

Class Notes

Module-5: Corrosion Science

Corrosion

Corrosion is a natural process, which converts a refined metal to a more chemically-stable form, such as its oxide, hydroxide, or sulfide. It is the gradual destruction of materials (usually metals) by chemical and/or electrochemical reaction with their environment.

Definition

Any process of deterioration (or destruction) and consequent loss of a solid metallic material, through an unwanted (or unintentional) chemical or electrochemical attack by its environment, starting at the surface, is called corrosion. Thus it can be called “reverse of extraction of metals”.

Examples:

1. Rusting of iron: Upon exposure of iron in atmospheric conditions, layers of reddish scale and powder of oxide (Fe_3O_4) is formed.
2. Formation of green film of basic carbonate ($\text{CuCO}_3 + \text{Cu}(\text{OH})_2$) on the surface of copper vessel/utensil upon exposed to moist-air containing CO_2 .

Types

Corrosion is mainly divided into two types-

- (i) **Chemical or dry corrosion**
 - (ii) **Electrochemical or wet corrosion**
- (i) **Chemical or dry corrosion:**

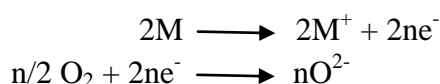
This type of corrosion occurs due to the direct chemical action of environment/atmospheric gases such as O_2 , halogen, H_2S , CO , SO_2 , N_2 or anhydrous inorganic liquid with metal surfaces in immediate proximity.

Three main types of chemical corrosion

(a) **Oxidation corrosion:**

It occurs due to direct action metal with O_2 at low or high temperature in absence of moisture. At ordinary temperature metals are not easily attacked. But alkaline (e.g. Li, Na, K, Rb etc.) and alkaline earth metals (e.g. Be, Ca, Sr etc.) are rapidly oxidized at low temperature. At high temperature, almost all metals (except Ag, Au & Pt) are oxidized.

The reactions are



Mechanism:

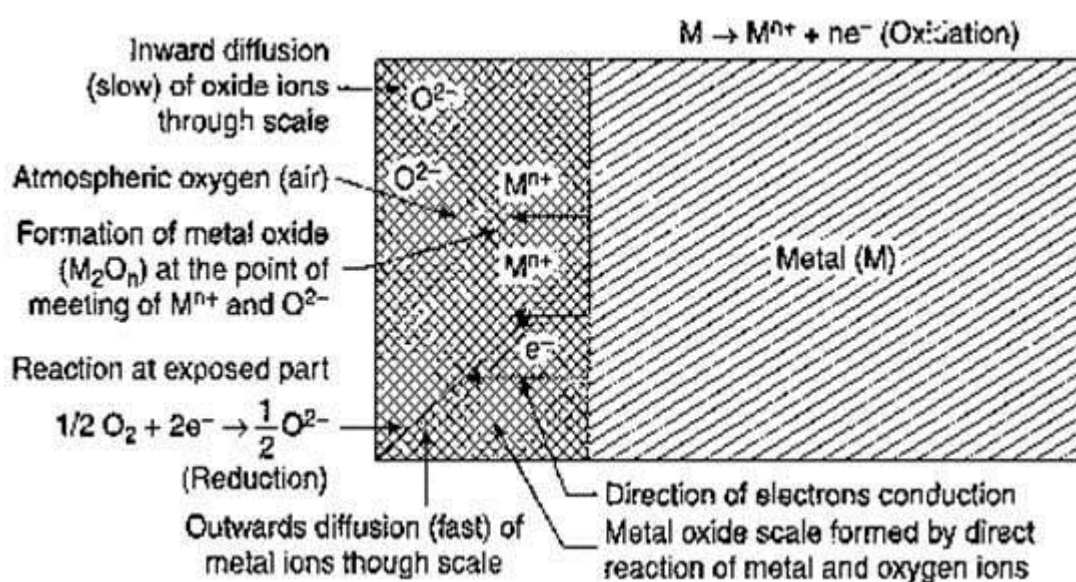
The oxidation of the metal occurs at the surface first resulting the formation of metal oxide layer. The nature of oxide layer formed on the metal surface decides the further action with the environment.

If the oxide film formed is continuous and rigidly adhered to the surface of metal is impervious in nature, and is called **stable oxide layer**. It is protective and shields the metal from further corrosion.

Ex: oxide films on Cu or Al acts as a protective coating and further corrosion is prevented.

If **unstable oxide film** is formed decomposes back into the metal and oxygen. Ex: noble metals like Pt, Au etc. corrosion is not possible, since oxide layer formed is very unstable and decomposes back to metal and oxygen.

If oxide layer formed is porous or volatile is non-protective and more feasible for further attack of environment, hence corrosion continues till the entire metal is converted to metal oxide. **Ex:** Mo forms a volatile oxide layer.



Pilling Bedworth rule:

An oxide is protective or non porous if the volume of oxide at least as great as the volume of the metal from which it is formed. On the other hand, if the volume of the oxide is less than the volume of the metal from which it is formed is called porous or non-protective oxide.

If the volume of metal oxide is less than the volume of the metal, the oxide layer is porous, non continuous and non-protective and faces strains. Hence cracks and pores are developed in the layer, creating access to atmospheric oxygen to reach the underlying metal. In this case corrosion is continuous and rapidly increases.

For example: Li, Na and K.

- (b) **Corrosion by other gases:** In the absence of moisture a few gases like SO_2 , CO_2 , Cl_2 , H_2S and F_2 etc. attack the metal. The degree of corrosion depends on the formation of protective or non-protective films on the metal surface.

If the film formed is protective or non-porous, the intensity or extent of attack decreases, because the film formed protects the metal from further attack.

Ex: AgCl film, resulting from the attack of Cl_2 on Ag .

If the film formed is non-protective or porous, the surface of the whole metal is gradually destroyed.

Ex: dry Cl_2 gas attacks on tin (Sn) forming volatile SnCl_4 .

(c) **Liquid Metal Corrosion:**

Chemical action of flowing liquid metal at high temperature on solid metal or alloy.

Involved by

- (i) Dissolution of solid metal by liquid metal.
- (ii) Internal penetration of liquid metal into the solid metal.

Especially in nuclear plants, liquid Al , Bi , Pb , Mg , Na , Sn , Zn , and Na-K alloys & fused sodium hydroxide have all been successfully used in nuclear power plants as heat transfer agents.

Electro-Chemical Corrosion (Wet Corrosion):

Wet corrosion or electrochemical corrosion takes place under wet or moist conditions through the formation of short circuited tiny electrochemical cells. Wet corrosion is more common than dry corrosion.

This type of corrosion can be observed

- (i) When a metal is in contact with conducting liquid.
- ii) When two dissimilar metals are dipped partially in a solution.

This corrosion occurs due to the existence of separate 'anodic' and 'cathodic' areas. Impact of corrosive environment on a portion of metal, changes its electrode potential compared to its original value of the electrode potential of the metal. This creates a potential difference within the metal system. The area of lower reduction potential created in the metal is known as the 'anodic area' and that with higher reduction potential value is called 'cathodic area'.

