

UNIT: 2 CORROSION AND ITS CONTROL

Lecture Session 10: Topics: Concepts of corrosion, its types, mechanism of chemical corrosion

Introduction

Corrosion is defined as the loss of materials as a result of chemical or electrochemical reaction with the environment. The process of corrosion is slow, but the losses due to it are enormous which cannot be measured in terms of the cost of metal alone, but also the cost of fabrication. Now-a-days it is necessary to pay more attention to corrosion because of increasing use of metals in all fields of engineering and technology. Therefore, knowledge about different forms of corrosion and prevention is essential to minimise the maintenance and replacement cost of the material.

“Corrosion is defined as the gradual destruction of metals or alloys by the chemical or electrochemical reaction with its environment.”

Causes of corrosion occurs

Most of the metals (except noble metals) naturally exist in combined form. During metallurgy the metal are extracted from their ores by reduction process. In the pure metallic state, the metals are unstable and considered to be in the excited (higher energy) state. Therefore, the extracted metals have a tendency to go to thermodynamically stable (lower energy) state, which is otherwise known as corrosion. Thus, corrosion is a process “reverse of extraction of metals.”

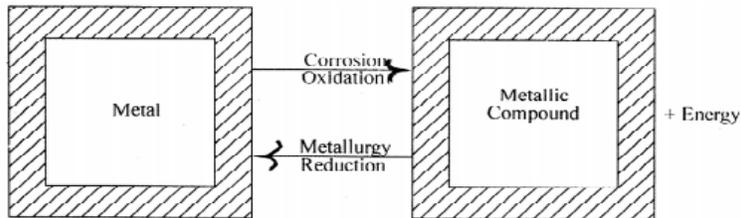
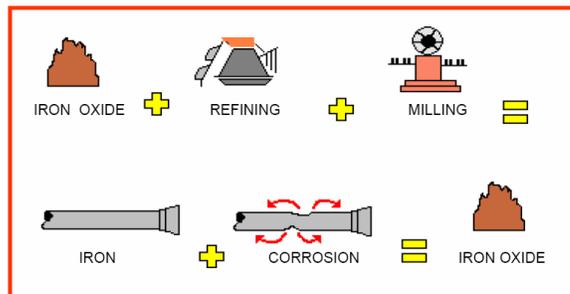


Illustration of Corrosion

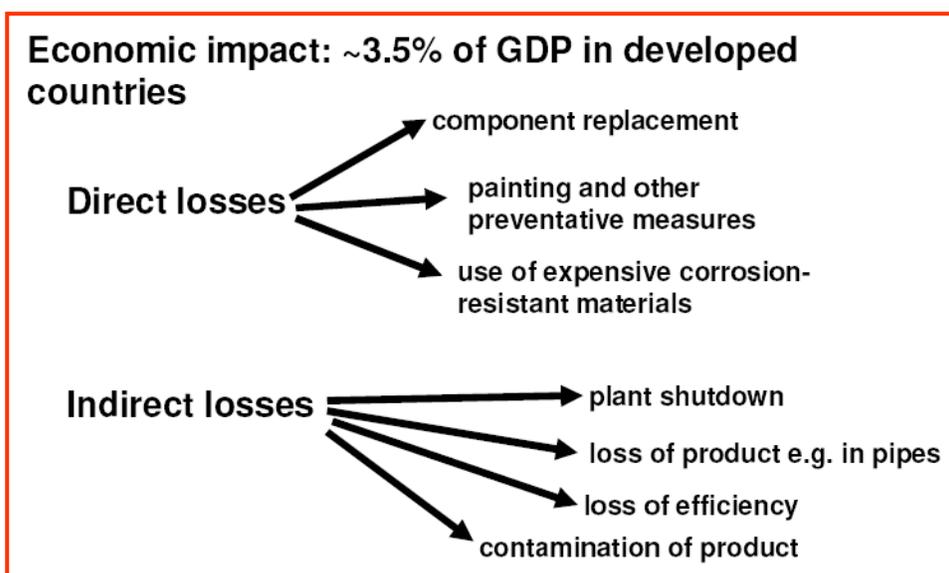


Corrosion – A natural process

Consequences of corrosion

- i. The efficiency of machine will be lost due to the loss of useful properties of metal.
- ii. The products gets contaminated due to corrosion.
- iii. Increase in maintenance and production cost.
- iv. Preventive maintenance like metallic (or) organic coating is required.
- v. Toxic products are released.

Loss due to corrosion



Corrosive environments

- All environments are corrosive to some degree
- Typical corrosive environments:
 - Air and humidity
 - Fresh, distilled, salt and marine water
 - Natural, urban, marine and industrial atmospheres.
 - Steam and gases, like chlorine
 - Ammonia
 - Hydrogen sulfide
 - Sulfur dioxide and oxides of nitrogen
 - Fuel gases
 - Acids Alkalies
 - Soils

Five Good Reasons to Study Corrosion

Reason 1 – Preservation of valuable resources

- Materials are precious resources of a country.
- Our material resources of iron, aluminum, copper, chromium, manganese, titanium, etc. are dwindling fast.
- Some day there will be an acute shortage of these materials.
- There is bound to be a metal crisis and we are getting the signals.
- To preserve these valuable resources, we need to understand how these resources are destroyed by corrosion and how they must be preserved by applying corrosion protection technology.

Reason 2 - Engineering knowledge is incomplete without an understanding of corrosion

- Aeroplanes, ships, automobiles and other transport carriers cannot be designed without any recourse to the corrosion behavior of materials used in these structures.

Reason 3 – Disaster prevention

- Several engineering disasters, such as crashing of civil and military aircraft, naval and passenger ships, explosion of oil pipelines and oil storage tanks, collapse of bridges and decks and failure of drilling platforms and tanker trucks have been witnessed in recent years
- Corrosion has been a very important factor in these disasters. Applying the knowledge of corrosion protection can minimize such disasters.
- Two million miles of pipe need to be corrosion-protected for safety

Reason 4 – Health care

- The designing of artificial implants for the human body requires a complete understanding of the corrosion science and engineering
- Surgical implants must be very corrosion-resistant because of corrosive nature of human body environment

Reason 5 - Threat to the environment

- Water can become contaminated by corrosion products and unsuitable for consumption
- Corrosion prevention is integral to stop contamination of air, water and soil.

TYPES OF CORROSION

Based on the environment, corrosion is classified into two types. (i)

Dry (or) Chemical corrosion

(ii) Wet (or) Electrochemical corrosion

Dry (or) Chemical corrosion

It is due to the direct chemical attack on metals by atmospheric gases such as oxygen, carbon-di-oxide, hydrogen sulphide, etc.

It follows adsorption mechanism. Corrosion product accumulate in the same spot of corrosion.

Example : Tarnishing of silver in H₂S gas, Action of dry HCl on iron surface.

There are three main types of chemical corrosion.

- (a) Oxidation corrosion
- (b) Corrosion by hydrogen
- (c) Liquid–Metal corrosion

(a) Oxidation corrosion

Oxygen present in atmosphere attacks metal surface resulting in the formation of metallic oxide which is a corrosion product and this is known as oxidation corrosion.

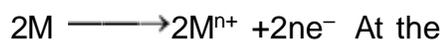
Alkali metals (Li, Na, K, etc.) and alkaline earth metals (Mg, Ca, etc.) are rapidly oxidised at low temperature. At high temperature almost all metals (except Ag, Au and Pt) are oxidised.

Mechanism of oxidation corrosion

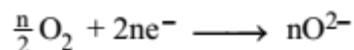
(i) Oxidation occurs first at the surface of the metal resulting in the formation of metal ions (Mⁿ⁺).

(ii) Oxygen changes to ionic form (O²⁻) and react with the metal ion to form the metallic oxide.

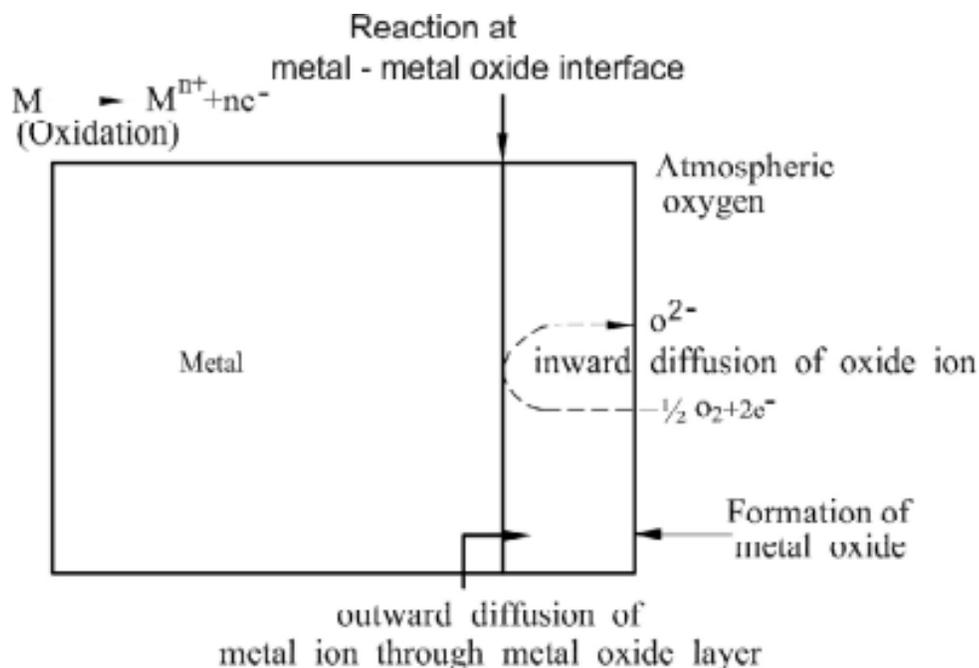
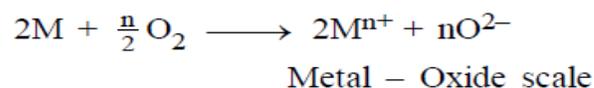
At the metal/oxide scale interface



oxide scale/environment interface



The over all reaction



Mechanism of oxidation corrosion

The metal oxide layer keeps on increasing in thickness as the corrosion progresses. The outward diffusion of metal is rapid than the inward diffusion of oxygen, this is because of higher mobility of smaller metal ions than the oxygen.

