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CHAPTER **1**

Introduction and Overview of Electrochemical Corrosion

Definition and Examples of Corrosion

The deterioration of materials due to reactions with their environments is the currently accepted broad definition of corrosion. From a practical standpoint, the term *materials* refers to those substances used in the construction of machines, process equipment, and other manufactured products. These materials include metals, polymers, and ceramics. The environments are liquids or gases, although under special circumstances certain solid-solid reactions might be included as corrosion. The breadth of this definition can best be appreciated by considering examples, starting with cases that are usually recognized as corrosion and proceeding to those that are less obvious or are not generally recognized as corrosion:

- Rusting of steel and cast iron in water, including humid air, as occurs with domestic and industrial water tanks and supply piping, automobiles, and exposed steel structures
- Corrosion of copper, aluminum, and cast iron in automotive cooling systems

- Corrosion of iron-base, copper-base, nickel-base, etc. alloys in the chemical process industry
- Corrosion of automobile exhaust systems by direct reaction of the metal with high-temperature gases and by condensation of water and absorption of the oxides of sulfur and nitrogen to produce aqueous acid environments
- Corrosion of turbine blades in gas turbines by hot combustion gases
- Corrosion of metallic surgical implant materials used in orthopedic, cardiovascular, and dental devices resulting in the release of metal ions to tissues, and degradation of the physical properties of polymeric implant materials due to interactions with tissue fluids and/or blood
- Corrosion of iron-base and nickel-base alloys by liquid metals used as heat transfer agents (e.g., liquid sodium, potassium, and lithium)
- Enhanced deterioration of structural concrete and stone by interaction with condensed moisture and acidic contaminants in the air, such as the oxides of sulfur and nitrogen
- Stress-corrosion cracking (SCC) of gold and brass by mercury
- SCC and pitting of stainless steel in sea water

The Need to Control Corrosion

The need to control corrosion almost always reduces to considerations of safety and economics. Machines, equipment, and functional products may fail due to corrosion in such a manner as to result in personal injury. Because the choice of materials, enforcement of manufacturing procedures, and control of products to minimize personal injury all involve economic considerations, implementation of safety measures not only involves humanitarian concerns but also economics. With all economic decisions, the basis for action is a compromise between the benefits generated by a certain level of corrosion control versus the costs that would result if that level of control were not maintained. Examples of economic decisions involving considerations of the consequences of corrosion include the following:

- Within limits of health and safety, materials should not be selected for individual products, or components of more complex products, if the corrosion resistance would permit the life of the part to be significantly longer than the life actually realized because of other factors. Thus, the muffler of an automobile could be made of materials that would permit it to outlast the use of some large fraction of all automobiles manufactured at a given time. Because driving habits

have a major influence on muffler life, and reasonable performance and ease of replacement can be realized by using relatively inexpensive materials, it is not economical to use more highly corrosion-resistant materials. This choice also is favored by the fact that the muffler is not a critical component from the safety standpoint. For example, a different set of criteria would be required for critical components of the steering mechanism.

- Design for corrosion resistance may be almost exclusively for appearance when favorable appearance is an economic advantage. Stainless steel and aluminum are frequently used for architectural applications and in food service largely for appearance. They also are used for trim on automobiles for the same reason.

- On the other hand, materials exhibiting very low corrosion rates may be selected for reasons of both health and appearance in the processing of foods, pharmaceuticals, and cosmetics. Even if health is not involved, corrosion products producing objectionable color or particles of foreign material are not acceptable to the consumer. For example, such product contamination in paint obviously can lead to totally unacceptable products.

- In some cases, severely corrosive environments are contained by metals such as gold and platinum, which, in spite of high costs, are required because of their inertness. The initial cost, however, is countered by the ease of recovery of the metals following use and their high recycle value.

- A major economic factor in designing for corrosion resistance is the avoidance of interruption of plant production. Failure due to corrosion of critical components such as pumps and heat exchangers may necessitate large sections of a process or entire plants to become inoperative, leading to costs associated with lost production far in excess of the cost of replacement of the failed component. Process design and materials selection to minimize plant outage is a major engineering consideration.

Corrosion Mechanisms

Particularly under the broad definition of corrosion as the deterioration of materials by reaction with the environment, the number of mechanisms whereby deterioration occurs is large. In general, a mechanism of corrosion is the actual atomic, molecular, or ionic transport process that takes place at the interface of a material. These processes usually involve more than one definable step, and the major interest is directed toward the slowest step that essentially controls the rate of the overall

reaction. In corrosion, of course, this rate should be as slow as possible. Because these processes cannot be observed directly on an atomic scale, it is necessary to infer possible mechanisms from indirect measurements and observations. Examples are the rate of change in weight or dimensions, the rate of buildup of corrosion products in the environment, changes in surface appearance examined by optical or electron microscopy, or changes in mechanical or physical properties. When electrochemical corrosion is occurring, mechanisms may be inferred from measurements of electrical potential and current.

