\text{-s}$).
- (b) Compute the corrosion potential for this reaction.
- 17.19** The influence of increasing solution velocity on the overvoltage-versus-log current density behavior for a solution that experiences combined activation–concentration polarization is indicated in Figure 17.26. On the basis of this behavior, make a schematic plot of corrosion rate versus solution velocity for the oxidation of a metal; assume that the oxidation reaction is controlled by activation polarization.

Passivity

- 17.20** Briefly describe the phenomenon of passivity. Name two common types of alloy that passivate.
- 17.21** Why does chromium in stainless steels make them more corrosion resistant in many environments than plain carbon steels?

Forms of Corrosion

- 17.22** For each form of corrosion, other than uniform, do the following:

(a) Describe why, where, and the conditions under which the corrosion occurs.

(b) Cite three measures that may be taken to prevent or control it.

- 17.23** Briefly explain why cold-worked metals are more susceptible to corrosion than noncold-worked metals.

- 17.24** Briefly explain why, for a small anode-to-cathode area ratio, the corrosion rate will be higher than for a large ratio.

- 17.25** For a concentration cell, briefly explain why corrosion occurs at that region having the lower concentration.

Corrosion Prevention

- 17.26** (a) What are inhibitors?
(b) What possible mechanisms account for their effectiveness?
- 17.27** Briefly describe the two techniques that are used for galvanic protection.

Oxidation

- 17.28** For each of the metals listed in the table, compute the Pilling–Bedworth ratio. Also, on the basis of this value, specify whether or not you would expect the oxide scale that forms on the surface to be protective, and then justify your decision. Density data for both the metal and its oxide are also tabulated.

Metal	Metal Density (g/cm^3)	Metal Oxide	Oxide Density (g/cm^3)
Mg	1.74	MgO	3.58
V	6.11	V ₂ O ₅	3.36
Zn	7.13	ZnO	5.61

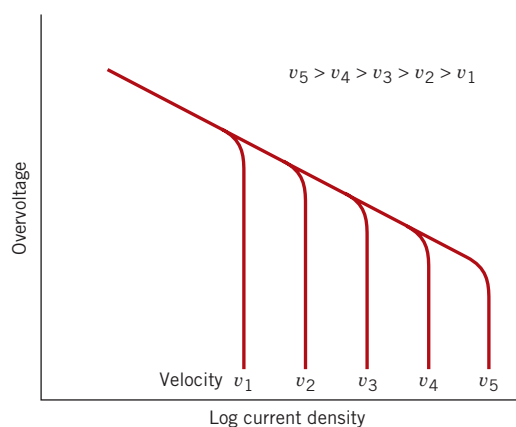


Figure 17.26 Plot of overvoltage versus logarithm of current density for a solution that experiences combined activation–concentration polarization at various solution velocities.

664 • Chapter 17 / Corrosion and Degradation of Materials

17.29 According to Table 17.3, the oxide coating that forms on silver should be nonprotective, and yet Ag does not oxidize appreciably at room temperature and in air. How do you explain this apparent discrepancy?

17.30 In the table, weight gain–time data for the oxidation of nickel at an elevated temperature are tabulated.

W (mg/cm ²)	Time (min)
0.527	10
0.857	30
1.526	100

(a) Determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression.

(b) Now compute W after a time of 600 min.

17.31 In the table, weight gain–time data for the oxidation of some metal at an elevated temperature are tabulated.

W (mg/cm ²)	Time (min)
6.16	100
8.59	250
12.72	1000

(a) Determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression.

(b) Now compute W after a time of 5000 min.

17.32 In the table, weight gain–time data for the oxidation of some metal at an elevated temperature are tabulated.

W (mg/cm ²)	Time (min)
1.54	10
23.24	150
95.37	620

(a) Determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression.

(b) Now compute W after a time of 1200 min.

Bond Rupture

17.33 Oil-based paints typically contain an unsaturated oil such as linseed oil. The “drying” of oil-based paints occurs by reactions with atmospheric oxygen that lead to crosslinking and hardening of the paint. In the table below, weight gain–time data for the oxidation of linseed oil at room temperature (298 K) are tabulated.

W (mg/cm ²)	Time (min)
0.053	18.6
0.100	39.0
0.158	57.1

(a) Determine whether the oxidation kinetics obey a linear, parabolic, or logarithmic rate expression.

(b) Compute the amount of time required for a weight gain of 0.120 mg/cm².

DESIGN PROBLEMS

17.D1 A brine solution is used as a cooling medium in a steel heat exchanger. The brine is circulated within the heat exchanger and contains some dissolved oxygen. Suggest three methods, other than cathodic protection, for reducing corrosion of the steel by the brine. Explain the rationale for each suggestion.

17.D2 Suggest an appropriate material for each of the following applications, and, if necessary, recommend corrosion prevention measures that should be taken. Justify your suggestions.

(a) Laboratory bottles to contain relatively dilute solutions of nitric acid

(b) Barrels to contain benzene

(c) Pipe to transport hot alkaline (basic) solutions

(d) Underground tanks to store large quantities of high-purity water

(e) Architectural trim for high-rise buildings

17.D3 Each student (or group of students) is to find a real-life corrosion problem that has not been solved, conduct a thorough investigation as to the cause(s) and type(s) of corrosion, and, finally, propose possible solutions for the problem, indicating which of the solutions is best and why. Submit a report that addresses the above issues.