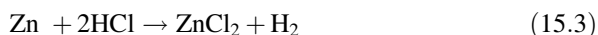# Chapter 15
Corrosion and Stress Corrosion Cracking Fundamentals

Corrosion can be broadly described as the destruction or deterioration of a metal or alloy by way of a chemical or electrochemical reaction with its environment. It can be considered as extractive metallurgy in reverse, or the process by which a metal is returned to its natural state—an oxide. Corrosion can occur in wet (aqueous) environments and also in dry (gaseous) environments, and can occur at a high rate or a very slow rate. It can also take many forms, as discussed in the next section.
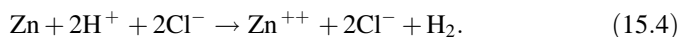
Nearly, all metallic corrosion processes involve the transfer of electronic charge in aqueous solutions. Consider the corrosion of zinc in hydrochloric (HCl) acid. Zinc reacts with the acid to form soluble zinc chloride and liberates hydrogen bubbles at the surface. It occurs by two reactions. The first is the oxidation of Zn to Zn^{++} and the liberation of 2 electrons, and the second is the combination of the two electrons with 2 hydrogen ions to yield 2 hydrogen atoms or H_2. The reactions are as follows:

$$Zn \rightarrow Zn^{++} + 2e^- \tag{15.1}$$

$$2H^+ + 2e^- \rightarrow H_2, \tag{15.2}$$

for a total reaction described by:

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \tag{15.3}$$

or in ionic form:

$$Zn + 2H^+ + 2Cl^- \rightarrow Zn^{++} + 2Cl^- + H_2. \tag{15.4}$$

The reaction in Eq. (15.1) is the anodic, or oxidation reaction in which the valence of Zn increases from 0 to +2 and liberates electrons. The reaction in Eq. (15.2) is the cathodic, or reduction reaction in which the oxidation state of H decreases from +1 to 0 by consuming electrons. Water is the carrier of ions, or the electrolyte. Note that the reactions shown in Eqs. (15.1) and (15.2) can occur simultaneously on the surface of a piece of Zn immersed in HCl. These reactions involve the transfer of charge or current. The relationship between current and mass of the reacting metal, M, is given by Faraday's law:

$$M = kIt, \tag{15.5}$$

where I is the current (amperes, A), t is the time (s), and k is the electrochemical equivalent (g/Coulomb or g/C) given by:

$$k = A/nF, \tag{15.6}$$

where A is the atomic weight, n is the number of equivalents exchanged, and F is Faraday's constant (96,500 C/eq). Recall that a Coulomb is the amount of charge transferred by a current of one ampere for 1 s. Hence, the corrosion rate of a metal is directly related to its reaction rate with the environment.

This chapter will focus on the fundamentals of aqueous corrosion by virtue of its importance in water reactor systems, and provide a foundation for understanding the interplay between corrosion and irradiation in the degradation of metals and alloys treated in Chap. 16. It begins with a description of the various forms of corrosion followed by the thermodynamics of corrosion including the use of potential–pH or Pourbaix diagrams, kinetics of corrosion, passivity, crevice corrosion, and then stress corrosion cracking. The latter two topics provide a basis for understanding the processes of irradiation accelerated corrosion (IAC) and irradiation-assisted stress corrosion cracking (IASCC).

15.1 Forms of Corrosion

While corrosion is most often envisioned as the loss of metal from a surface exposed to the electrolyte, corrosion can take many forms as summarized in Fig. 15.1. The eight forms of corrosion include uniform corrosion, crevice corrosion, pitting, intergranular attack, selective leaching or dealloying, erosion corrosion, stress corrosion cracking, and hydrogen damage.

Uniform corrosion

Uniform corrosion is characterized by a reaction that proceeds uniformly over the entire surface of the component, e.g., rusting of iron or tarnishing of silver. Various units are used to describe the uniform removal of metal, such as the thinning rate in mm/yr or the mass loss per unit area in g/m^2yr. Uniform corrosion is not really uniform on a microscopic level. In fact, the orientation of grain faces on the surface will determine which corrodes the fastest. As grains dissolve away, preferential sites for attack will alternate. All other forms of corrosion can be broadly classified as localized corrosion.

