

Ancillary Chemistry-II



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CORROSION AND ELECTROCHEMICAL PROCESS

Corrosion

Corrosion is defined as the gradual deterioration of a metal or alloy by the chemical or electrochemical reaction with the environment.

Causes of corrosion

Metals occur in nature either in (i) native state (or) (ii) in combined state

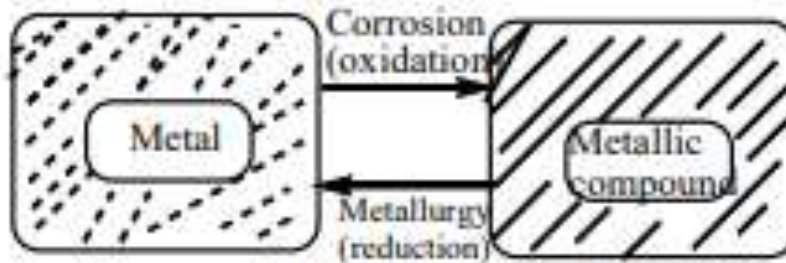
i. Native state

Metal those occurring in nature in native (or) free (or) uncombined state are non – reactive with the environment. They are noble metals. They do not undergo corrosion. Example: Au, Pt, Ag

ii. Combined state

Except noble metals, all the other metals are reactive and react with the environment and form compounds such as oxides, sulphides, chlorides and carbonates by reaction with the environment. They exist in nature in the form of their stable compounds (ores). Example: Fe_2O_3 , ZnO , PbS , CaCO_3

How and why corrosion occurs



Metals are extracted from the ores by reduction. In pure metallic state these are unstable. The reverse

Process, oxidation resulting corrosion takes place.

When the metals are used in various environments, such as corrosive gases, moisture, the metal surface tends to decay, which is the reason for corrosion

Due to corrosion, some of the useful properties of metals such as electrical conductivity, ductility, malleability are lost

Consequences of corrosion

- i. Formation of corrosion parts on the machinery the efficiency will be lost
- ii. Products get contaminated
- iii. Results in plant failure
- iv. Necessity arises for overdesign
- v. Toxic products are released

Classification (Theories of corrosion)

Based on the environment, corrosion is classified into

- (i) Dry (or) chemical corrosion (ii) Wet (or) Electrochemical corrosion

Dry (or) Chemical corrosion

This process is due to the attack of metal surfaces by atmospheric gases such as O_2 , H_2S , SO_2 , NO_2

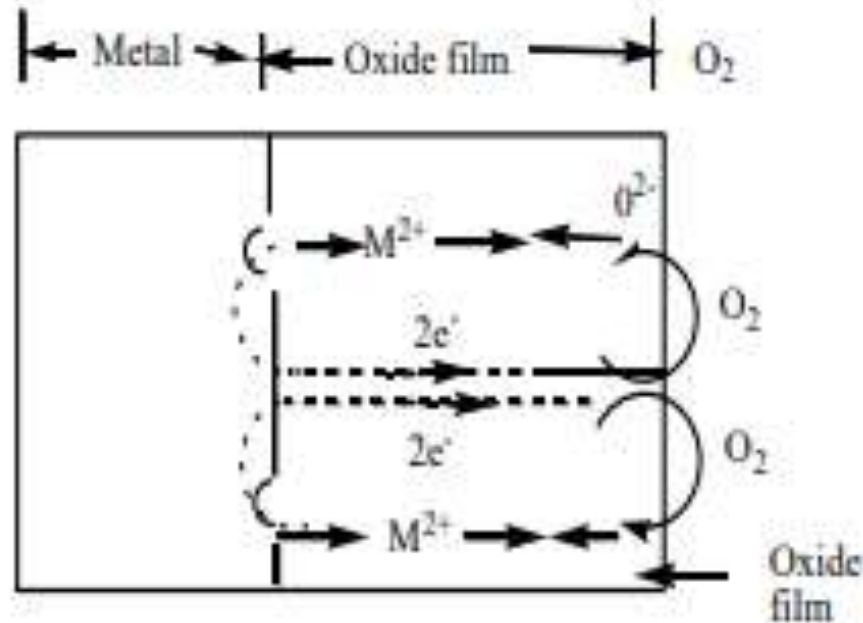
There are 3 main types of dry corrosion

- i. Oxidation corrosion ii. Corrosion by hydrogen iii. Liquid – metal corrosion

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Mechanism of dry corrosion Oxidation corrosion

Oxidation corrosion is brought by the direct attack of oxygen at low or high T, on metal surfaces in the absence of moisture. Alkali metals and alkaline earth metals are rapidly oxidised at low T. At high T, almost all metals except Ag, Au and Pt are oxidised



Mechanism of dry corrosion

Oxidation occurs first at the surface of the metal resulting in the formation of metal ion (M^+). Oxygen changes to ionic form (O^-) and reacts with metal ions for form oxide film. Once the metal surface

covered with a monolayer of metal oxide, for further corrosion, the metal ion diffuses outward through the metal – oxide barrier. Thus, the growth of the oxide film commences perpendicular to metal surface

At the metal / oxide film interface $M \longrightarrow M^{2+} + 2e^{-}$

At the oxide film / environment interface



The overall reaction is $M + \frac{1}{2} O_2 \longrightarrow M^{2+} + O^{2-} \equiv MO$
(oxide film)

Nature of metal oxide film

Nature of metal oxide film on the metal surface plays an important role in oxidation corrosion

i. Stable oxide layer : Stable oxide layer is a fine grained structure, and gets adsorbed tightly to the metal surface. Such layer is impervious and stops further oxygen attack. Such a film behaves as a protective coating and further corrosion is prevented

Examples: Oxides of Al, Sn, Pb, Cu form stable oxide layers

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Examples: Oxides of Al, Sn, Pb, Cu form stable oxide layers

ii. Unstable oxide layer: Unstable oxide layer is formed on noble metals, which decomposes back into metal and oxygen

Examples: Oxides of Pt, Ag

iii. Volatile oxide layer: The oxide layer volatilizes as soon as it is formed leaving the fresh metal surface for further corrosion

Example : Molybdenum oxide

iv. Protective or non-protective oxide film: (Pilling – Bedworth ratio)

Ratio of the volume of the oxide formed to the volume of metal consumed is called as **Pilling – Bedworth ratio**

If the volume of the oxide layer formed is less than the volume of the metal, the oxide layer is porous and non protective. **Examples** : Na, Mg, Ca

If the volume of the oxide layer formed is greater than the volume of the metal, the oxide layer is non porous and protective,

Examples : Pb, Sn

Corrosion by hydrogen

i. Hydrogen embrittlement

Contact of metals with H_2S at ordinary T causes evolution of atomic hydrogen : $\text{Fe} + \text{H}_2\text{S} \longrightarrow \text{FeS} + 2\text{H}$

Atomic hydrogen diffuses into the metal and collects in the voids, where it recombines into molecular hydrogen.



Collection of these gases in voids develop very high pressure, which causes cracks and blisters in the metal.

ii. Decarburisation

At higher T, atomic hydrogen is formed by the thermal decomposition of molecular hydrogen : $\text{H}_2 \longrightarrow 2\text{H}$

When steel is exposed to this environment, atomic hydrogen combines with carbon of steel to produce methane gas :



Accumulation of these gases leads to high pressure, which causes cracking. The process of decrease in carbon content of steel is called as '**decarburisation of steel**'

Liquid – metal corrosion

This is due to the flowing action of liquid metal at high T. Corrosion reaction involves

- i. Dissolution of solid metal by liquid metal
- ii. Liquid metal penetrating into solid metal

Wet corrosion (Electrochemical corrosion)

Conditions

- i. When two dissimilar metals or alloys are in contact with each other in the presence of an aqueous solution or moisture
- ii. When a metal is exposed to varying concentrations of oxygen or an electrolyte

Under these conditions, one part of the metal becomes anode and another part becomes cathode.

