

CHAPTER II

CORROSION PRINCIPLES[21]

Corrosion Aspects

1. Definition of Corrosion

Corrosion may be defined in several ways :

(1) destruction or deterioration of a material because of reaction with its environment; (2) destruction of material by means other than straight mechanical; and (3) extractive metallurgy in reverse. Definitions (1) and (2) are preferred for purposes of this research. Figure 2.1 illustrates definition (3). Extractive metallurgy is concerned primarily with the winning of the metal from the ore and refining or alloying the metal for use. Most iron ores contain oxides of iron, and rusting of steel by water and oxygen results in a hydrated iron oxide. Rusting is a term reserved for steel and iron corrosion, although many other metals form their oxides when corrosion occurs.

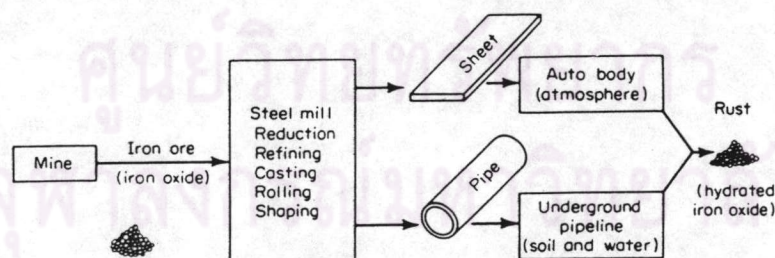
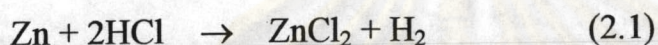


Figure 2.1 Metallurgy in reverse

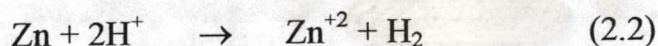
2. Electrochemical Aspects

2.1 Electrochemical Reactions

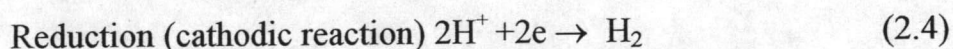
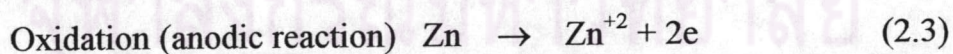
The electrochemical nature of corrosion can be illustrated by the attack of zinc by hydrochloric acid. When zinc is placed in dilute hydrochloric acid, a vigorous reaction occurs; hydrogen gas is evolved and the zinc dissolves, forming a solution of zinc chloride. The reaction is :



Noting that the chloride ion is not involved in the reaction, this equation can be written in the simplified form :



Hence, zinc reacts with the hydrogen ions of the acid solution to form zinc ions and hydrogen gas. Examining the above equation, it can be seen that during the reaction, zinc is oxidized to zinc ions and hydrogen ions are reduced to hydrogen. Thus Eq. (2.2) can be conveniently divided into two reactions, the oxidation of zinc and the reduction of hydrogen ions :



An oxidation or anodic reaction is indicated by an increase in valence or a production of electrons. A decrease in valence charge or the consumption of electrons signifies a reduction or cathodic reaction. Equations (2.3) and (2.4) are partial reactions-both must occur simultaneously and at the same rate on the

metal surface. If this were not true, the metal would spontaneously become electrically charged, which is clearly impossible. This leads to one of the most

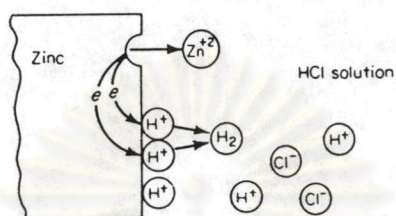


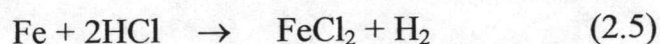
Figure 2.2 Electrochemical reactions occurring during corrosion of zinc in airfree hydrochloric acid.

important basic principles of corrosion : during metallic corrosion, the rate of oxidation equals the rate of reduction (in terms of electron production and consumption).

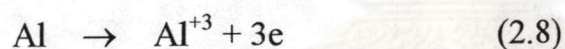
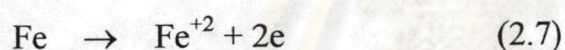
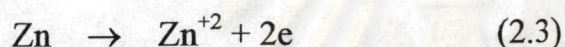
The above concept is illustrated in Fig. 2.2. Here a zinc atom has been transformed into a zinc ion and two electrons. These electrons which remain in the metal are immediately consumed during the reduction of hydrogen ions. Figure 2.2 shows these two processes spatially separated for clarity. Whether or not they are actually separated or occur at the same point on the surface does not affect the above principle of charge conservation. In some corrosion reactions the oxidation reaction occurs uniformly on the surface, while in other cases it is localized and occurs at specific areas. These effects are described in detail later.

