

ASSIGNMENT - 3
ENGINEERING CHEMISTRY

Submitted By : **YASH VINAYVANSHI**
B.TECH (2nd SEM)
SECTION **C** ; SR : **72** ; ROLL NO. : **19BCS081**
JAMIA MILLIA ISLAMIA FET
E-Mail : yash.vinayvanshi@gmail.com

Submitted To : **PROF. MASOOD ALAM**
DEPT. OF APPLIED SCIENCES AND HUMANITIES
JMI FET

1. What is Electrochemical corrosion? Describe the mechanism of electrochemical corrosion by hydrogen evolution and oxygen absorption.

1.1 ELECTROCHEMICAL CORROSION

Electrochemical corrosion is the deterioration of metals by redox process which occurs :

- 1. Where a conducting liquid is in contact with a metal or**
- 2. When two dissimilar metals or alloys are either immersed or dipped partially in a solution.**

This corrosion occurs due to existence of separate anodic and cathodic areas / parts between which current flows through the conducting solution. At the anodic area, an oxidation reaction takes place, so anodic metal is destroyed by coming to ionic form by and dissolving or assuming combined state such as oxides etc. Hence corrosion always occurs at anodic areas :

**At anode : $M \rightarrow M(n+) + ne^-$
 $M(n+) \rightarrow$ Dissolves in solution / forms compounds such as oxides.**

On the other hand at cathodic areas, reduction reaction takes place. Usually cathode reactions do not affect the cathode, since most of the metals cannot be further reduced. So, at cathodic part, dissolved constituents in the conducting medium accepts the electrons to form some ions (like OH⁻, O₂⁻). The metallic ions (at anodic part) and non metallic ions (formed at cathode part) diffuse towards each other through conducting medium and form a corrosion product somewhere between anode and cathode. The electrons set free at the anode flows through the metal and are finally consumed in the cathodic reaction. Thus we can say that the electrochemical corrosion involves :

- 1. The formation of anodic and cathodic areas or parts in contact with each other;**
- 2. Presence of a conducting medium ;**
- 3. Corrosion of anodic areas only ;**
- 4. Formation of corrosion product somewhere between anodic and cathodic areas.**

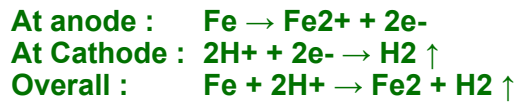
MECHANISM of electrochemical corrosion involves flow of electron current between the anodic and cathodic areas. The anodic reaction involves the dissolution metal as corresponding metal ions with liberation of free electrons . The the other hand the Cathodic reaction consumes electrons with either by :

- 1. Evolution of hydrogen or**
- 2. Absorption of oxygen**

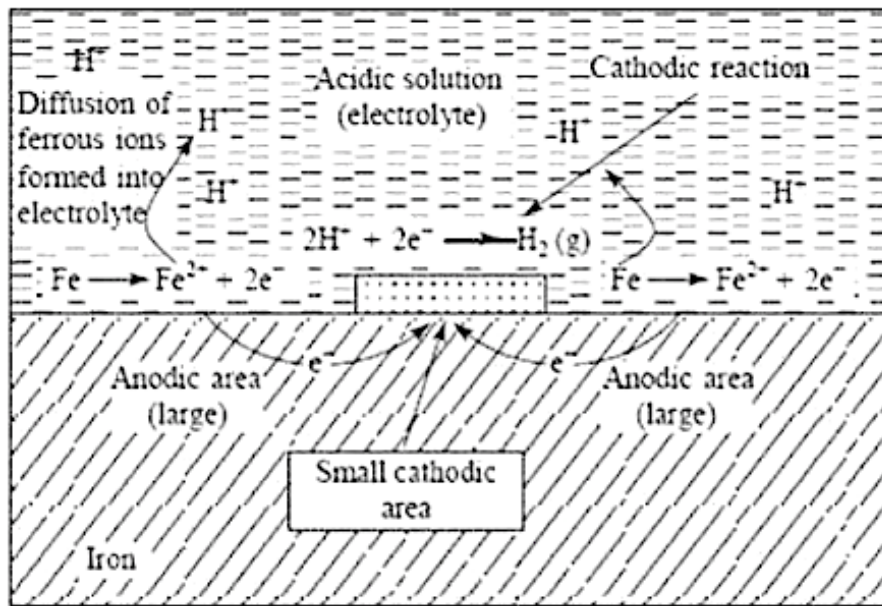
Depending upon the nature of the corrosive environment.