The nature of oxide film formed on the metal surface plays an important role in oxidation corrosion.

Nature of oxide layer and its role

1. Stable : The oxide layer formed in some cases stick firmly to the parent metal surface. Such layers naturally do not allow penetration of oxygen to the underlying metal surface and thus act as protective films.

Example : Al, Sn, Pb, Cu, etc.

2. Unstable : In case of some metals, elemental or uncombined state is naturally more stable than the combined state such as oxide, sulphide, sulphate, etc.



Only forward reaction is favoured. So, oxidation corrosion is not possible in those metals.

Example : Ag, Au and Pt.

3. Volatile : In some metals the oxide layers formed are volatile. They leave the metal surface as soon as they are formed. That means, the fresh metal surface is kept exposed all the time for further attack. This makes the corrosion continuous and rapid.

Example : Mo (MoO₃ is volatile).

4. Porous : The oxide layer formed in some cases are porous. Atmospheric oxygen gets free access to underlying metal surface. Consequently corrosion goes non-stop till the entire metal is converted into its oxide. *Example* : Alkali metals (Li, Na, K etc.)

Pilling–Bed worth rule

An oxide layer is protective (or) non-porous, if the volume of the metal oxide formed is atleast as great as the volume of the metal from which it is formed.

Protective or non-porous : *Example* : Al, Sn, Pb, Cu, etc.

$$V_{MO} > V_M$$

An oxide layer is non-protective (or) porous, if the volume of the metal oxide formed is less than the volume of the metal from which it is formed.

$$V_{MO} < V_M$$

Non-protective or Porous :

Example : Alkali metals : Li, Na, K, etc.

Alkaline earth metals : Mg, Ca, Si etc.

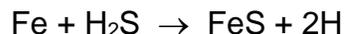
(b) Corrosion by hydrogen

Atomic hydrogen (H) can more easily penetrate steel and other metals than molecular hydrogen (H₂), which is chemically more active.

(i) Hydrogen embrittlement : At ordinary temperatures, some reactions produce atomic hydrogen which attack metals and reduce their strength.

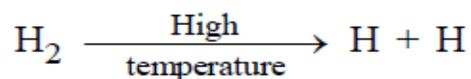
Example :

Aqueous solution of H₂S liberates atomic hydrogen at iron-surfaces.



Atomic hydrogen so produced penetrates the metal body and collects in voids, if any. There it again gets converted into molecular hydrogen ($H + H \rightarrow H_2$). When this process continues, the pressure inside the voids increase sufficiently to cause blisters and fissures consequently the metal is made weak.

(ii) Decarburization: At high temperatures, atomic hydrogen is produced by thermal dissociation.



Atomic hydrogen so produced at this high temperature condition is chemically very active. It easily combines with C, S, O or N which are normally present in metals in small amounts. For example, atomic hydrogen combines with 'C' of steel at high temperature forming CH_4 gas.



The gas collects in gaps and voids and causes blisters and fissures. Consequently the metal becomes weak.

(ii) By other gases : Gases like, SO_2 , CO_2 , H_2S , F_2 and Cl_2 are also corrosive.

(c) Liquid–Metal corrosion

This is brought about by chemical action of flowing liquid metals at high temperatures over solid metal or alloy. The corrosion involves either

- (i) dissolution of a solid metal by a liquid metal or
- (ii) internal penetration of the liquid metal into the solid metal.

Example: Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactor.

Lecture Session 11: Topics: Electrochemical corrosion, its mechanism – Hydrogen evolution type and Oxygen Absorption type.

Wet (or) Electrochemical Corrosion

This type of corrosion occurs when

- (i) Metal is in contact with electrolyte or varying concentration of oxygen.
- (ii) Two dissimilar metals or alloys are immersed or partially dipped in a solution.

Under the above conditions, metals lead to form different anodic and cathodic areas resulting an electrochemical cell.

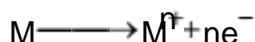
At anode – Oxidation takes place (loss of electron)

At Cathode – reduction takes place (gain of electron)

i.e. It involves flow of current between anodic and cathodic areas.

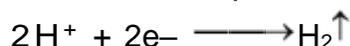
Mechanism of electrochemical corrosion

In an electrochemical corrosion, the anodic reaction involves dissolution (oxidation) of metal to metal ion.

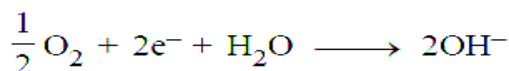


The cathodic reaction involves reduction which depends on the nature of corroding environment. If the medium is

(i) acidic, cathodic reaction is accompanied by evolution of hydrogen. $2H^{+}$



(ii) alkaline (or) neutral, absorption of oxygen is the cathodic reaction.



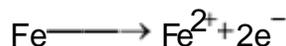
(i) Evolution of Hydrogen type corrosion

This occurs when metal comes in contact with acidic environment.

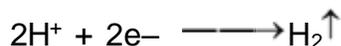
(i.e.) All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic medium with the evolution of hydrogen gas.

(e.g.) Iron comes in contact with acids like HCl, H₂SO₄, HNO₃, etc.

At anode : Oxidation of Iron takes place with the liberation of electrons.

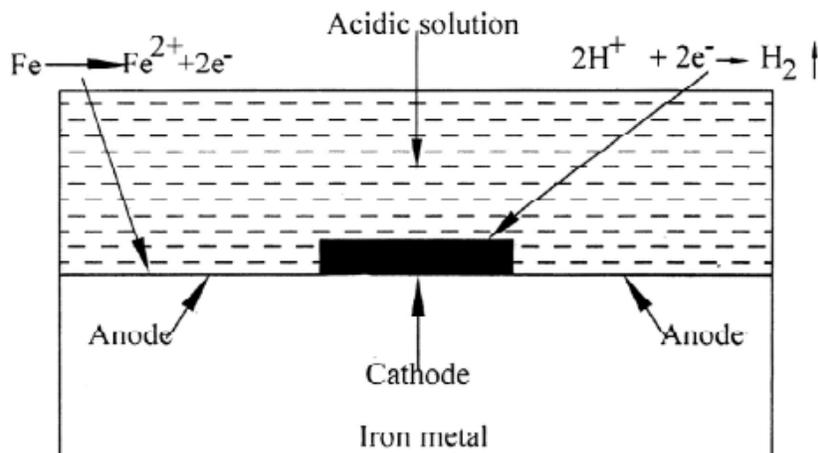


At cathode : The liberated electrons flow from anode to cathode, where H⁺ ions get reduced to hydrogen gas.



The Overall reaction is



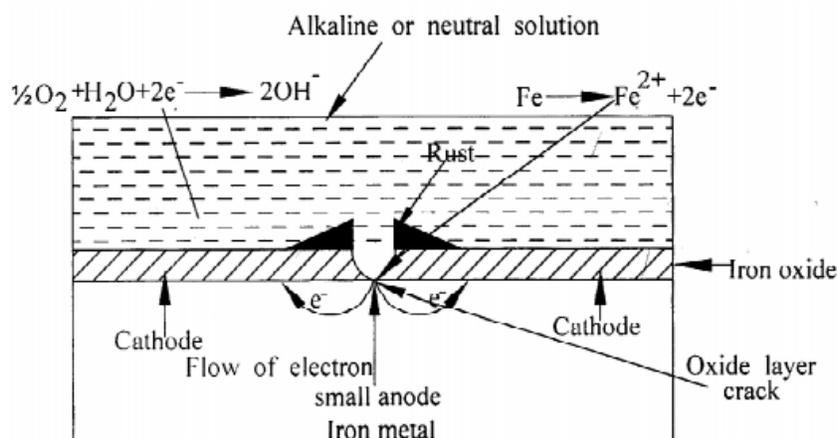


Hydrogen evolution corrosion

(ii) Absorption of oxygen (Rusting of Iron) type corrosion

This type of corrosion occurs when metal comes in contact with neutral or alkaline medium.

(e.g) The surface of iron is usually coated with a thin film of iron oxide. However if iron oxide film develops some cracks, anodic areas are created on the surface, while the other parts of metal acts as cathode.



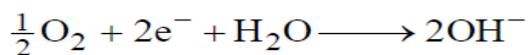
Oxygen absorption corrosion

Reactions

At anode : Iron dissolves as Fe^{2+} ions with the liberation of electrons.



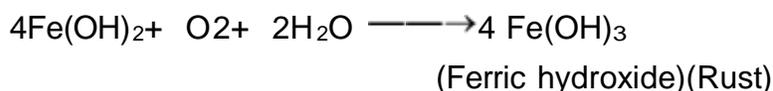
At cathode : The electrons liberated from anode are intercepted by the dissolved oxygen at cathode to form OH⁻ ions..



The Fe²⁺ from anode and OH⁻ ions from cathode diffuse to form ferrous hydroxide



If excess oxygen is present in the corroding medium, ferrous hydroxide is oxidised to ferric hydroxide (rust).