The current flows from the anodic area to the cathodic area through the conducting solution. A galvanic cell is created in the metal.

At anodic area, oxidation reaction takes place, so metal is destroyed by either dissolving or assuming combined state. Hence, corrosion always occurs at anodic area.

At anodic area: $\text{M} \longrightarrow \text{M}^{n+} + n\text{e}^-$ (Oxidation)

$\text{M}^{n+} \longrightarrow$ Dissolves in solution or forms compound such as oxide.

At cathodic area, reduction reaction takes place. Usually, cathode reactions do not affect the cathode, since most metals cannot be further reduced. So, at cathodic part, dissolved constituents in the conducting medium accept the electrons to form some ions like OH^- , O^{2-} .

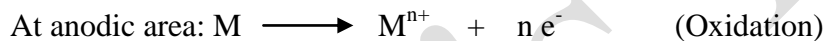
The metallic ion formed at anodic part and non-metallic ions formed at cathode part diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode. The electrons set free at the anode flow through the metal and are finally consumed in the cathodic reaction.

Thus, we may sum up that electrochemical corrosion involves:

- i) The formation of anodic and cathodic areas or parts in contact with each other,
- ii) Presence of a conducting medium,
- iii) Corrosion of anodic areas only,
- iv) Formation of corrosion product somewhere between anodic and cathodic areas.

Mechanism:

Electrochemical corrosion involves flow of electron-current between the anodic and cathodic areas. The anodic reaction involves in dissolution of metal as corresponding metallic ions with the liberation of free electrons.



The anodic reaction consumes electrons with either by i) evolution of hydrogen, or ii) absorption of oxygen depending on the nature of the corrosive environment.

i) Evolution of hydrogen: In absence of oxygen.

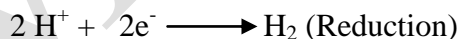


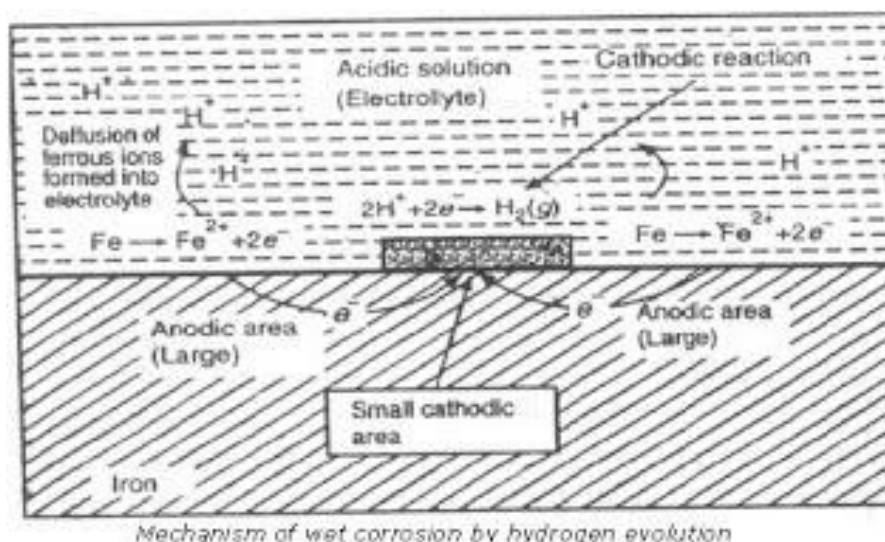
Considering metal like Fe,

At the anodic reaction is dissolution of iron as ferrous ion with the liberation of electrons.



These electrons flow through the metal, from anode to cathode, where H^+ ions are eliminated as hydrogen gas from acidic solution.





Thus, this type of corrosion causes “displacement of hydrogen ions from the acidic solution by metal ions. “ Consequently, all metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen.

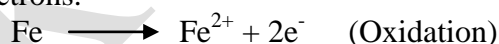
The overall reaction: $\text{Fe} + 2\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2$

ii) Absorption of oxygen: in presence of dissolved oxygen.

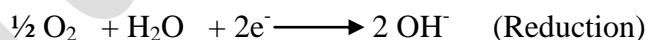
In acidic medium: $4\text{H}^+ + \text{O}_2 + 4\text{e}^- \longrightarrow 2\text{H}_2\text{O}$

In neutral or alkaline medium: $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \longrightarrow 4\text{OH}^-$

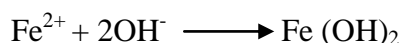
By considering Rusting of iron in neutral aqueous solution of electrolytes in the presence of atmospheric oxygen. At the anodic areas of the metal (iron) dissolve as ferrous ions with liberation of electrons.



The liberated electrons flow from anodic to cathodic areas, through iron metal, where electrons are intercepted by the dissolved oxygen as:



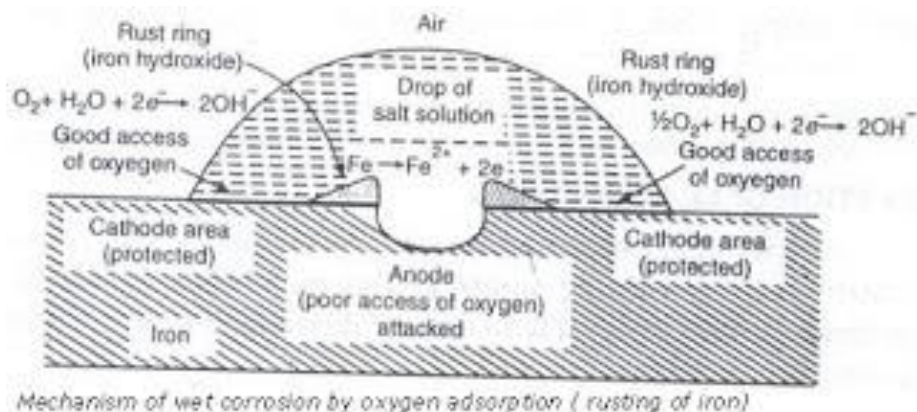
The Fe^{2+} ion at anode and OH^- ions at cathode diffuse and when they meet, ferrous hydroxide is precipitated.



If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.



This product is called yellow rust, actually corresponds to $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$



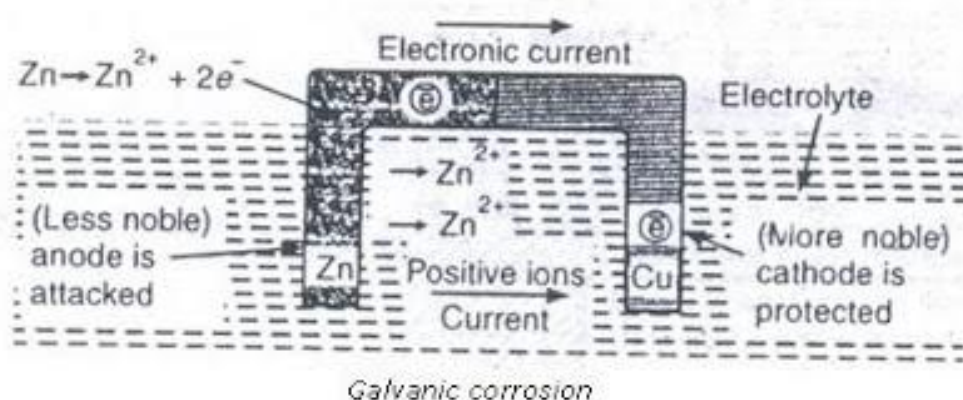
If the supply of oxygen is limited the corrosion product may be even black anhydrous magnetite, Fe_3O_4 .