1.2 EVOLUTION OF HYDROGEN TYPE

This type of corrosion occurs usually in acidic environments. Considering metal like Fe, the anodic reaction is dissolution of iron as ferrous ions with liberation of electrons which flow through the metal from anode to cathode, where H⁺ ions of acidic solution are eliminated as hydrogen gas :



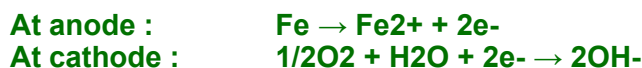
Thus, this type of corrosion causes displacement of hydrogen ions from the acidic solution by metal ions. Consequently, all metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solutions with simultaneous evolution of hydrogen. It may also be noted that in this process anodes are usually very large areas, whereas cathodes are small areas.



1.3 ABSORPTION OF OXYGEN TYPE

A common example of this type of corrosion is rusting of iron in neutral aqueous solution of electrolytes like NaCl solution etc. 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 well metal parts act as cathodes. It follows that the anodic areas are small surface parts, while nearly the rest of the surface of metal forms large cathodes.

At anodic areas of metal (iron) dissolves as ferrous ions with liberation of electrons which flows to cathodic areas, through the metal itself where the electrons are intercepted by dissolved oxygen :

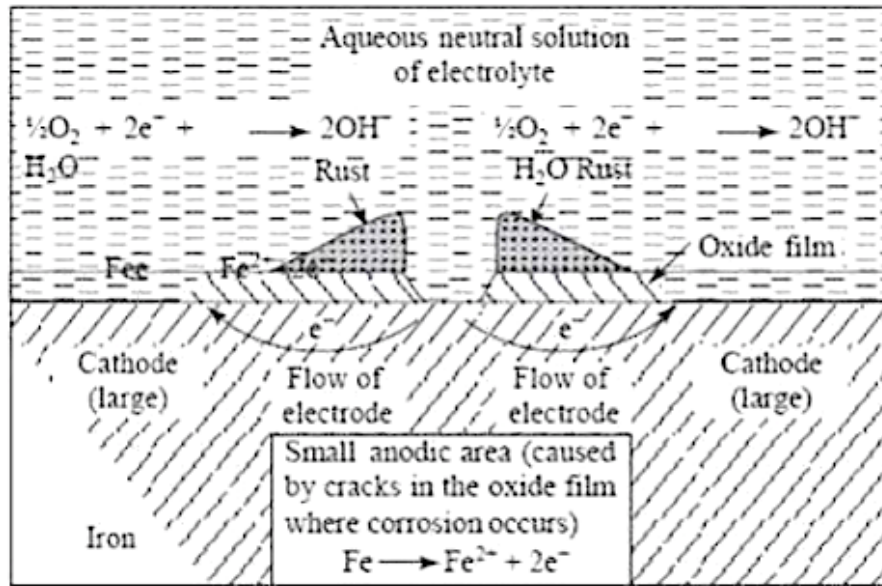


Further, Fe^{2+} ions at the anode and OH^- at cathode diffuse and ferrous hydroxide is precipitated:



Oxidation happens in presence of oxygen :