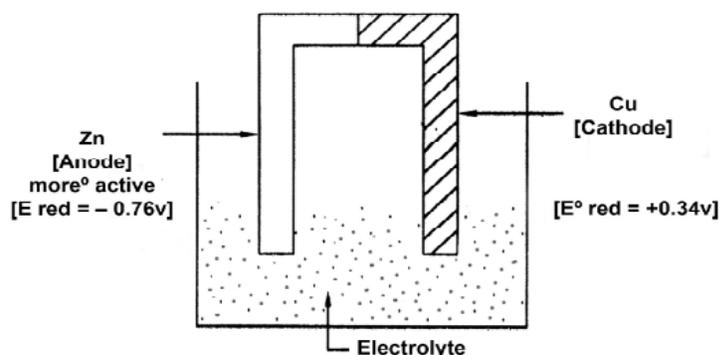
Here corrosion occurs at anode but the corrosion product get deposited at cathode. This is because, ionic diffusion through the conducting medium is more for smaller Fe²⁺ than OH⁻.

Lecture Session 12: Topics: Types of electrochemical corrosion – Galvanic, Differential aeration, Pitting, Waterline, Stress corrosion.

TYPES OF ELECTROCHEMICAL CORROSION

Galvanic (or) Bimetallic corrosion

When two different metals comes in contact with each other in presence of electrolyte (conducting solution), galvanic corrosion occurs. The more active metal (metal with high negative electrode potential) acts as anode and less active metal acts as cathode. Corrosion occurs at the anodic area.



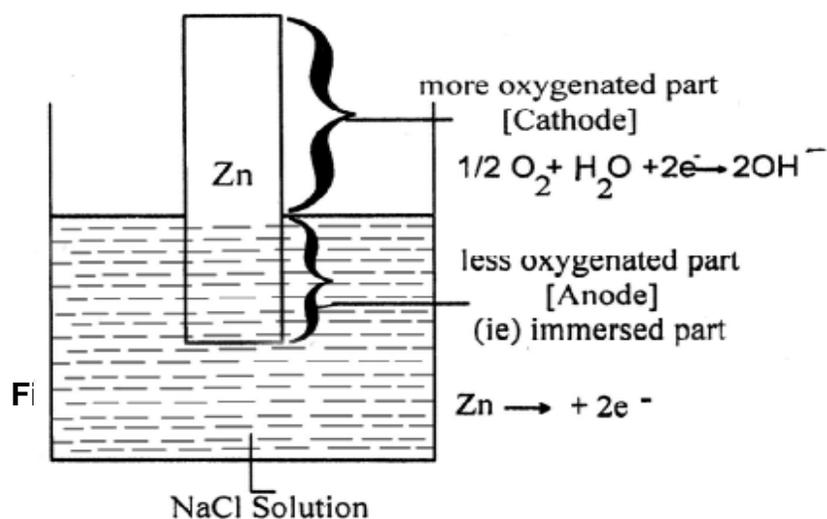
In Zn–Cu couple, Zn acts as anode [$E^{\circ}_{\text{Zn}} = -0.76\text{V}$] and Copper acts as cathode [$E^{\circ}_{\text{Cu}} = +0.34\text{V}$]

(e.g.) Steel screws in a brass marine hardware.

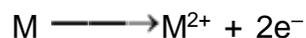
2. Differential aeration (or) Concentration cell corrosion

This type of corrosion occurs when metal is exposed to varying concentration of oxygen or an electrolyte.

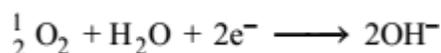
When a metal is partially immersed in a conducting solution, the immersed part which has less access to oxygen (air) acts as anode and the metal part above the solution has more access to oxygen acts as cathode. So a potential is created and causes a current flow within the same metal.



At anode (less aerated part) corrosion occurs

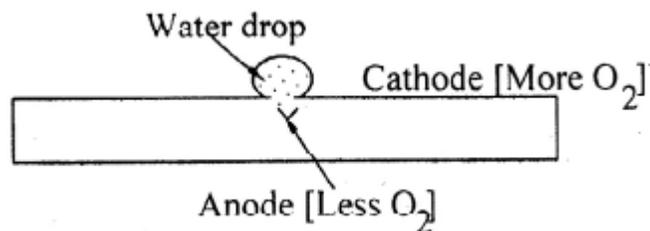


At cathode (more aerated part) OH^- ions are produced.

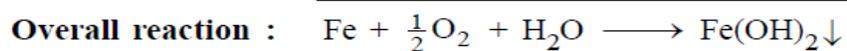
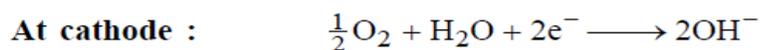


3. Pitting corrosion

Pitting is a localised attack, resulting in the formation of a hole around which the metal is relatively unaffected. The mechanism involved is differential aeration corrosion.



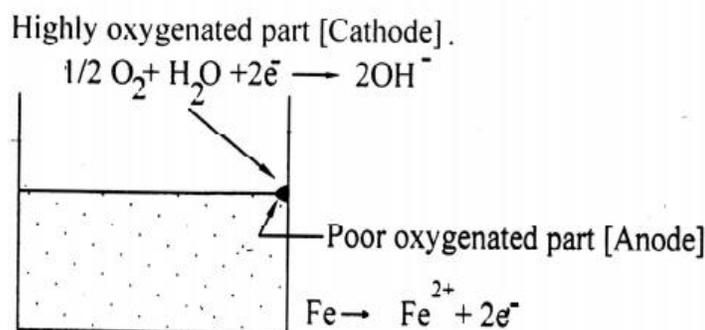
Pitting corrosion



Consider a drop of water resting on iron surface. The area covered by the drop of water is less oxygenated, acts as anode and the remaining area acts as cathode.

Water line corrosion

It is also a type of differential aeration corrosion. When water is stored in a steel tank, it is generally found that maximum amount of corrosion takes place along a line just beneath the level of the water (i.e.) The metal just above the water level is cathodic and the corrosion occurs at metal just below the water level which is anodic.



Water line corrosion

Stress corrosion cracking (stress corrosion)

Stress-corrosion cracking is the cracking of a metal or alloy by the combined action of stress and the environment.

Stress-corrosion cracking (SCC) can occur in stressed structures such as bridges and support cables, aircraft, pressure vessels, pipelines, and turbine blades. Instances of stress-corrosion cracking are especially serious when they involve critical structures such as bridges or aircraft as because they involve the loss of life or personal injury.

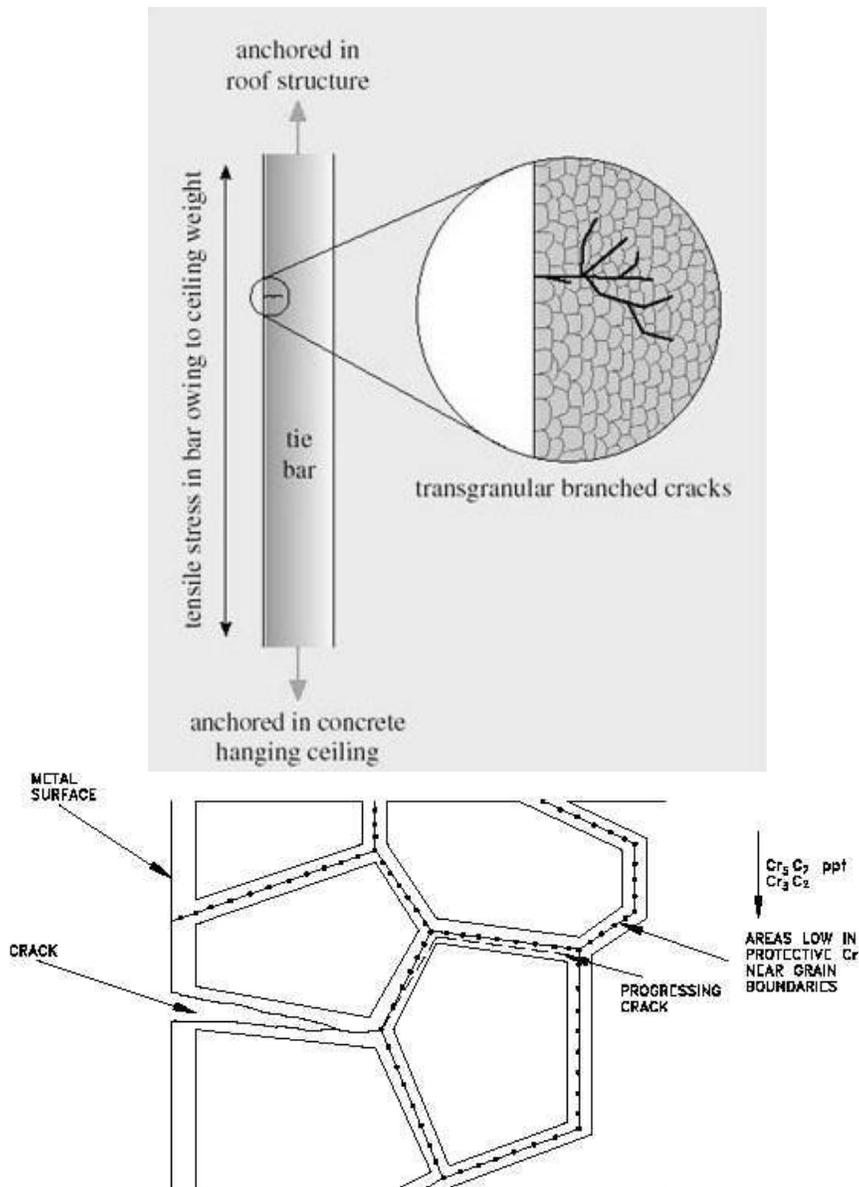


Fig. shows the failure of a high strength rocket motor case due to stress-corrosion cracking in tap water.