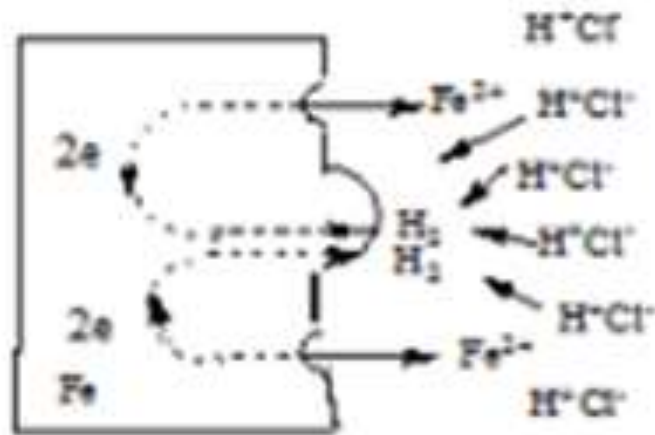
Mechanism of Wet corrosion

- i. In the anodic part, oxidation (or) dissolution of metal occurs : $M \rightarrow M^{2+} + 2e^-$
- ii. In the cathodic part, reduction occurs, which depends on the nature of the corrosive environment
 - (a) If the corrosion environment is acidic, hydrogen evolution occurs $2H^+ + 2e^- \rightarrow H_2$
 - (b) If the corrosive environment is slightly alkaline or neutral, hydroxyl ion is formed : $\frac{1}{2} O_2 + 2e^- + H_2O \rightarrow 2OH^-$

The metal ions from the anodic part and non metallic ions from cathodic part diffuse towards each other through conducting medium and form a corrosion product between anode and cathode

(a) Hydrogen evolution corrosion

All the metals above hydrogen in the electrochemical series have a tendency to dissolve in acidic solutions with evolution of hydrogen gas



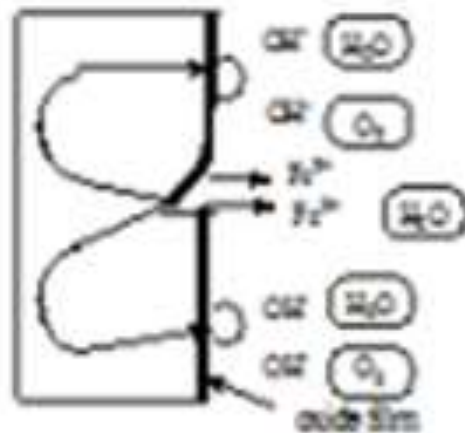
At anode: Iron undergoes dissolution to give Fe^{2+} ions with the liberation of e^-



At cathode: Liberated electrons flow from anodic to cathodic part where H^+ is reduced to H_2



(b) Adsorption of oxygen corrosion



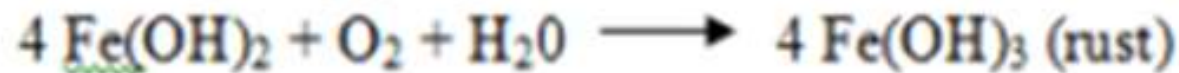
The surface of iron is generally coated with a thin film of oxide. However, if the oxide film develops some crack, some anodic areas will be created on the surface and the remaining part acts as cathode

At anode: Iron dissolves with liberation of e^-

At cathode: Liberated e^- flow from cathodic to anodic part through metal, where they are taken up by dissolved oxygen to form OH^- .

Nett corrosion reaction is $Fe^{2+} + OH^- \longrightarrow \underline{Fe(OH)_2}$

If enough oxygen present



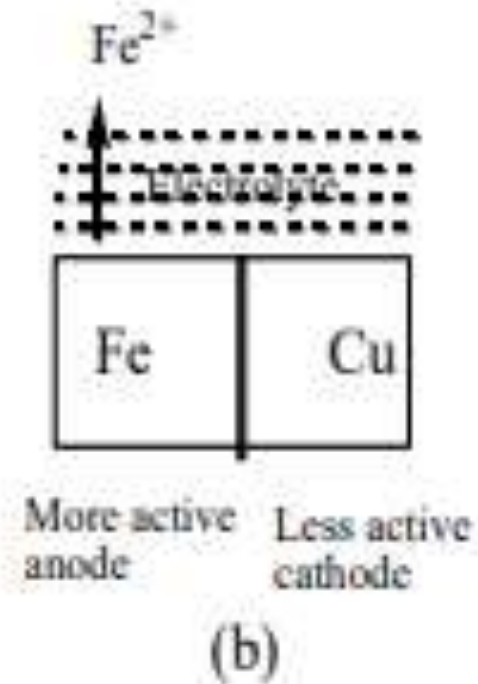
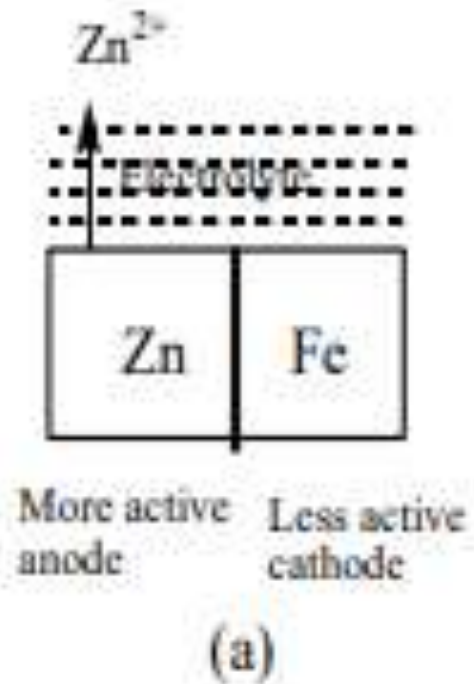
Types of electrochemical corrosion:

i. Galvanic corrosion

When two metals are in contact with each other in presence of an aqueous solution or moisture, galvanic corrosion occurs

More active metal (more -ve electrode potential) acts as anode

Less active metal (less -ve electrode potential) acts as cathode



(a) Zn – Fe couple :
Zn is more active and
dissolves in preference
to Fe

(b) Fe – Cu couple:
Iron is more active
than Cu and
undergoes corrosion
in preference to Cu

Other examples

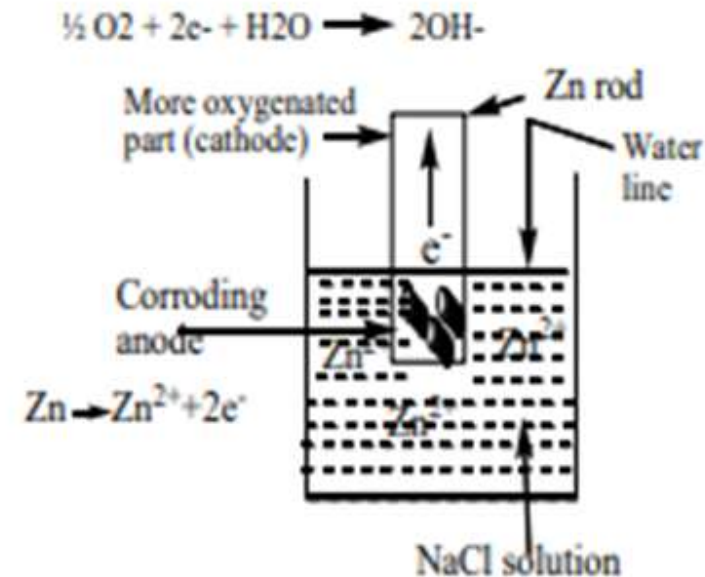
Steel screw in brass marine hardware corrodes