The corrosion of zinc in hydrochloric acid is an electrochemical process. That is, any reaction which can be divided into two (or more) partial reactions of oxidation and reduction is termed electrochemical. Dividing corrosion or other electrochemical reactions into partial reactions makes them

simpler to understand. Iron and aluminium, like zinc, are also rapidly corroded by hydrochloric acid. The reactions are :

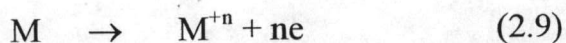


Although at first sight these appear quite different, comparing the partial processes of oxidation and reduction indicates that reactions (2.1), (2.5), and (2.6) are quite similar. All involve the hydrogen ion reduction and they differ only in their oxidation or anodic reactions :

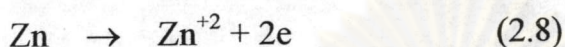
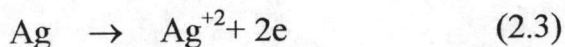


Hence, the problem of hydrochloric acid corrosion is simplified since in every case the cathodic reaction is the evolution of hydrogen gas according to reaction (2.4). This also applies to corrosion in other acids such as sulfuric, phosphoric, hydrofluoric, and water-soluble organic acids such as formic and acetic. In each case, only the hydrogen ion is active, the other ions such as sulfate, phosphate, and acetate do not participate in the electrochemical reaction.

When viewed from the standpoint of partial processes of oxidation and reduction, all corrosion can be classified into a few generalized reactions. The anodic reaction in every corrosion reaction is the oxidation of a metal to its ion. This can be written in the general form :

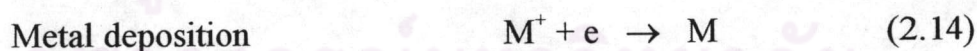
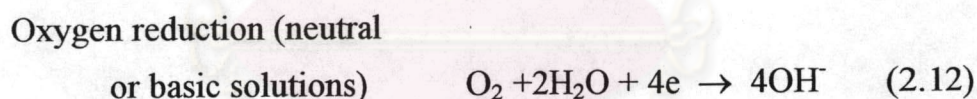
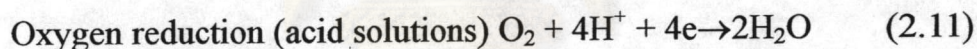


A few examples are :



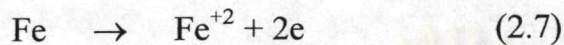
In each the number of electrons produced equals the valence of the ion.

There are several different cathodic reactions which are frequently encountered in metallic corrosion. The most common cathodic reactions are :

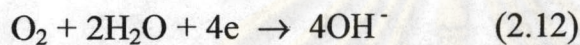


Hydrogen evolution is a common cathodic reaction since acid or acidic media are frequently encountered. Oxygen reduction is very common, since any aqueous solution in contact with air is capable of producing this reaction. Metal ion reduction and metal deposition are less common reactions and are most frequently found in chemical process streams. All of the above reactions are quite similar—they consume electrons.

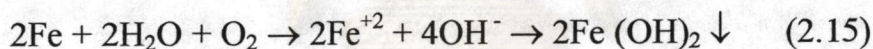
The above partial reactions can be used to interpret virtually all corrosion problems. Consider what happens when iron is immersed in water or seawater which is exposed to the atmosphere (an automobile fender or a steel pier piling are examples). Corrosion occurs. The anodic reaction is :



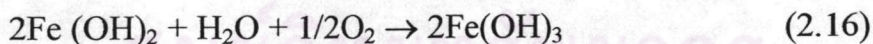
Since the medium is exposed to the atmosphere, it contains dissolved oxygen. Water and seawater are nearly neutral, and thus the cathodic reaction is :



Remembering that sodium and chloride ions do not participate in the reaction, the overall reaction can be obtained by adding (2.7) and (2.12)

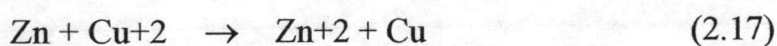


Ferrous hydroxide precipitates from solution. However, this compound is unstable in oxygenated solutions and is oxidized to the ferric salt :

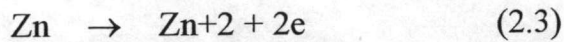


The final product is the familiar rust.

The classic example of a replacement reaction, the interaction of zinc with copper sulfate solution, illustrates metal deposition :



or, viewed as partial reactions :



The zinc initially becomes plated with copper and eventually the products are copper sponge and zinc sulfate solution.

