Mechanical Engineering

Material Science

Comprehensive Theory

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Material Science

First Edition : 2018
Second Edition : 2019
Third Edition: 2020

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Corrosion

10.1 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. 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).

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. The consequences of corrosion are all too common. Familiar examples include the rusting of automotive body panels and radiator and exhaust components.

10.2 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. Examples in which metal oxidizes are,

$$Fe \rightarrow Fe^{2+} + 2e^-$$
$$Al \rightarrow Al^{3+} + 3e^-$$
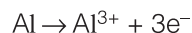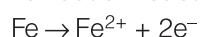
The site at which oxidation takes place is called the anode; oxidation is sometimes called an anodic reaction. The electrons generated from each metal atom that is oxidized must be transferred to and become a part of another chemical species in what is termed a reduction reaction. For example, some metals undergo corrosion in acid solutions, which have a high concentration of hydrogen (H^+) ions; the H^+ ions are reduced as follows:

$$2H^+ + 2e^- \rightarrow H_2$$

and hydrogen gas (H_2) is evolved.
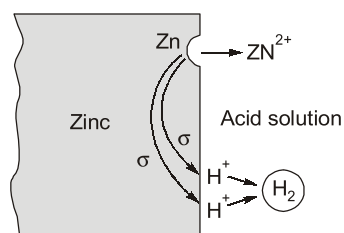
Figure 10.1: The electrochemical reactions associated with the corrosion of zinc in an acid solution.

The location at which reduction occurs is called the cathode. Furthermore, it is possible for two or more of the preceding reduction reactions 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 10.1 and according to the reaction.

$$Zn \rightarrow Zn^{2+} + 2e^- \qquad ...(i)$$

Because 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

$$2H^+ + 2e^- \rightarrow H_2 \text{(gas)} \qquad ...(ii)$$

If no other oxidation or reduction reactions occur, the total electrochemical reaction is just the sum of reactions (i) and (ii).

$$Zn \rightarrow Zn^{2+} + 2e^-$$
$$\underline{2H^+ + 2e^- \rightarrow H_2 \text{(gas)}}$$
$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \text{(gas)} \qquad ...(iii)$$
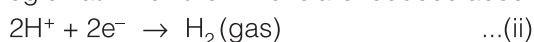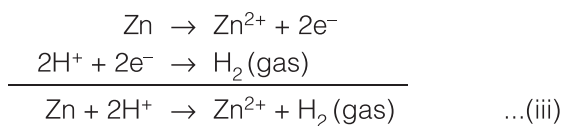
Another example is the oxidation or rusting of iron in water, which contains dissolved oxygen. This process occurs in two steps; in the first, Fe is oxidized to Fe^{2+}

$$Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \quad ...(iv)$$
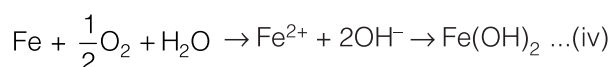
and, in the second stage, to Fe^{3+} [as $Fe(OH)_3$] according to

$$2Fe(OH_2) + \frac{1}{2}O_2 + H_2O \rightarrow 2Fe(OH)_3 \qquad ...(v)$$
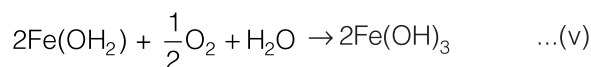
The compound $Fe(OH)_3$ is the all-too-familiar rust.

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

Figure 10.2: An electrochemical cell consisting of iron and copper electrodes, each of which is immersed in a M solution of its ion. Iron corrodes while copper electrodeposits.

10.3 The Galvanic Series

The Galvanic series represents the relative reactivities of a number of metals and commercial alloys in seawater. The alloys near the top are cathodic and unreactive, 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.

10.4 Corrosion Rate

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

$$\text{CPR} = \frac{KW}{\rho At}$$

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). 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 mol/m^2 s, is determined using the expression

$$r = \frac{i}{nF}$$

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

Table 10.1: 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)

↑ Increasingly inert (cathodic)

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

Increasingly active (anodic) ↓

10.5 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 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 re-forms 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.

10.6 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. The rates of most chemical reactions rise with increasing temperature; this also holds for most 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.

10.7 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.

10.7.1 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 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.

10.7.2 Galvanic Corrosion

Galvanic corrosion occurs when two metals or alloys having different compositions are electrically coupled while exposed to an electrolyte. 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. Again, the galvanic series (Table 10.1) 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 (Galvanic series) 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.

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, 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.

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

10.7.4 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 undetected and with very little material loss until failure occurs.

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

intergranular fracture is observed for some alloy systems. Hydrogen embrittlement is similar to stress corrosion 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 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: pickling 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 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, 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.

10.8 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 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 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.

10.9 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.