Galvanic corrosion can be prevented by providing an insulating material between the two metals

(ii) Differential aeration (Concentration cell corrosion)

This type of corrosion occurs when a metal is exposed to varying concentration of oxygen or any electrolyte on the surface of the base metal

Example: Metals partly immersed in water or conducting solution
(Water line corrosion)

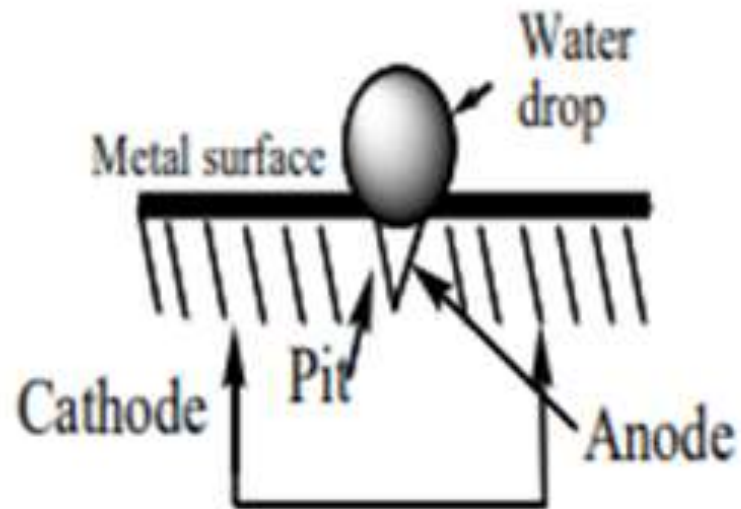


If the metal is partially immersed in the conducting solution, the metal part above the solution is more aerated and hence becomes cathode. The metal part inside the solution is less aerated and thus, become acidic and suffers corrosion

1. Pitting corrosion

Pitting is localised attack, resulting in the formation of a hole around which the metal is relatively unattacked cathode due to high oxygen concentration.

The rate of corrosion will be more, when the area of cathode is larger and the area of anode is smaller. A small pit is formed at the surface of the metal



Consider a drop of water or aqueous NaCl resting on a metal surface. The area covered by the drop acts as an anode due to less oxygen concentration and suffers corrosion. Uncovered area acts as

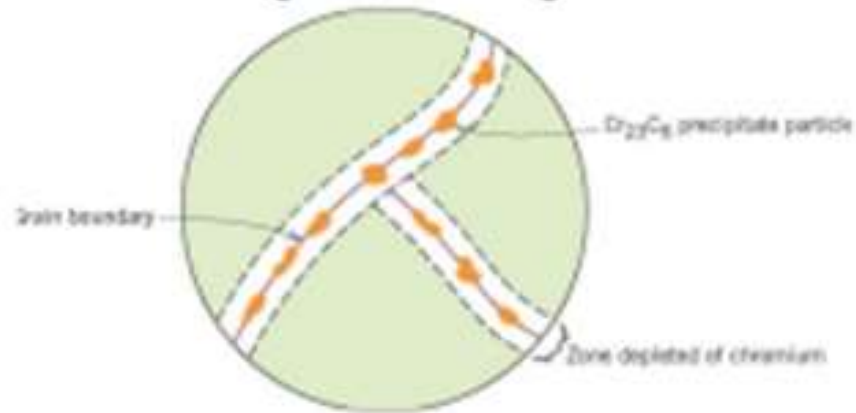
2. Intergranular Corrosion (IGC)

- This type of corrosion occurs along the grain boundaries. When a metal is solidified the solidification starts at a number of randomly distributed nuclei within the molten mass.
- Each of them grows in a regular pattern or atomic array to form grains. Because of random distribution of the nuclei, the planes of atoms in adjacent grains do not match and these mismatched areas between grains are known as grain boundaries.
- Certain compounds precipitate along the grain boundaries. The precipitated compounds as well as the grain centers behave as cathode, whereas the grain boundaries behave as anode.

- Owing to the precipitation of certain compounds at the grain boundaries the solid metal solution adjacent to the boundary becomes depleted in those constituents. Thus, a potential difference is created leading to the corrosion at the anodic grain boundaries.

It is common in stainless steel and other heat treated alloys
The presence of **mismatching of grains** leads to highly active grain boundaries.

Due to this high activity along the boundaries, the Cr and C present in SS react to give Chromium Carbide, which precipitates along the boundary. This decreases the % of Cr at the boundary and hence the **boundary becomes anodic** with respect to the bulk of the grain, resulting of corrosion at boundary.



Adopting proper and controlled heat treatment methods can minimize IGC.

3. Stress Cracking Corrosion

It occurs because of the combined effect of

- Static tensile stress and
- Corrosive environment near the metal

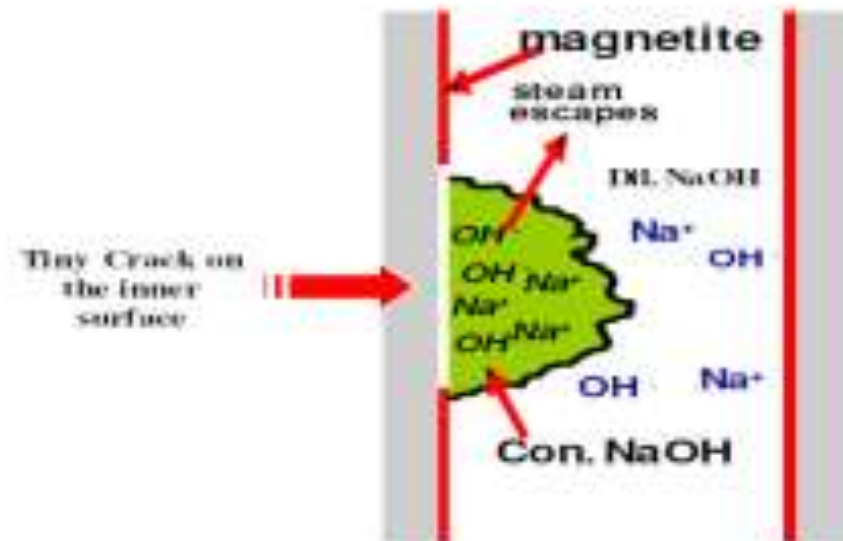
The metal develops internal stress during manufacture process like fabrication, heat treatment, rolling insufficient annealing etc.

Thermodynamically, areas under stress are at higher energy level. Therefore, they have high electrode potential and act as anode. The stress-free areas are at lower electrode potential and act as cathode. The difference in potential of these two is quite low and corrosion is concentrated in small path that is anodic. The anodic area

become highly reactive and is attacked even by a mild corrosive environment resulting in the formation of a crack.

The corrosive agents are very specific like

- Caustic alkalies and strong nitrate solution for mild steel
- Brass undergoes corrosion easily in the presence of traces of NH_3 .
- Acid chloride for stainless steel.



For example caustic embrittlement is a type of SCC occurring in boilers. In high pressure boilers, Na_2CO_3 , used for treating hard water is converted to NaOH .



High pressure

Due to the repeated heating and cooling, the walls of the boiler contain lot of tiny cracks.

The NaOH formed as above, enters these cracks and evaporates. Thus the cracks contain higher concentration of NaOH and attack the surrounding area, dissolving iron of boiler forming sodium ferroate. This causes embrittlement of boiler parts, particularly stressed parts like bends, joints, and rivets.

Another example is the corrosion of brass in presence of NH_3 .

