

## MATERIALS SCIENCE

### CORROSION AND DEGRADATION

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#### Corrosion of Metals

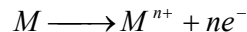
Corrosion is defined as the destructive and unintentional attack of a metal; it is electrochemical and ordinarily begins at the surface.

- It has been estimated that approximately 5% of an industrialized nation's income is spent on corrosion prevention and the maintenance or replacement of products lost or contaminated as a result of corrosion reactions.

#### Electrochemical Considerations

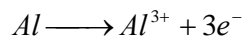
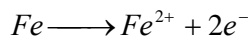
The corrosion process is normally electrochemical – a chemical reaction in which there is transfer of electrons from one chemical species to another.

Metals usually give up its electrons in what is called an oxidation reaction.



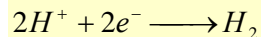
Where in the process of loosing n valance electrons, M becomes an n+ positively charged ion.

E.g.:



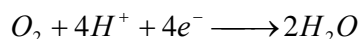
The side at which corrosion takes place is called anode, hence oxidation is sometimes called **anodic reaction**.

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

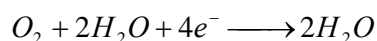


and hydrogen gas ( $H_2$ ) is the by product.

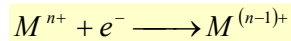
Other reduction reactions are possible depending on the solution the metal is in contact with. For an acidic solution having dissolved oxygen



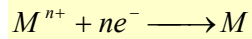
Or for a neutral solution such as oxygen (such as water) having dissolved oxygen



Any metal ions present in the solution may also be reduced by



Or a metal may be totally reduced from ionic to a neutral metallic state according to

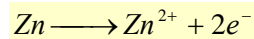


The location at which reduction occurs is called the **cathode**.

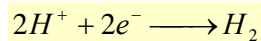
For corrosion to take place at least one oxidation and one reduction reaction must take place – the individual oxidation and reductions reactions are termed **half reactions**. Hence, all electrons generated through oxidation must be consumed in the reduction reaction.

Example: Zinc in acid solution containing  $H^{+}$  ions.

Oxidation or corrosion of Zinc

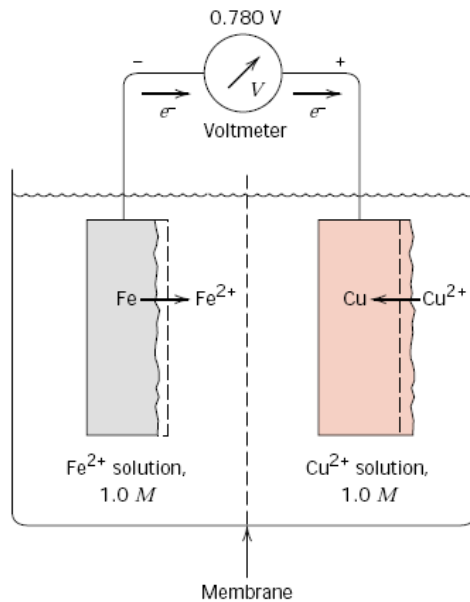


Reduction of  $H^{+}$  ions

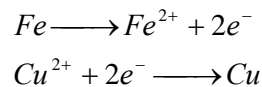


### Electrode Potentials

Not all metallic materials oxidize to form ions as easily as the next metal. Consider the electrochemical cell in Figure 17.2.



**FIGURE 16.2** An electrochemical cell consisting of iron and copper electrodes, each of which is immersed in a 1M solution of its ion. Iron corrodes while copper electrodeposits.



Two half cells

This is a galvanic couple – two metals electrically connected in a liquid electrolyte wherein one metal becomes an anode and corrodes, while the other acts as a cathode.

## The Standard emf Series

The standard emf series was established to create a reference point to which other cells halves may be compared.

The reference cell consists of an inert platinum electrode in a 1M solution of  $H^+$  ions, saturated with hydrogen gas that is bubbled through the solution at a pressure of 1 atm and a temperature of 25 °C.

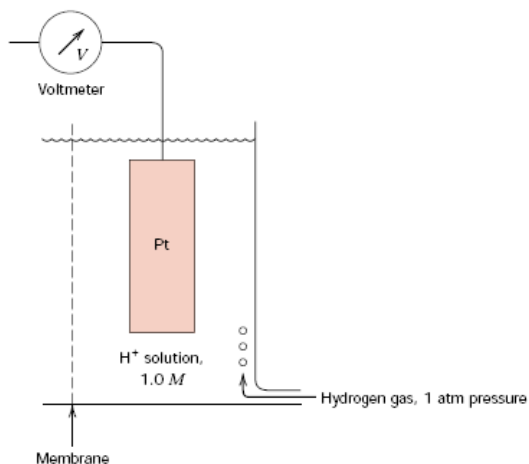


FIGURE 16.4 The standard hydrogen reference half-cell.