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. Several mechanisms 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. Because dissolved oxygen may enhance the corrosivity of many solutions, the design should, if possible, include provision for the exclusion of air. 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.

10.9.1 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 earlier and may, in some situations, completely stop corrosion. Again, oxidation or corrosion of a metal M occurs by the generalized reaction

$$M \rightarrow M^{n+} + ne^-$$

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

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 10.4 (a).

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 10.5). 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.
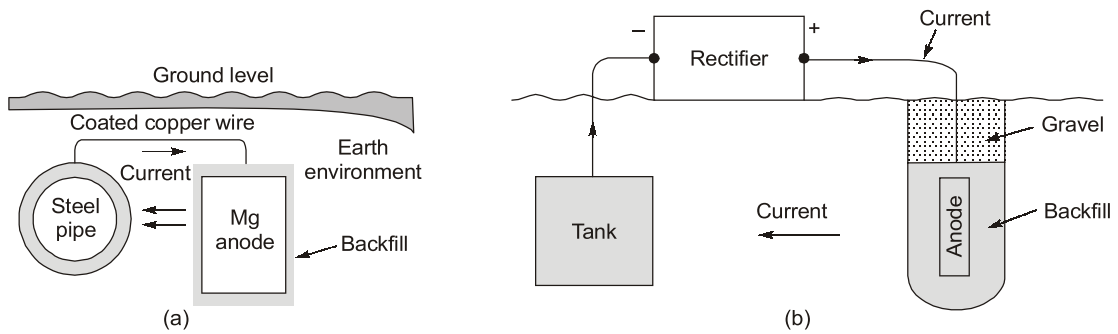
Figure 10.4: Cathodic protection of (a) an underground pipeline using a magnesium sacrificial anode, and (b) an underground tank using an impressed current.

For another method of cathodic protection, the source of electrons is an impressed current from an external dc power source, as represented in Figure 10.4 (b) 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 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.
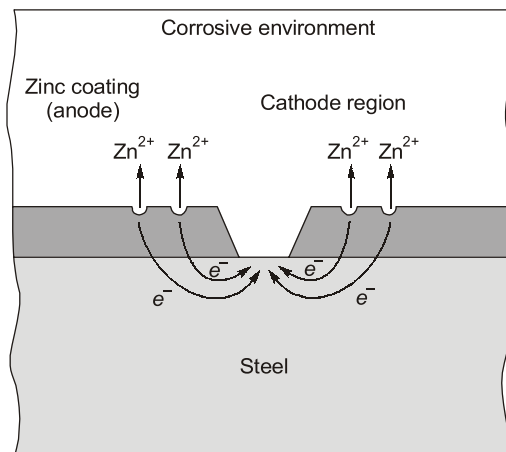

Figure 10.5: Galvanic protection of steel as provided by a coating of zinc.

10.10 Oxidation

The corrosion of metallic materials in terms of electrochemical reactions 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.

10.10.1 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:

$$M + \frac{1}{2}O_2 \rightarrow MO$$
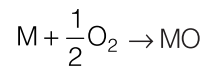
Furthermore, the preceding reaction consists of oxidation and reduction halfreactions. The former, with the formation of metal ions, occurs at the metal–scale interface. The reduction half-reaction produces oxygen ions as follows:

$$M \rightarrow M^{2+} + 2e^-$$

$$\frac{1}{2}O_2 + 2e^- \rightarrow O^{2-}$$
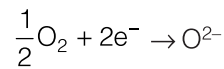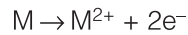
and takes place at the scale–gas interface.

For the oxide layer to increase in thickness, 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. 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.
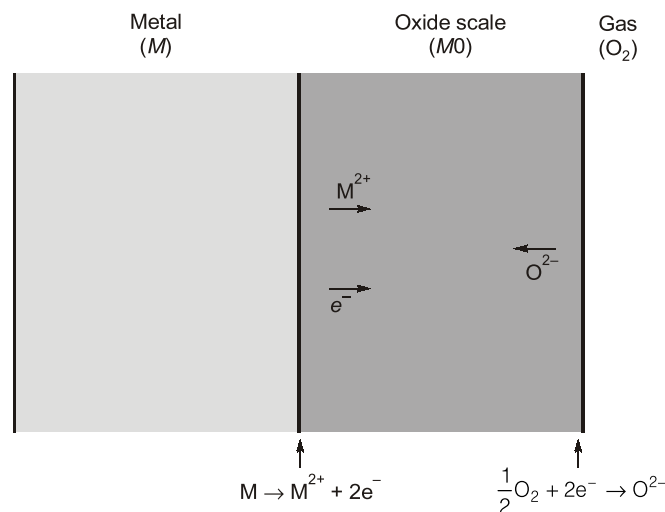

Figure 10.6: Schematic representation of processes that are involved in gaseous oxidation at a metal surface.

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