Module -2

Corrosion and Metal Finishing

J K Prasannakumar
Asst.Professor
Department of Chemistry
BIET, Davanagere

Introduction:

- Corrosion is defined as the processes whereby a metal or alloy used as a material of construction is transformed from metallic to the combined state due to interaction with the environment through chemical or electrochemical attack (or) “The spontaneous destruction and consequent loss of a metal/alloy due to unavoidable chemical/electrochemical attack by the environment”

Example:

- When Cu is exposed to the industrial environment it forms an adherent protective green deposit which isolates the metal from the environment, hence the further action is very slow.
- When iron metal is exposed to the industrial environment, the metal forms a loosely adherent product of hydrated ferric oxide called rust, which is relatively non- protective.

Dry corrosion (Chemical corrosion):

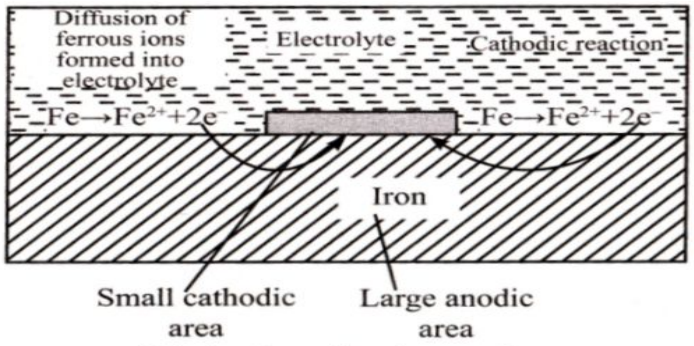
- It occurs by direct attack of atmospheric gases such as oxygen, sulphide, halogens and sulphur dioxide on the metal forming oxide layer (chemical reaction).

Wet corrosion (Electro chemical corrosion):

- Wet corrosion occurs in presence of an aqueous solution of electrolyte and atmospheric oxygen by setting up of tiny galvanic cells on the metal surface.

Electrochemical Theory of Corrosion

- According to this theory, when a metal such as iron, is exposed to atmospheric air, the following electrochemical changes occur gradually.
- Formation of galvanic cells: Anodic and cathodic areas are formed resulting in minute galvanic cells.



Mechanism of wet corrosion

Anodic reactions: At the anodic area, oxidation takes place resulting in the corrosion of iron.

$$Fe \text{ -----------> } Fe2+ + 2e$$

Cathodic reactions:

- The electrons flow form anodic to cathodic areas and cause reduction. There are three possible ways in which the reduction can take place.

- If the solution is aerated and almost neutral, oxygen is reduced in presence of water to form OH^- ions of according to the equation.

  $$O_2 + 2H_2O + 4e \text{ ---------> } 4OH^-$$

- If the solution is deaerated and almost neutral, water is reduced to H_2 and OH^-.

  $$2H_2O + 2e \text{ -----------> } H_2 + 2OH^-$$

- If the solution is deaerated and almost acidic, the H^+ ions are reduced to H_2.

  $$2H^+ + 2e \text{ ----------> } H_2$$

- The metal ions (formed at the anode) combine with the OH^- ions to form the metal hydroxide and finally the hydrated metal oxide (rust).

  $$2Fe^{2+} + 4OH^- \text{ ----------> } 2Fe(OH)_2$$

  $$4Fe(OH)_2 + O_2 + 2H_2O \text{ ---------> } 2[Fe_2O_3.3H_2O] \quad \text{Rust}$$

Factors affecting the rate of corrosion

Ratio of anodic to cathodic area: -

- If the anodic area is smaller and the cathodic area is larger, the rate of corrosion is much greater compared to the usual sizes of the anodic and cathodic area. This is because the reduction occurs at the cathode.
- The greater demand for electrons by the large cathodic area will have to be met by smaller anode by undergoing brisk corrosion. Similarly, if anodic area is larger and cathodic area is smaller the rate of corrosion is less.

Nature of corrosion product (Protective film):-

- Metals like Al, Ti, Cr etc are passive in nature and these exhibit much higher corrosion resistance than expected from their position in the galvanic series since they have highly protective oxide films.
- The product of corrosion is usually the oxide of the metal. This forms a thin layer on the surface of the metal. The nature of the oxide layer determines the corrosion rate.
- If its composition is stoichiometric, stable, uniform and non porous, highly insoluble the layer formed effectively prevents further corrosion. For example, aluminium, titanium and chromium develop such a layer on their surfaces and become passive to further corrosion.
- Stainless steel (18% Cr, 8%Ni) builds up a thin but a highly protective film of $Cr2O3$ which resists attack in a highly corrosive environment. If the oxide layer is non-stoichiometric, unstable, soluble, non-uniform and porous, it cannot control further corrosion. Ex: Fe, Zn, Mg etc.

Nature of the medium:

pH :-

- The rate of corrosion increases with decrease of pH. Lower the pH (highly acidic) of the corrosion environment, higher the rate of corrosion. But, between pH 3 & 10, the presence of O2 is essential for corrosion of iron.
- Higher the pH (>10, highly alkaline) corrosion of iron ceases due to the formation of protective coating of hydroxides of iron.

Temperature:

- The rate of corrosion increases with increase in temperature. Increase in temperature increases conductance of the aqueous medium and results in an increase in the diffusions rate. Hence, corrosion rate increases.