During corrosion, more than one oxidation and one reduction reaction may occur. When an alloy is corroded, its component metals go into solution as their respective ions. More importantly, more than one reduction reaction can occur during corrosion. Consider the corrosion of zinc in aerated hydrochloric acid. Two cathodic reactions are possible : the evolution of hydrogen and the reduction of oxygen. This is illustrated schematically in Fig. 2.3. On the surface of the zinc there are two electron-consuming reactions. Since the rates of oxidation and reduction must be equal, increasing the total reduction rate increased the rate of zinc solution. Hence, acid solutions containing simply provides a new means of “electron disposal.” The same effect is observed if

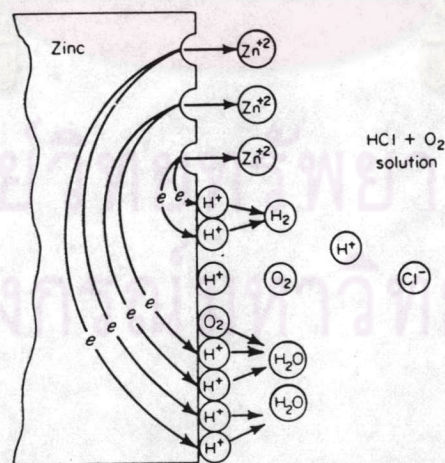
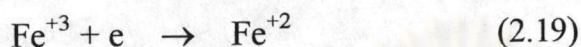


Figure 2.3 Electrochemical reactions occurring during corrosion of zinc in aerated hydrochloric acid.

any oxidizer is present in acid solutions. A frequent impurity in commercial hydrochloric acid is ferric ion, present as ferric chloride. Metals corrode much more rapidly in such impure acid because there are two cathodic reactions, hydrogen evolution and ferric ion reduction :



Since the anodic and cathodic reactions occurring during corrosion are mutually dependent, it is possible to reduce corrosion by reducing the rates of either reaction. In the above case of impure hydrochloric acid, it can be made less corrosive by removing the ferric ions and consequently reducing the total rate of cathodic reduction. Oxygen reduction is eliminated by preventing air from contacting the aqueous solution or by removing air which has been dissolved. Iron will not corrode in air-free water or seawater because there is no cathodic reaction possible.

If the surface of the metal is coated with paint or other nonconduction film, the rates of both anodic and cathodic reactions will be greatly reduced and corrosion will be retarded. A corrosion inhibitor is a substance which when added in small amounts to a corrosive, reduces its corrosivity. Corrosion inhibitors function by interfering with either the anodic or cathodic reactions or both. Many of these inhibitors are organic compounds; they function by forming an impervious film on the metal surface or by interfering with either the anodic or cathodic reactions. High-molecular-weight amines retard the hydrogen-evolution reaction and subsequently reduce corrosion rate. It is obvious that good conductivity must be maintained in both the metal and the electrolyte during the corrosion reaction. Of course it is not practical to increase the electrical resistance of the metal, since the sites of the anodic and cathodic reactions are not known, nor are they predictable. However, it is possible to increase the electrical resistance of the electrolyte or corrosive and thereby reduce corrosion. Very pure water is much less corrosive than impure or natural

waters. The low corrosivity of high-purity water is primarily due to its high electrical resistance.

2.2 Polarization

The concept of polarization is briefly discussed here because of its importance in understanding corrosion behavior and corrosion reactions.

The rate of and electrochemical reaction is limited by various physical and chemical factors. Hence, and electrochemical reaction is said to be polarized or retarded by these environmental factors. Polarization can be conveniently divided into two different types, activation polarization and concentration polarization.

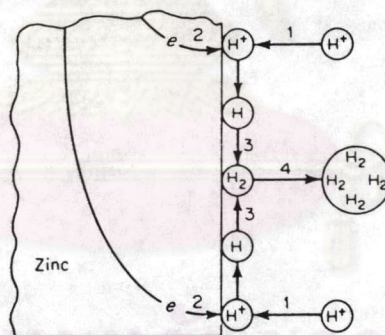


Figure. 2.4 Hydrogen-reduction reaction under activation control (simplified).

Activation polarization refers to an electrochemical process which is controlled by the reaction sequence at the metal-electrolyte interface. This is easily illustrated by considering hydrogen-evolution reaction on zinc during corrosion in acid solution. Figure 2.4 schematically shows some of the possible steps in hydrogen reduction on a zinc surface. These steps can also be applied to the reduction of any species on a metal surface. The species must first be

adsorbed or attached to the surface before the reaction can proceed according to step 1. Following this, electron transfer (step 2) must occur, resulting in a reduction of the species. As shown in step 3, two hydrogen atoms then combine to form a hydrogen molecule. These hydrogen molecules then combine to form a bubble of hydrogen gas (step 4). The speed of reduction of the hydrogen ions will be controlled by the slowest of these steps. This is a highly simplified picture of the reduction of hydrogen; numerous mechanisms have been proposed, most of which are much more complex than that shown in Fig. 2.4.