Types of Electro-Chemical Corrosion (Wet Corrosion):

(i) Galvanic or bimetallic corrosion:

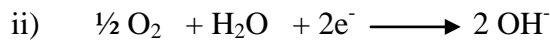
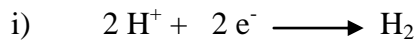
It occurs when two dissimilar metals are in contact with each other in a corrosive conducting medium. The two metals differ in their tendencies to undergo oxidation; the one with lower electrode potential or the more active metal (higher up in electrochemical series) acts as anode and the one with higher electrode potential acts as cathode. The potential difference between two metals is the cause or driving force for corrosion. The anodic metal undergoes corrosion and the cathodic metal is generally unattacked.

Ex: When Zn and Cu are connected and exposed to corroding atmosphere Zn becomes anodic because of its higher oxidation potential or higher position in the electrochemical series. Zn undergoes oxidation and corroded, whereas Cu undergoes reduction and protected. The electrons released by Zn reach Cu through the metal.



Anodic metal: $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$ (Oxidation)
(More active metal)

At cathodic metal: depending on nature of the corrosion environment the cathode reaction (reduction) may be either hydrogen evolution or oxygen absorption.



Galvanic corrosion can be minimized by

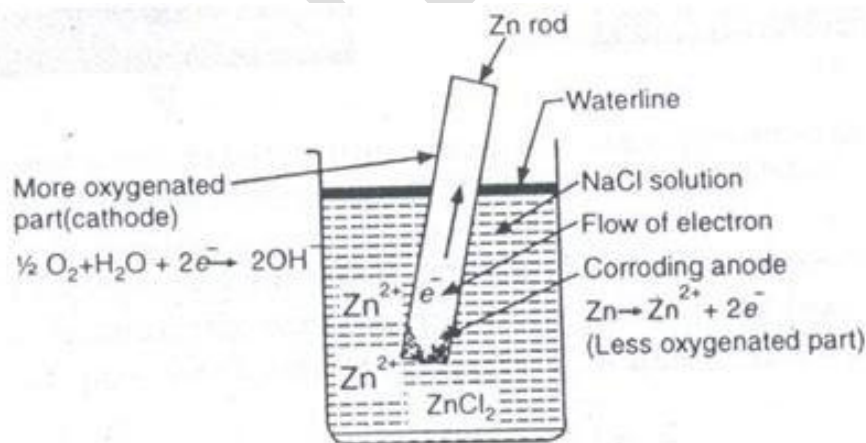
1. Avoiding galvanic couples.
2. Providing an insulating material between two metals.

Some more examples:

- Steel screws/ rivets in copper sheet.
- Steel pipe connected to copper plumbing.
- Lead antimony solder around copper wire.

(ii) **Differential aeration corrosion:**

It occurs when a metal is exposed to different air concentrations or oxygen concentrations. The part of the metal exposed to higher oxygen concentration acts as cathodic region, and part of the metal exposed to lower oxygen concentration acts as anodic region. Consequently, the poorly oxygenated region undergoes corrosion. Corrosion of metals arising as a result of the formation of a oxygen concentration cell due to the uneven supply of air on the metal surface.



Differential aeration corrosion

Ex: The Zn metal partially immersed in a NaCl solution. The parts above the waterline more oxygenated are more strongly aerated and hence, become cathodic. On the other hand, parts immersed to greater depth show a smaller oxygen concentration and thus become anodic. So, a difference of potential is created, which causes a flow of current between the two differently aerated areas of the same metal. Zn will dissolve at anodic area, and oxygen will take up electrons at the cathode areas to form hydroxyl ions. Thus, Zn undergoes corrosion at poorly oxygenated part.

At anode: $\text{Zn} \longrightarrow \text{Zn}^{2+} + 2\text{e}^-$ (poorly oxygenated part)

At cathode: $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 2\text{OH}^-$ (well oxygenated part)

Examples:

- Parts of the nail inside the wall, being exposed to lower oxygen concentration than the exposed part, undergo corrosion.
- Window rods inside the frame suffer corrosion but not the exposed region.
- Paper pins inside the paper gets corroded, and the exposed parts is free from corrosion.
- Metal under dirt, dust, scale or water undergoes corrosion.
- Partially buried pipeline in soil or submerged in water undergoes corrosion below the soil or water where as the exposed part is free from corrosion.

Passivity

Passivation involves creation of an outer layer of shield material that is applied as a microcoating, created by chemical reaction with the base material, or allowed to build from spontaneous oxidation in the air. As a technique, passivation is the use of a light coat of a protective material, such as metal oxide, to create a shell against corrosion. Passivation can occur only in certain conditions, and is used in microelectronics to enhance silicon. The technique of passivation strengthens and preserves the appearance of metallics. In electrochemical treatment of water, passivation reduces the effectiveness of the treatment by increasing the circuit resistance, and active measures are typically used to overcome this effect, the most common being polarity reversal, which results in limited rejection of the fouling layer. Other proprietary systems to avoid electrode passivation, several discussed below, are the subject of ongoing research and development.

Corrosion coating reduces the rate of corrosion by varying degrees, depending on the kind of base metal and its environment, and is notably slower in room-temperature air for aluminium, chromium, zinc, titanium, and silicon (a metalloid); the shell of corrosion inhibits deeper corrosion, and operates as one form passivation. The inert surface layer, termed the ‘native oxide layer’, is usually an oxide or a nitride, with a thickness of a monolayer of 0.1-0.3 nm (1-3 Å) for a noble metal such as platinum, about 1.5 nm (15 Å) for silicon, and nearer to 5 nm (50 Å) for aluminium after several years.