The electromotive force (emf) series is generated by coupling to the standard hydrogen electrode, standard half-cells for various metals and ranking them according to measure voltage.

Table 16.1 The Standard emf Series

	Electrode Reaction	Standard Electrode Potential, $V^0$ (V)
	$Au^{3+} + 3e^- \longrightarrow Au$	+1.420
	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
	$Pt^{2+} + 2e^- \longrightarrow Pt$	~+1.2
	$Ag^+ + e^- \longrightarrow Ag$	+0.800
	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH^-)$	+0.401
	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.340
	$2H^+ + 2e^- \longrightarrow H_2$	0.000
	$Pb^{2+} + 2e^- \longrightarrow Pb$	-0.126
	$Sn^{2+} + 2e^- \longrightarrow Sn$	-0.136
	$Ni^{2+} + 2e^- \longrightarrow Ni$	-0.250
	$Co^{2+} + 2e^- \longrightarrow Co$	-0.277
	$Cd^{2+} + 2e^- \longrightarrow Cd$	-0.403
	$Fe^{2+} + 2e^- \longrightarrow Fe$	-0.440
	$Cr^{3+} + 3e^- \longrightarrow Cr$	-0.744
	$Zn^{2+} + 2e^- \longrightarrow Zn$	-0.763
	$Al^{3+} + 3e^- \longrightarrow Al$	-1.662
	$Mg^{2+} + 2e^- \longrightarrow Mg$	-2.363
	$Na^+ + e^- \longrightarrow Na$	-2.714
	$K^+ + e^- \longrightarrow K$	-2.924

This table relates the susceptibility of a metal to oxidation.

## The Galvanic Series

The standard emf series was generated under highly idealized conditions and has limited use. A more realistic and practical ranking is provided by the galvanic series - it represents the reactivity of a number of metal in seawater.

**Table 16.2** The Galvanic Series

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

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

## Corrosion Rates

The corrosion penetration rate (CPR) is expressed as

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

Where  $W$  is the weight loss after exposure time  $t$ ,  $\rho$  and  $A$  represent the density and exposed specimen area, respectively, and  $K$  is a constant.

CPR can be expressed as mills per year (mpy) or millimeter per year (mm/yr).

## Passivity

Some normally active metals and alloys, under particular environment conditions, lose their chemical reactivity and become extremely inert - this is termed passivity.

Passivity results from the formation of a highly adherent and very thin oxide film on the metal surface, which serve as a protective barrier. Stainless steels are a common example of stainless steels.

If damages, the protective film normally reforms very rapidly but subsequent damage to a preexisting passive film could result in substantial increase in corrosion rate, by as much as 100,000 times.

## Forms of Corrosion

The eight forms of corrosion

1. Uniform
2. Galvanic
3. Crevice
4. Pitting
5. Intergranular
6. Selective leaching
7. Erosion-corrosion
8. Stress corrosion cracking

## Uniform Attack

Uniform attack occurs with equivalent intensity over the entire exposed surface and often leaves behind a scale or deposit. Examples include rusting of steel and iron and the tarnishing of silverware.

## Galvanic Corrosion

This occurs when two metals or alloys having different compositions are electrically coupled while exposed to an electrolyte. The more reactive metal will experience corrosion (more rapid than usual) and the inert metal will be protected.

There is little danger when two metals within a single bracket are put together.

The rate of galvanic attack depends on the relative anode-to-cathode surface areas that are exposed to the electrolyte. That is, for a given cathode area, a smaller anode will corrode more rapidly than a large one.

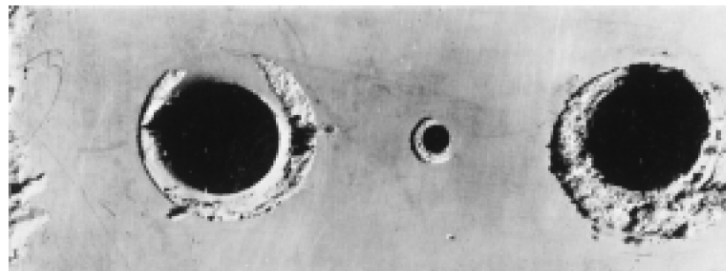
A number of measures can be taken to significantly reduce the effects of galvanic corrosion. These include the following:

1. If it is a must to couple to dissimilar metals, choose two that are close together in the galvanic series.
2. Avoid unfavorable anode-to-cathode surface area; 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.