Concentration polarization refers to electrochemical reactions which are controlled by the diffusion in the electrolyte. This is illustrated in Fig. 2.5 for the case of hydrogen evolution. Here, the number of hydrogen ions in solution is quite small, and the reduction rate is controlled by the diffusion of hydrogen

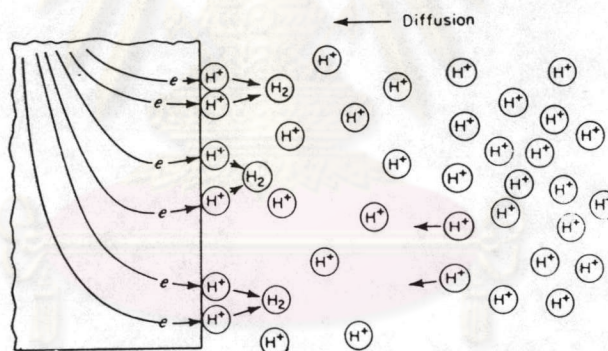


Figure 2.5 Concentration polarization during hydrogen reduction.

ions to the metal surface. Note that in this case the reduction rate is controlled by processes occurring within the bulk solution rather than at the metal surface. Activation polarization usually is the controlling factor during corrosion in media containing a high concentration of active species (e.g., concentrated acids). Concentration polarization generally predominates when the concentration of the reducible species is small (e.g., dilute acids, aerated salt solutions). In most instances concentration polarization during metal dissolution is usually small and can be neglected; it is only important during reduction reactions.

The importance of distinguishing between activation and concentration polarization cannot be overemphasized. Depending on what kind of polarization is controlling the reduction reaction, environmental variables produce different effects. For example, any changes in the system which increase the diffusion rate will decrease the effects of concentration polarization and hence increase reaction rate. Thus, increasing the velocity or agitation of the corrosive medium will increase rate only if the cathodic reactions are controlled by activation polarization. If both the anodic and cathodic reactions are controlled by activation polarization, agitation will have no influence on corrosion rate.

2.3 Passivity

The phenomenon of metallic passivity has fascinated scientists and engineers for over 120 years, since the days of Faraday. The phenomenon itself is rather difficult to define because of its complex nature and the specific conditions under which it occurs. Essentially, passivity refers to the loss of chemical reactivity experienced by certain metals and alloys under particular environmental conditions. That is, certain metals and alloys become essentially inert and act as if they were noble metals such as platinum and gold. Fortunately, from an engineering standpoint, the metals most susceptible to this kind of behavior are the common engineering and structural materials, including iron, nickel, silicon, chromium, titanium, and alloys containing these metals. Also, under limited conditions other metals such as zinc, cadmium, tin, uranium, and thorium have also been observed to exhibit passivity effects.

Passivity, although difficult to define, can be quantitatively described by characterizing the behavior of metals which show this unusual effect. First, consider the behavior of what can be called a normal metal, that is, a metal which does not show passivity effects. In Fig. 2.6 the behavior of such a metal is illustrated. Let us assume that we have a metal immersed in an air-free acid

solution with an oxidizing power corresponding to point A and a corrosion rate corresponding to this point. If the oxidizing power of this solution is increased, say, by adding oxygen or ferric ions, the corrosion rate of the metal will increase rapidly. Note that for such a metal, the corrosion rate increases as the oxidizing power of the solution increases. This increase in rate is exponential and yields a straight line when plotted on a semilogarithmic scale as in Fig. 2.6. The oxidizing power of the solution is controlled by both the specific oxidizing power of the reagents and the concentration of these reagents. Oxidizing power can be precisely defined by electrode potential.

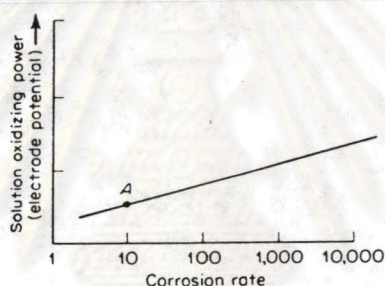


Figure 2.6 Corrosion rate of a metal as a function of solution oxidizing power (electrode potential).

Figure 2.7 illustrates the typical behavior of a metal which demonstrates passivity effects. The behavior of this metal or alloy can be conveniently divided into three regions, active, passive, and transpassive. In the active region, the behavior of this material is identical to that of a normal metal. Slight increase in the corrosion rate. If more oxidizing agents produce little if any change in the corrosion rate of the material. Finally, at very high concentrations of oxidizers, or in the presence of very powerful oxidizers, the corrosion rate again increases with increasing oxidizer power. This region is termed the transpassive region.

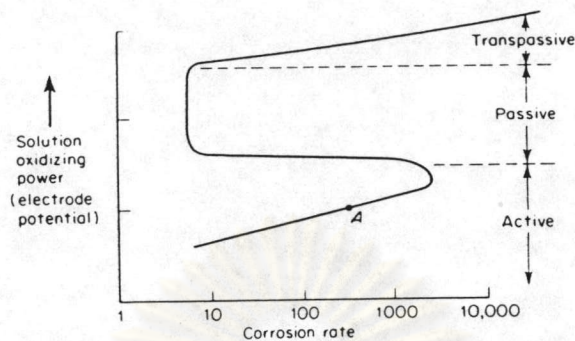


Figure 2.7 Corrosion characteristics of an active-passive metal as a function of solution oxidizing (electrode potential).