Conductance of the medium:

- The corrosion rate increases in the presence of conducting species in the atmosphere. This is because corrosion is an electrochemical phenomenon.
- The rate of corrosion in a dry atmosphere is less than that in a wet atmosphere since the latter is the more conducting.
- Ex: The corrosion of the metal structures is more in ocean water (more conducting) than in river water (less conducting).

Types of corrosion:

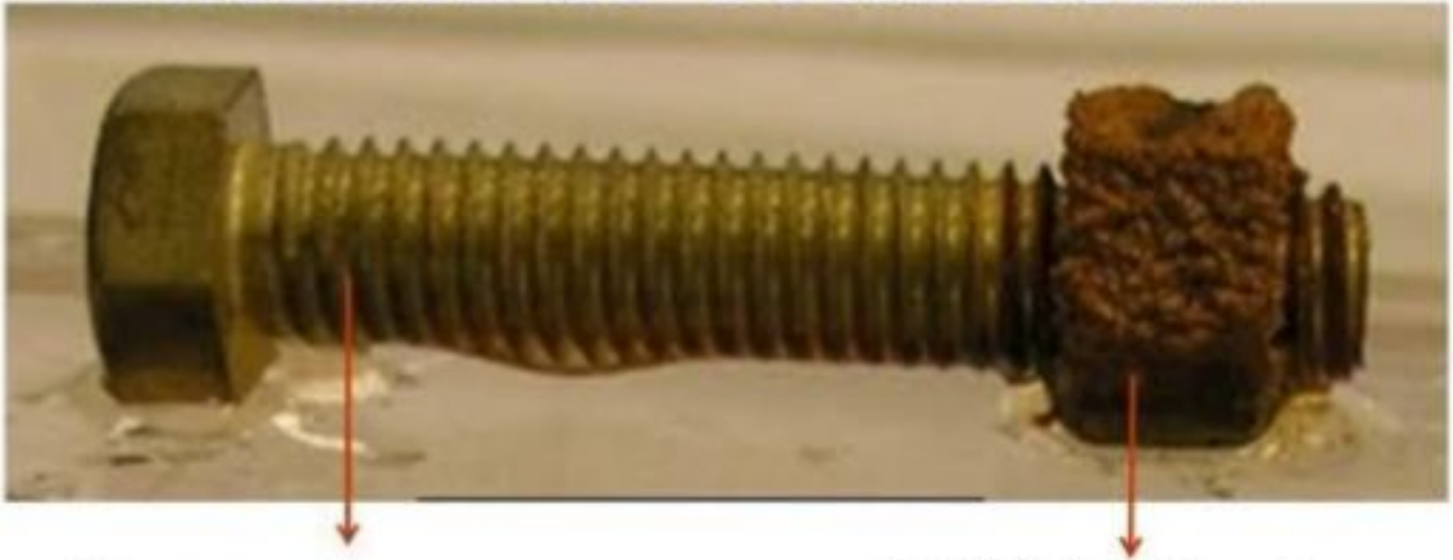
There are three types of corrosion

- Differential metal corrosion
- Differential aeration corrosion
- Stress corrosion

Differential metal corrosion (Galvanic corrosion):-

- This arises when two dissimilar metals are in contact with each other. Ex: zinc coated on mild steel. Under this condition, a potential difference is set up resulting in a galvanic current.
- The metal placed higher in the electrochemical series is anodic to one below it. For example, the iron is anodic to copper, nickel and tin but cathodic to zinc and magnesium.
- Therefore, iron corrodes in contact with copper whereas zinc and magnesium corrode in presence of iron. The rate of differential metal corrosion depends upon the amount of current passing from the anode to the cathode, that is, on the difference in the potentials; higher the difference faster is the rate of corrosion.
- To generalize "When two metals are in contact with each other, a galvanic cell is set up and a current flows. The metal acting as anode undergoes corrosion and the metal acting as cathode is unaffected". So, bolts and nuts are always made of similar metal.

GALVANIC CORROSION/ BIMETALLIC CORROSION

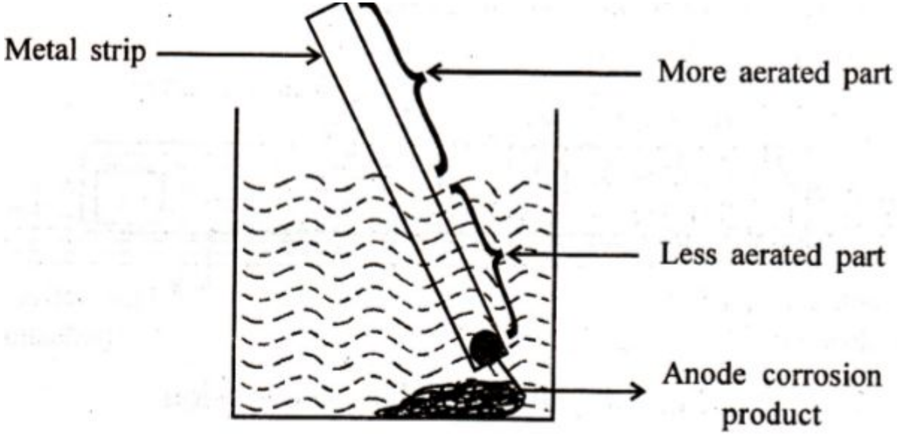


Brass screw
Cathode-protected

Mild steel nut
Anode - undergoes corrosion

Differential aeration corrosion:

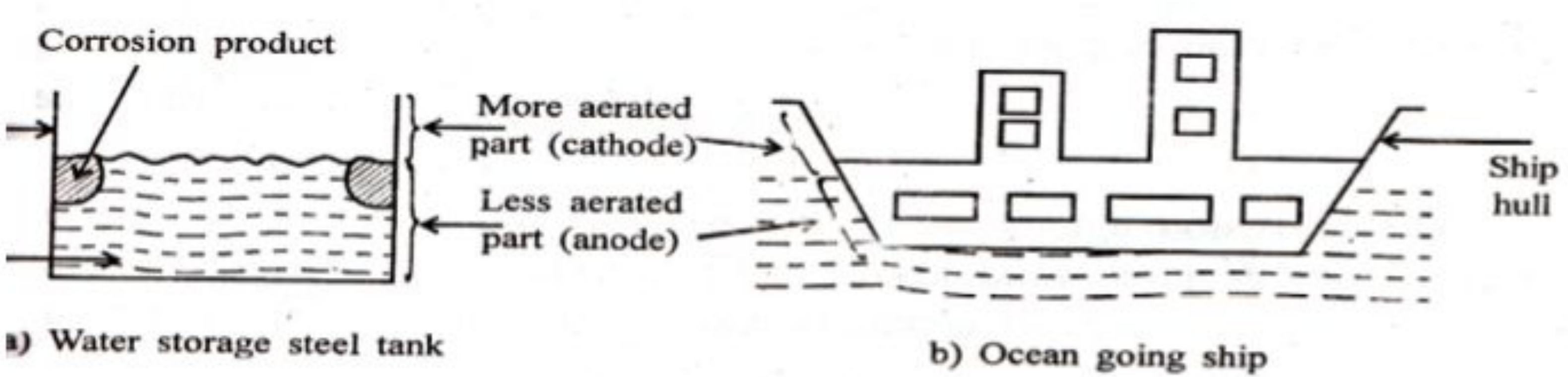
- This occurs due to difference in concentration of air over the surface of a metal.
- Consider a strip of pure iron partially immersed in an aerated sea water as shown in the figure. The concentration of oxygen is high at the surface than that inside the solution.
- Since the cathodic reaction involves the use of oxygen, the cathodic area tends to concentrate near the water–line as shown in the figure. Therefore, the bottom portion of the iron strip acts as anode where the corrosion process begins.
- Electrons pass from the bottom of the strip to the top of the strip. The corrosion product (rust) is formed between the anodic and cathodic areas and not on the active electrode surface.
- The anodic and cathodic reactions are
  Anode : Fe--------> $Fe^{2+} + 2e$
  Cathode : $O_2 + 2H_2O + 2e$ ----------> $4OH^-$



Differential aeration corrosion

Water line corrosion:

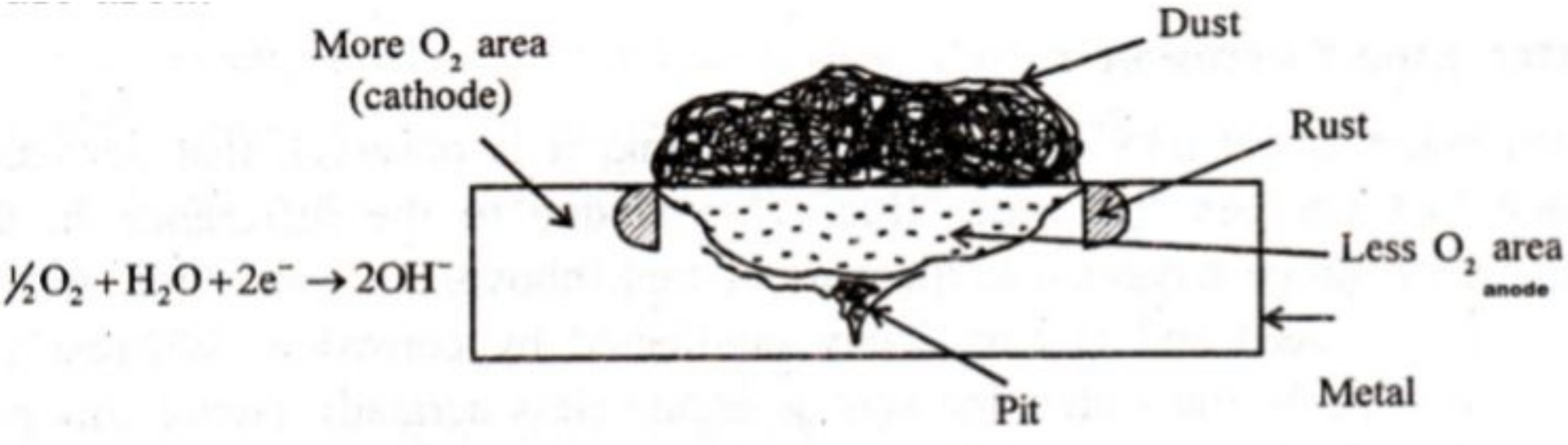
- This type of corrosion commonly observed in steel water tanks. The part of the metal below the water line is exposed only to the dissolved oxygen while the part above the water is exposed to higher oxygen concentration of the atmosphere.
- Thus part of the metal below the water acts as the anode (less oxygenated) and undergoes corrosion and the part above the water line acts as the cathode (more oxygenated) and is unaffected. The anodic area moves gradually upwards and entire tank corrodes with an intense corrosion (creep) just below the waterline. The size of the creep determines the rate of corrosion.
- Ex: This type of corrosion is commonly observed in ships floating in sea water long period of time.