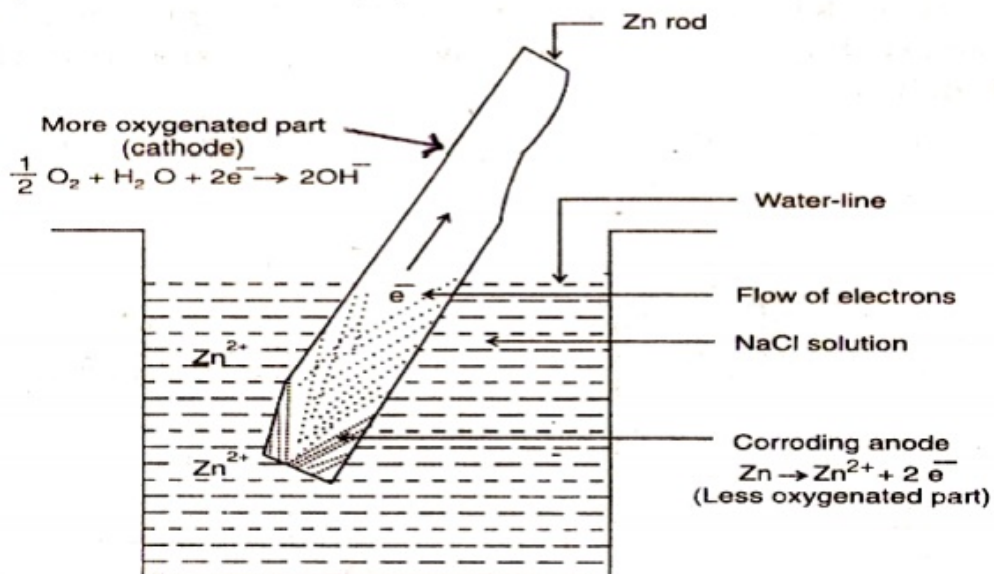




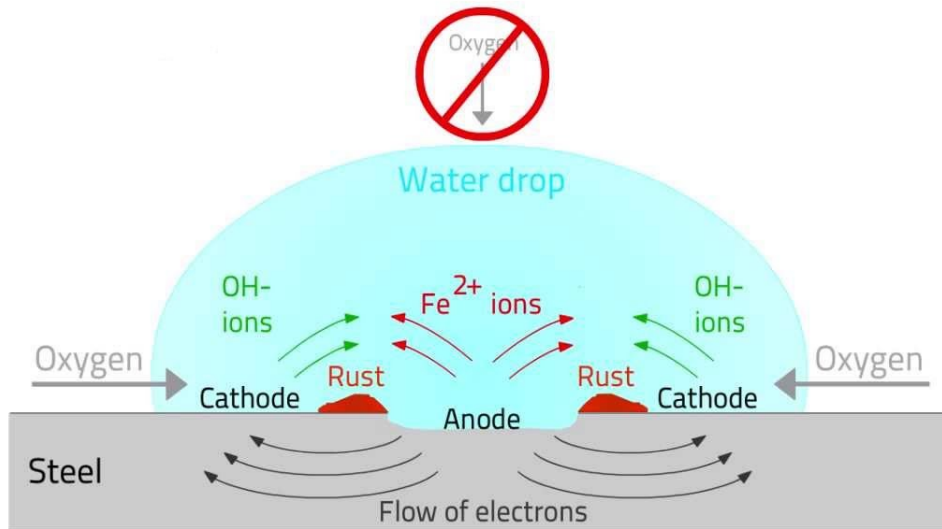
2. Explain the mechanism of differential aeration. Give two examples where differential aeration effect are seen.

Differential aeration accounts for the corrosion of metals, partially immersed in a solution, just below the waterline. Thus if a metal (Say Zinc) is partially immersed in a dilute solution of a neutral salt (Say NaCl) and the solutions not agitated properly, then **the parts above and closely adjacent to the waterline are more strongly aerated (because of easy access to oxygen) and hence become cathodic. On the other hand parts immerse to greater depth (which have less access of oxygen) show a small oxygen concentration and thus become anodic. So, a difference in potential is created, which causes a flow of current between the two differentially aerated areas of the same metal.** Some observations of differential aeration are :

2.1 Zinc rod in partially immersed in brine. Zinc will dissolve at the anodic areas, and oxygen will take up electrons at the cathodic areas to form hydroxide ions.



2.2 In a similar way, iron corrodes under the drops of water (or salt solution). Areas covered by droplets, having no access of oxygen become anodic with respect to other areas, which are freely exposed to air.



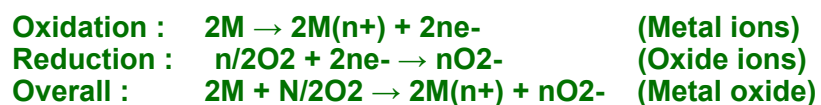
3 Explain chemical corrosion and its types. Discuss the role of nature of oxide film formed in oxidation corrosion. Explain Pitting Bedworth rule.