Prevention Methods:

i. Adopting **Phosphate Conditioning** as an alternative to Carbonate conditioning

ii. By **sealing the hair line cracks** with Sodium sulphate , Tannin, Lignin etc. (can be done easily by adding a little amount of sealants in water)

Other examples

- i. Corrosion occurs under metal washers, where oxygen cannot diffuse easily.
- ii. Lead pipeline passing through clay to cinders undergo corrosion. The pipeline under cinders is more aerated.

Difference between chemical and electrochemical corrosion

Chemical corrosion	Electrochemical corrosion
Occurs only in dry condition	Occurs in the presence of moisture or electrolyte
Due to direct chemical attack of the metal by environment	Due the setting up of large number of anodic and cathodic areas
Even a homogeneous metal surface gets corroded	Heterogeneous surface (or) bimetallic contact is necessary
Corrosion products accumulate in the same place where corrosion occurs	Corrosion occurs at the anode, while product formed elsewhere
Self controlled	Continuous process
Follows adsorption mechanism	Follows electrochemical reaction

Factors influencing the rate of corrosion:

- i. Nature of the metal
- ii. Nature of the environment

Nature of the metal

(a) Position in the emf series:

Rate of corrosion $\propto T$, as the rate of chemical reaction and the rate of diffusion of the ions increases with increase in T

(b) Humidity:

Rate of corrosion will be more when the humidity of the environment is high

Moisture acts as the solvent for oxygen in air, to produce the electrolyte essential for corrosion

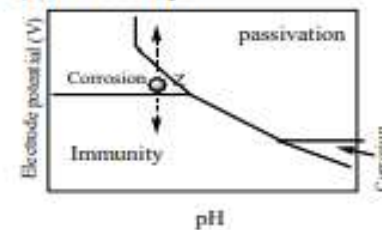
(c) Presence of corrosive gases

Acidic gases like CO_2 , SO_2 , H_2S and fumes of HCl produce electrolytes, which are acidic and increases electrochemical corrosion

(d) Presence of suspended particles

Particles like NaCl , $(\text{NH}_4)_2\text{SO}_4$ along with moisture act as powerful electrolytes and accelerate electrochemical corrosion

(e) Effect of pH



Pourbaix Diagram

Explains the possibility of corrosion with respect to pH and the electrode potential of the metal

Pourbaix diagram for iron in water clearly shows the zones of corrosion, immunity and passivity. In the diagram Z is

the point at $\text{pH} = 7$ and electrode potential = -0.4 V . It is in the corrosion zone, indicating that iron rusts in water under this condition.

The rate of corrosion can be altered by shifting the point Z into immunity and passivity zones, if the potential is changed to -0.8 V by applying an external current

On the other hand, corrosion of iron can be reduced by moving into the passivity region by applying +ve potential

Rate of corrosion will be maximum, when the environment is acidic.

Electroplating:

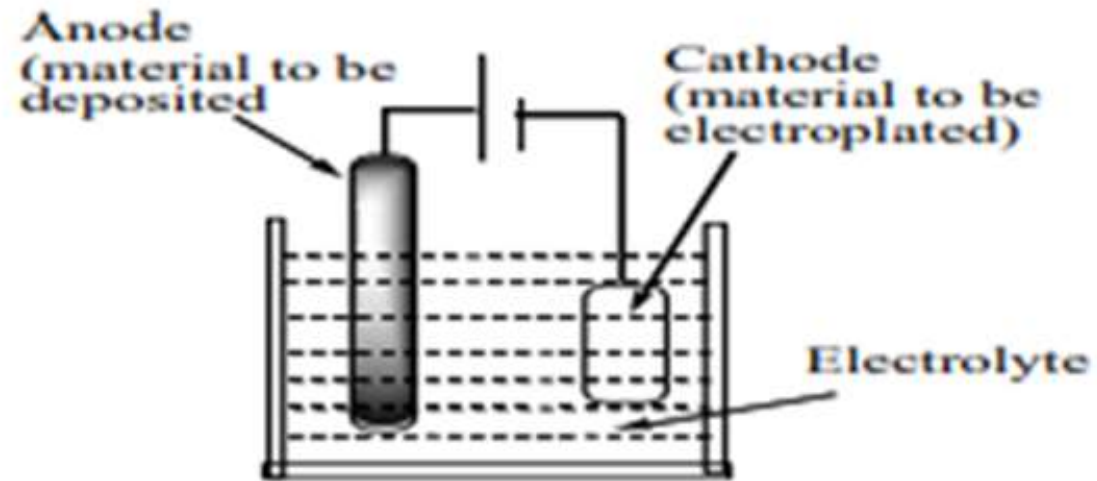
Electroplating is the process of deposition of a metal on a metal, non-metal or alloy by passing electric current through an electrolytic solution containing soluble salt of the coating metal.

In this method, the base metal to be coated or electroplated is made the cathode and the coating metal is made the anode.

The process of electroplating consists of two steps.

(i) Surface preparation: In this step, the surface of the metal to be electroplated is cleaned by several chemical and mechanical methods.

(ii) Electrodeposition: In this step, the coating metal is electroplated over the base metal.



Electroplating of Copper:

For copper plating, the anode is made of copper and the cathode is the material to be electroplated. The electroplating bath may be acidic or alkaline.

(a) **Acidic bath:** Also called sulphate bath, it consists of 200-250 g/l CuSO_4 , 50-75 g/l H_2SO_4 and rest water. The additives are gelatin or dextrin, sulphur containing brightener and sulphonic acid. The operating temperature is $20-40^\circ\text{C}$. The pH is low and the current density is about $20-50 \text{ mA/cm}^2$.

This bath is used for coating in printed circuit boards (PCB) and is not suitable for electroplating iron and its alloys.

(b) **Alkaline bath:** It is also called cyanide bath. The composition per liter of the bath is as follows: CuCN : 40-50g, KCN : 20-30g, 10g K_2CO_3 and rest water. Brighteners like Al_2O_3 and thiosulphate are also added to the electrolytic bath. The pH is maintained between 12 and 13, current density used is $10-40 \text{ mA/cm}^2$ and the temperature of the bath is $40-50^\circ\text{C}$.

This bath finds application in the coating of printed circuit boards and is also suitable for plating iron and its alloys. It is used as an undercoating for chromium plating.

If during electrolysis, the anode is made of the coating metal itself, concentration of the electrolyte remains unchanged, as the metal ions deposited from the bath are replaced continuously from the anode

Example:

If CuSO_4 solution is used as an electrolyte, it ionizes as



On passing current, Cu^{2+} ions get deposited at the cathode



The free SO_4^{2-} ions migrate to the copper anode and dissolve an equivalent amount of Cu from CuSO_4 :



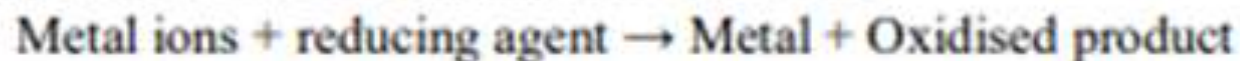
CuSO_4 formed gets dissolved in the electrolyte. Thus, there is a continuous replenishment of electrolyte during electrolysis.

Process:

The article to be plated is cleaned with dilute acid. The article made cathode in the electrolytic cell. The anode is the coating metal. When dc current is passed from battery, coating metal ions migrate to the cathode and get deposited. A thin layer of coating metal is obtained on the article to be coated. To get strong, adherent smooth deposit, certain additives (glue, gelatin) are added to the bath. Optimum conditions for plating (T, current density and concentration of electrolyte) are maintained.