Considering engineering materials as metals, polymers, and ceramics, transport of mass across the interface to the environment may be broadly considered as electrochemical, chemical, or physical. Since electrochemical corrosion involves the release of ions to the environment and movement of electrons within the material, this mechanism can occur only if the environment can contain ions and the material can conduct electrons. The most important case of electrochemical mechanisms is the simple corrosion of metals in aqueous solutions, where atoms at the surface of the metal enter the solution as metal ions and electrons migrate through the metal to a site where, to sustain the reaction, they are consumed by species in contact with the metal. In more complicated cases, the metal ions move into solution by forming complex ions, or they combine with other species in the solution and precipitate compounds such as hydroxides, oxides, or sulfides. At sufficiently high temperatures, metals corrode in gases, particularly oxygen to form oxides. Whereas the mechanism in this case appears to be one of direct chemical attack, the mechanism may still be electrochemical in nature, with ions and electrons moving in the oxide which acts as the electrolyte supporting the electrochemical mechanism.

Polymeric and ceramic materials generally do not support electron conduction and hence corrode by either direct chemical or physical mechanisms. Chemical attack of polymers breaks bonds responsible for the properties of these materials, resulting in changes of molecular structure, possible transfer of material to the environment, and degradation of properties. In the case of chemical attack of ceramic materials, the composition of the environment may cause the ceramic or components in the ceramic to either become soluble or to be changed into soluble corrosion products. An example is the attack of sulfurous and sulfuric acid on limestone. Corrosion by direct chemical attack often results in the material being transported into the environment—polymers in certain organic solvents or metals in liquid metals. Direct physical attack often is the result of the mechanical action of the environment, which can remove protective films or actually disintegrate the material by intense local forces. Thus, cavitation corrosion results from the forces of collapsing vapor bubbles in a liquid impinging on the surface

of the material. If the environment contains suspended matter, abrasive wear may cause a form of failure classified as erosion-corrosion.
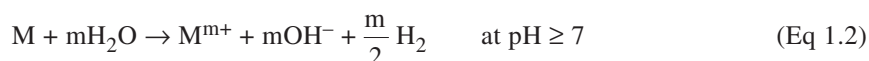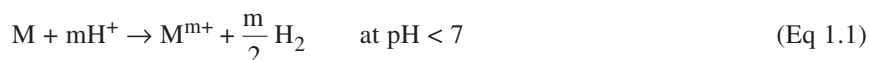
In the present treatment, the fundamental mechanisms involved in aqueous electrochemical corrosion of metals and alloys and the effects of direct chemical and physical processes will be emphasized.

Electrochemical Corrosion Processes and Variables

Before examining in detail the theories of aqueous corrosion processes and the bases for making quantitative calculations of corrosion rates, it will be useful to develop qualitatively the major phenomena involved. The following sections review several general types of metal/corrosive-environment combinations, the chemical reactions involved, idealized mechanisms for the transfer of metal ions to the environment, and the electrochemical processes occurring at the interface between the metal and the aqueous environment.

Uniform Corrosion with pH as the Major Variable

For metals, M, that are thermodynamically unstable in water, the simplest corrosion reactions are:

$$M + mH^+ \rightarrow M^{m+} + \frac{m}{2} H_2 \qquad \text{at pH} < 7 \qquad\qquad \text{(Eq 1.1)}$$

$$M + mH_2O \rightarrow M^{m+} + mOH^- + \frac{m}{2} H_2 \qquad \text{at pH} \geq 7 \qquad \text{(Eq 1.2)}$$