3.1 CHEMICAL CORROSION

The process of deterioration and consequent loss of a solid metallic material by direct chemical action of environment/atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen or anhydrous inorganic liquid with metal surfaces in immediate proximity is called chemical corrosion. There are three types of chemical corrosion :

3.1.1 OXIDATION CORROSION

It is brought about by the direct action of oxygen at low or high temperatures on metals, usually in absence of moisture. At ordinary temperatures, metals, in general, are very slightly attacked. However alkali and alkaline earth metals are rapidly oxidised even at low temperatures. At high temperature almost all metals except Au, Ag, Pt are oxidised. The reactions of oxidation corrosion are :



3.1.1.1 ROLE OF OXIDE FILM

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of of this film decides the further action. Following films has effects as described :

1. STABLE

A stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Hence, such a layer can be of impervious nature and **consequently prevents further oxidation process. Ex : Oxide films on Al, Sn, Pb, Cu, etc.**

2. UNSTABLE

The metal oxide layer is formed, decomposed back into metal and oxygen. **Consequently, oxidation corrosion is not possible in such a case. Ex : Ag, Au, Pt.**

3. VOLATILE

The oxide layer volatilises as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion, leading to excessive corrosion. Ex : MoO_3 Molybdenum oxide.

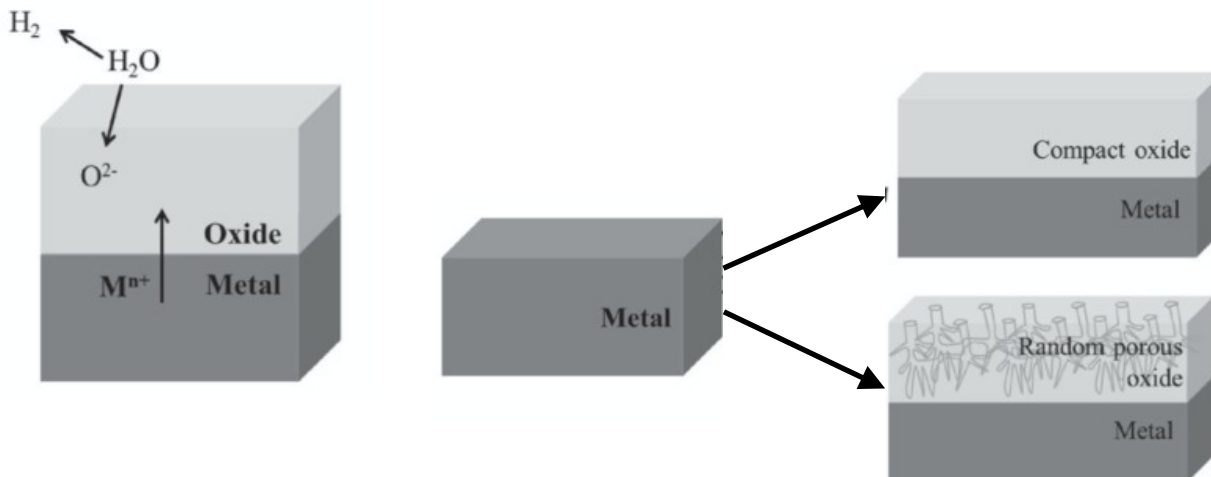
4. POROUS

Oxide layer have pores or cracks. In such a case the atmospheric oxygen have access to the underlying metal surface, through these pores or cracks of oxide layer. Thereby the corrosion continues unobstructed, till the entire metal is converted into oxide.

3.1.1.2 PITTING BEDFORTH RULE

According to this rule, an oxide is protective or non-porous, if the volume of the oxide is at least as great as the volume of the metal form which it is formed. On the other hand is the volume of the oxide is less than the volume of metal, the oxide layer is porous (non-continuous and hence non-protective, because it cannot prevent the access of oxygen to the fresh metal surface below.

Alkali and Alkaline earth metals form oxides of volume less than the volume of metals. Consequently the oxide layer faces stress and strains, thereby developing cracks and pores in its structure. Porous oxide scale permits free access of oxygen to the underlying metal surface and thus corrosion continues non stop.



On the other hand, metals like Al forms oxide, whose volume is greater than the volume of metal (Al). Consequently an extremely tightly adhering non porous layer is formed. Due to absence of any pores or cracks in the oxide film, the rate of oxidation rapidly decreases to zero.

3.1.2 CORROSION BY OTHER GASES (like SO_2 , CO_2 , Cl_2 , H_2S , F_2 etc)

The extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation of protective or non protective (porous) films on the metal surface.

3.1.3 LIQUID METAL CORROSION

It is due to the chemical action of flowing liquid metal at high temperatures on solid metal or alloy . Such corrosion occur in devices used for smelting and nuclear power. The corrosion reaction involves either :

1. Dissolution of a solid metal by liquid metal.

2. Internal penetration of the liquid metal into the solid metal .

Both these modes of corrosion cause weakening of of the solid metal.