Characteristics of Stress-Corrosion Cracking

(1) A tensile stress is required.

- The tensile stress may be external, as with an applied load, or the stress may be a residual stress due to metal-working processes, such as machining or welding.
- The stress may also be self-generated, as may be caused by the wedging action of solid corrosion products within an emerging crack.

(2) Metals or alloys which undergo SC usually have a good resistance to general corrosion.

For example, stainless steels, aluminum alloys, and titanium all undergo SCC but are usually resistant to general corrosion (in neutral solutions). One exception is that high-strength low-alloy steels may undergo both general corrosion and SCC at the same time.

(3) Specific environments cause SCC in certain alloys.

- For example, Cl^- solutions (but not NO_3^- solutions) cause SCC of type 304 stainless steels. On the other hand NO_3^- solutions (but not Cl^- solutions) cause SCC of mild steel.
- In addition, ammonia or amines are specific reagents for
- the SCC of brasses (Cu–Zn alloys). Some specific environments which cause SCC for various metals are listed in Table 1.

(4) The necessary corroding species can be present in small concentrations.

- For example, a few ppm of Cl^- in high-temperature water can cause SCC in certain stainless steels.

(5) A threshold stress or stress intensity must be exceeded for SCC to occur

Types of alloys	Environments
High-strength steels [33]	Seawater chloride solutions solutions containing H ₂ S NO ₃ ⁻ solutions
Stainless steels [20]	Cl ⁻ , Br ⁻ , F ⁻ solutions hydroxide solutions polythionic acids (H ₂ S _x O ₆ , x = 3, 4, 5) thiosulfate solutions
Aluminum alloys [24]	Chloride solutions most aqueous solutions organic liquids
Titanium alloys [1, 66, 37, 34]	Seawater Cl ⁻ , Br ⁻ , I ⁻ solutions carbon tetrachloride and other organic solvents, including alcohols fuming nitric acid
Brass (Cu–Zn alloys) [41, 40]	Ammonia solutions amines citrate solutions tartrate solutions

How can SCC be controlled?

- ❖ By selecting a material that is not susceptible to the service environment and by ensuring that any changes to the environment caused by cleaning etc are not detrimental.
- ❖ By controlling the service stresses through careful design and minimising stress concentrations to keep them below the critical value. Residual stresses can be reduced by heat treatments and careful design for manufacturing.
- ❖ By using corrosion inhibitors during cleaning operations or to control the environment in a closed system
- ❖ By coating the material and effectively isolating the material from the environment.

Difference between Chemical and Electrochemical corrosion

S.N	Chemical or Dry corrosion	Electrochemical or Wet
1.	It occurs in dry condition	It occurs in the presence of moisture or
2.	It involves the direct chemical attack of metals by dry gases.	It involves the setting up of large number of electrochemical cells.
3.	Corrosion products accumulate in the same	Corrosion occurs at the anode, products gather at
4.	Corrosion is uniform throughout the	Corrosion is not uniform, which depends on anodic
5.	It follows adsorption	It follows mechanism of electrochemical
6.	It is a slow process.	It is a fast process.

Lecture session 13: Factors influencing corrosion (metal and environmental based)

FACTORS INFLUENCING THE RATE OF CORROSION

The rate and extent of corrosion depends on

- (i) Nature of the metal
- (ii) Nature of the environment

Nature of the metal

- (a) Position in galvanic series
- (b) Over voltage
- (c) Purity of metal
- (d) Relative areas of anode and cathode
- (e) Nature of oxide film (surface film)
- (f) Nature of corrosion product
- (g) Physical state of metal

(a) Position in galvanic series

Metals above hydrogen in emf series get corroded vigorously. When two metals are in contact with each other in presence of an electrolyte, the more active metal or metal having high negative potential undergoes corrosion. The extent of corrosion depends on the difference on their position. Greater the difference, faster is the corrosion rate.

Cathodic ↑ ↓ Anodic	Least Active	Platinum
	High Potential	Gold
		Carbon (graphite)
		Titanium
		Type 316 or 304 stainless steel (passive)
		Monel metal (70% nickel, 30% copper)
		Silver
		Nickel
		Lead
		Bronze, Copper, Brass
		Tin
		Lead/Tin solder
	Most Active	Type 316 or 304 stainless steel (active)
	Low Potential	Cast Iron/Mild Steel
	Cadmium	
	Aluminium	
	Zinc	
	Magnesium	

(b) Over voltage

If hydrogen overvoltage of the cathodic metal is very high, corrosion rate is lesser. When the voltage in a circuit of part of it raised above its upper design limit - over voltage.

$$(i.e.) \text{ Over voltage of a metal} \propto \frac{1}{\text{Corrosion rate}}$$

(e.g.) When Zn dipped in 1 N H₂SO₄, the hydrogen over voltage is 0.70 volts. Here, the rate of corrosion is low. However if we add a drop of CuSO₄ to H₂SO₄, the hydrogen over voltage drops to 0.33V, which accelerates corrosion of zinc by forming a minute cathode. As the over voltage of metal decreases corrosion increases.

(c) Purity of metal

The 100% pure metal will not undergo any types of corrosion. But presence of impurity may lead to heterogeneity in metal, resulting large number of galvanic cells at different parts of metal. The higher the percentage of impurity, higher the rate of corrosion.

(eg.)

Zn containing impurities Pb (or) Fe undergoes corrosion due to formation of local galvanic cells.

%Purity of Zn	99.9999	99.99	99.95
Corrosion rate	1	2650	5000

(d) Relative areas of anode and cathode

Corrosion is severe, if the anodic area is smaller than cathodic area. (i.e) Larger the cathodic area, greater will be the demand for electrons for reduction to occur at cathode. So cathode induces anode to provide more electrons (oxidation).

(e) Nature of oxide film (surface film)

The nature of surface film formed decides the extent of corrosion. In the case of alkali and alkaline earth metals the oxide film formed is porous (non-protective) further corrosion occurs. But, in heavy metals, the oxide film formed is non-porous (protective) further corrosion is prevented (e.g. Al/Cr metal oxide).

(f) Nature of corrosion product

The corrosion product formed is soluble in corroding medium, the corrosion rate will be greater. Similarly, if the corrosion product is volatile (e.g.) MoO_3 , SnCl_4 both are volatile corrosion rate will be faster.

(g) Physical state of metal

The rate of corrosion depends on physical state of metal (i.e) grain size, stress, orientation of crystals.

The smaller the grain size of metal or alloy greater will be its solubility and corrosion. Areas under stress (bends, joints, rivets) tend to be anodic and leads to corrosion.

Nature of the environment

- (a) Temperature
- (b) Humidity
- (c) Presence of impurity in atmosphere
- (d) Presence of suspended particles
- (e) Nature of ions present
- (f) pH

(a) Temperature

The rate and extent of corrosion is directly proportional to temperature.

Reason: Increase of temperature increases diffusion of ions in corrosive medium, and increases the corrosion rate. (i.e) dissolution of metal is faster.

(b) Humidity

The greater is the humidity, the greater is the rate and extent of corrosion. This is due to the fact that moisture acts as a solvent for O_2 , H_2S , SO_2 and NaCl etc., resulting an electrochemical cell.

(c) Presence of impurity in atmosphere

Presence of gases like CO_2 , H_2S , SO_2 and fumes of HCl , H_2SO_4 makes the environment acidic so corrosion is accelerated.

Presence of Na^+ and Cl^- in marine environment leads to high conductivities and increases the corrosion.

(d) Presence of suspended particles

If the environment contains chemically active particles (NaCl , $(\text{NH}_4)_2\text{SO}_4$) they absorb moisture and act as strong electrolytes. So rate of corrosion is high.

If charcoal (inactive) is present, it absorbs sulphur gases, moisture and slowly enhances the corrosion.

(e) Nature of ions present

Presence of silicate (anion) in the medium leads to insoluble products (silica gel), which prevents corrosion.

Presence of chloride ions in electrolyte destroys the protective films and enhances corrosion.

If ammonium salts are present in corroding medium that will lead to corrosion of many metals.

(f) Effect of pH

Generally acidic medium is more corrosive than alkaline medium. The corrosion of iron in oxygen free water is very slow upto $\text{pH} = 5$. But in presence of oxygen the corrosion rate of iron is very high at $\text{pH} = 5$. But at $\text{pH} = 4$ the corrosion rate of iron is considerably increased due to the change in oxidation states of iron from Fe^{2+} to Fe^{3+} . Zinc which is readily corroded in acidic solution suffers very less corrosion in alkaline medium i.e. $\text{pH} = 11$. Aluminium has less corrosion at $\text{pH} = 5.5$ which corrodes rapidly at $\text{pH} = 8.5$.

Lecture session 14: Corrosion control – Sacrificial anode & impressed current cathodic protection and corrosion inhibitors.**CORROSION CONTROL**

The corrosion process depends on the metal and the environment. So control measures are aimed at the metal and environment.

(i.e.) (i) Metal based controlled measures and (ii) Environment based controlled measures.