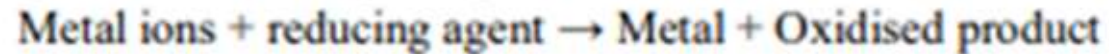
Electroless plating:

In electroless plating, a noble metal (less reactive metal) is deposited on a less noble metal (more reactive metal) without the passage of electric current. It involves a redox reaction catalyzed by the metal of the alloy being deposited; hence it is also termed as autocatalytic coating. The method employs a suitable reducing agent to bring about the reduction of metal ions to metal that gets deposited over catalytically active surface.



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This technique has been used for manufacturing mirrors by the reduction of a complexed metal with the help of a mild reducing agent like formaldehyde.

Advantages:

1. Electrical energy is not used
2. It helps in coating non-conducting objects, non-metallic surfaces like plastic, semiconductors.
3. The throwing power is unlimited.
4. No excess deposit at joints.

5. Edges, inside holes, irregular objects and objects of complex geometries and shapes can easily be coated evenly. It is difficult to coat these surfaces by electroplating.
6. Hydrogen gas is not trapped in the blind holes.
7. Resulting deposits have unique physical, chemical, mechanical and magnetic properties.
8. Coating is harder and less porous than regular coating.

Disadvantages

1. Process is expensive as the chemicals used cost high.
2. Rate of deposition is rather slow.
3. A careful analytical control of the bath is required.

Electroless plating of Nickel

Surface to be plated	Chemical used for activation
Al, Cu, Fe, brass, Au, Ag, Pt, Rh and Co	No activation required and nickel is plated directly on their surface
Stainless steel	By dipping in hot solution of 50% dilute H_2SO_4
Magnesium alloy	Thin coating of Zn and Cu over it
Non-metallic articles like plastics, glass or quartz	They are first dipped in $SnCl_2$, solution containing HCl followed by dipping in palladium chloride so that a thin activating surface layer of Pd is formed on their surface.

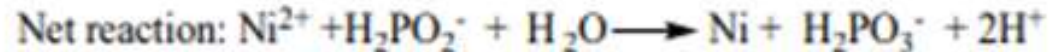
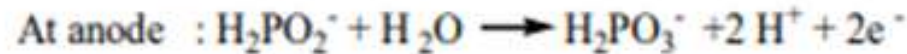
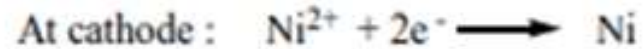
Bath

The coating bath contains the following

- Coating solution – 20 g/l of NiCl_2
- Reducing agent – 20 g/l of sodium hypophosphite
- Complexing agents cum exhalant – 15 g/l sodium succinate
- Buffer – 10 g/l of sodium acetate

The pH of the bath is maintained at 4.5 and temperature is 93°C .

Following reactions take place when the activated surface is dipped in the bath



As seen above H^+ ions are liberated in the reaction hence the pH of the bath goes down which adversely affects the quality of the plating. Consequently continuous addition of the buffer is essential to maintain the pH. NiCl_2 and hypophosphite are also consumed and need to be replenished continuously. In addition to the above reactions there may be formation of phosphorous which results in Ni-P alloy deposition.

Applications

1. Owing to excellent throwing power, this method is applied for coating objects with complex geometrical shapes and also on the internal diameter of tubular parts that are otherwise difficult to access.
2. It is used for plating several components like pistons, fasteners, pipes, valves, shafts and hydraulic systems, fuel injection assemblies.

3. Electroless nickel plating finds use in jewellery, electroless nickel plating on acrylonitrile butadiene styrene polymer is used in decorative items.

4. In electrical industry electroless Ni-P coating is used in making magnetic components.

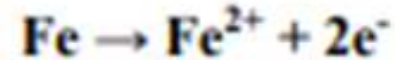
Electrochemical machining :

Electrochemical machining is a process of a selective dissolution of the anodically connected work piece material submerged in an electrolyte together with an anodically connected tool.

Principally electrochemical machining is similar to Electro polishing where the work piece surface roughness decreases due to the conversion of the atoms into ions and their removal from the surface as a result of a passage of an electric current. Electrochemical machining is generally opposite to electroplating where the metallic ions traveling through the electrolyte solution deposit on the surface of the cathodically connected work piece.

The electrochemical reactions occurring in the electrochemical machining process are as follows:

At the anode the iron atoms convert into the iron ions (cations):

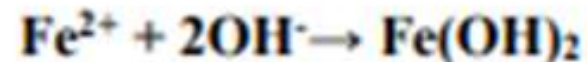


The electrons lost by the iron atoms travel to the cathode through the DC power supply.

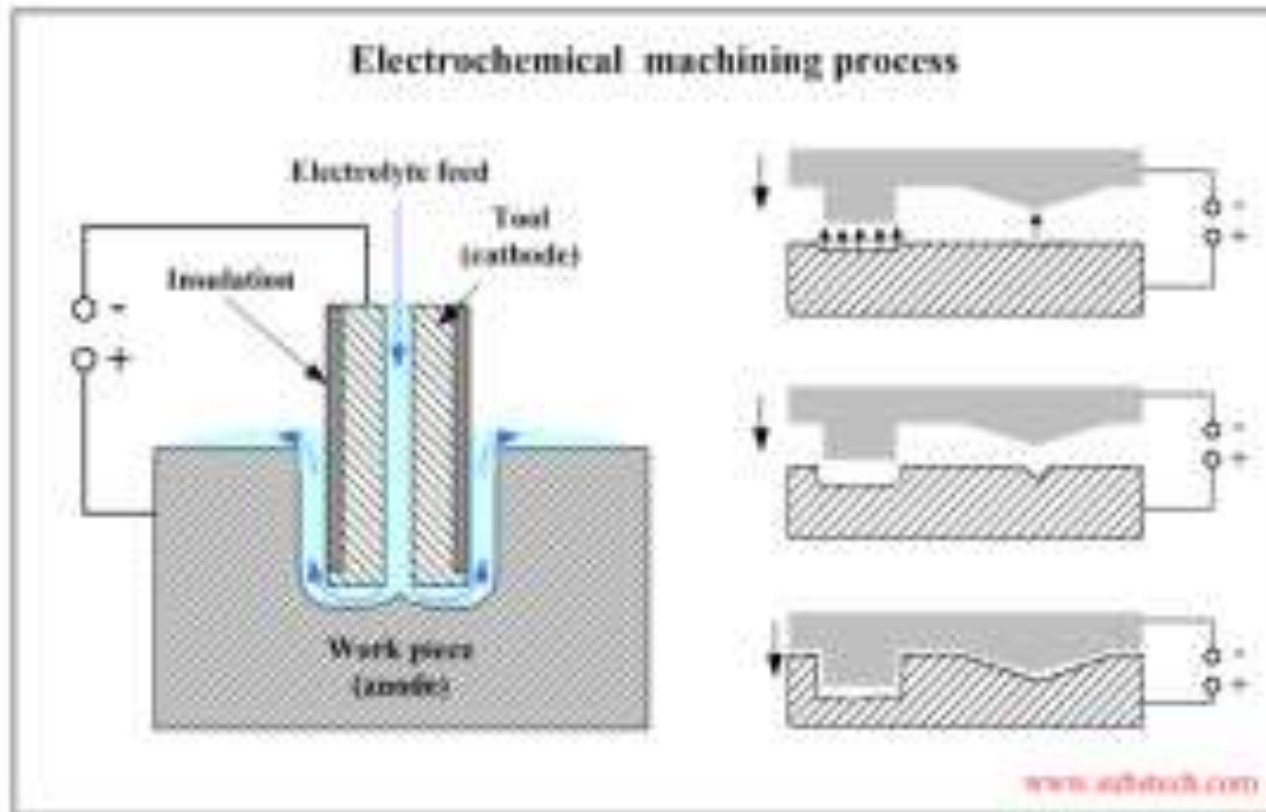
At the cathode the electrons react with water molecules forming gaseous Hydrogen and hydroxyl ions (anions) according to the reaction:



The cations and the anions react in the aqueous solution and create insoluble ferrous hydroxide:



The insoluble hydroxide is taken away by the flowing electrolyte and then it precipitates at the tank bottom forming the sludge. The principle scheme of electrochemical process is presented in the figure below.