It is important to note that during the transition from the active to the passive region, a 10^3 to 10^6 reduction in corrosion rate is usually observed. The precise cause for this unusual active-passive-transpassive transition is not completely understood. It is a special case of activation polarization due to the formation of a surface film or protective barrier which is stable over a considerable range of oxidizing power and is eventually destroyed in strong oxidizing solutions. The exact nature of this barrier is not understood. However, for the purposes of engineering application, it is not necessary to understand the mechanism of this unusual effect completely, since it can be readily characterized by data such as are shown in Fig. 2.7.

To summarize, metals which possess an active-passive transition become passive or very corrosion resistant in moderately to strongly oxidizing environments. Under extremely strong oxidizing conditions, these materials lose their corrosion-resistant properties. These characteristics have been successfully used to develop new methods of preventing corrosion and to predict corrosion resistance.

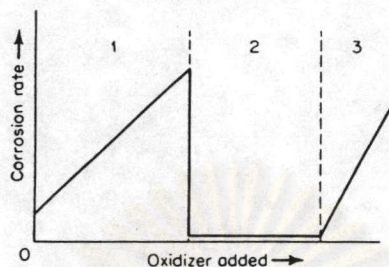
Environment Effects on Corrosion

Frequently in the process industries, it is desirable to change process variables. One of the most frequent questions is : What effect will this change have on corrosion rates? In the following section some of the more common environmental variables are considered on the basis of the concepts developed above.

1. Effect of Oxygen and Oxidizers

The effect of oxidizers and oxidizing power was discussed above in connection with the behavior of active-passive shown in Fig. 2.8. Note that the shape of this graph is similar to that of Fig. 2.7 and that this figure is divided into three different sections. Behavior corresponding to section 1 is characteristic of normal metals and also of active-passive metals when they exist only in the active state. For metals which demonstrate active-passive transition, passivity is achieved only if a sufficient quantity of oxidizer or a sufficiently powerful oxidizer is added to the medium. Increasing corrosion rate with increasing oxidizer concentrations as shown in section 1 is characteristic of Monel and copper in acid solutions containing oxygen. Both of these materials do not passivate. Although iron can be made to passivate in water, the solubility of oxygen is limited, and in most cases it is insufficient to produce a passive state as shown in Fig 2.7.

An increase in corrosion rate, followed by a rapid decrease, and then a corrosion rate which is essentially independent of oxidizer concentration, is characteristic of such active-passive metals and alloys as 18Cr-8Ni stainless steel and titanium.



Examples

1 : Monel in $\text{HCl} + \text{O}_2$

Cu in $\text{H}_2\text{SO}_4 + \text{O}_2$

Fe in $\text{H}_2\text{O} + \text{O}_2$

1-2 : 18Cr-8Ni in $\text{H}_2\text{SO}_4 + \text{Fe}^{+3}$

Ti in $\text{HCl} + \text{Cu}^{+2}$

2 : 18Cr-8Ni in HNO_3

1-2-3 : 18Cr-8Ni in concentrated

$\text{H}_2\text{SO}_4 + \text{HNO}_3$ mixtures

at elevated temperatures

Figure 2.8 Effect of oxidizers and aeration on corrosion rate.

If an active-passive metal is initially passive in a corrosive medium, the addition of further oxidizing agents has only a negligible effect on corrosion rate. This condition frequently occurs when an active-passive metal is immersed in an oxidizing medium such as nitric acid or ferric chloride. The behavior represented by sections 2 and 3 results when a metal, initially in the passive state, is exposed to very powerful oxidizers and makes a transition into the transpassive region. This kind of behavior is frequently observed with stainless steel when very powerful oxidizing agents such as chromates are added to the corrosive medium. In hot nitration mixtures containing

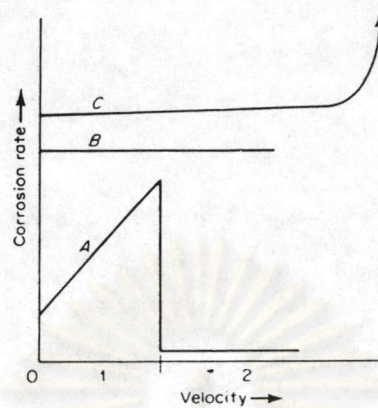
concentrated sulfuric and nitric acids, the entire active-passive-transpassive transition can be observed with the increased ratios of nitric to sulfuric acid.

It is readily seen that the effect of oxidizer additions or the presence of oxygen on corrosion rate depends on both the medium and the metals involved. The corrosion rate may be increased by the addition of oxidizers, oxidizers may have no effect on the corrosion rate, or a very complex behavior may be observed.

By knowing the basic characteristics of a metal or alloy and the environment to which it is exposed, it is possible to predict in many instances the effect of oxidizer additions.