Crevice corrosion

Crevice corrosion is characterized by intense localized corrosion that occurs most frequently within crevices or shielded areas on metal surfaces exposed to corrosives. The attack is usually associated with small volumes of stagnant solution.
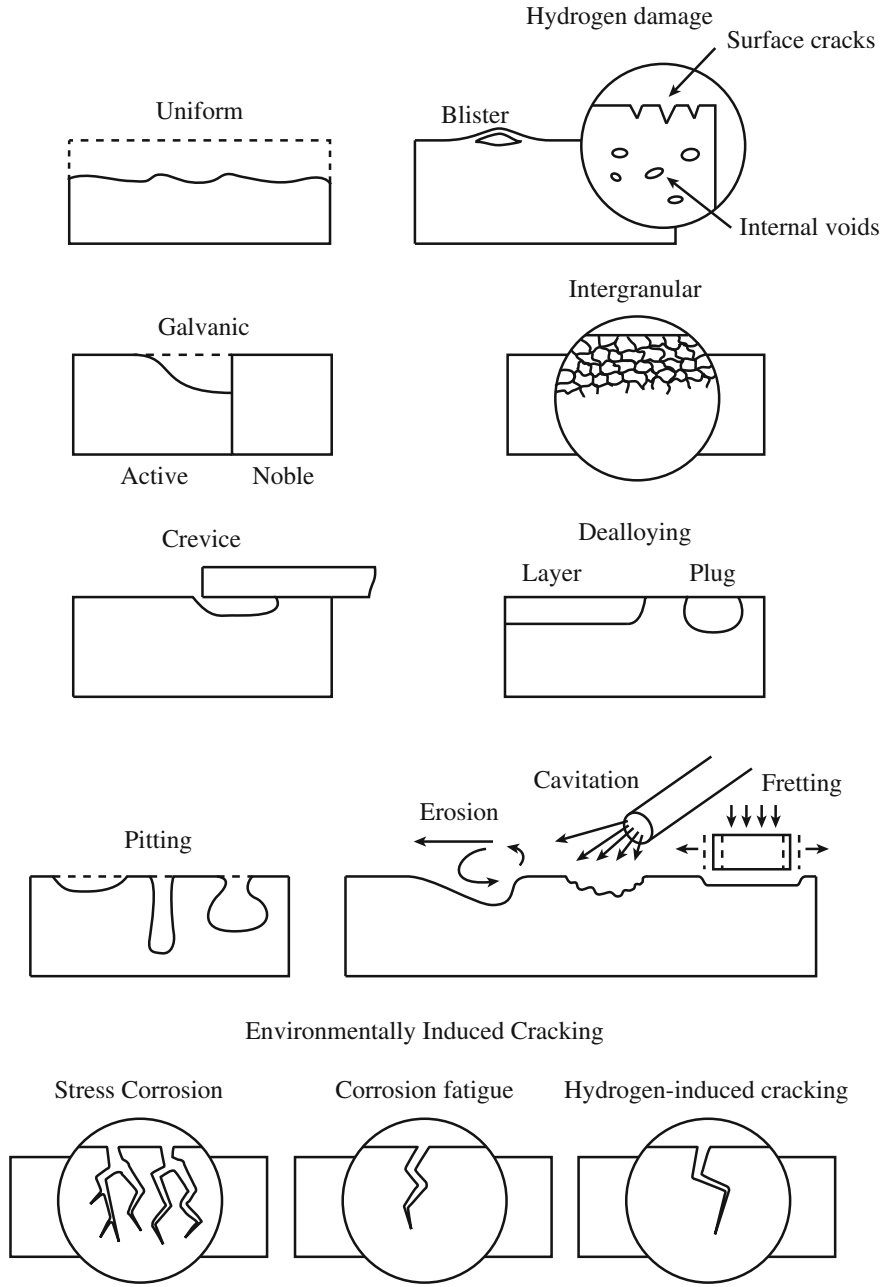
Fig. 15.1 Eight forms of corrosion (after [2])