Metal based controlled measures

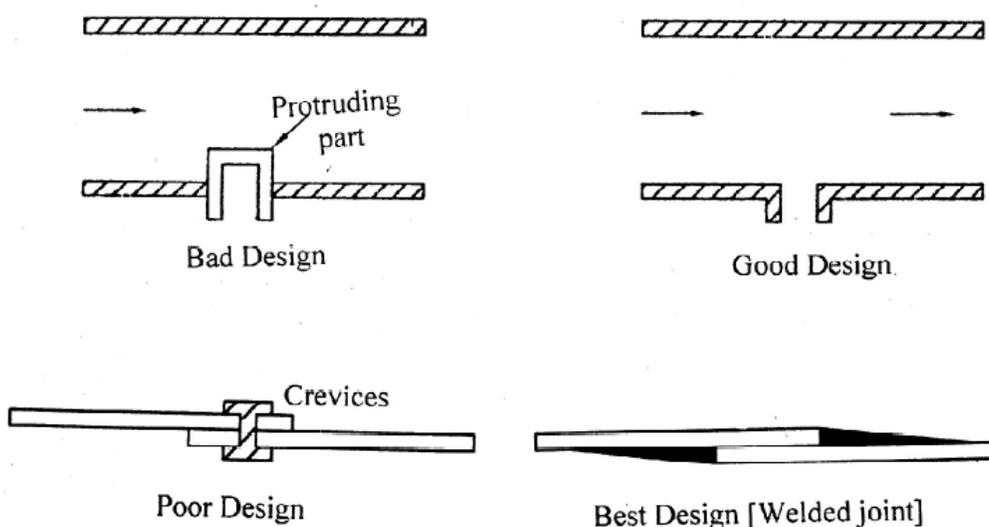
- (a) Proper choice (or) Selection of metal
- (b) Proper design
- (c) Cathodic protection

(a) Proper choice (or) Selection of metal

- (i) Before fabrication of equipments, proper selection of metal or alloy have to be studied according to the environmental conditions.
- (ii) Noble metals (Pt, Au, Ag) almost inert in all environmental conditions, but also too expensive if we used for common purpose.
- (iii) Some of the metals are inert in certain environmental conditions.

(e.g) <u>Metals</u>	<u>Not affected by</u>
Stainless steel	HNO ₃
Steel	Con.H ₂ SO ₄
Ti	Hot acids and alkalies

- (iv) Corrosion can be avoided by replacing the metal parts by plastics, rubbers, ceramics etc. as far as possible.

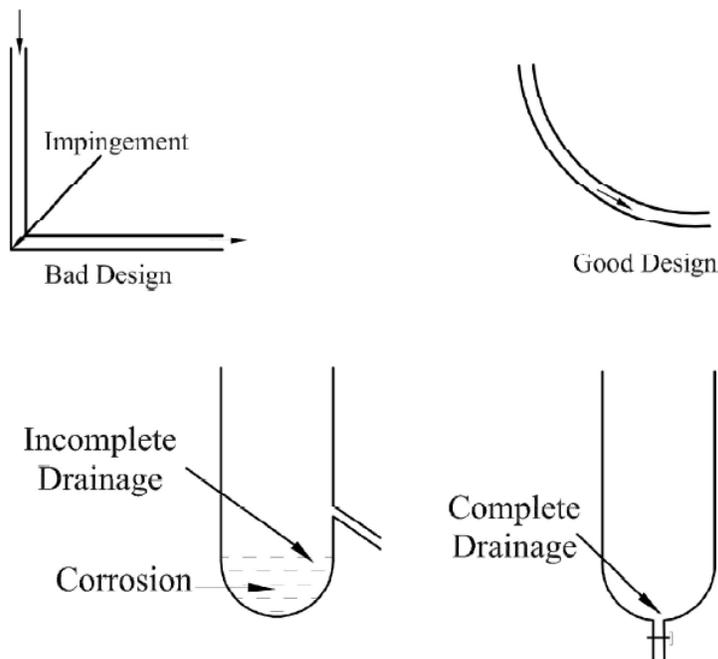
(b) Proper design**Corrosion prevention using curved pipeline**

Design plays an important role in corrosion control. Important design principles are –

- Avoid direct contact of dissimilar metals by using adhesives.
- When two dissimilar metals are in contact, the anodic part should have large area than the cathodic part.
- Care must be taken in designing an equipment so that the liquid can be drained off completely.
- Crevice corrosion and caustic embrittlement can be prevented by avoiding

hair cracks, gaps and protruding parts (rivets etc).

- Single crystalline solids avoid inter granular corrosion.
- Stress corrosion can be avoided by heat treatment technique (annealing).
- Heterogeneity is reduced by using pure metals, which decreases corrosion rate.



Minimizing crevice corrosion

(c) **Cathodic protection**

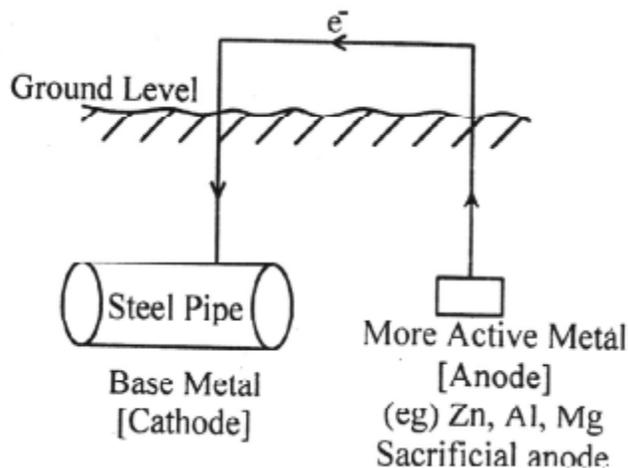
In cathodic protection, the corroding metal is forced to act as cathode. (i.e) The base metal to be protected can be converted into cathode.

This is achieved by the following methods.

- Sacrificial anodic protection
- Impressed current cathodic protection

(i) **Sacrificial anodic protection**

The metal to be protected is converted into cathode by connecting it with more active metal (anode), The artificially made anode thus gets gradually corroded protecting the base metallic structure. This process is known as sacrificial anodic protection. The metals commonly used as sacrificial anode are Zn, Mg, Al and their alloys.



Sacrificial anodic protection

e.g.,

- (i) Protection of pipe lines, cables from soil corrosion.
- (ii) Protection of ship hulls from marine corrosion.

Advantages

- (i) No need of external power supply.
- (ii) Installation and maintenance cost is low.

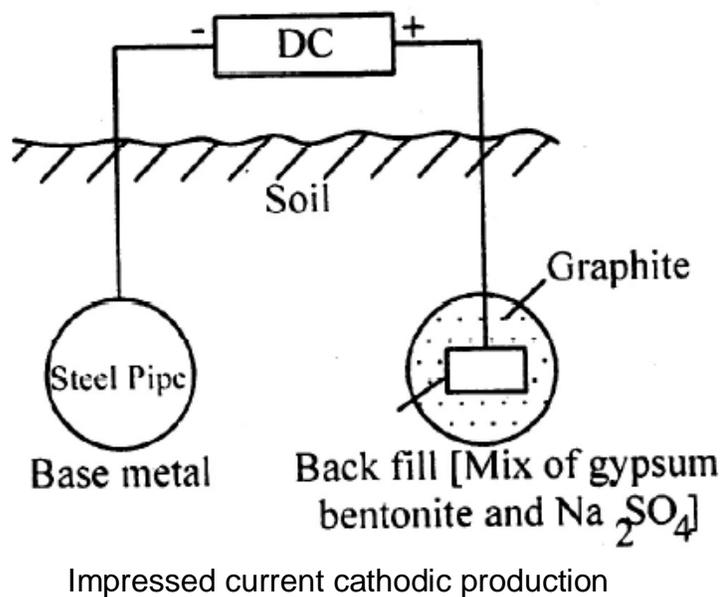
Limitations

- (i) Not suited for large objects due to limited driving potential.
- (ii) Uncoated parts cannot be protected.

(ii) Impressed current cathodic protection

In this method an impressed current is applied in the opposite direction of the corrosion current to nullify it, which converts corroding metal from anode to cathode.

The negative terminal of DC source is connected to metallic structure to be protected and positive terminal to an inert anode graphite surrounded by back fill. The backfill provides good electrical contact to anode. Hence the current from the external system is impressed on the metallic structure to be protected which act as the cathode.



Advantages

- (i) Larger objects can be protected due to larger driving voltage.
- (ii) Uncoated parts can be protected.

Limitations

- (i) Larger installation cost.
- (i) Higher maintenance cost.

Environment based controlled measures

Corrosion Inhibitors

A corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate.

(Or) A corrosion inhibitor is any chemical substance which when added to a solution (usually in small amounts) increases the corrosion resistance.

The efficiency of an inhibitor can be expressed by a measuring Inhibitor efficiency

$$\text{Inhibitor efficiency (\%)} = 100 \times (\text{CR}_{\text{uninhibited}} - \text{CR}_{\text{inhibited}}) / \text{CR}_{\text{uninhibited}}$$

where , $\text{CR}_{\text{uninhibited}}$ -corrosion rate of the uninhibited system

$\text{CR}_{\text{inhibited}}$ -corrosion rate of the inhibited system

Corrosion inhibitors are used in various industrial applications, including potable (drinking) water, cooling water systems, automobile engine coolants, acid pickling (cleaning) solutions, to protect reinforcing steel bars in concrete, and in oil recovery and storage.

Inhibitors are also used in the surface treatment of metals to improve the corrosion resistance (chromates on aluminum alloys or galvanized steel) or to improve their paint adhesion (phosphates on autobody steel sheet). Corrosion inhibitors can also be incorporated into paints or organic coatings.