2. Effects of Velocity

The effects of velocity on corrosion rate are, like the effects of oxidizer additions, complex and depend on the characteristics of the metal and the environment to which it is exposed. Figure 2.9 shows typical observation when agitation or solution velocity are increased. For corrosion processes which are controlled by activation polarization, agitation and velocity have no effect on the corrosion rate as illustrated in curve B. If the corrosion process is under cathodic diffusion control, then agitation increases the corrosion rate as shown in curve A, section, 1. This effect generally occurs when an oxidizer is present in very small amounts, as is the case for dissolved oxygen in acids or water.



Examples

Curve A :

1 : Fe in $H_2O + O_2$

Cu in $H_2O + O_2$

1-2 : 18Cr-8Ni in $H_2SO_4 + Fe^{+3}$

Ti in $HCl + Cu^{+2}$

Curve B : Fe in dilute HCl

18Cr-8Ni in H_2SO_4

Curve C : Pb in dilute H_2SO_4

Fe in concentrated H_2SO_4

Figure 2.9 Effect of velocity on corrosion rate.

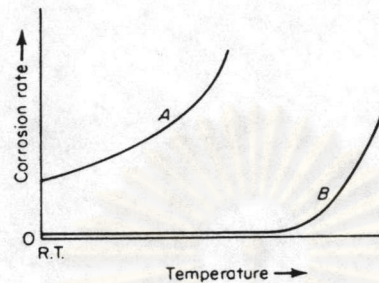
If the process is under diffusion control and the metal is readily passivated, then the behavior corresponding to curve A, sections 1 and 2, will be observed. That is, with increasing agitation, the metal will undergo an active-to-passive transition. Easily passivated materials such as stainless steel and titanium frequently are more corrosion resistant when the velocity of the corrosion medium is high.

Some metals owe their corrosion resistance in certain mediums to the formation of massive bulk protective films on their surfaces. These films differ

from the usual passivation films in that they are readily visible and much less tenacious. It is believed that both lead and steel are protected from attack in sulfuric acid by insoluble sulfate films. When materials such as these are exposed to extremely high corrosive velocities, mechanical damage or removal of these films can occur, resulting in accelerated attack as shown in curve C. This is called erosion corrosion and is discussed in next section. In the case of curve C, note that until mechanical damage actually occurs, the effect of agitation or velocity is virtually negligible.

3. Effect of Temperature

Temperature increased the rate of almost all chemical reactions. Figure 2.10 illustrates two common observations on the effect of temperature on the corrosion rates of metals. Curve A represents the behavior noted above, a very rapid or exponential rise in corrosion rate with increasing temperature. Behavior such as noted in curve B is also quite frequently observed. That is, an almost negligible temperature effect followed by a very rapid rise in corrosion rate at higher temperatures. In the case of 18.8 stainless steel in nitric acid, this effect is readily explained. Increasing the temperature of nitric acid greatly increases its oxidizing power. At low or moderate temperatures, stainless steels exposed to nitric acid are in the passive state very close to the transpassive region. Hence, an increase in oxidizing power causes a very rapid increase in the corrosion rate of these materials. A similar sort of mechanism may explain the behavior of Monel and nickel, as noted in fig. 2.10. However, it is possible that curves such as B in many instances erroneously represent actual behavior. If the corrosion rate at low temperature is very low, and increases exponentially, linear plots will appear as curve B. That is, corrosion rate increases rapidly with temperature; this is not evident in the usual plots of corrosion rate versus temperature because of the choice of scales.



Examples

Curve A : 18Cr-8Ni H_2SO_4

Ni in HCl

Fe in HF

Curve B : 18Cr-8Ni in HNO_3

Monel in HF

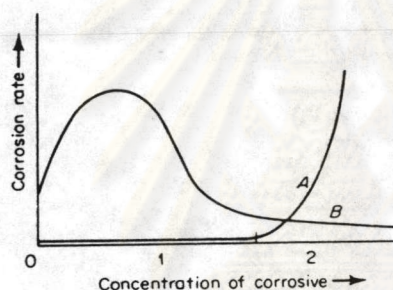
Ni in NaOH

Figure 2.10 Effect of temperatur on corrosion rate.

4. Effects of Corrosive Concentration

Figure 2.11 shows schematically the effects of corrosive concentration on corrosion rate. Note that curve A has two sections, 1 and 2. Many materials which exhibit passivity effects are only negligibly affected by wide changes in corrosive concentration as shown in curve A, Section 1. Other materials show similar behavior except at very high corrosive concentrations, when the corrosion rate increases rapidly as shown in curve A, sections 1 and 2. Lead is a material which shows this effect, and it is believed to be due to the fact that lead sulfate, which forms a protective film in low concentrations of sulfuric acid, is soluble in concentrated sulfuric acid. The behavior of acids which are soluble in all concentrations of water offer yield curves similar to

curve B in Fig. 2.11. Initially, as the concentration of corrosive is increased, the corrosion rate is likewise increased. This is primarily due to the fact that the amount of hydrogen ions which are the active species are increased as acid concentration is increased. However, as acid concentration is increased further, corrosion rate reaches a maximum and then decreases. This is undoubtedly due to the fact that at very high concentrations of acids ionization is reduced. Because of this, many of the common acids such as sulfuric, acetic, hydrofluoric, and others, are virtually inert when in the pure state, or 100% concentration, and at moderate temperatures.