The work piece is mounted in a fixture electrically isolated from the tank and other machine parts. The work piece is connected to the positive terminal (anode) of the Power Supply. The tool is connected to the negative terminal (cathode).

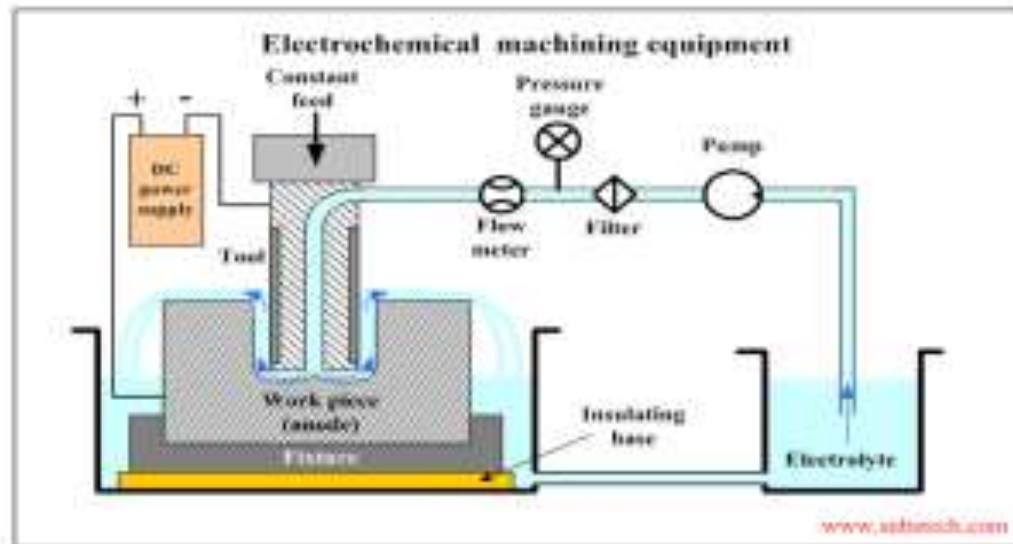
The electrolyte is continuously flowing through a hole in the tool to the gap between the work piece and the tool surfaces.

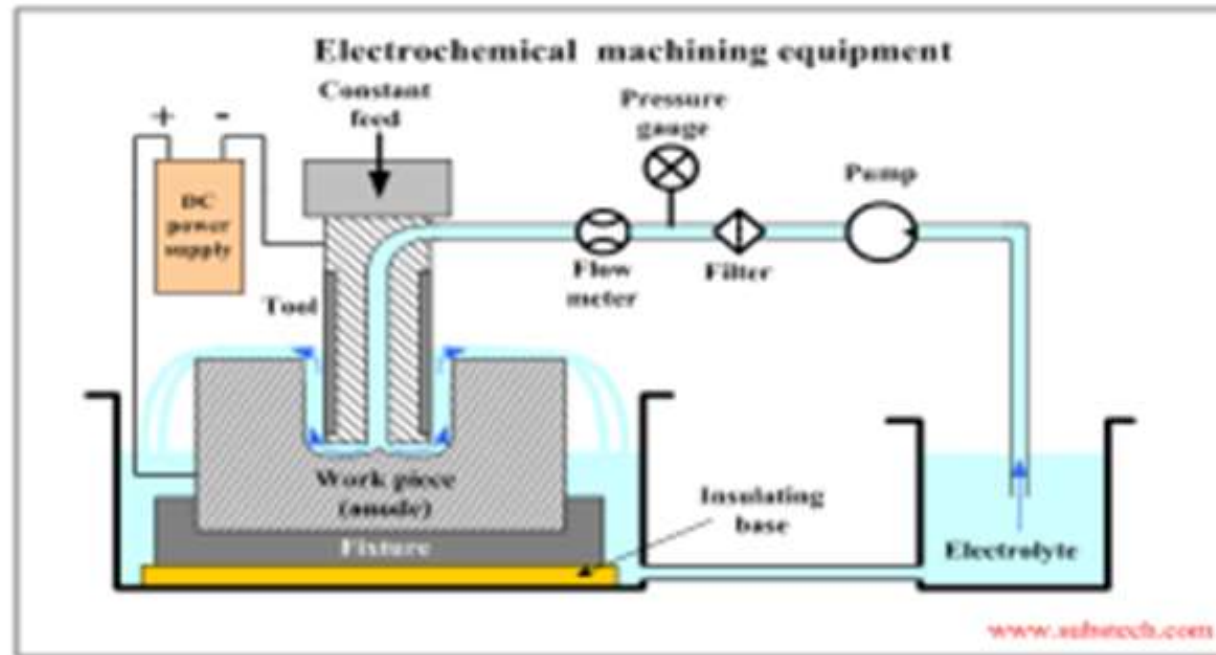
The tool is moving towards the work piece at a constant speed of about $0.05''/\text{min}$ (1.25 mm/min). The gap between the tool and the work piece is kept constant. Stable behavior of the process is a result of a control of the power supply voltage.

The final shape of the work piece formed as a result of the electrochemical machining process conforms the shape of the tool.

Electrolytes used in electrochemical machining:

- Sodium chloride (**NaCl**) at the concentration of 20% - for ferrous alloys(e.g. Steels and cast irons and cobalt alloys.
- Sodium nitrate (**NaNO₃**) - for ferrous alloys.
- Hydrochloric acid (**HCl**) - for Nickel alloys.
- A mixture of sodium chloride (**NaCl**) and sulfuric acid (**H₂SO₄**) - for nickel alloys.
- A mixture of 10% hydrofluoric acid (**HF**), 10% hydrochloric acid (**HCl**), 10% nitric acid (**HNO₃**) - for Titanium alloys.
- Sodium hydroxide (**NaOH**) - for tungsten carbide (**WC**).





Applications of electrochemical machining

- Machining of hard materials. The process parameters and the tool life time do not depend on the hardness of the work piece therefore electrochemical machining is often used for machining hard materials. Turbine blades and rifle barrels are fabricated by electrochemical machining.
- Producing holes and cavities which cannot be obtained by conventional machining methods.

- Die sinking. Electrochemical machining is often used as an alternative to the cavity type electric discharge machining (EDM).
- Fabrication of thin walled parts. Electrochemical machining does not produce surface stress in the work piece therefore even very brittle and easily deformed materials may be machined in thin walled shapes.
- Grinding of a work piece by a rotating wheel, which performs grinding operation through an electrolyte. The wheel is conductive and cathodically connected. Non-conductive hard particles are set on the wheel surface. The particles provide a constant gap through which an electrolyte is continuously fed. Hard and brittle materials are ground by the method.

Advantages of electrochemical machining:

- The rate of machining does not depend on the hardness of the work piece material.
- The tool does not wear. Soft materials (e.g., copper) may be used for tool fabrication.
- No stresses are produced on the work piece surface.
- No burrs form in the machining operation.
- High surface quality may be achieved.
- High accuracy of the machining operation.

Disadvantages of electrochemical machining:

- Higher cost.
- Electrolyte may cause corrosion of the equipment.
- Large production floor is required.
- Only electrically conductive materials may be machined.
- Not environmentally friendly process.