Types of Inhibitors

Inhibitors can be classified in several different ways. The two main types are

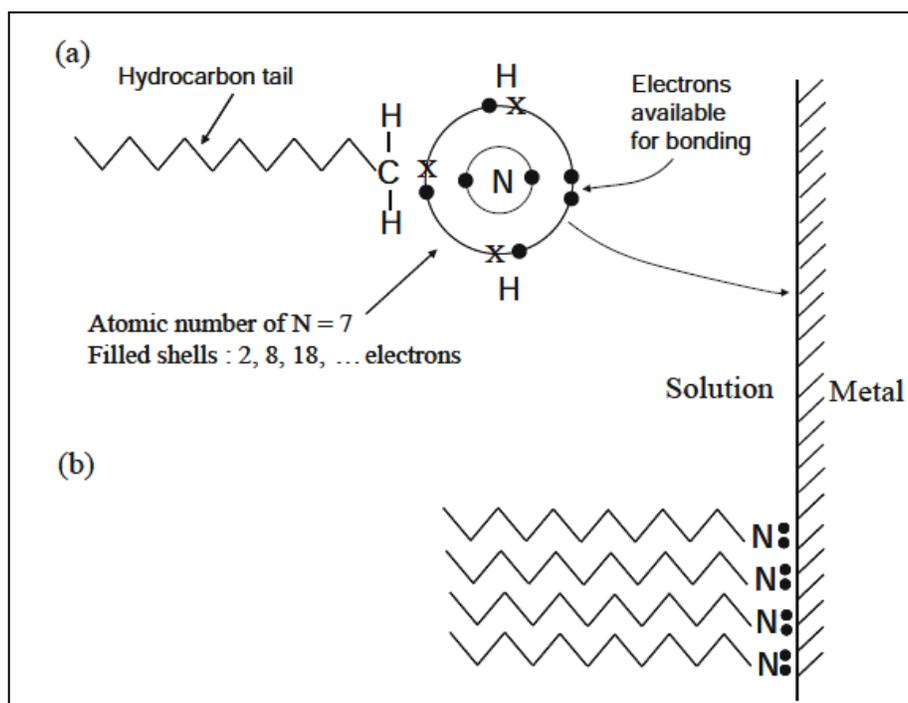
- (i) adsorption inhibitors and
- (ii) film-forming inhibitors.

Adsorption inhibitors form a chemisorptive bond with the metal surface and impede ongoing electrochemical dissolution reactions.

Most organic inhibitors are chemisorption-type inhibitors. For example, Fig. (a) shows schematically that an aliphatic organic amine has an electron pair on the nitrogen atom which is available for donation to the metal surface.

In addition, the hydrocarbon tails of the molecule are oriented away from the interface toward the solution so that further protection is provided by the formation of an array of hydrophobic hydrocarbon tails located on adjacently adsorbed amines.

This hydrophobic network serves to keep water molecules and aggressive anions, such as Cl^- , away from the metal surface, as shown in Fig. (b)



(a) Chemisorption of amines at a metal surface. The solid black dots denote electrons belonging to the N atom, whereas the Xs refer to electrons from H or C atoms. (The size of the nitrogen atom is exaggerated relative to the rest of the molecule.) (b) Formation of a close-packed monolayer on the metal surface

There are two types of film-forming inhibitors:

- (i) passivating inhibitors and
- (ii) precipitation inhibitors.

As implied by their name, passivating inhibitors function by promoting the formation of a passive film on the surface.

Passivating inhibitors may be oxidizing or non-oxidizing agents. (Oxidizing agents themselves are reduced in the process of oxidizing another molecule). Chromates are typical oxidizing inhibitors, and with iron or steels, the chromate ion is reduced to Cr_2O_3 or $\text{Cr}(\text{OH})_3$ on the metal surface to produce a protective mixed oxide of chromium and iron oxides.

Adsorption is also important with oxidizing inhibitors because they are usually adsorbed on the metal surface prior to their reduction and formation of the passive film. Non-oxidizing passivators like benzoates, azelates, and phosphates also first adsorb on the surface before forming the passive film.

With precipitation inhibitors, a precipitation reaction between cations of the corroding metal and the inhibitor deposits a three-dimensional barrier film on the metal surface.

Such a film is formed when the solubility product is exceeded for the salt formed between the cations of the metal and the anions of the inhibitor. Phosphates and silicates are examples of precipitation-type inhibitors.

From another point of view, inhibitors can be classified as anodic, cathodic, or mixed inhibitors, depending on which partial electrochemical reaction is affected. As examples, chromates are anodic inhibitors, some phosphates are cathodic inhibitors, and most organic compounds are mixed inhibitors

Lecture session 15: Coatings – surface preparation for metallic coating – Electroplating objective, method of electroplating of copper.

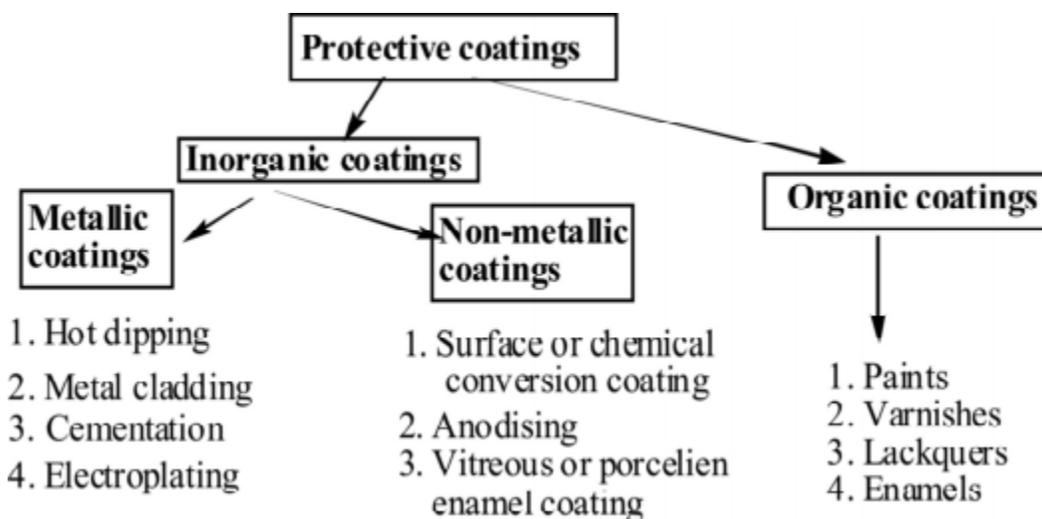
PROTECTIVE COATINGS

Protective coatings are the physical barrier between the metal surface and the environment which prevents corrosion. They are also used for decorative purpose and to impart some special properties such as hardness, electrical properties, oxidation resistance, and thermal insulation

Classification

They are broadly classified in to two types:

1. Inorganic coatings
2. Organic coatings



Electroplating (Electrodeposition)

Electroplating is the process of deposition of coating metal on the base metal by passing a direct current through an electrolytic solution which contains the soluble salt of the coating metal.

Objectives of electroplating

On metals

- To increase the resistance to corrosion of the plated metal.
- To improve the hardness and physical appearance.
- To increase the decorative and commercial values of the metal.
- To increase resistance to chemical attack.
- To improve the surface properties.

On non-metals

- To increase strength.
- To decorate surfaces of non metals like wood, plastic, glass.
- For obtaining surface conductivity.

Principle

It follows electrolytic cell principle. In electroplating the base metal to be plated is taken as cathode and the metal to be coated is taken as anode. The soluble salt of coat metal is used as electrolyte.

During electrolysis, concentration of the electrolyte remains unchanged, as the metal ions deposited from the electrolyte solution on the cathode are replenished continuously by the ions from the anode.

Example: copper plating

Step1. Pretreatment and activation of the surface (surface preparation): The surface to be plated is decreased first by using an organic solvent or alkali followed by acid treatment.

Example:

- (i) Surface of stainless steel is activated by dipping in hot solution of 50% H₂SO₄.
- (ii) Surface of Mg alloy is activated by thin coating of Zn or Cu.
- (iii) Activation is not necessary for metals and alloys like Al, Cu, Fe, brass.
- (iv) Non metallic articles (plastics, glass) are activated by dipping them in the solution containing SnCl₂+ HCl followed by dipping in PdCl₂ solution. On drying, a thin layer of Pd is formed on the surface.

Step 2: Bath conditions

Sl.No.	Nature of the content	Sulphate bath
1.	Plating bath composition (Per lit.)	200-250g-CuSO ₄ , 50-75g-H ₂ SO ₄ + Rest Water
2.	Additive	Gelatin/ dextrin (Req.)
3.	Temperature (°C)	20-40
4.	Current density (mA/cm ²)	20-50

To get strong, adherent smooth deposit, certain additives (boric acid, gelatin) are added to the bath. The favourable conditions for a good electro deposits are normal temperature and current density (20-30 mA/cm²) and low metal ion concentrations are maintained.

Step 3 : plating procedure

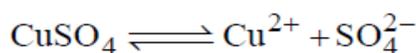
It consists of

Cathode : Material to be plated

Anode : Copper Rod (metal to be

Electrolyte : Copper Sulphate

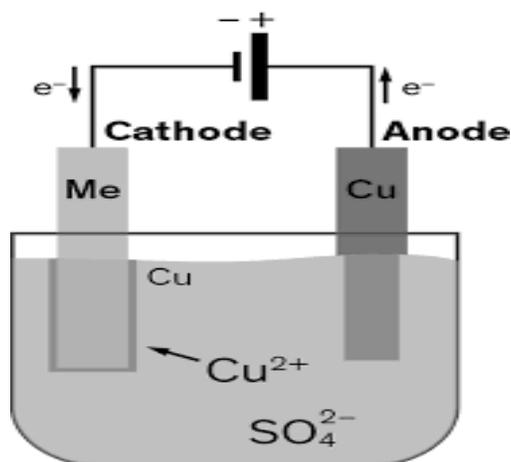
The chemical reactions involved during plating are CuSO₄ solution ionizes as



On passing current Cu²⁺ ions of the electrolyte get deposited at the cathode.