Thus, the metal passes from the metallic state to ions of valence m in solution with the evolution of hydrogen. The reaction is considered to be directly with hydrogen ions in acid solution and progressively with water molecules as the pH increases to neutral and alkaline conditions. Two processes are involved in the reaction, with each involving a change in charge: M to M^{m+} and mH^+ to $m/2$ H_2 (in acid solution). The changes in charge are accomplished by electron transfer from M to H^+. Because the metallic phase is an electron conductor, it supports the electron transfer, allowing the two processes to occur at separate sites on the metal surface. In limiting cases, these processes occur within a few atom diameters on the surface with the sites constantly changing with time, thus producing uniform corrosion. Otherwise, the corrosion is nonuniform. Uniform corrosion supported by pH is represented schematically in Fig. 1.1. In this example, oxygen is excluded by a nitrogen gas purge and overblanket.
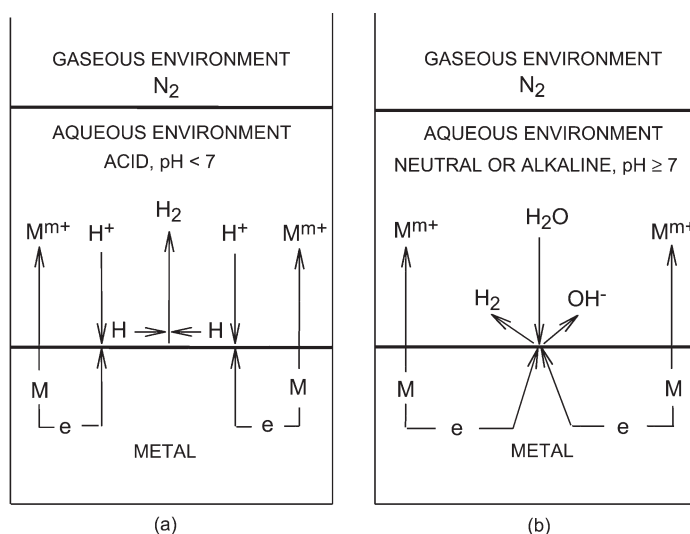
Fig. 1.1 Uniform corrosion supported by controlled pH (oxygen excluded, deaerated). (a) Acid, pH < 7. (b) Neutral or alkaline, pH ≥ 7

Uniform Corrosion with pH and Dissolved Oxygen as Variables

When dissolved oxygen is present in the solution, usually from contact with air (aerated environment), the following reactions apply *in addition* to those just considered:

$$M + \frac{m}{4} O_2 + mH^+ \rightarrow M^{m+} + \frac{m}{2} H_2O \qquad \text{at pH < 7} \qquad \text{(Eq 1.3)}$$

$$M + \frac{m}{4} O_2 + \frac{m}{2} H_2O \rightarrow M^{m+} + mOH^- \qquad \text{at pH} \geq 7 \qquad \text{(Eq 1.4)}$$

Uniform corrosion supported by dissolved oxygen and pH is represented schematically in Fig. 1.2. Since electrons are now consumed by two reactions, the rate of corrosion of the metal increases. In the case of iron, dissolved oxygen is more important in supporting corrosion than the presence of hydrogen ions when the pH is greater than approximately 4. This is an initial illustration of the role of dissolved oxygen (aeration of solutions) in corrosion.