Examples

Curve A :

1 : Ni in NaOH

18Cr-8Ni HNO₃

Hastelloy B in HCl

Ta in HCl

1-2 : Monel in HCl

Pb in

Curve B :

Al in acetic acid and HNO₃

18Cr-8Ni in H₂SO₄

Fe in H₂SO₄

Figure 2.11 Effect of corrosive concentration on corrosion rate.

5. Effect of Galvanic Coupling

In many practical applications, the contact of dissimilar materials is unavoidable. In complex process streams and piping arrangements, different metals and alloys are frequently in contact with each other and the corrosive medium. The effects of galvanic coupling will be only briefly mentioned here. Consider a piece of zinc immersed in a hydrochloric acid solution and contacted to a noble metal such as platinum (Fig. 2.12). Since platinum is inert in this medium, it tends to increase the surface area at which hydrogen evolution can occur. Further, hydrogen evolution occurs much more readily on the surface of platinum than on zinc. These two factors increase the rate of the cathodic reaction and consequently increase the corrosion rate of the zinc. Note that the effect of galvanic coupling in this instance is virtually identical to that of adding an oxidizer to a corrosive solution. In both instances, the rate of electron consumption is increased and hence the rate of metal dissolution increases. It is important to recognize the galvanic coupling does not always increase the corrosion rate of a given metal; in some cases it decreased the corrosion rate of the metal.

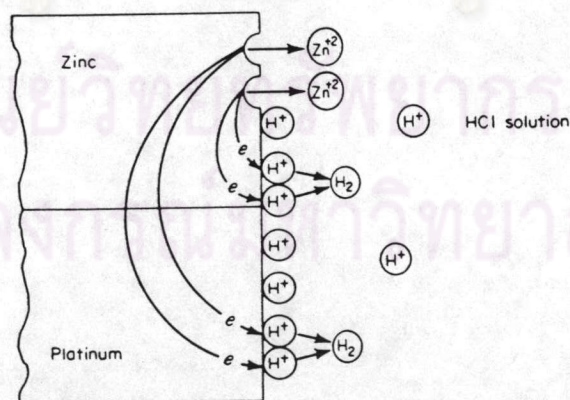


Figure 2.12 Electrochemical reactions occurring on galvanic couple of zinc and platinum.

Metallurgical Aspects

1. Metallic Properties

Metals and alloys are crystalline solids. That is, the atoms of a metal are arranged in a regular, repeating array. The three most common crystalline arrangements of metals are illustrated in Fig. 2.13. Iron and steel have a body-centered cubic structure, the austenitic stainless steels are face-centered cubic, and magnesium possesses a hexagonal close-packed lattice structure. Metallic properties differ from those of other crystalline solids such as ceramics and chemical salts. They are ductile (can be deformed plastically without fracturing) and are good conductors of electricity and heat. These properties result from the nondirectional bonding of metals—each atom is bonded to many of its neighbors. Hence, the crystal structures are simple and closely packed as shown in Fig. 2.13. Ductility is probably the most important property of metals. Their ductility permits almost unlimited fabrication. Further, when highly stressed, metals usually yield plastically before fracturing. This property is, of course, invaluable in engineering applications.

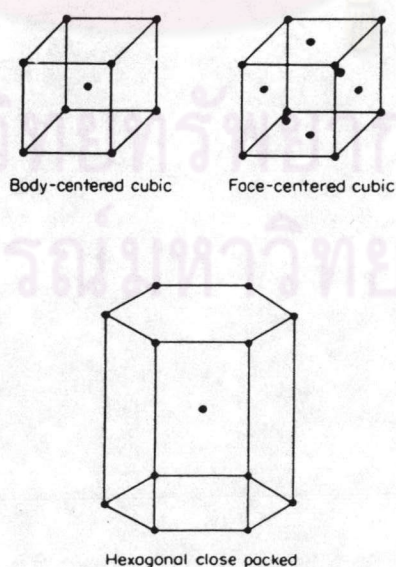


Figure. 2.13 Metallic crystal structures.

When a metal solidifies during casting, the atoms, which are randomly distributed in the liquid state, arrange themselves in a crystalline array. However, this ordering usually begins at many points in the liquid, and as these blocks of crystals or grains meet, there is a mismatch at their boundary. When the metal has solidified and cooled, there will be numerous regions of mismatch between each grain. These regions are called grain boundaries. Figure 2.14 shows this using a two-dimensional representation of a grain boundary. Since the most stable configuration of the metal is its particular crystal lattice, grain boundaries are high-energy areas and are more active chemically. Hence, grain boundaries are usually attacked slightly more rapidly than grain faces when exposed to a corrosive. Metallographic etching, in many cases, depends on this difference in chemical reactivity to develop contrast between grains. Figure 2.15 shows a magnified view of 18.8 stainless steel which has been etched in acid solution. The grain boundaries appear dark because they have been more severely attacked than the grains.