At cathode : Cu²⁺ + 2e⁻ → Cu

At anode : Cu + SO₄²⁻ → CuSO₄



Electroplating of copper

Applications

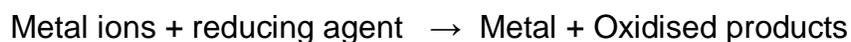
1. Under coat for Ni-Cr electrodeposit for smoothening out the irregularities
2. Protective coating for steel
3. Coated at the bottom of Stainless Steel cooking utensils to effect better heat transfer

Lecture session 16: Electroless plating - advantages, electroless plating of nickel

Electroless Plating:

Principle

Electroless plating is a technique of depositing a noble metal (noble metal salt solution) on a catalytically active surface of the base metal by using a suitable reducing agent without electric current. The reducing agent reduces the noble metal ions to metal, which gets plated over the catalytically activated surface giving a uniform coating.



Steps involved in electroless plating:

Step 1: Pretreatment and activation of the surface (surface preparation)

The surface to be plated is degreased first by using an organic solvent or alkali followed by acid treatment.

Example:

- (i) Surface of stainless steel is activated by dipping in hot solution of 50% H_2SO_4 .
- (ii) Surface of Mg alloy is activated by thin coating of Zn or Cu.
- (iii) Activation is not necessary for metals and alloys like Al, Cu, Fe, brass.

(iv) Non metallic articles (plastics, glass) are activated by dipping them in the solution containing $\text{SnCl}_2 + \text{HCl}$ followed by dipping in PdCl_2 solution. On drying, a thin layer of Pd is formed on the surface.

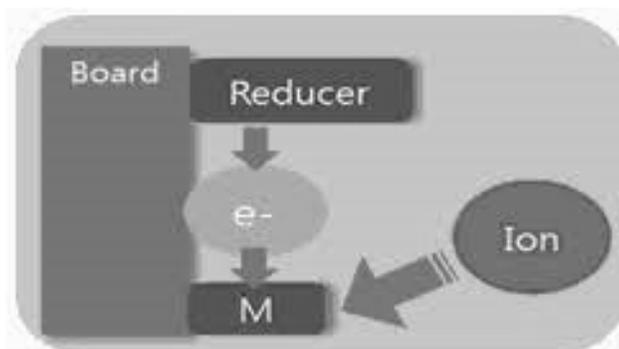
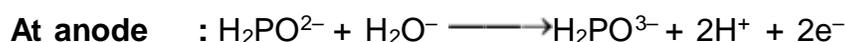
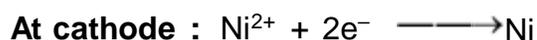
Step 2: Plating bath

Sl.N	Nature of the	Compound	Quantity (g/L)
1.	Coating solution	NiCl_2	20
2.	Reducing agent	Sodium	20
3.	Complexing agent cum	Sodium succinate	15
4.	Buffer	Sodium acetate	10
5.	pH	4.5	-
6.	Temperature	93°C	-

Step 3: Plating Procedure

The pretreated object is placed in the plating bath for the required time. The reduction reaction occurs and nickel gets coated over the object, which is shown in Fig.

Reactions



Electroless plating of nickel

Applications

- i. It is extensively used in electronic appliances.
- ii. It is used in domestic and automotive fields (eg., jewellery, tops of perfume bottle)
- iii. Electroless nickel coated polymers are used as decorative material.
- iv. Copper and nickel coated plastic cabinets are used in digital and electronic instruments.

Advantages of electroless plating over electroplating

- i. No electricity is required
- ii. It can be easily plated on insulators
- iii. Complicated parts can be plated uniformly.
- iv. This coating possess unique mechanical, chemical and magnetic features.

Difference between Electroplating and Electroless plating

S. No.	Electroplating	Electroless Plating
1.	It is carried out by passing current.	It is carried out by auto catalytic redox reaction.
2.	Separate anode is employed.	Catalytic surface of the substrate acts as an anode.
3.	Object to be coated is cathode.	Object to be coated, after making its surface catalytically active.
4.	It is not satisfactory for the object having irregular shape.	It is satisfactory for all parts.
5.	It is carried out on conducting materials.	It is carried out on conducting semil conducting (plastics)
6.	Thickness of the plating is 1 – 100 μm	Thickness of the plating is 1 – 100 μm

Lecture session 17: Chemical conversion coatings – phosphating, chromate coating and anodizing.

Chemical conversion coatings

Chemical conversion coatings are inorganic surface-barriers, produced by chemical or electrochemical reactions, brought at the surface of the base metal. Such coatings are particularly used as an excellent base for paints, lacquers, oils, and enamels

Impartment conversion coatings are

1. Phosphate conversion coatings
2. Chromate conversion coatings
3. Anodizing

1. Phosphate conversion coating

Phosphate coatings are produced by the chemical reactions of a base metal with aqueous solutions of phosphoric acid and phosphates. The coating is formed by either spraying or immersing of the substrate in to a solution of dilute phosphoric acid combined with other chemicals that assist in the coating process.

Phosphate coatings are made up of thin crystalline layers of phosphate compounds that adhere to the surface of the metal substrate. The phosphate crystals are porous and can be formed from zinc, manganese or iron phosphate solutions, which can be applied to zinc, cadmium, aluminium, tin and galvanized steels.

The main components of a phosphating solution are:

- phosphoric acid (H_3PO_4)
- ions (cations) of bivalent metals: Zn^{2+} , Fe^{2+} , Mn^{2+}
- accelerator – an oxidizing reagent (nitrate, nitrite, peroxide) increasing the coating process rate and reducing the grain size of the deposit.

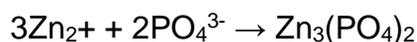
Chemistry of phosphating

When a metal part is immersed into a phosphating solution (for example zinc phosphate) the following chemical reactions start:

Iron dissolves in the phosphoric acid solution:



Consumption of phosphoric acid for the reaction causes reduction of the acidity of the solution in the layer adjacent to the metal surface. Solubility of zinc phosphate in the neutralized solution is lowering resulting in precipitation of the salt and its deposition on the substrate surface:



Process:

In general, phosphating sequence comprises of seven operations, as indicated in the flow chart. However, depending upon the surface conditions of the base metal, some of these operations may be omitted or additional operations may be incorporated into the system. A typical seven-stage sequence of phosphate pretreatment process is given as a flow chart below.

1. Cleaning

Perhaps, the most important requisite for proper coating formation is a clean substrate, free from contaminants such as oils, greases, waxes, corrosion products and other soils. Many coating failures can be attributed to the poor metal surface preparation. An ideal cleaning agent is the one, which is capable of removing all the contaminants from the metal surface, and prevents their redeposition or the formation of other detrimental reaction products. A variety of methods such as sand blasting, solvent degreasing, vapour degreasing, alkaline cleaning and pickling have been used to achieve this end.

2. Rinsing

The rinsing step followed by cleaning plays a vital role in the phosphating sequence. Rinsing prevents the drag-out of chemicals used in the earlier cleaning that may contaminate the subsequent stages.

3. Phosphating

Suitably cleaned surfaces are next subjected to phosphating, which causes the formation of an insoluble, corrosion resistant phosphate layer on the substrate surface. A wide variety of phosphating compositions are available. However, the right choice of the components and the operating conditions of the phosphating bath are made based on the nature of the material to be treated and its end use.

4. Rinsing after phosphating

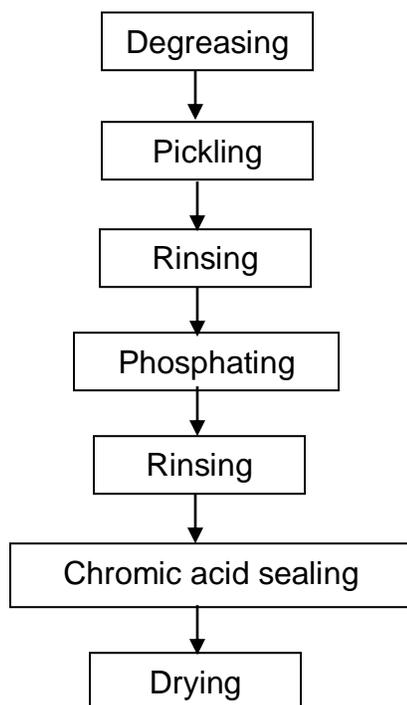
The surface that has been subjected to phosphating should be thoroughly rinsed with deionized water to remove any acid residue, soluble salts and non-adherent particles present on it which would otherwise promote blistering of paint films used for finishing. Generally overflow rinsing and spray rinsing are preferred.

5. Chromic acid sealing

The phosphate coatings are usually porous in nature. The porous nature will have a detrimental influence on the corrosion resistance of the phosphate coating unless they are sealed. A hot (70-80 °C) dilute chromic acid rinse is usually used for this purpose. This treatment reduces the porosity by about 50%. It improves the corrosion resistance by the deposition of insoluble chromates on the bare areas of the coating.

6. Drying

After chromic acid rinsing the parts must be dried before finishing, the conventional methods used being simple evaporation, forced drying by blowing air or by heating. Where evaporation conditions are good, warm air circulating fans and compressed air blow offs are the most economical methods. After drying the phosphated panels are ready for application of further finishes such as paints, oils, varnishes, etc.



Flow chart depicting the operating sequence involved in phosphating process (same can be followed for Chromate Conversion Coating depends on the materials)

Uses of phosphate coating

- Phosphate coatings are often used to provide corrosion resistance.
- Zinc and manganese coatings are used to help prevent wear and galling.