Water line corrosion

Pitting corrosion:

- When a large drop of water or an electrolyte or dust particles is placed on the surface of a clean sheet of iron, the concentration of oxygen will be less at the bottom of the drop and becomes anode, while oxygen will be more at the surface area and becomes cathode.
- In the presence of electrolyte and moisture, corrosion starts at the bottom of the drop causing pits or cavities at the bottom. Once a pit is formed, the corrosion progresses rapidly.
- This is because of the formation of a small anodic area (pit) compared to a large cathodic area (surface)
- The latter induces the small anodic area to corrode faster by accepting electrons from the anodic area.
- Anode :. Fe --------> Fe2+ + 2e
- Cathode : ½O2 + H2O + 2e --------> 2OH-



Pitting corrosion

Corrosion control:

- Corrosion can be controlled by preventing the formation of galvanic cells. The methods commonly used to control corrosion of metals are the following.
- In this process care must be taken to cover the surface of the base metal completely with cathodic metal because even a small pin hole or scratch on the coated surface creates a large cathodic area and tiny anodic area causing rapid reduction at larger cathodic area thereby resulting in rapid corrosion. Cathodic metal coating is done by tinning process as follows.

Anodizing:

- When metals like aluminium, titanium, chromium, vanadium and zirconium etc are made as anode in presence of chromic acid and sulphuric acid, a thin layer of oxide is formed, which acts as a protective layer. This phenomenon is known as anodizing. (Inorganic coatings are generally are chemical conversion coatings).

Anodizing aluminium:

- Degreased and polished aluminium metal object is made as anode and electrolyzed in 5-10% chromic acid by passing a current of 40V at 350C (Steel or copper is made the cathode).
- A thin oxide layer (Al2O3.H2O) of 2-8 microns thickness is obtained. Higher thickness is obtained by addition of 10% H2SO4 at 220C and maintaining a potential of 24 V. Further the article is dipped in aqueous solution of dye at 50-600C which gives color.
- Finally the object is treated with nickel acetate followed by boiling water to improve corrosion resistance.

Applications:

- Widely used in industrial, commercial and domestic materials like air craft, window frames utensils, roofs, ceilings, computer hardware, scientific instruments etc.

Cathodic protection:

- Cathodic protection is a method of protecting a metal or alloy from corrosion by converting it completely into cathode and no part of it allowed acting as anode.
- The corrosion of the metal takes place at the anodic region whereas at the cathodic region, the metal is unaffected. Therefore, corrosion can be prevented by eliminating the anodic sites and converting the entire metal into cathodic area.

Cathodic protection can be achieved by the following methods.

Sacrificial anode method:

- In this method the metal to be protected is connected by a wire to more anodic metal. More anodic metal undergoes corrosion supplying electrons to the base metal thereby making the base metal as cathode and protecting the base metal.
- The more anodic metals get corroded and hence are called sacrificial anodes. So, this is called as sacrificial anode method. After continuous use these sacrificial anodes have to be replaced.
- Base metals: - Fe, Cu and alloys like brass.
- Anodic metals: - Mg, Zn and Al.
- Sacrificial anode method is used to protect buried pipe lines, ship hull, industrial water tanks and steel rods in R.C.C by connecting to a more anodic metal using a wire

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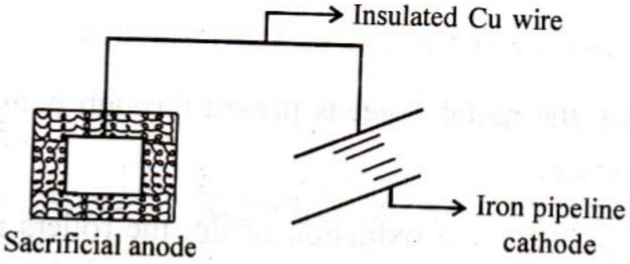


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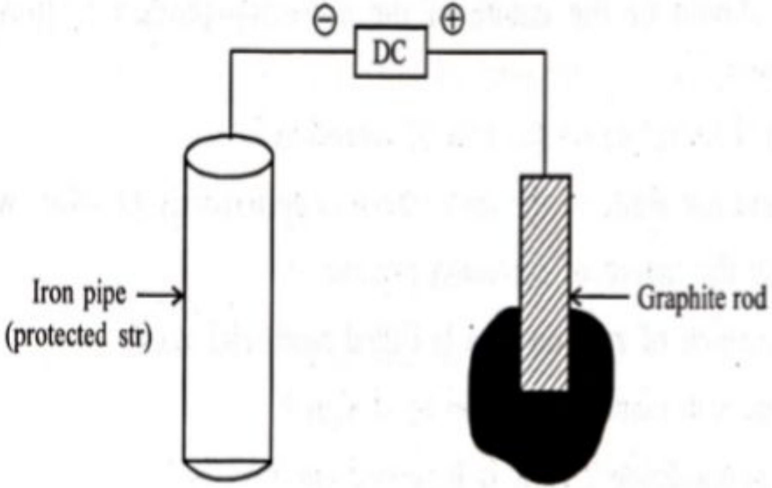
Impressed current method:

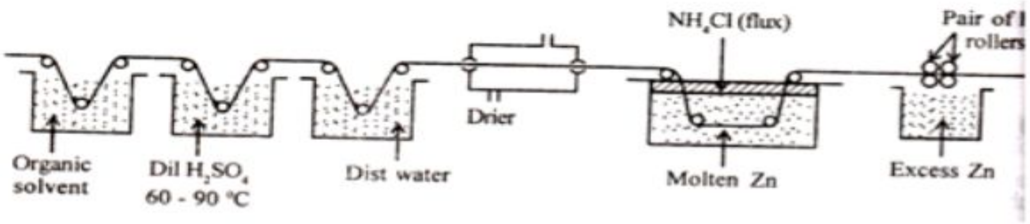
- In this method an impressed anodic current is applied in opposite direction to nullify the corrosion current and converting the corroding metal from anode to cathode which remains unaffected (Applied impressed anodic current should be more than the corrosion current).
- Metal to be protected is made cathode by connecting to negative terminal of a D.C battery. The electron supplied by the –ve terminal of the D.C. battery convert the corroding metal form anode to cathode and prevents corrosion. Graphite rod, stainless steel or platinum is used as inert anode by connecting it to the +ve terminal which remains unaffected.
- Ex: Buried tanks, pipelines, water storage tanks and marine structures are given cathodic



Impressed current cathodic protection

Metal coatings:

- Corrosion of metals can be controlled by isolating them from the environment. This can be brought about by the covering the substrate or base metal with a layer of another metal. The process is referred to metal coating.
- **Anodic metal coating**:-
- Anodic coatings are produced by coating a base metal with more active metals which are anodic to the base metal. In anodic metal coating, a base metal Fe is coated with more anodic metal in the galvanic series to protect the base metal Fe from corrosion, so that more anodic metals like Mg, Zn, Al & Cd undergo corrosion protecting the base metal (Fe). A characteristic feature of anodic coating is that the base metal on which the coating is done will not get corroded even if coating peels off. This is due to the formation of large anodic and small cathodic areas. Hot dipping or galvanizing is an example of anodic metal coating.
- **Galvanization or Hot dipping:**
- Hot dipping involves dipping the base metal into the molten anodic metal. The process of coating zinc on iron by hot dipping is called galvanizing. It is carried as follows.The iron sheet is subjected to pretreatment by degreasing with organic solvents.The sheet is passed through dilute sulphuric acid (pickling) and rinsed with water.The sheet is treated with a mixture of aqueous solution of zinc chloride and ammonium chloride and dried.The treated sheet is dried and dipped in molten zinc at 4300 -4700C. Excess Zinc is removed by rolling, wiping or passing blast of air.



Metal Finishing

Introduction:

- The materials such as metals/alloys are required for various engineering applications. These materials should be ideal and must meet several requirements like resistance to corrosion, wear resistance, mechanical properties, etc.
- It is impossible to have all these properties in a single metal. Hence, to improve the lacking properties in these materials, metal finishing is one of the methods employed for the purpose. Metal finishing is the process carried out to modify the surface properties of a metal by electro deposition of a layer of another metal on the substrate.

The principles of metal finishing are used in the

- Electroplating of metals, alloys and composites.
- Manufacture of electronic components such as printed circuit boards, capacitors and plating of metal over cheap materials like plastics and other insulators.

Important electrochemical metal finishing techniques are

- Electroplating of metals, alloys and composites
- Electroless plating of metals, alloys and composites

Technological Importance of metal finishing:

It is carried out,

- To give a decorative finish to the articles.
- To impart the following desirable characteristics to metals, alloys or composites. to offer corrosion resistance
- To enhance abrasion and wear resistance
- T!o impart thermal resistance and resistance to impact
- To provide electrical and thermal conduction
- To offer the surface a thermal or optical reflectivity
- In the manufacture the electrical and electronic components such as printed circuit boards (PCB), capacitors and contacts.
- To manufacture the metal articles entirely by electroplating
- To reproduce finely engraved dies or similar finely divided articles such as gramophone records and
- In the electrochemical machining, polishing and etching.

Electroplating:

Introduction:

- It is the process of coating a metal object with another metal, using electrical current passed through a chemical solution.
- This process produces a thin, metallic coating on the surface of the metal object. They dissolve in the solution as metal is taken away by plating.
- Anode : Dissolution of metal : M -------> M+ + ne (Oxidation)
- Cathode : Deposition of metal M+ + me -------> M (Reduction)

Principles governing Electro plating:

The fundamental principles governing metal finishing are

Polarization:

- Polarization is an electrode phenomenon. The electrode potential is determined by the Nernst equation,

$$E= E0 + 0.0591/n \log [Mn+]$$

Where Mn+ is the concentration of the metal ions surrounding the electrode surface at equilibrium.