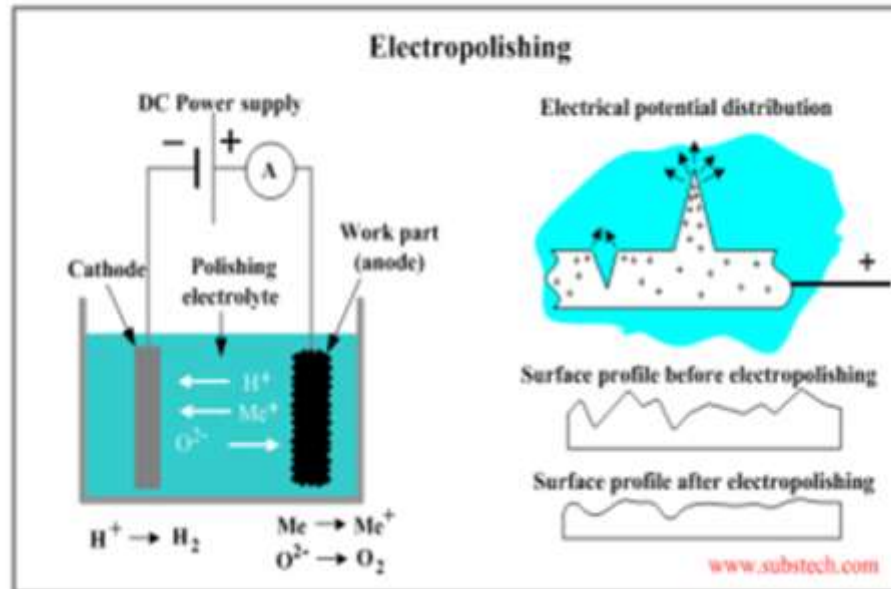
Electropolishing:

Electropolishing is an electrochemical process in which the atoms of a work piece submerged in an electrolyte convert into ions and are removed from the surface as a result of a passage of an electric current.

In electropolishing the metallic work piece dissolves in the electrolyte in contrast to Electroplating where the metallic ions traveling through the electrolyte solution deposit on the work piece surface.

In an electropolishing cell (see the figure below) the work piece is anode. It is connected to the positive terminal of the direct current power supply. The negative terminal is connected to a cathode plate commonly made of stainless steel, copper or lead. The anode and the cathode are immersed into an electrolyte solution.

Principally electropolishing is similar to Electrochemical machining where the work piece material is removed due to the conversion of the atoms into ions, formation of an insoluble precipitate and its transfer from the surface. The DC power supply, the anodically connected work piece, the electrolyte and the cathode form an electric circuit.



According to Faraday's law the amount of the removed material is directly proportional to the amount of electric charge, passed through the circuit. The amount of electric charge $Q=I*t$ (I – electric current, t – time).

The amount of the metal removed from the work piece surface in an electropolishing process varies from 0.1 to 2.5 mil (2.5-64 μm).

The important feature of the electropolishing process is its ability to dissolve asperities (peaks) on the work surface much faster than the material in "micro-valleys". Such selective dissolution is a result of different values of the electrical potential of the peaks and valleys. The positive charge of the anodically connected work piece is concentrated in the peaks where the current density is higher than average which causes a selective dissolution of the peaks and smoothening the surface.

Brightening:

- Brightening is an effect of lower surface roughness produced by electropolishing operation.
 - The surface of the parts produced by metalworking operations (cutting, Rolling, stamping, Drawing) is relatively rough and has to be improved by a polishing operation.
 - One of the polishing techniques is a mechanical polishing. However mechanical polishing produces scratches, debris and may leave the abrasive particles on the work surface. Additionally mechanical polishing causes a formation of residual stresses in the surface layer.
 - In contrast to mechanical polishing electropolishing produces a surface free of both mechanical defects and residual stresses.
 - Surface roughness is a parameter of the surface quality commonly measured as the average deviation of the surface profile from the mean line.
 - Electropolishing reduces the profile peaks resulting in smootheningthesurface.
- The improvement of the surface roughness achieved by electropolishing is commonly a half of the original roughness value.

Deburring:

The selective dissolution of prominent point (peaks) on the work surface in the electropolishing process is utilized in deburring operation.

Small burrs (up to 0.5 mil/13 μm) produced in some various metalworking operations may be effectively removed by electropolishing.

Like in the peaks on the surface the density of the electric current passing through burrs is higher than the average value

therefore the burrs material is removed much faster. The resulting surface is electropolished and free of burrs.

In contrast to mechanical deburring (e.g. vibratory deburring) electropolishing does not produce scratches and residual stresses on the work surface.

Passivating:

Passivation is a chemical process of a restoration of the corrosion resistance of a contaminated stainless steel part.

The contaminant particles embedded into the surface disturb the protecting layer of chromium oxide and allow oxidation of iron (rust formation).

In the conventional passivation process the contaminants are removed by a treatment in 20% nitric acid.

The contaminating particles may also be removed by electropolishing. Additionally electropolishing produces higher surface concentration of chromium due to the preferential dissolution of iron and nickel atoms. In contrast to the treatment by nitric acid the passivation by electropolishing does not produce distortion and does not cause hydrogen embrittlement.

Stress relieving:

Tensile stresses concentrated in the part surface reduce its Fatigue.

The stresses may be induced in various fabrication stages: metalworking operations (stamping, Rolling, Drawing, grinding), heat treatment, vibratory deburring, Electroplating. The thickness of the layer with the surface stresses is about 1 mil (25 μm).

Electropolishing allows to remove the stressed surface skin from the work piece. The fatigue strength is additionally improved due to smoothening the surface of electropolishing. The surface

defects such as scratches, foreign particles embedded into the surface, tool produce notch effect decreasing the fatigue limit.

Defects free electropolished surface provides an increased fatigue strength.

Benefits of electropolishing:

- Bright appearance;
- Absence of abrasive scratches;
- Improved fatigue strength due to stress relieving and defects free surface;
- Lower coefficient of friction due to smoother surface (reduced microasperities);
- Better corrosion resistance;
- Allows processing fragile and delicate parts.

Disadvantages of electropolishing:

- Rough surface defects cannot be removed;
- Electropolishing multiphase alloys may cause roughening due to selective dissolution of different phases.

Electrophoretic deposition EPD

Electrophoretic deposition EPD is a method of coating a conductive part with particles suspended in a fluid dispersion under the influence of an electric field applied between the work part and the counter electrode.

Similar to Electroplating coating electrophoretic deposition utilizes electrically charged particles moving between two electrodes (an anode and a cathode) immersed in a liquid media. However in contrast to conductive electrolytes used in electroplating, the fluids of electrophoretic dispersions are dielectric.

In addition the electroplating coatings are built from metallic ions converted into atoms when discharged at the cathode, whereas

in electrophoretic process the coating is formed by a deposition of relatively large powder particles which may be polymeric, ceramic or metallic.

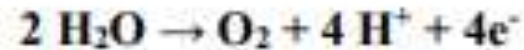
The following characteristic features define electrophoretic deposition:

- There is a stable dispersion of particles in a solvent (a colloid).
- The particles gain a surface charge as a result of an electrostatic interaction with the molecules of the solvent.
- The particles are capable to move in the suspension towards the work part under the influence of a voltage imposed between the work part and the counter electrode (the phenomenon called electrophoresis).
- A rigid deposition composed of condensed particles is built up on the work part surface in contrast to dip coating - a painting process in which the concentration of particles in the layer adhered to the work part is the same as the concentration of the particles in the bulk suspension.
- The deposited coating is adhered to the surface of the work part.