Uniform Corrosion with Corrosion Product Formation

An example of corrosion product formation is the rusting of iron as illustrated in Fig. 1.3. When the pH is greater than approximately 4, and under aerated conditions, a layer of black Fe_3O_4, and possibly $Fe(OH)_2$, forms in contact with the iron substrate. In the presence of the dissolved oxygen, an outer layer of red Fe_2O_3 or FeOOH forms. The adherence
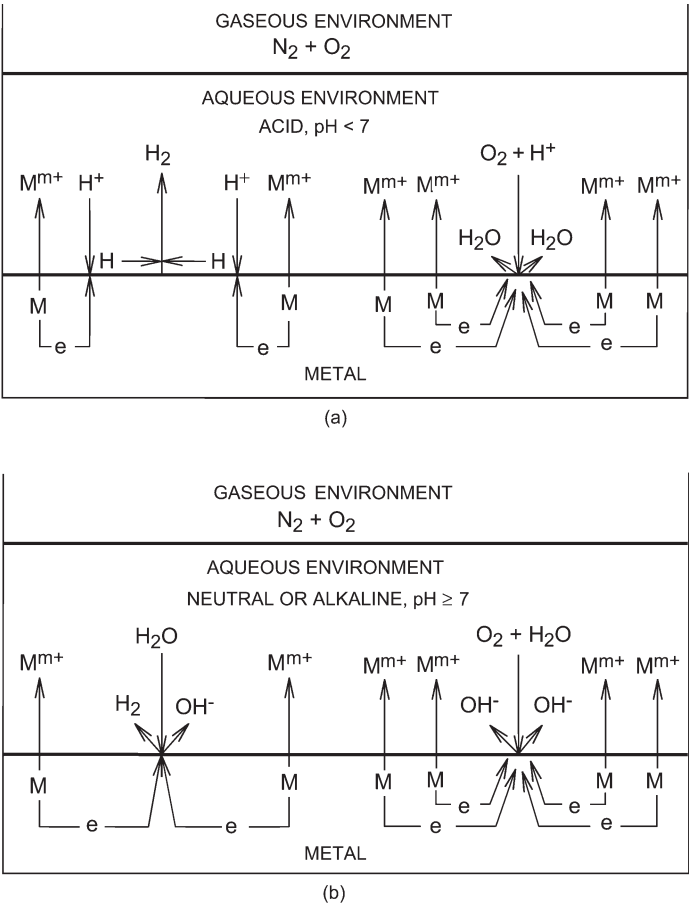
Fig. 1.2 Uniform corrosion supported by pH and dissolved oxygen (aerated). (a) Acid, pH < 7. (b) Neutral or alkaline, pH ≥ 7
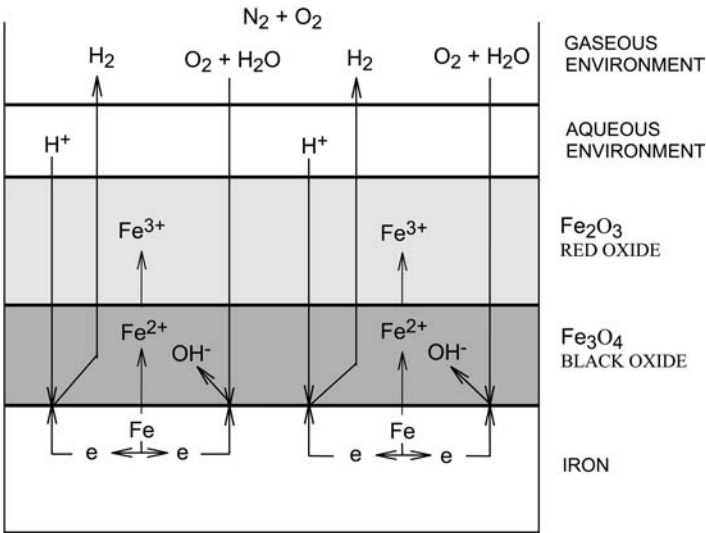

Fig. 1.3 Uniform corrosion with solid corrosion product deposit. Details of the formation of oxide species are not considered at this point.

and porosity of these layers change with time and can be influenced by other chemical species in the environment, such as chloride and sulfate ions. In any case, the formation of the corrosion product layer influences the corrosion rate by introducing a barrier through which ions and oxygen must diffuse to sustain the corrosion process.

Some Basic Terminology, Reactions, and Variables in Aqueous Corrosion

The basic corrosion process is represented in Fig. 1.4. In the simplest case, the corrosion reaction is the transfer of metal atoms from the solid to the solution where they exist as ions (i.e., $M \rightarrow M^{m+} + me$). Because there is a loss of electrons from the metal atom in this transfer, the metal has undergone oxidation. The oxidation is sustained by the consumption of the electrons by another reaction, generalized in this case as $X^{x+} + xe \rightarrow X$. The oxidation occurs at a site on the metal surface referred to as the anodic reaction site and is the location of the loss of metal by corrosion. The electrons are picked up at a cathodic reaction site. The areas over which the anodic and cathodic reactions occur individually vary greatly and may extend from positions a few atom distances apart on the surfaces to microscopic areas, and even to macroscopic areas extending to hundreds of square meters. When the sites are so close together that they cannot be distinguished, and when the sites undergo changes and reversals with time, uniform corrosion is said to occur. With resolvable areas and/or with anodic and cathodic sites that do not change with time, the corrosion will be largely identified by the anode areas only, and localized corrosion is said to occur. Obviously, there are large differences in interpretation of what is uniform corrosion and what is localized corrosion. It frequently depends on the scale of obser-
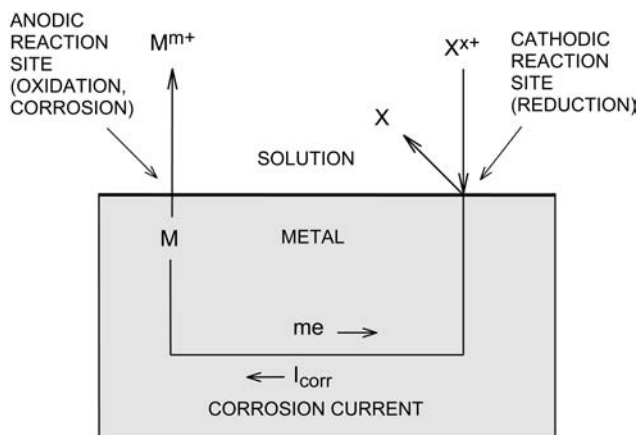

Fig. 1.4 The basic corrosion process

vation, or the magnitude of the difference in corrosion rate between areas that are predominantly anodic and areas that are predominantly cathodic because both reactions often occur over the entire surface. If the two processes are occurring on a microscale, then the anodic and cathodic areas are considered the same and equal to the total area, A. If the two processes are occurring over separate areas, an anodic reaction area, A_a, is distinguished from a cathodic reaction area, A_c.