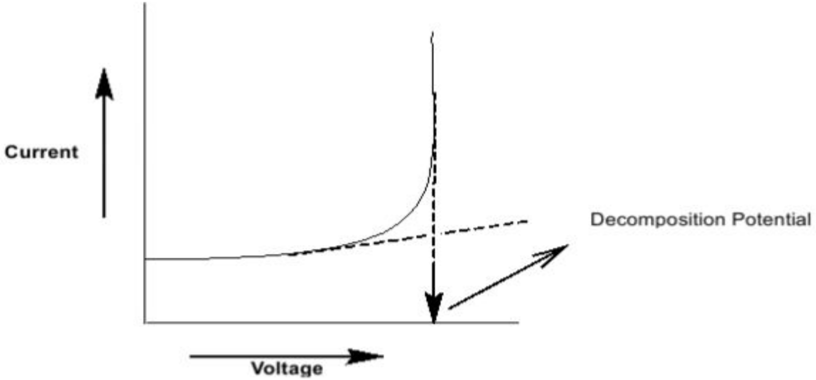
- When there is a passage of current, the metal ion concentration in the vicinity of the electrode surface decreases due to the reduction of metal ions.
- Therefore, there is a shift in the equilibrium and a change in the electrode potential. The concentration gradient between the bulk of the solution and the area surrounding the electrode surface leads to diffusion of ions from the bulk of the solution towards the electrode surface.
- This reestablishes the equilibrium.If the diffusion is slow, the electrode potential changes and the electrode is said to be polarized. Therefore, Polarization is defined as a process in which there is a variation in electrode potential due to slow supply of ions from the bulk of the solution to the electrode.

Electrode polarization depends on several factors.

- Nature i.e., size, shape and composition of the electrode.
- Concentration of electrolyte and its conductivity.
- Temperature
- Products formed at the electrodes
- Rate of stirring of the electrolyte.
- Large electrode surface and highly conducting solutions at low concentrations decrease the polarization effects.

Decomposition Potential:

- When a small voltage (say 0.5 V) is applied between two Pt electrodes in 1M H2SO4, an appreciable current flows at the beginning.
- The current decreases rapidly and becomes almost equal to zero in a short time. When the voltage is gradually increased, there is a slight increase in the current. Beyond a certain voltage called decomposition potential (Ed), the current abruptly increases due to commencement of electrolysis. Below this voltage no electrolysis occurs.
- Therefore decomposition potential (Ed) is defined as “The minimum voltage that must be applied to bring about continuous electrolysis of an electrolyte”.
- Decomposition potential can be determined by the current >< voltage curve as shown in the figure. When the voltage is gradually increased, there is a slight increase in the current.
- Beyond a certain voltage called decomposition potential (Ed), the current abruptly increases due to commencement of electrolysis. Below this voltage no electrolysis occurs. Ed can be obtained by extrapolation of the curve as shown in the figure.



Over voltage (η):

- Continuous electrolysis takes place when the applied voltage is slightly more than the decomposition potential (Ed). In a few cases, the applied voltage has to exceed the theoretically value by at least 1V for continuous electrolysis.
- This is known as over voltage or over potential, represented by η.
- It can be defined as “the excess voltage that has to be applied above the theoretical decomposition potential for continuous electrolysis”.

$$\eta = \text{experimental decomposition potential} - \text{theoretical decomposition potential}$$

- Decomposition potential is given by

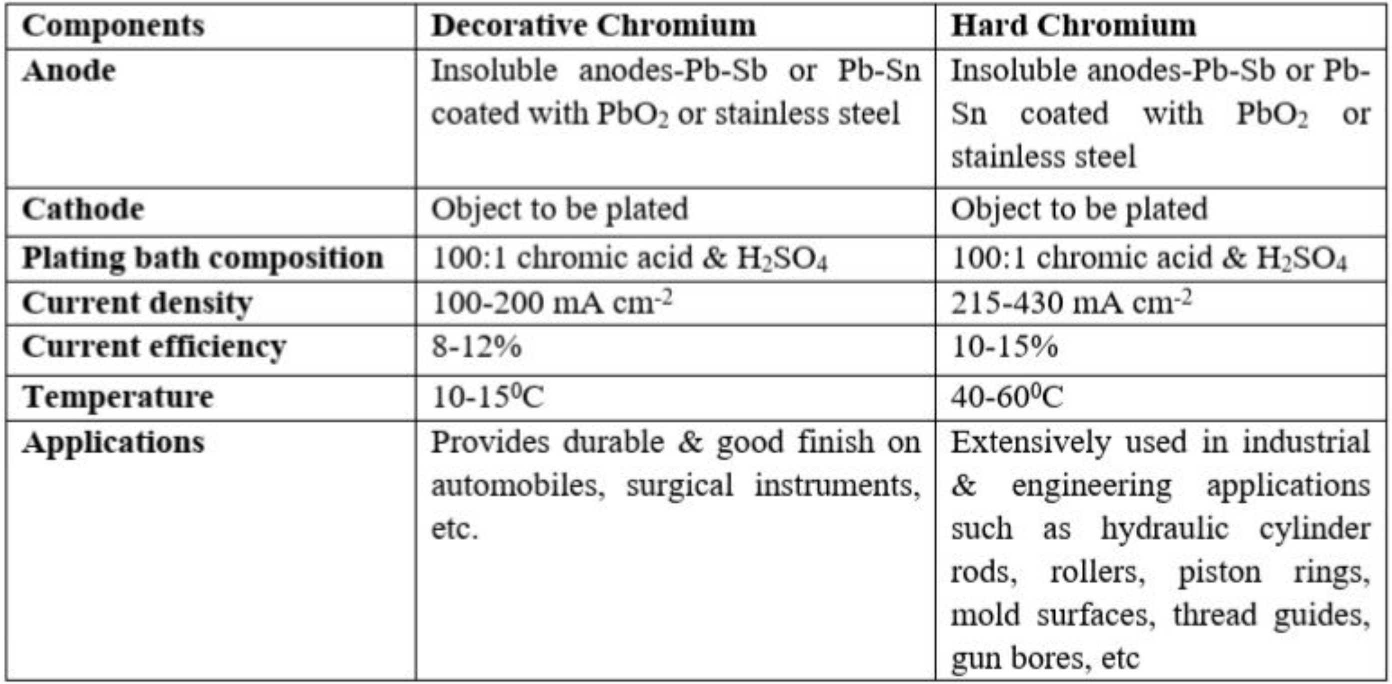
$$E_d = E_{cathode} - E_{anode} + \eta$$