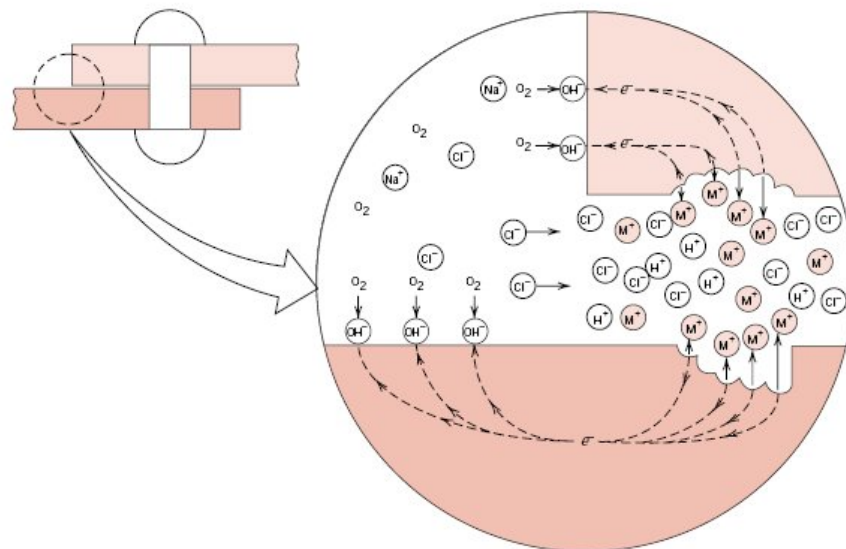
### Crevice Corrosion

Crevice corrosion occurs due to difference of ions or dissolved gases in the electrolyte solution, and between two regions of the same metal piece.

It 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



**FIGURE 16.15** On this plate, which was immersed in seawater, crevice corrosion has occurred at the regions that were covered by washers. (Photograph courtesy of LaQue Center for Corrosion Technology, Inc.)



**FIGURE 16.16** Schematic illustration of the mechanism of crevice corrosion between two riveted sheets. (From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

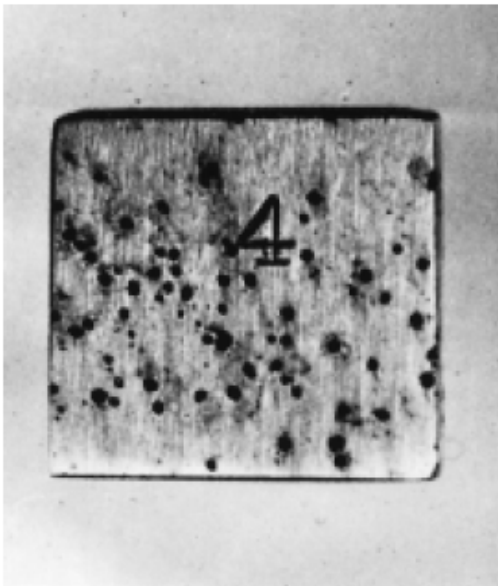
Crevice corrosion can be prevented by using welded instead of riveted or bolted joints, use non-absorbing gaskets, removing accumulated deposits frequently, and designing containment vessels to avoid stagnant areas and ensure complete drainage.

### **Pitting**

Pitting is form localized corrosion attack in which pits or holes form. They penetrate from the top of a horizontal surface downward in a nearly vertical direction. It is a very dangerous form of corrosion that usually goes undetected with very little material loss until failure.

The mechanism for pitting is the same as for crevice corrosion. Gravity causes the pit to grow downwards where the solution at the bottom of the pit becomes more and more concentrated as the pit progresses.

Pitting is initiated by localized surface defects such as scratch or slight variation in composition.



**FIGURE 16.17** The pitting of a 304 stainless steel plate by an acid-chloride solution. (Photograph courtesy of Mars G. Fontana. From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

### **Intergranular Corrosion**

Intergranular corrosion occurs preferentially along grain boundaries. Hence, the metal disintegrates along the grain boundaries.