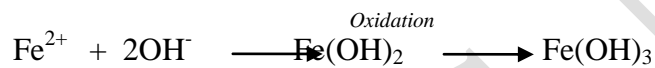
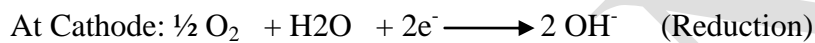
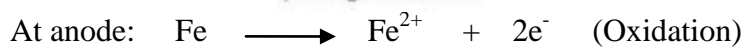
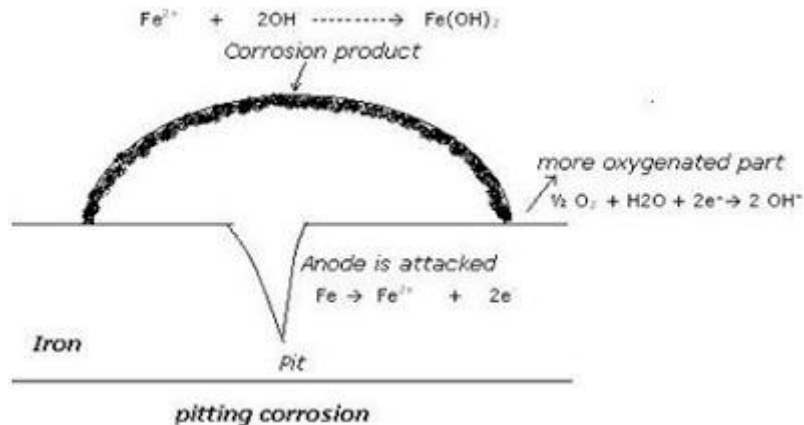
(iii) **Pitting Corrosion:**

Pitting corrosion is a localized and accelerated corrosion, resulting in the formation of pits or pin holes around which the metal is relatively unattacked.

It is characterized by small anodic and large cathodic areas, resulting in accelerated corrosion at the anodic area. It is an auto catalytic process, with the initially formed pit produces conditions which are both stimulating and necessary for the continuing activity of the pit.

It is generally initiated by the deposition of extraneous matter such as sand, scale, water drop, dust etc, or due to the breakdown of the protective film on metal surface. The metal below the deposit is exposed to lower oxygen concentration, acts as anode and undergoes corrosion. The metal surrounding the deposit acts as cathode since it is exposed to higher concentration of oxygen.

Consider a drop of water resting on the surface of metal, the metal surface which is covered by the drop has low oxygen concentration and thus acts as an anode and suffers corrosion. The uncovered metal surface due to high O_2 concentration acts as cathode.



Because of small anode and large cathode accelerated corrosion takes place below the deposit. Once the corrosion product is formed, it further provides the condition for differential aeration below the corrosion product and the surrounding metal parts. The pit grows and ultimately may cause failure of metal.

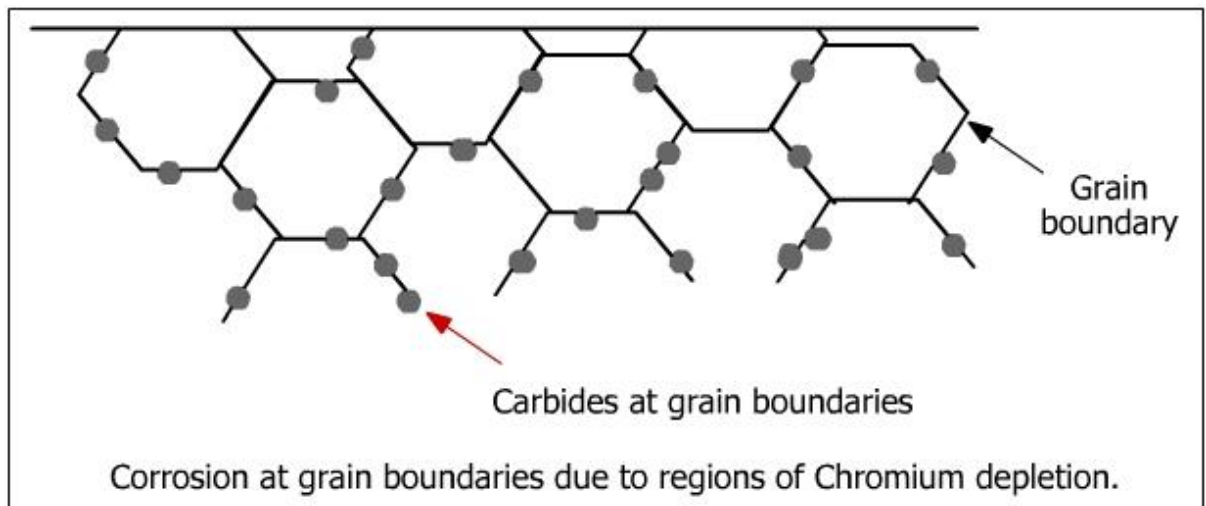
Pitting is one of the most destructive forms of corrosion. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. It is often difficult to detect pits because of their small size and also because pits are covered with corrosion products.

Pitting is dangerous because it is localized and intense of corrosion and failures often occur with extreme suddenness. As such, it is rather difficult to assess precisely the life of metal component undergoing pitting corrosion. Loss of metal due to pitting is of the little significance when compared to indirect losses such as production, repairs and replacements.

(iv) **Inter granular corrosion:**

This type of corrosion occurs along grain boundaries and only where the material, especially sensitive to corrosive attack exists, and corrosive liquid, the liquid possesses a selective character of attacking only at the grain boundaries, but leaving the grain interiors untouched or slightly attacked.

This situation can happen in otherwise corrosion-resistant alloys, when the grain boundaries are depleted, known as grain boundary depletion, of the corrosion-inhibiting elements.



Examples:

- In nickel alloys and austenitic stainless steels, where chromium is added for corrosion resistance, the mechanism involved is precipitation of chromium carbide at the grain boundaries, resulting in the formation of chromium-depleted zones adjacent to the grain boundaries (this process is called sensitization). Around 12% chromium is minimally required to ensure passivation, a mechanism by which an ultra thin invisible film, known as passive film, forms on the surface of stainless steels. This passive film protects the metal from corrosive environments. The self-healing property of the passive film makes the steel stainless. Selective leaching often involves grain boundary depletion mechanisms.
- Stainless steels can be stabilized against this behavior by addition of titanium, niobium, or tantalum, which form titanium carbide, niobium carbide and tantalum carbide preferentially to chromium carbide, by lowering the content of carbon in the steel and in case of welding also in the filler metal under 0.02%, or by heating the entire part above 1000 °C and quenching it in water, leading to dissolution of the chromium carbide in the grains and then preventing its precipitation.

(v) **Waterline corrosion:**

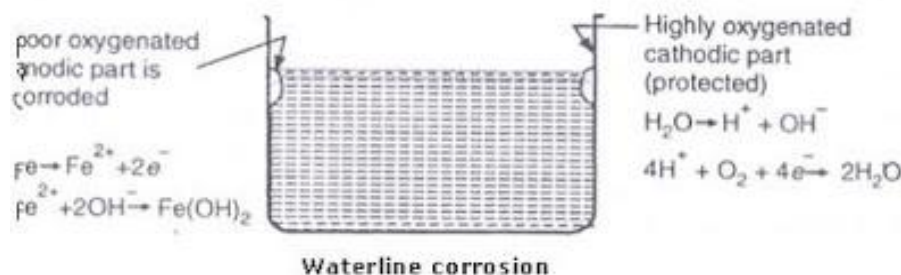
It is a case of differential aeration corrosion. More prevalent in cases such as ocean going ships, water storage steel tanks etc, in which a portion of metal is always under water.

The water line corrosion takes place due to the formation of differential oxygen concentration cell. The part of the metal below the water line exposed only to the dissolved oxygen while the part above the water is exposed to higher concentration of the atmosphere of the atmosphere. Thus, part of the metal below the water acts as anode and undergoes corrosion and the part above the water line is free from corrosion.