For a specific example, such as the corrosion of iron in an aerated acid solution, the net reaction due to acidity is:

Anodic reaction:
$$Fe \rightarrow Fe^{2+} + 2e \tag{Eq 1.5}$$

Cathodic reaction:
$$2H^+ + 2e \rightarrow H_2 \tag{Eq 1.6}$$

Overall reaction:
$$Fe + 2H^+ \rightarrow Fe^{2+} + H_2 \tag{Eq 1.7}$$

and the reaction due to dissolved oxygen is:

Anodic reaction:
$$Fe \rightarrow Fe^{2+} + 2e \tag{Eq 1.8}$$

Cathodic reaction:
$$\frac{1}{2}O_2 + 2H^+ + 2e \rightarrow H_2O \tag{Eq 1.9}$$

Overall reaction:
$$Fe + \frac{1}{2}O_2 + 2H^+ \rightarrow Fe^{2+} + H_2O \tag{Eq 1.10}$$
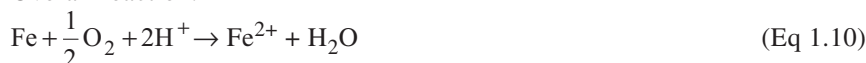
To show that these reactions actually proceed to the right (i.e., to show that corrosion actually occurs), it is necessary to calculate the Gibbs free-energy change and find that it is negative. To make this calculation requires quantitative information on the activity or effective concentration of iron ions ($a_{Fe^{2+}}$) in the solution, the acidity, or pH, and the concentration of dissolved oxygen that is related to the partial pressure of the oxygen, P_{O_2}, in contact with the solution. It is demonstrated in the following chapter that the change in the Gibbs free energy is negative for these reactions at all values of pH, and hence, iron tends to corrode at all pH values. The rate of corrosion, however, depends on factors influencing the kinetic mechanisms of the several processes involved in the transport of ions from metal to solution and in the supporting cathodic reactions. In addition to the species in solution relating directly to the above reactions (Fe^{2+}, H^+, and O_2), other species in solution can affect both the tendency to corrode in terms of thermodynamic driving forces and the kinetics of the several steps involved. For example,

complexing agents reacting with metal ions in solution reduce the concentration of free metal ions and make it more favorable thermodynamically for metal ions to pass into solution, thereby increasing the corrosion rate. Conversely, if species in solution can form precipitates with metal ions and form protective diffusion barriers at the interface, corrosion rates may be decreased significantly.

The important processes, terminology, and variables associated with the anodic and cathodic reactions, and which characterize the environment, are summarized in Table 1.1.

Table 1.1   Summary of processes, terminology, and variables associated with aqueous corrosion(a)

Anode

Area, A_a
Reactions (oxidation)
   General, $M \rightarrow M^{m+} + me$
   Reduced state $\rightarrow$ oxidized state
   Example, $Fe \rightarrow Fe^{2+} + 2e$

Cathode

Area, A_c
Reactions (reduction)
   General, $X^{x+} + xe \rightarrow X$
   Oxidized state $\rightarrow$ reduced state
   Examples
     Deaerated
       Acid, $H^+ + e \rightarrow \frac{1}{2} H_2$
       Neutral or alkaline
         $H_2O + e \rightarrow \frac{1}{2} H_2 + OH^-$
     Aerated (additive to above)
       Acid, $O_2 + 4H^+ + 4e \rightarrow 2H_2O$
       Neutral or alkaline
         $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

Aqueous phase variables

Acidity
   H^+ concentration
   C_{H^+}, molal concentration
   a_{H^+}, activity
   $pH = -\log a_{H^+}$
   $(a_{H^+})(a_{OH^-}) = 10^{-14}$
Dissolved gases
   H_2, $C_{H_2} \propto P_{H_2}$
   O_2, $C_{O_2} \propto P_{O_2}$

Other dissolved species

Fe^{2+}, Cl^-, SO_4^{2-}, etc., with activities $a_{Fe^{2+}}$, etc.

Note: C_Z = Molal concentration of species Z; a_Z = Activity or effective concentration of species Z; P_Z = Partial pressure of species Z. (a) Figure 1.4 shows a schematic representation of the interrelationships of the processes characterized in this table.