Over voltage for a given electrolyte depends on following factors,

- Nature and physical state of the metal electrode
- Nature of the substance deposited
- Current density (current per unit area of the electrode surface)
- Temperature
- Rate of stirring of the electrolyte

Electroplating of Chromium:

- It is the most commonly used for decorative purpose because of fixed durability, resistance to chemical corrosion and flexibility in its usage.
- Chromium cannot be used in chromium plating because chromium metal passivates strongly in acidic medium and it dissolves gives Cr3+ ion which leads for black deposit



Components	**Decorative Chromium**	**Hard Chromium**
Anode	Insoluble anodes-Pb-Sb or Pb-Sn coated with PbO_2 or stainless steel	Insoluble anodes-Pb-Sb or Pb-Sn coated with PbO_2 or stainless steel
Cathode	Object to be plated	Object to be plated
Plating bath composition	100:1 chromic acid & H_2SO_4	100:1 chromic acid & H_2SO_4
Current density	100-200 mA cm^{-2}	215-430 mA cm^{-2}
Current efficiency	8-12%	10-15%
Temperature	10-15^{0}C	40-60^{0}C
Applications	Provides durable & good finish on automobiles, surgical instruments, etc.	Extensively used in industrial & engineering applications such as hydraulic cylinder rods, rollers, piston rings, mold surfaces, thread guides, gun bores, etc

- The plating bath contains CrO_3 in which Cr is in +6 oxidation state. This is reduced to +3 oxidation state by a series of complex reactions in the presence of SO_4^{2-} furnished by H_2SO_4. Cr^{3+} ions are reduced to elemental Cr which gets deposited on the substrate. The reactions taking place during chromium plating are given below.
- The amount of Cr^{3+} ions should be restricted in order to obtain good deposit. Insoluble anodes like Pb-Sb or Pb-Sn alloys covered with a layer PbO_2 which oxidize Cr^{3+} to hexavalent Cr are used thus controlling the Cr^{3+} ion concentration.

$$Cr_2O_7^{2-} + 14H^+ + 6e \longrightarrow 3Cr^{3+} + 7H_2O$$

Applications

- It is mainly used in automobile industry as decorative & protective coating.

Electroless Plating:

- Electroless plating is a method of depositing a metal or alloy over a substrate by controlled reduction of the metal ions by a suitable reducing agents without electrical energy.
- Reducing agent converts to metal ions (M^{n+}) to the metal (M) which get plated over the catalytically active surface.
- In electro less plating, driving force is auto catalytic redox reaction on a pretreated active surface.

$$M^{n+} + \text{Reducing Agent} \longrightarrow M + \text{Oxidised Product}$$

The pretreatment is done by one of the following techniques.

- Acid treatment (etching)
- Electroplating a thin layer of the metal followed by heat treatment
- For non conducting surfaces like plastics/PCB, the surface in treated with $SnCl_2$ & $PdCl_2$ solution.

Electroless plating of Nickel:

- The metal surface is first cleaned by using organic solvents followed by acid treatment.
- Aluminum can be directly plated without any activation.

Plating Bath Solution:

- solution of $NiCl_2$ (20 g/L),
- sodium hypophosphite as a reducing agent (20 g/L),
- sodium acetate buffer (10g/L),
- sodium succinate behaves as a complexing agent and exhaultant,
- is maintained around 4.5 and the temperature is around 93oC.

Electrode reactions are:

At anode: $NaH_2PO_2 + H_2O \rightarrow NaH_2PO_3 + 2H^+ + 2e^-$

cathode: $Ni^{+2} + 2e^- \rightarrow Ni$

Net redox reaction : $NaH_2PO_2 + H_2O + Ni^{+2} \rightarrow NaH_2PO_3 + 2H^+ + Ni$

- The H^+ ions are released in the above redox reaction, decreases the pH of the medium. This affects the quality of the deposit.
- Therefore, addition of buffer is very essential to maintain the pH.Further, Ni^{+2} ions and sodium hypophosphite are consumed during the redox reaction, and hence it should be replenished periodically.