A distinct brown line is formed just below the water line due to the deposition of rust.

At anode: $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$ (Oxidation)

At cathode: $\frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 2 \text{OH}^-$



Factors Effecting Rate of Corrosion –

1. Nature of metal

(a) Nature of metal- Position of Metal in Galvanic Series:

When the metal is higher up in the galvanic series, greater is the oxidation potential. Thus, greater is its tendency to become anodic and hence greater is the rate of corrosion. Thus, extent of corrosion depends upon the position of the metal in the galvanic series. When two metals are in electrical contact, greater is the difference in their positions in the electrochemical series, faster is the corrosion of anodic metal.

(b) Overvoltage

Reduction in overvoltage of the corroding metal or alloy accelerates the corrosion rate

(c) Relative areas of Anode & Cathode

If a metal has small anodic area and large cathodic area, then the corrosion is more intensive and faster is the corrosion rate at the anodic region. The corrosion in anodic part is directly proportional to the ratio of areas of the cathodic part and the anodic part.

As this ratio increases, the corrosion rate increases rapidly. At anode, oxidation takes place and electrons are liberated. At the cathode, these electrons are consumed. When anode is smaller and cathode region is large all the electrons liberated at the anode are rapidly consumed at the cathode. This process makes the anodic reaction to take place at its maximum rate, thus increasing the corrosion rate. If the cathode is smaller, the consumption of electrons will be slower and the corrosion reaction as a whole will be slower.

(d) Purity of sample.

Impurities in metal, generally cause heterogeneity and form a minute /tiny electrochemical cells and results is the corrosion.

(e) Physical state of metal

The rate of corrosion is influenced by physical state of the metal (E.g. grain size, orientation of crystal, stress etc.). Smaller grain size-high solubility-high rate of corrosion.

(f) Nature of surface film

Nature of layer form at the surface of the metal (According to Pilling-Bedworth rule)

(g) Passive character of metal

Passive character of metal has high corrosion resistance power (Ti, Al, Cr, Mg, Ni, Co)

(h) Solubility of corrosion products

In electrochemical corrosion, if the corrosion product is soluble in the corroding medium, then the corrosion proceeds at a faster rate.

(i) Volatility of corrosion products

Volatile corrosion product (MoO_3) increases the rate of corrosion.

2. Nature of the corroding environment

(a) Temperature

With increasing temperature of environment, the reaction as well as diffusion rate increase, thereby corrosion rate is generally enhanced.

(b) Humidity of air

Critical humidity can be defined as the relative humidity above which the atmospheric corrosion rate of metal increases sharply. The value of critical humidity depends on the physical characteristics of the metal as well as nature of the corrosion products.

(b) Presence of impurities in atmosphere

Atmospheric gases like CO_2 , H_2S , SO_2 and fumes of HCl , H_2SO_4 increases the corrosion rate.

(c) Presence of suspended particles in atmosphere

In atmospheric corrosion (a) if the suspended particles are chemically active in nature [like NaCl , $(\text{NH}_4)_2\text{SO}_4$], they absorb moisture and acts as strong electrolyte, thereby causing enhanced corrosion. (b) if the suspended particles are chemically inactive in nature (e.g. charcoal), they both absorb sulphur gases, moisture and slowly enhance corrosion rate.

(d) Influence of pH

Generally acidic media are more corrosive than alkaline and neutral media. However, amphoteric metals (like Al , Zn , Pb) dissolve in alkaline solutions as complex ions. The corrosion rate of iron in oxygen-free water is slow, until the pH is below 5. The corresponding corrosion rate in presence of oxygen is much higher

(e) Nature of ions present

Presence of anions like silicate in the medium leads to the formation of insoluble reaction products (e.g. silica gel), which inhibits further corrosion. On the other hand presence of chloride ion in media, destroy the protective or passive surface film and results in the corrosion.

(f) Conductance of corroding medium

Conductance of dry sandy-soils is lower than those of clayey and mineralized soils. Consequently, stray currents will cause more severe damage to the metallic structures, buried under clayey and mineralized soils than those under dry sandy soil.

(g) Formation of oxygen concentration cell

With increase in supply of oxygen/air to the moist-metal surface, the corrosion is promoted. Less oxygen concentrated area will behave as anodic part and more concentrated area will behave as cathode. Thus it forms oxygen-concentration cell.

(h) Flow velocity process stream

When a metal that does not passivate, is under diffusion control, an increase in the velocity of the medium enhances diffusion rate, thereby increasing the corrosion rate.

(i) Polarization of electrode

The potential difference between the anode and the cathode is the driving force of an electrochemical corrosion process, but corrosion rate is controlled by the current flowing through the circuit. The extent of corrosion can be reduced by adding certain inorganic or organic substances (called inhibitors) to the corroding environment.

Corrosion Control Methods:

1. Proper designing

- I. Avoid contact of dissimilar metals in presence of conducting liquid
- II. Anodic metal should be high for two dissimilar metals in presence of conducting liquid
- III. For two dissimilar metals, the metals should be as close as possible to each other in the electrochemical series in presence of conducting liquid.
- IV. Avoid direct contact of two metals in presence of conducting liquid and this can be done by placing insulating material between the two metals.
- V. The anodic metal should not be painted or coated.
- VI. Prevent the occurrence of inhomogeneities.
- VII. It is desirable that the design allows for adequate cleaning and flushing of the critical parts.
- VIII. Whenever possible, the equipment should be supported on legs to allow free circulation of air and prevent the formation of stagnant pools or damp areas.
- IX. Uniform flow of a corrosion liquid is desirable, since both stagnant areas and highly turbulent flow and high velocities can cause accelerated corrosion.
- X. A proper design should prevent condition subjecting some areas of structure to stress (cold worked part).

2. Using pure metal

Corrosion can be prevented by increasing purity of the metal.

3. Using metal alloys

Corrosion of metals can be prevented by alloying with some suitable elements. But alloy should be homogeneous. **Ex.** Cr is best in alloying with iron.

4. Modifying environment

- I. **Deaeration:** Exclusion of O_2 from aqueous environment reduces metal corrosion.
- II. **Deactivation:** Addition of chemicals.
$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$
- III. **Dehumidification:** Reducing moisture content.
- IV. **Alkaline neutralization:** Prevention of corrosion by neutralization of acidic solution by adding NH_3 , $NaOH$ etc.