4 How corrosion of metal can be prevented? Discuss in details.

1. Proper designing

- 1.1 Avoid contact of dissimilar metals In presence of corroding solution
- 1.2 In case two dissimilar metals are in contact :
 - A. Anodic material area should be maximised, while cathodic material area should be minimised;
 - B. They should be as close as possible to each other in the electrochemical series ;
 - C. An insulating fitting may be applied in between them to avoid direct electric contact.
 - D. The anodic material should not be coated or painted because any break in paint will lead to rapid localised corrosion
- 1.3 Prevent the occurrence of inhomogeneities as crevices permit some concentration differences. Crevices may be painted with an impervious material.
- 1.4 Sharp corners and recesses should be avoided., because the favour the formation of stagnant areas and accumulation of solids etc.
- 1.5 Equipment should be supported in legs to allow circulation of air and prevent formation of stagnant pools or damp areas.

2. Using Pure metal

Impurities in metals cause heterogeneity, which decreases corrosion resistance of the metal. Purification of metals like Mg, Al provides a coherent and impervious protective oxide film on their surfaces, when exposed to the environment. Corrosion resistance of a purified metal depends hence upon the nature corrosive environment. It is usually helpful in against corrosion by electrochemical mechanism and not direct chemical attack.

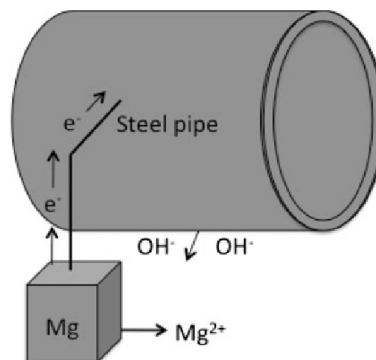
3. Using Metal Alloy

4. Cathodic Protection

The principle involved in this method is to force the metal behave like a cathode , so that its corrosion does not occur. There are two types of cathodic protection :

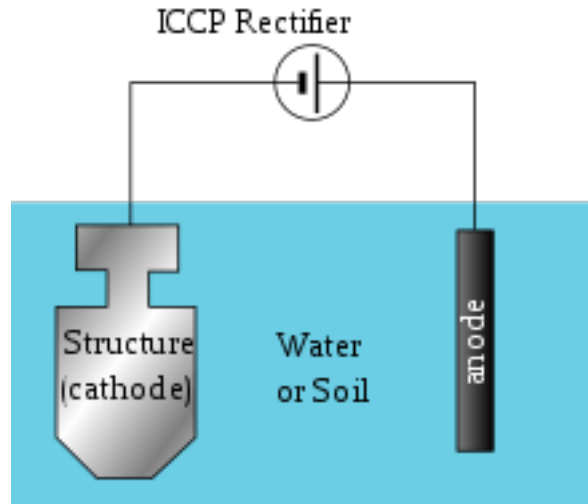
4.1 Sacrificial anodic protection method

The metallic structure (to be protected) is connected by a wire to a more anodic metal, so that the corrosion is concentrated at this more active metal. The more active metal itself gets corroded slowly; while the parent structure (cathodic) is protected. The more active metal so employed is called "sacrificial anode". Metals commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys. Applications of this method include protection of buried pipelines, underground cables, marine structures, ship hulls, rather tanks etc



4.2 Impressed current cathodic protection method

In this method an **impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.** Usually, impressed current is derived from a DC source (like battery or rectifier on an AC Line). With an insoluble anode (like graphite, stainless steel etc.). This type of protection is particularly useful for large structures for long term operation and is used for open water box coolers, water tanks, buried pipelines, condensers, transmission line towers etc.



5. Modifying the environment

5.1 Deaeration

Exclusion of oxygen from aqueous environment reduces metal corrosion.

5.2 Deactivation

Addition of chemicals capable of combining rapidly with oxygen.

5.3 Dehumidification

Reducing the moisture content of air to such an extent that the amount of water condensed on metal is too small to cause corrosion.

5.4 Alkaline Neutralisation

Prevention corrosion by neutralising the acidic character of corrosive environment.