Advantages:

- Possesses excellent throwing power, hence method is suitable for plating the objects having intricate shapes.
- The deposits are free from pores, hence possesses better corrosion resistance.
- The plating gives harder surface, hence it gives good wear resistance.
- This plating on Al enhances the solderability, also provides a non- magnetic underlay in magnetic components.

Applications:

- Electroless Ni plating is extensively used in electronic appliances
- Electroless Ni plating is used in domestic as well as automotive fields.
- Electroless Ni plated polymers are used for decorative purposes.
- Electroless Ni plating is also preferred in hydraulic compressors, pressure vessels, pumps, etc.

Electro less plating of Copper:

- Copper will deposit spontaneously in presence of a suitable reducing agent on metals such as gold, silver, platinum, palladium, rhodium, iron, cobalt and nickel. Insulators like plastics and glass are to be activated before subjecting to electroless plating.

Pretreatment and Activation of the surface:

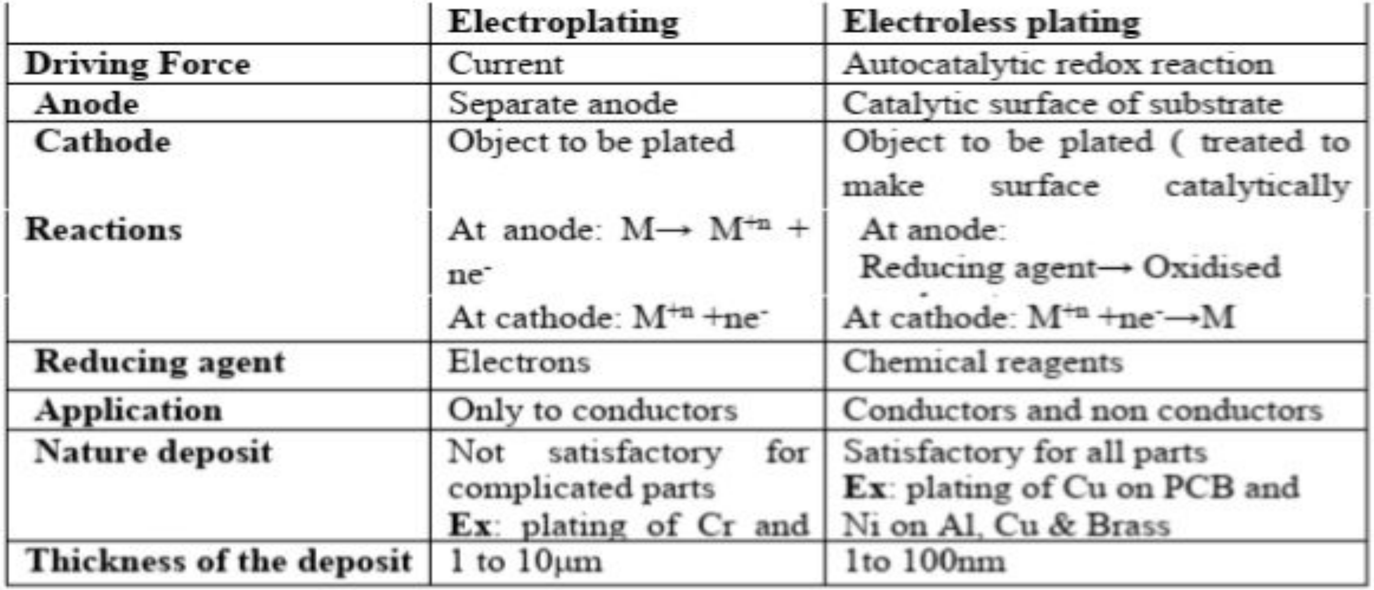
- The plastic board is degreased and etched in acid.
- It is activated by dipping in SnCl2 solution containing HCl at 25OC followed by dipping in PdCl2. Then the surface is dried to get layer of palladium.

Plating Bath Solution:

- Solution of copper sulphte- (12 g per L)
- Reducing agent – formaldehyde (8 g per L)
- EDTA – complexing agent and exaltant (20 g per L)
- Buffer-Sodium hydroxide (15 g per L) and Rochelle salt (14 g per L)
- pH-11
- Temperature- 250C

Anode: $2HCHO + 4OH^- \text{---------}> 2HCOO^- + 2H_2O + H_2 + 2e$

Cathode : $Cu^{2+} + 2e \text{---------}> Cu$



	Electroplating	**Electroless plating**
Driving Force	Current	Autocatalytic redox reaction
Anode	Separate anode	Catalytic surface of substrate
Cathode	Object to be plated	Object to be plated (treated to make surface catalytically
Reactions	At anode: M→ M^{+n} + ne^- At cathode: M^{+n} +ne^-	At anode: Reducing agent→ Oxidised At cathode: M^{+n} +ne^-→M
Reducing agent	Electrons	Chemical reagents
Application	Only to conductors	Conductors and non conductors
Nature deposit	Not satisfactory for complicated parts **Ex**: plating of Cr and	Satisfactory for all parts **Ex**: plating of Cu on PCB and Ni on Al, Cu & Brass
Thickness of the deposit	1 to 10µm	1to 100nm

Advantages of electroless playing

- No electrical power is required,
- Plating may also be obtained on insulators and semiconductors,
- Better throwing power compared to electroplating,
- These coatings possess unique mechanical, chemical and magnetic features.