5. Use of inhibitors

- I. **Anodic inhibitors:** They stifle the corrosion reaction, occurring at the anode by forming a sparingly soluble compound with a newly produced metal ion. **Eg.** Chromates, Phosphates, Tungstates.
- II. **Cathodic inhibitors:** Corrosion may be reduced by slowing down the diffusion rate of hydrated H^+ ions. **E.g.** Eliminating oxygen (Na_2SO_3 , N_2H_4), Adding Mg, Zn, Ni (form insoluble hydroxides)

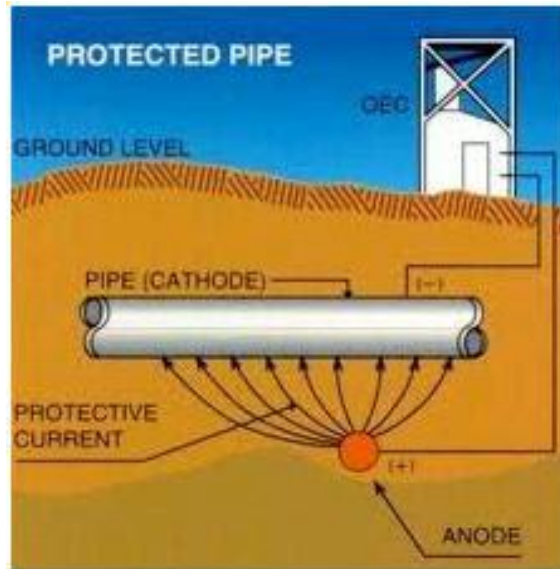
6. Cathodic protection: The method of protection given to a metal by forcibly making it to behave like a cathode is called cathodic protection. There are two types of cathodic protection.

I. Sacrificial anodic protection:

In this method of protection, the metallic structure to be protected called "base metal" is connected to more anodic metal through a wire, so that all the corrosion is concentrated at the more anodic metal.

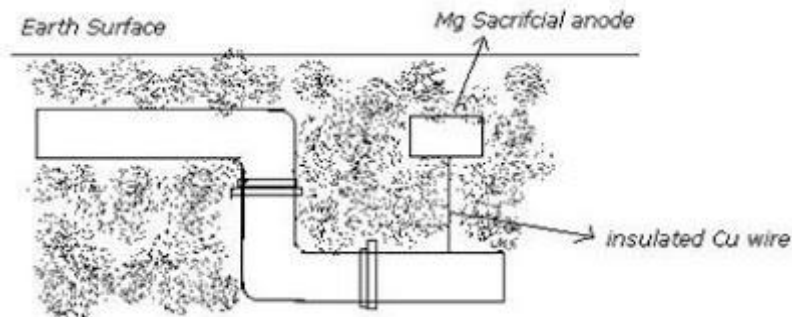
As the more anodic metal is sacrificed in the process of saving base metal from corrosion. Hence, it is known as **sacrificial anode**. The corroded sacrificial anode block is replaced by a fresh one.

Metals commonly used as sacrificial anodes are Zn, Al, Mg and their alloys. Mg is used in high resistivity electrolytes such as soils due to its most negative potential and it can provide highest current output. **Example:** Railway tracks are protected from corrosion by this method.

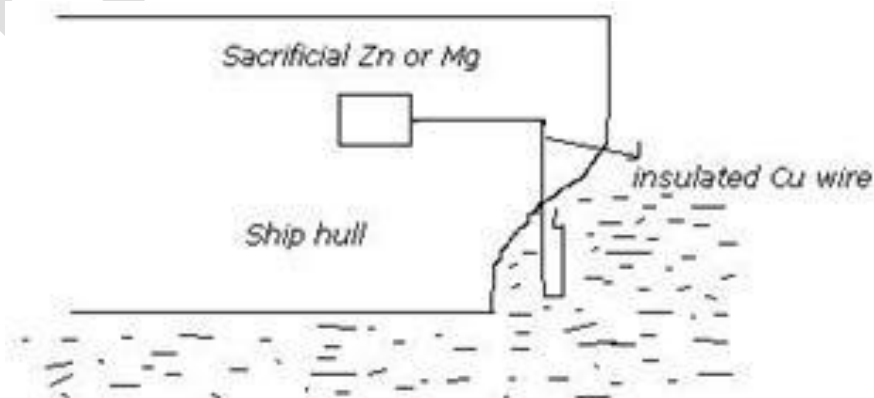


Applications: Important applications of this technique are

- Protection of underground cables and pipelines from soil corrosion.



- Protection of ships and boat hulls from marine corrosion. Sheets of Mg or Zn are hung around the ship hull, these sheets being anodic to corrosion so these sheets get corroded, when consumed completely; these are replaced by fresh one.



II. **Impressed current cathodic protections:**

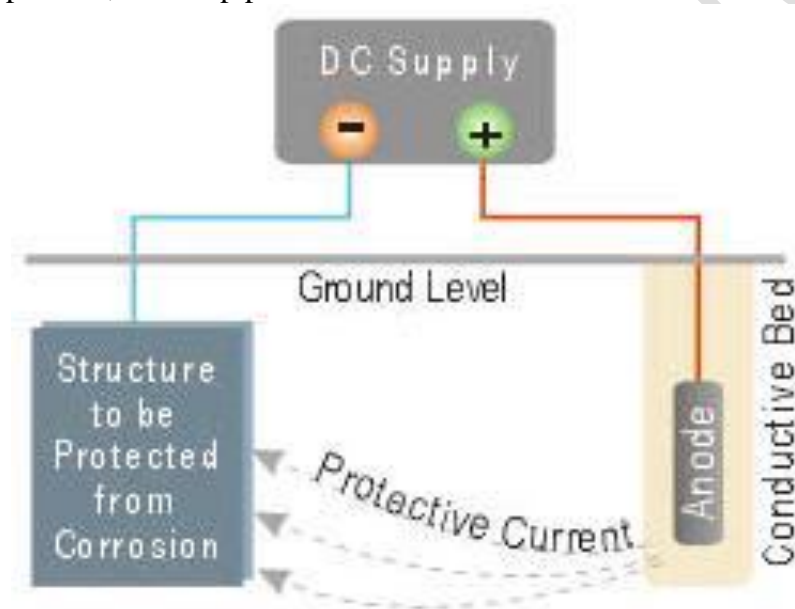
In this method current from an external source is impressed (applied in the opposite direction) to nullify the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.

The anode may be either an inert metal or one which deteriorates and will have to be replaced periodically. The commonly used anodic materials are graphite, carbon, stainless steel, scrap iron, high silica iron and platinum. The anode is buried in back fill such as gypsum to increase the electrical contact between itself and the surrounding soil.

Applications:

This protection method is useful when electrolyte resistivity and current requirements are high. It is well suited for large structures and long-term applications.

This protection technique is employed in the case of open water box coolers, water tanks, buried pipe-lines, marine pipes etc.



7. Application of protective coating

I. Metal Coatings:

Deposition of protective metal over the surface of a base metal is called metallic coating. It is a valuable and well tried method for improving the corrosion life of the underlying metal. Metal coatings are applied by electro deposition, flame spraying, cladding, hot dipping, diffusion coating and vapor deposition. From the corrosion point of view, metal coatings can be divided into two classes – **anodic coatings and cathodic coatings**.

Anodic coatings: Anodic coatings are produced by coating a base metal with more active metals which are cathodic to the base metal.

Ex: Iron is coated with anodic and more active metal such as zinc, magnesium and aluminium.

The one of the important characteristic of anodic coating is that, even if the coating is ruptured, the base metal does not undergo corrosion. The exposed surface of the metal is cathodic with respect to the coating metal and the coating metal preferentially undergoes corrosion. The protection is ensured as long as the anodic coating metal is still present on the surface. Therefore, anodic coating also known as sacrificial coating.