- it performs effectively with excellent adhesion and electric isolation
- The porosity allows the additional materials to seep into the phosphate coating and become mechanically interlocked after drying.

2. Chromate Conversion Coating

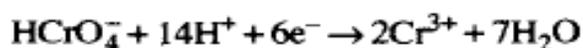
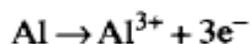
- Chromate Conversion Coatings are formed on metal surfaces as a result of the chemical attack that occurs when a metal is immersed in or sprayed with an aqueous solution of chromic acid, chromium salts such as sodium or potassium chromate or dichromate, hydrofluoric acid or hydrofluoric acid salts, phosphoric acid, or other mineral acids.
- The chemical attack facilitates the dissolution of some surface metal and the formation of a protective film containing complex chromium compounds.
- This type of coating is applicable to zinc, aluminum, magnesium and cadmium. This coating typically provides superior corrosive resistance and is broadly used in giving protection to usual household products such as hinges, screws and other hardware items.

Bath conditions

- Coated components were immersed in acidic baths (pH < 1.8) with chromates, dihydrogen phosphates and fluorides.
- The temperature of these baths was maintained at 25 – 30 °C and the immersion time was only 2 – 5 minutes.
- Modern working baths are based on these acidic baths with addition of other anions (fluorides, phosphates, ferricyanides etc.) to speed up the formation of coating.

Chemistry of Chromating

Chromate conversion treatments actually use of a strong oxidizing agent such as chromic acid, CrO_3 , a redox reaction occurs at acidic pH (pH~2) where hexavalent chromium, either in the form of $\text{Cr}_2\text{O}_7^{2-}$ or HCrO_4^- , is reduced to trivalent chromium while aluminum is oxidized to trivalent aluminum:



Probably due to the presence of fluoride ion, another reduction reaction besides that involving chromic acid can occur. This reaction involves the reduction of water, hydronium ion, or dissolved oxygen to form hydroxyl ions at the metal surface. This surface-localized increase in pH results in the precipitation of an amorphous mixture of hydrated aluminum plus chromium oxides.

The presence of fluoride ion is important for building films of significant thickness; without its presence, film growth is extremely slow. Fluoride presumably serves two roles. First, it solubilizes the aluminum oxide initially present on the surface and allows the redox and deposition reactions to proceed. Second, it solubilizes a portion of the growing film, which allows penetration of the electrolyte to the surface and ion transport from the surface into the growing film.

Uses of chromate coating

- Low-cost option for corrosion and wear protection
- A bonding agent for paint and adhesives
- A lubrication carrier
- Final finish
- Minimal electrical resistance

Characteristics of chromate coating

- Electrical conducting coating.
- Effective protection against oxidation in the case of products applied internally in machines.
- As a result of the excellent adhesive characteristics, chromating is a suitable pre-treatment for further coating processes.
- Chromating has hardly any negative consequences for dimensions.
- Applications Aircraft building, aerospace industry, automotive, electrical engineering, etc

3. Anodizing

- It is an electrochemical treatment that produces stable oxide layer on the metal/alloy (anode) surface.
- The bath usually contains sulphuric acid, chromic, phosphoric oxalic and boric acids
- Generally non-ferrous metals such as Al, Zn, Mg, and their alloys can be anodized
- Other metals can be also anodized such as Titanium, niobium, tantalum, tungsten, zirconium

Purpose of Anodizing

- Grow an oxide layer on the metals, so it can be dyed (Dye goes into pores, results in bright colors)
- Corrosion and wear resistance
- Hardening
- Protects from further oxidation

Common Process Steps

1. Racking

- Provides a secure connection for transportation of the parts through the various chemical solutions
- Provides a secure connection for the flow of electricity through each individual part
- Allows for uniformity and consistency of current flow from part to part

2. **Cleaning**- heated, nonetching alkaline cleaner (10 min)

- removal of most shop residues and fabrication oils
- no removal of adhesives, greases, or buffing compounds

3. **Etching** - heated sodium hydroxide (0-20 min)

- roughens the surface to provide a matte finish
- limited success at obscuring scratches, die lines, and bearing marks
- removal of aluminum 0-2.5 mil (0-65 microns) per side

4. **Anodizing**

- Immersion in chilled 10% (v/v) sulfuric acid bath
- DC current applied at densities of 8-20 amps/ft²
 - Time varies based on coating thickness (10-60 minutes)
- Barrier layer formed first to a 0.0005 mil thickness
- Coating builds to a 1.0 mil (25.4 mm) max. thickness
- Pores develop as the acid solution dissolves the coating
 - 250 - 500 billion pores per square inch
- Part dimensions increase as the coating is 40% penetration and 60% build-up from the pre-anodized surface

5. **Coloring**

- Absorption of either organic or inorganic molecules into the pores of the coating (2-30 min)
- Limitless range of colors
- Typically less fade resistance than other colored anodic finishes

6. Sealing

- Unsealed - Excellent base for paint and adhesives
- Hydrothermal Seal - 200-205 F (15-60 min)
 - Temperature drives coating hydration causing coating expansion to squeeze shut the pores at the surface
- Mid-Temperature Seal with Metal Salts - 180 F (15 min)
 - Deposition of metal salts in pores and some sealing by hydration
- Room Temperature Seal - 90 F (15 min)
 - Creation of a “super molecule” at the surface consisting of coating, metal salts, and fluoride
 - Prone to causing green tints or a fuzzy surface
 -

7. Unracking- First Inspection Point

- Appearance
- Coating Thickness
- Seal Quality

8. Packing- Second Inspection Point and Packaging

- Type
- Size
- Materials

10. Lab Testing-

- Coating Thickness - ASTM B244 - Eddy Current
- Coating Weight - ASTM B137 - Acid Dissolution
- Seal Quality
 - ASTM B136 -Modified Dye Stain
 - ASTM B680 - Acid Dissolution
- Abrasion Resistance - FED-STD-141 Method 6192.1
- Corrosion Resistance
 - ASTM B117 - Salt Spray

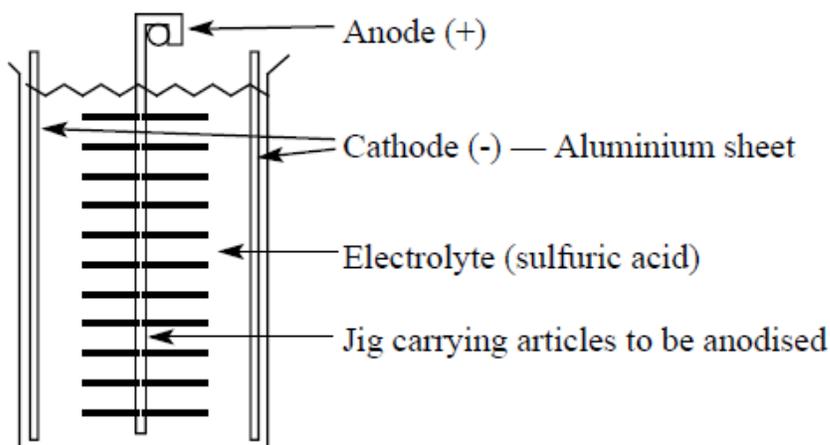
Chemistry of anodizing

When the current is flowing in the cell the following sequence of events is believed to occur. Sulphuric acid begins to decompose, the hydrogen ions moving to the cathode where they are reduced to hydrogen gas:

Cathode reaction



Simultaneously, negatively charged anions, i.e. hydroxide, sulphate and maybe oxide ions move to the anode. The electrical charge in the circuit causes positively charged aluminium ions (Al^{3+}) to be generated in the anode and in turn move toward the cathode. At the anode surface they react with the oxide/hydroxide ions to form aluminium oxide (in the case of the hydroxide ion, hydrogen ions are released into the solution).



Anodizing process

Types of oxide films

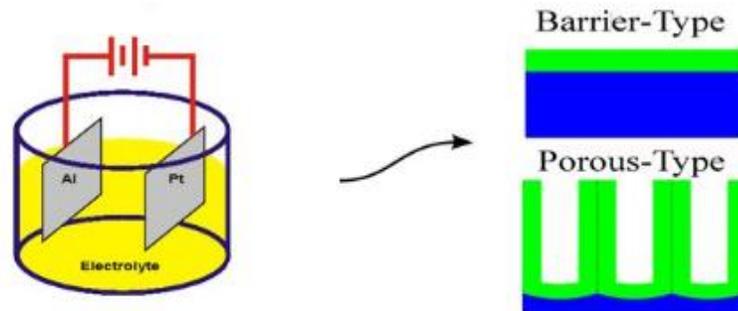
There are two main types of anodic oxide films can be grown depending on the nature of the electrolytes

Barrier type-films

- Grown oxide insoluble in electrolytes
- Nearly neutral electrolytes (5-7 pH)

Porous type-films

- Grown oxide slightly soluble in electrolytes
- Aqueous sulfuric, oxalic and phosphoric acid electrolytes



Characteristics properties

- Abrasion Resistance
- Corrosion Resistance
- Wear resistance
- Thermal Resistance
- Electrical Resistance
- Improve adhesive bonding
- Improve lubricity
- Porous
 - Increase paint adhesion allows for the coloring and sealing of the coating

Is corrosion always a problem?- No

- Anodizing – formation of TiO_2 nanoporous structure – nanotubes – controlled drug delivery
- AAO membranes for preparing metallic nanowires and nanotubes
- Etching of metals – metallography
- Cathodic protection – sacrificial anodes
- Dry cell batteries