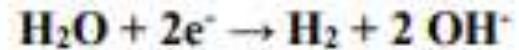
When a voltage is applied between the electrophoretic electrodes the charged particles start to migrate towards the electrode with the opposite electric polarity. The particles are deposited first of all at the surface areas with the highest electric potential. The formed coating decreases the potential of such areas and equalizes the potential distribution over the part surface. As a result a uniform and even film forms over the whole part surface including the surface of cavities, edges and corners. The coating thickness is determined by the voltage value which is typically 25-400 V. After a coating of a certain thickness is built the deposition process stops.

If the electrophoretic dispersion is aqueous, the voltage applied between the immersed electrodes immersed causes water molecules to decompose.

At the anode Oxygen is generated according to the oxidation reaction:



The reduction reaction at the cathode results in a formation of Hydrogen:



As a result of electrolysis the solution surrounding the anode becomes acidic and in the cathode region - alkaline. Changes of the solution PH destabilize the colloid causing the particles to coagulate and deposit on the electrode surface.

Polarity of electrophoretic deposition. The electric charge of the dispersed particles may be either positive or negative. The positively charged particles are attracted to the cathode. The process of a deposition of positively charged particles is classified as cathodic electrophoretic coating in contrast to anodic electrophoretic coating related to the deposition of negatively charged particles.

Anodic electrophoretic process: is less expensive. It produces coatings of good aesthetic appearance. However the anode metal slightly dissolves in the solvent producing metallic ions which are incorporated in the coated film. The metallic contamination of anodic coatings decreases their corrosion resistance. Therefore anodic electrophoretic coatings are mostly used in indoor applications.

Cathodic electrophoretic process: results in a deposition of coatings with very low metallic contamination. Cathodic coatings are characterized by high corrosion resistance and durability in both indoor and outdoor applications.

Electrophoretic coating process: The industrial applications of electrophoretic deposition are referred to as e-coating, electrocoating, electrophoretic painting or electrophoretic coating.

The deposition process includes the following stages:

- Hanging the work parts
- Alkaline cleaning
- Rinsing
- Acid cleaning
- Immersion in adhesion promoter (wetting agent)
- Electrophoretic deposition
- Rinsing and dispersion recovery
- Rinsing in de-ionized water
- Dehydration oven
- Curing

The most popular applications of electrophoretic deposition are cathodic coating of automotive parts with epoxy, acrylic and polyurethane films.

The coatings have excellent scratch resistance and corrosion resistance. Acrylic and polyurethane coatings are also resistant against ultra-violet light.

Etching:

Etching PCB is to use the materials of chemical reactions or physical impact of technologies that are removed. Etching techniques can be divided into wet etching and dry etching, chemical solution used in wet etching through chemical reactions in order to achieve the purpose of etching, dry etching is usually a plasma etching, its effect may be the impact chips by plasma surface physics, or possibly a plasma activated chemical reaction between base and surface atoms, or even role may be a composite of the two.

PCB Etching:

Currently used for print circuit board etching of solvents are iron (Ferric Chloride), cupric chloride (Cupric Chloride), alkaline ammonia (Alkaline Ammonia), sulfuric acid hydrogen peroxide (Sulfuric Acid + Hydrogen Peroxide) etching fluid, ammonium persulfate, sulfuric acid – chromic acid etching solution. Like the PCB manufacturing in Fusion PCB of Seed, Etching liquid are mainly copper chloride solution, ferric chloride liquid, alkaline etching, acid/hydrogen peroxide (hydrogen peroxide) etching.

Chloride copper etched liquid by chloride copper (CuCl_2 Castle, $2\text{H}_2\text{O}$) + hydrochloride (HCl) + hydrogen peroxide (H_2O_2) + water (H_2O) composition; three ferric chloride etched liquid is by three ferric chloride (FeCl_3) + hydrochloride (HCl) + water (H_2O) composition of; alkaline etched liquid of main components has copper ammonia complex ion; sulfuric acid/hydrogen peroxide (hydrogen peroxide) etched liquid to sulfuric acid and hydrogen peroxide (hydrogen peroxide) mainly components.

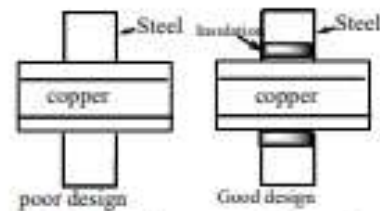
PCB etching process and copper chloride and ferric chloride market, PCB manufacturers some 95% using copper chloride (CuCl_2), IC substrate maker about 80% using ferric chloride (FeCl_3), 20% using copper chloride (CuCl_2). You can try etching PCB at home.

Corrosion control

Control of corrosion by modifying metal

1. **By selection of the metal** : Noble metals are used in ornaments and surgical instruments
2. **By using pure metal** : Pure metals have high corrosion resistance
3. **By alloying** : Stainless steel containing Cr produces a coherent oxide film, which protects steel
4. **By proper design** :

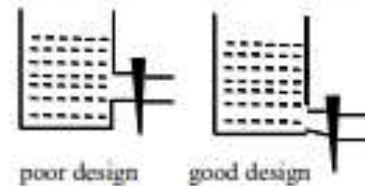
(i) Avoid galvanic corrosion



: If two metals are in contact, galvanic corrosion occurs. Galvanic corrosion can be prevented by

- (a) Selecting metals as close as possible in the emf series
- (b) Providing smaller area for cathode
- (c) Inserting an insulating material between two metals

(ii) Drainage affects corrosion



Tanks and other containers must be designed in such a way that the whole of the liquid be drained off completely

(iii) Avoid sharp corners and edges

(iv) Avoid crevices

Welded joints should be preferred to riveted joints

5. By cathodic protection

The metal is forced to behave like cathode

Sacrificial anodic protection method

The metallic structure to be protected is made cathode by connecting it with more active metal

Corrosion will be concentrated only on more active metal

The artificial anode gets oxidised protecting the original metallic structure

Hence, this process is called Sacrificial anodic protection

Al, Zn and Mg are used as sacrificial anodes

This method is used for the protection of ships and boats

Applications

- i. Protection of underground pipelines
- ii. Insertion of Mg sheets in boilers to prevent formation of rust
- iii. Ca metal is used to reduce engine corrosion

Corrosion inhibitors

Corrosion inhibitor is a substance which reduces the corrosion of a metal, when it is added to corrosive environment

Types of inhibitors

1. Anodic inhibitors :

Examples : Chromates, nitrates and tungstates of transition metal ions with high oxygen content

Anodic inhibitors are those that prevent corrosion occurring at the anode by forming an insoluble compound with the metal ions.

These precipitates get adsorbed on to the metal surface forming a protective film and hence reduce corrosion

2. Cathodic inhibitors :

In electrochemical corrosion, the cathodic reactions are of two types, depending on the environment

(a) In an acidic solution :

Examples : Organic inhibitors like amines, mercaptans, thiourea, heavy metal soaps

In the acidic solution, the cathodic reaction is evolution of H_2

The corrosion can be reduced in 2 ways

- (i) By slowing down the diffusion of H^+ to the cathode. This is done by organic inhibitors
- (i) By increasing the overvoltage of H_2 evolution. This can be done by adding antimony or arsenic oxides, which deposit adherent film of metallic As or Sb at the cathodic areas.

(b) In neutral solution:

Example : Sodium sulphite, hydrazine

Corrosion can be reduced by

- i. By eliminating oxygen from neutral solution using a reducing agent
- ii. Eliminating OH^- by adding Mg, Zn or Ni salts.

III. Vapour phase inhibitors

Examples : Dicyclohexyl ammonium nitrate, benzotriazole

Vapour phase inhibitors readily vaporise and form a protective layer on the metal surface.

These are used in storage containers, packing materials, sophisticated instruments