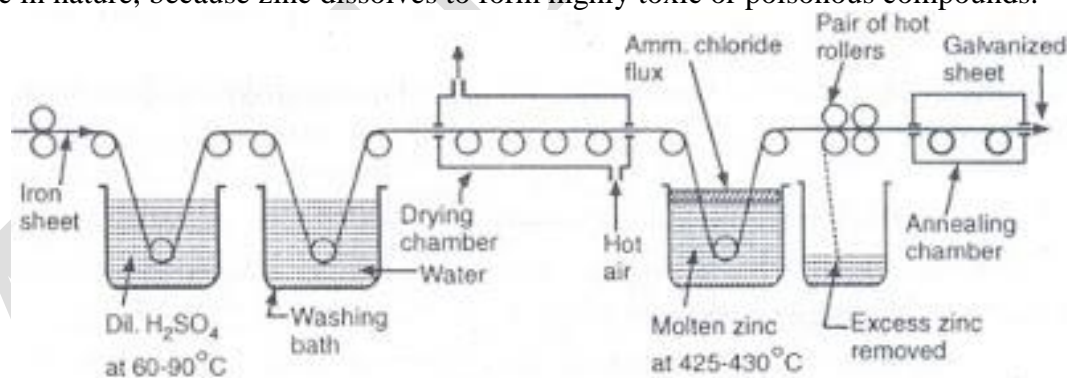
Galvanization is a familiar example for anodic coating and is extensively used to protect iron and steel objects.

Galvanizing:

It is a process of coating iron or steel sheets with a thin coat of Zn to prevent iron from rusting. The base metal iron or steel sheet is cleaned by acid pickling method with dil. H_2SO_4 for 15-20 minutes at 60-90 °C. The sheet is then washed well and dried. It is dipped in a bath of molten zinc maintained at 425-435 °C. The surface of the bath is kept covered with ammonium chloride flux to prevent oxide formation. The sheet is taken out and excess Zn is removed by passing it between a pair of hot rollers. Then the sheet is subjected to annealing process at 650 °C and cooled slowly. An alloy of iron and zinc were formed at the junction of the base metal and coating metal.

Applications: It is mostly used to protect iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets and tubes.

Galvanizing utensils cannot be used for preparing and storing food stuffs especially acidic in nature, because zinc dissolves to form highly toxic or poisonous compounds.



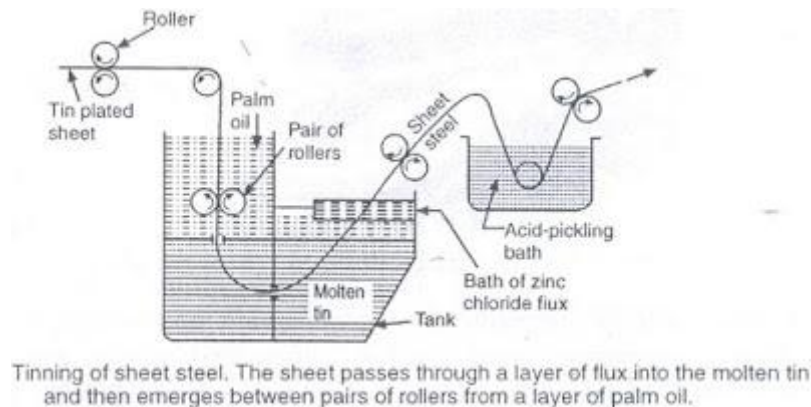
Galvanizing of sheet steel.

ii. Cathodic coating: Cathodic coatings are produced by coating a base metal with a more noble metal which is cathodic. The metal such as copper, nickel, tin, silver is commonly used as cathodic coatings on steel. These coating metals are less reactive than the base metal and are less susceptible for corrosion.

The cathodic coating provides protection only when it is undamaged, continuous and non porous. When the coating is discontinuous, an intense localized corrosion occurs due to the setting up of a galvanic cell that consists of a large cathodic area and a small anodic area. Tinning is most commonly used surface coating on steel surfaces.

Tinning:

Coating tin over iron or steel articles is called tinning. In this process the surface of the base metal i.e., iron sheet is cleaned by acidic pickling with $\text{dil. H}_2\text{SO}_4$ and passed through a bath of zinc chloride flux. The flux helps the molten metal to adhere to the metal surface. Then the sheet is passed through molten tin bath and pressed in between two rollers from a layer of palm oil. Palm oil helps to protect the tin coated surface against oxidation. The rollers remove excess of tin and produce a thin film of uniform concentration. An alloy of the base metal coating metal at their junction.



Applications: Tin metal possess good resistance against atmospheric corrosion. Tin is non toxic and widely used for coating steel, copper, and brass sheet.

The containers coated with tin is used for storing food stuffs, ghee, oils etc. and packing food materials.

Tinned copper sheets are used for making cooking utensils and refrigeration equipment.

Metal Cladding:

It is the process by which a dense, homogeneous layer of coating metal is bonded firmly and permanently to the base metal on one or both side.

The advantage of cladding is that the process as well as the material can be chosen as per the needs of the application and the bond strength required. The laser beam method of cladding can be used for ceramic coating as well as metallic coating. Effective cooling in such cases ensures better micro-structure, and hence only a smaller area is thermally affected. With metal cladding, the surfaces can develop adequate wear resistance. The method is suitable for complex shapes as well.

Eg. Copper-clad aluminum wires are extensively used in electrical applications due to the cost advantage as well as an improved electrical conductivity. Metal cladding is also used on the outer surfaces of structures as well as buildings for corrosion and abrasion protection. Aluminum cladding is advantageous for buildings as it is self-cleaning. The earliest type of metal cladding used in buildings was called "corrugated sheeting," which was used for roofs and walls. In some cases, the cladding is chosen for its aesthetic advantage.

Electroplating:

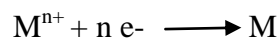
The process of deposition of a metal on to the surface of another metal, alloy or any conductor metal by the electrolysis is called electroplating.

It consists of a process, by which a metal is deposited on another metal or alloy by passing a direct current through an electrolyte solution containing the metal ions to be deposited. The common coating metals used is Zn, Cu, Ni, Cr, Ag, Pt, Au, etc.

The electroplating device is essentially an electrolytic cell, in which two electrodes, anode and cathode are dipped in an electrolyte solution. The principal components of an electroplating process are:

- An electroplating bath containing a conducting salt and the metal to be plated in a soluble form as well as a buffer and additives.
- The electronically conducting cathode, i.e., the article to be plated.
- The electronically conducting anode, the coating metal itself or an inert material of good electrical conductivity like graphite.
- An inert vessel to contain the above mentioned materials, made up of either rubber lined steel, plastic, concrete or wood.

In this process the object to be plated is made the cathode in an electrolyte bath containing a metal ion, M^{n+} so that the simplest reaction at the cathode is



Wherever possible, the preferred anode reaction is the dissolution of the same metal in the solution.