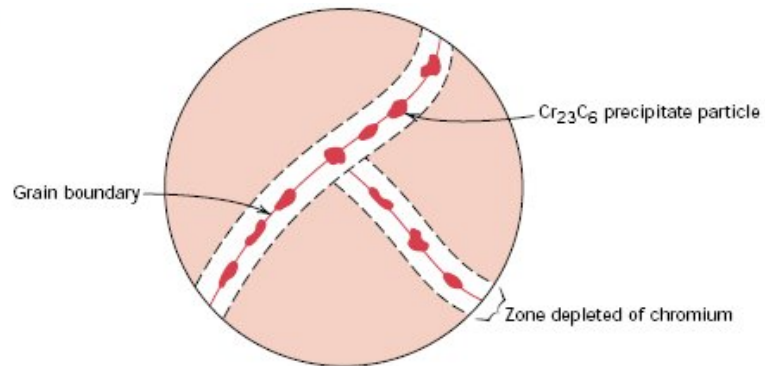
It is especially seen in stainless steels when operating between the temperatures of 500 °C to 800 °C for long periods of time. At this temperature, the chromium and carbon in the alloy react to form chromium carbide. This reaction takes place and precipitate at the grain boundaries. This leaves the grain boundaries depleted of chromium hence more susceptible to corrosion. They are more severe at the heat affected zones of a weld.

Stainless steels can be protected by

- 1) Heat treating to high temperatures hence chromium carbide particles are re-dissolved.
- 2) Lowering the carbon content – reduce number of atom that can react with chromium.
- 3) Alloying with other metals such as niobium or titanium which react with carbon more easily than chromium.

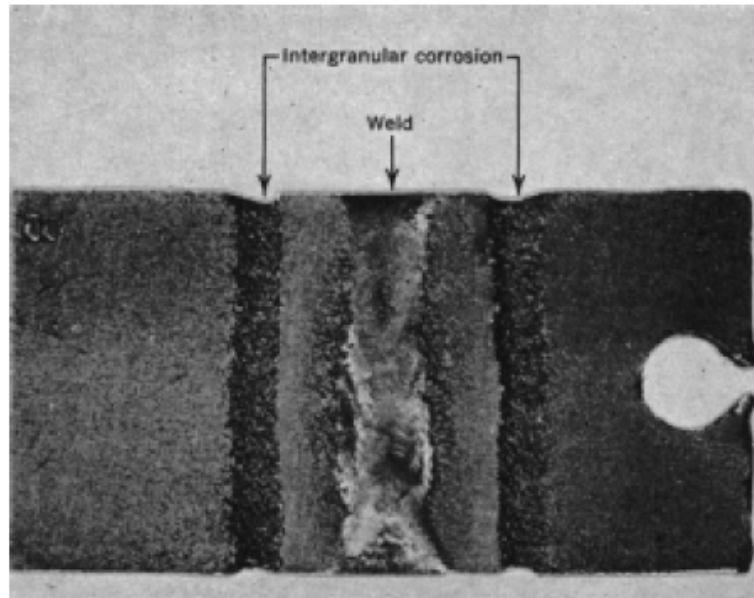
**FIGURE 16.18**

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



**FIGURE 16.19**

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





## Selective Leaching

Selective leaching occurs when one element or constituent is preferentially removed as a consequent of corrosion.

A common example is the selective removal of zinc from copper-zinc brass alloy. This greatly impairs the mechanical properties of the specimen due to porosity. Colour change may be noticeable.

## Erosion-Corrosion

This is a combination of chemical attack and mechanical abrasion as a consequence of fluid motion. This is more prominent in metal that passivates because the passive film is eroded away. If the metal cannot form a new layer fast enough corrosion can be severe.

Increasing fluid velocity enhances the corrosion rate. Bubbles and suspended solids in the fluid can also enhance erosion.

Erosion-corrosion is commonly found in piping, especially at bends, elbows and abrupt changes in the pipe diameter – where turbulence is greater.

Erosion-corrosion can be reduced by changing the design to eliminate turbulence or by removing suspended solids.



**FIGURE 16.20** Impingement failure of an elbow that was part of a steam condensate line. (Photograph courtesy of Mars G. Fontana. From M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright © 1986 by McGraw-Hill Book Company. Reproduced with permission.)

### **Stress Corrosion**

Also called stress corrosion cracking, result from the combined action of an applied tensile stress and a corrosive environment. Small cracks form and then propagate in a direction perpendicular to the stress.

Cracks may form at moderate stress levels and stress corrosion is environment specific. Stainless steels experience stress corrosion in solutions containing chlorine, brass is more susceptible in ammonia.

Stress applied may not necessarily be applied externally – high temperature and pressure can create stress.

**FIGURE 16.21**

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