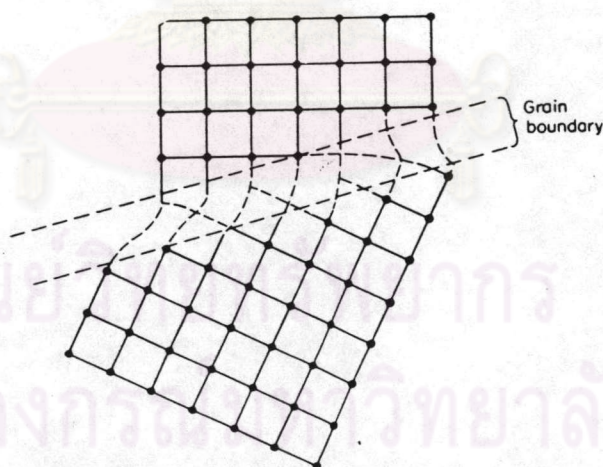


Fig. 2.14 Grain boundary in a polycrystalline metal (two-dimensional representation).

Alloys are mixtures of two or more metals or elements. There are two kinds of alloys-homogeneous and heterogeneous. Homogeneous alloys are solid solutions. That is, the components are completely soluble in one another, and the

material has only one phase. 18.8 stainless steel (Fig. 2.15) is an example of a homogeneous or solid-solution alloy. The iron, nickel, chromium, and carbon are dissolved completely, and the alloy has a uniform composition. Heterogeneous alloys are mixtures of two or more separate phases. The components of such alloys are not completely soluble and exist as separate phases. The composition and structure of these alloys are not uniform. Figure 2.16 shows a photomicrograph of low-carbon steel. The carbon combines with some of the iron to form iron carbide, which usually appears in a lamellar form. Each type of alloy has advantages and disadvantages. Solid-solution alloys are generally more ductile and have lower strength than heterogeneous alloys. The choice between these two types depends on the mechanical properties desired. Solid-solution alloys are usually more corrosion resistant than alloys with two (or more) phases, since galvanic coupling effects are not present. However, there are important exceptions to this generalization which can study increasing on textbooks of corrosion.



Fig. 2.15 Photomicrograph of 18Cr-8Ni stainless steel etched to reveal grain boundaries (100X)

Alloys are quite similar to aqueous solution. Some substances can be dissolved, while others are insoluble. Solubility usually increases rapidly with increasing temperature. For example, iron carbide is completely soluble in iron at high temperatures; hence steel becomes a solid solution when heated to a high temperature. Precipitation of a phase can occur from supersaturated solid

solutions as it does in the case of liquid solutions. As noted above, grain boundaries are high-energy areas, so precipitation frequently begins at the grain interfaces.

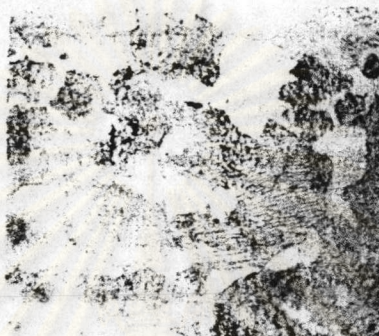


Figure 2.16 Photomicrograph of carbon steel etched to reveal iron carbide platelets (600X)

Other differences in the metal can be chemical, metallurgical, or mechanical in nature. Examples are impurities such as oxides and other inclusions, mill scale, orientation of grains, dislocation arrays, differences in composition of the microstructure, precipitated phases, localized stresses, scratches, and nicks. Highly polished surfaces are used in only special cases. Very pure metals are more corrosion resistant than commercial materials. For example, very pure and smooth zinc will not corrode in very pure hydrochloric acid, yet their commercial counterparts react rapidly. However, pure metals are expensive, and they are usually weak-one would not build a bridge of pure iron.

The following table shows the effect of purity of aluminum on corrosion by hydrochloric acid

% aluminum	Relative corrosion rate
99.998	1
99.97	1,000
99.2	30,000

The eight forms of the corrosion

It is convenient to classify corrosion by the forms in which it manifests itself, the basis for this classification being the appearance of the corroded metal. Each form can be identified by mere visual observation. In most cases the naked eye is sufficient, but sometimes magnification is helpful or required. Valuable information for the solution of a corrosion problem can often be obtained through careful observation of the corroded test specimens or failed equipment. Examination before cleaning is particularly desirable.

Some of the eight forms of corrosion are unique, but all of them are more or less interrelated. The eight forms are; (1) uniform, or general attack, (2) galvanic, or two-metal corrosion, (3) crevice corrosion, (4) pitting, (5) intergranular corrosion, (6) selective leaching, or parting, (7) erosion corrosion, and (8) stress corrosion. This listing is arbitrary but covers practically all corrosion failures and problems. The forms are not listed in any particular order of importance.