In such cases, there is a continuous replenishment of electrolyte during electrolysis. However, if the anode is made of an inert material that does not pass into the solution, the electrolyte salt is added continuously in order to maintain optimum metal ion concentration in the solution.

Ex: Nickel electroplating

Electroplating of Nickel:

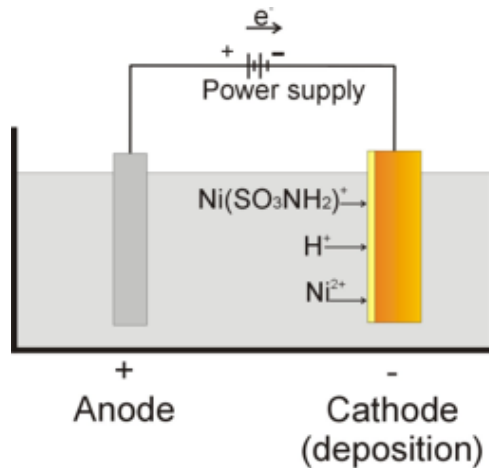
Nickel is a widely plated metal in plating industry, for both decorative and protective applications. To electroplate nickel on other surfaces different bath compositions are used.

Watt's bath: It is an all purpose bath, used both for decorative and protective applications of nickel deposit, as well as for making up worn out parts and for electroforming.

Composition: $NiSO_4 + NiCl_2 + \text{boric acid} + \text{sodium lauryl sulfate}$

Sulfamate bath: For heavy nickel deposits are required, sulfamate bath is preferred.

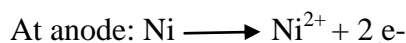
Composition: Nickel sulfamate + $NiCl_2$ + Boric acid



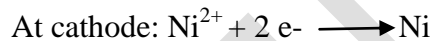
The article to be electroplated is subjected to solvent cleaning to remove oil, greases etc. then it is subjected to acid pickling with dil.HCl or dil.H₂SO₄ to remove any scales, oxides etc.

The cleaned article is made cathode of the electrolytic cell and the anode can be made of the high purity Nickel pellets or pieces in titanium mesh basket/cotton/terylene bath. The electrodes are dipped in solution of an electrolytic bath.

When direct current is passed Ni metal is dissolved into the solution as Ni²⁺ ions at anode.



Ni²⁺ ions migrate to the cathode and deposit on the base metal article in the form of a thin layer.



Nickel plating forms a corrosion resistant, wear resistant, hard surface. When nickel is co-deposited with insoluble materials such as alumina, zirconia, silicon carbide, etc., the wear and abrasion resistance is enhanced.

Application:

- For decorative as well as protective applications
- Used as an undercoat for the decorative chromium finish on components made of steel, brass, zinc die castings, plastics and to a limited extent on Al and Mg alloys.
- Used as an undercoat for brass, gold and rhodium plating.
- Thick deposits of nickel – heavy nickel – are used in electroforming, for corrosion and wear resistance purpose, for high temperature oxidation resistance, and to build up worn out or mismachined parts.
- Black nickel plating is used for making name plates, type writer parts, camera components, optical and electrical instruments, military hardware.

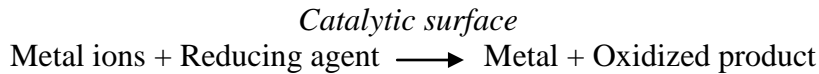
Electroless plating:

It is a method of depositing a metal or alloy over a substrate by controlled chemical reduction of the metal ions by a suitable reducing agent without using electrical energy. The process is a chemical reaction and is autocatalytic.

The reduction of metal ions by the reducing agent is catalyzed by the metal atoms being plated. Therefore, electroless plating is also termed as autocatalytic plating.

The surface to be plated should be catalytically active so that in the beginning of the plating reaction, the surface of the substrate catalyses the reduction. Once the substrate is covered by the metal or alloy coating, the coating catalyses the reduction. The process continues with building of successive layers of the metal or alloy.

The electroless plating process can be represented as,



The catalytic metals such as Ni, Co, Steel, Fe, Rh, Pd, Al, etc., do not require any surface preparation before electroless plating on them. Non-catalytic metal such as Cu, Brass, Ag, etc., need activation.

Electroless plating of Copper:

The composition of an electrolyte bath for electroless plating comprises the following:

Salt: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, Reducing agent: Formaldehyde (HCHO)

Buffer: NaOH + Rochelle salt, $\text{pH}=11$ (Potassium sodium tartrate, $\text{NaKC}_4\text{H}_4\text{O}_6$)

Complexing agent: EDTA, Temperature: 298°K

The redox reaction takes place as



The metallic copper obtained as a reduced product in the bath deposits on the metal surface.

However, the reduction proceeds through a cuprous state. An excess of cuprous oxide formation will cause the reduction reaction to proceed out of control. To inhibit the formation of cuprous oxide, air is bubbled slowly through the electroless copper solution and small complexing agents are added to the solution. The presence of these complexing agents turns the electroless copper bath into a chelated solution. Furthermore, in order for the reaction to progress, certain concentration levels of copper sulphate, formaldehyde, sodium hydroxide, and chelating agent, and the correct chemical ratios of these chemical components must be maintained. The electroless copper bath must be analyzed at least every four hours to make sure that optimum concentration and ratios are maintained. Replenishment of copper sulfate, formaldehyde, sodium persulfate, and chelating agent must be provided as needed. Constant monitoring and maintenance are required to properly operate the electroless copper bath.

Applications:

- Widely used for metalising printed circuit boards.
- For producing through-hole connections.
- For plating on non conductors.
- As a base for subsequent conventional electroplating.
- Applied on wave guides and for decorative plating on plastics.

Questions:

1. Define corrosion.
2. What is meant by rusting of iron?
3. What is dry and wet corrosion?
4. Define Pilling-Bedworth rule?
5. The rate of metallic corrosion increases with increasing temperature. Give reason.
6. What is meant by passivity?
7. A steel screw in a brass marine hardware corrodes. Give reasons.
8. What is differential aeration corrosion?
9. Give examples of metal which has volume of oxide is greater than the metal. (**Hint-** Cr, Ni, Al, Ti)
10. Why does a steel pipe in a larger copper tank corrode causing rapid destruction?
11. What are different types of corrosion? Explain the electrochemical theory of wet corrosion, giving its mechanism.
12. Explain the rusting of iron 'with the help of electrochemical theory of corrosion'
13. Illustrate the reactions involved in differential aeration corrosion with reference to the iron materials.
14. How iron corrodes in neutral or alkaline solution?
15. Discuss the various factors affecting rate of corrosion.
16. Discuss the various methods of preventing corrosion.
17. Why coating of zinc on iron is called Sacrificial anode?
18. What is galvanizing?
19. Explain the mechanism of following types of corrosion
(a) Water-line (b) Pitting (c) Bimetallic or galvanic (d) Inter granular (e) Concentration cell corrosion.

Text Book & References

1. Engineering Chemistry by Jain and Jain
2. A test Book of Engineering Chemistry by Shashi Chawla