6. Use of Inhibitors

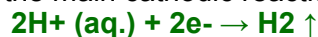
A corrosion inhibitor is a substance which when added in small quantities to the aqueous corrosive environment, effectively decreases the corrosion of a metal. Inhibitors are :

6.1 Anodic Inhibitors

These are those that stifle the corrosion reaction, occurring the anode by forming a sparingly soluble compound which is newly produced metal ion. They are adsorbed on the metal surface forming a protective film or barrier, thereby reducing the corrosion rate. Although, this type of control is effective, yet it may be dangerous, since severe local attack can occur, if certain areas are left unprotected by depletion of the inhibitors. Ex : chromates, phosphates, tungstate or other ions of transition elements with a high oxygen content.

6.2 Cathodic Inhibitors

1. In acidic solutions, the main cathodic reaction is evolution of hydrogen.



Consequently, corrosion may be reduced either by slowing down the diffusion of hydrated H^+ ion to the cathode and / or by increasing the over voltage of hydrogen evolution.

2. In neutral solutions, The cathodic reaction is :



The corrosion can, therefore, be controlled either by elimination oxygen from the corroding medium or by retarding its diffusion to the cathodic areas.

7. Application of Protective Coatings

A coated surface isolates the underlying metal from the corroding environment.

7.1 Anodic Coatings

These are produced from coating metals, which are anodic to the base metal (i.e. which is to be protected). Ex : Coating of Zn, Al and Cd on the steel are anodic, because their electrode potentials are lower than that of the base metal, Iron. If any pores, breaks or discontinuities occur in such an anodic coating, a galvanic cell is formed between coating metal and the exposed part of the base metal. Ex : In the case of galvanised steel, zinc, the coating metal (being anodic) is attacked; leaving the underlying cathodic metal unattacked. Galvanic cell is formed between Zn and the exposed iron. Zn (being anodic to Iron) dissolved anodically; where's the iron (being cathodic) is protected. Thus, no attack on the iron occurs, until practically all the zinc has first corroded in the vicinity of the exposed iron spot. So Zinc coating protect iron sacrificially.

7.2 Cathodic Coatings

These are obtained by coating a more Noble metal (i.e. having higher electrode potential) than the base metal. They protect the base metal because they have higher corrosion resistance than the base metal. The cathodic coating provides effective protection to the base metal only when they are completely continuous and free from pores, breaks and discontinuities.

7.3 Hot dipping

It is used for producing a coating of low melting metal such as Zn (M.P. : 419 degree celsius), Sn (M.P. : 232 degree celsius), Pb, Al, etc, on Iron, steel and copper, which have relatively higher melting points. The process, in general, consists of immersing the base metal in a bath of the molten coating metal, covered by a molten flux layer (usually $ZnCl_2$). The flux cleans the base metal's surface and prevents the oxidation of molten coating metal. For good adhesion, the base metal surface must be very clean; otherwise it cannot be properly wetted by the molten metal. Two most widely applied hot dipping methods are :

7.3.1 Galvanisation

It is the process of coating iron or steel sheets with a thin coat of Zinc to prevent them from rusting.

7.3.2 Tinning

Tinning is the process of thinly coating sheets of wrought iron or steel with tin, and the resulting product is known as tinplate. It is most often used to prevent rust. While once more widely used, the primary use of tinplate now is the manufacture of tin cans.

7.4 Electroplating

7.5 Metal Cladding

8. Potentiostatic Anodic protection

5 Write short notes on

- (i) Galvanic corrosion
- (ii) Intergranular corrosion
- (iii) Effect of pH on the rate of corrosion

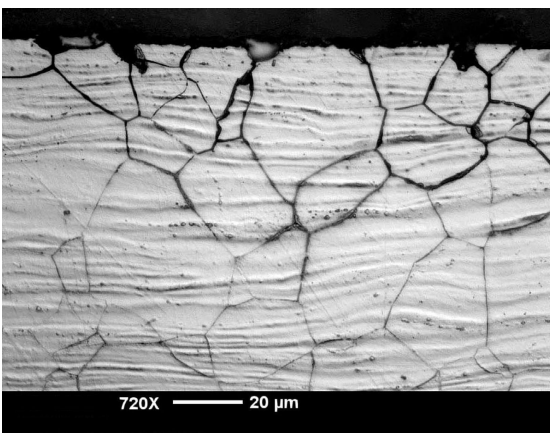
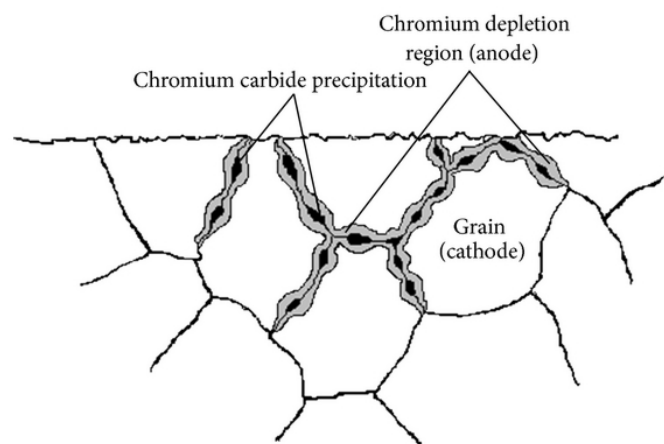
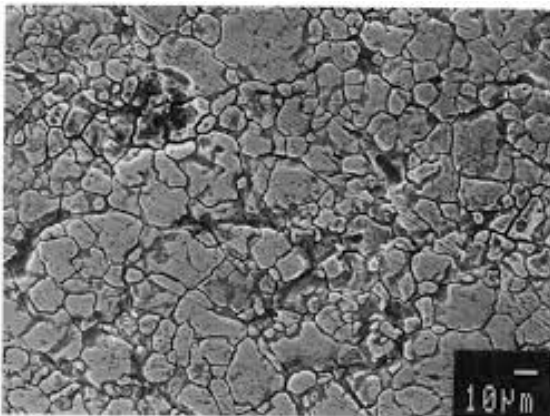
5.1 GALVANIC CORROSION

Galvanic corrosion occurs when two different metals electrically contact each other and are immersed in an electrolyte. In order for galvanic corrosion to occur, an electrically conductive path and an ionically conductive path are necessary. This effects a galvanic couple where the more active metal corrodes at an accelerated rate and the more noble metal corrodes at a retarded rate. When immersed, neither metal would normally corrode as quickly without the electrically conductive connection (usually via a wire or direct contact). Galvanic corrosion is often utilized in sacrificial anodes. What type of metal(s) to use is readily determined by following the galvanic series. For example, zinc is often used as a sacrificial anode for steel structures, such as pipelines or docked naval ships. Galvanic corrosion is of major interest to the marine industry and also anywhere water can contact pipes or metal structures. Factors

such as relative size of anode (smaller is generally less desirable), types of metal, and operating conditions (temperature, humidity, salinity, etc.) will affect galvanic corrosion. The surface area ratio of the anode and cathode will directly affect the corrosion rates of the materials.

5.2 INTERGRANULAR CORROSION

This type of corrosion occurs along grain boundaries and only where the material, especially sensitive to corrosive attack exists, and the corrosive liquid possesses a selective character of attacking only at the grain boundaries, but leaving the grain interiors untouched or only slightly attacked. This type of corrosion is due to the fact that grain boundaries contain material, which shows electrode potential more anodic than that of the grain centre in the particular corroding medium. This may be due to precipitation of certain compounds at the grain boundaries, thereby leaving the solid metal solution (just adjacent to the grain boundary) depleted in one constituent. The depleted solid solution is anodic with respect to the grain centres as well as to the precipitated compound, so that it will be attacked preferentially by the corrosive environment. This type of corrosion is generally encountered in alloys. Ex : During the welding of stainless steel (An alloy of Fe, C and Cr), chromium carbide is precipitated at the grain boundaries, thereby, region just adjacent to the grain boundaries becomes depleted in chromium composition and is more anodic wrt the solid solution within the grain (which is richer in chromium). For the same reason, it is also anodic to the particles of chromium carbide so precipitated.



5.3 EFFECT OF PH ON RATE OF CORROSION

Generally acidic media ($\text{pH} > 7$) are more corrosive than alkaline and neutral medium. However amphoteric metals (like Al, Pb, etc) dissolve in alkaline solutions as complex ions. The corrosion rate of iron in oxygen free water is slow, until the pH is below 5. The corresponding corrosion rate on presence of oxygen is much higher. **Consequently, corrosion of metals, readily attacked by acid, can be reduced by increasing the pH of the attacking environment.** Ex : Zn which is rapidly corroded, even in weakly acidic solutions such as carbonic acid suffers minimum corrosion at $\text{pH} = 11$.