[III] Theories of Corrosion

The different theories of corrosion are :

(1) Direct chemical attack (2) The electrochemical theory (3) The acid theory

- **(1) Direct Chemical Attack**

This theory is also known as ***chemical or dry corrosion.*** According to this theory, when a metal is corroded by direct chemical action, an insoluble, soluble or a liquid corrosion product is formed. If it is insoluble, it means that a solid film of the corrosion product is usually formed on the surface of the metal which then protects the metal from further corrosion. When the corrosion product is soluble or is liquid, it goes on dissolving or it is removed as it is being formed. Thus, the surface is left exposed for further attack. For example, chlorine and iodine attack silver generating a protective film of silver halide. Similarly, during de-tinning of tinned low-carbon steel cans using chlorine gas at high temperatures, volatile $SnCl_4$ is formed and so all the tin is readily removed from the metal surface. However, the base metal, iron is very little affected or attached by dry chlorine because it reacts with iron to form solid ferric chloride (non-volatile) which protects the rest of the metal. There are three main types of chemical corrosion, *i.e.*,

(A) Oxidation corrosion (B) Corrosion by other gases (C) Liquid metal corrosion

(A) Oxidation corrosion : It is one of the most common ways in which metals are attacked by direct action with oxygen, usually, in the absence of moisture. At ordinary temperatures, most of the metals are very slightly attacked, but alkali and alkaline earth metals are, however, rapidly oxidised at low temperature, whereas at high temperatures, practically all metals except Ag, Au and Pt are oxidised.

Practically, all metals on exposure to air get covered with a film of oxide which is a few Angstrom unit thick. The thickness of the oxide film varies with the metal and the temperature.

The reactions in the oxidation corrosion are :

$$\underset{\text{Metal}}{2M} \longrightarrow \underset{\text{Metal ion}}{2M^{n+}} + 2ne^- \qquad \text{(Loss of electrons or oxidation)}$$

$$\underset{\text{Oxygen}}{nO_2} + 2ne^- \longrightarrow \underset{\text{Oxide ion}}{2nO^{2-}}$$

$$\underset{\text{Metal}}{2M} + \underset{\text{Oxygen}}{nO_2} \longrightarrow \underbrace{\underset{\text{Metal ion}}{2M^{n+}} + \underset{\text{Oxide ion}}{2nO^{2-}}}_{\text{Metal oxide}} \qquad \text{(Gain of electrons or reduction)}$$

Mechanism : The oxidation occurs first at the surface of the metal and the resulting metal oxide scale forms a barrier, that tends to restrict further oxidation. All the gas molecules are adsorbed rapidly by the surface of the metal as atoms, ions or molecules. This is followed by diffusion of the gas in metal (Fig. 1). This layer of adsorbed gas is only one molecule thick and the

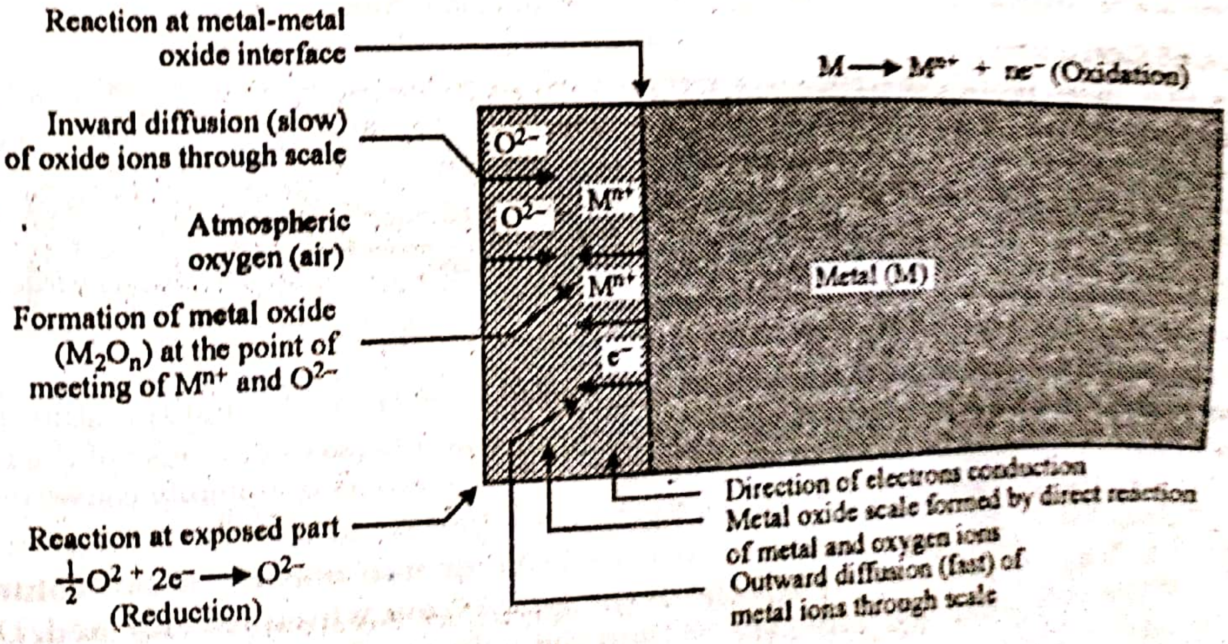

Fig. 1.

gas molecules are held by the molecules of the metal through the residual valency of surface molecules. For oxidation to continue, either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal. The outward diffusion of metal is, generally much more rapid than the inward diffusion of oxygen, since the metal ion is appreciably smaller than the oxygen ion and consequently, of much higher mobility.

Nature of the oxide formed plays an important part in oxidation corrosion process.

$$\text{Metal} + \text{Oxygen} \longrightarrow \text{Metal oxide (corrosion product)}$$

When the oxidation strats, a thin layer of oxide is formed on the metal surface. If the thickness of this layer is approximately less than 300Å (1Å = 10^{-8} cm), then such layer is called a ***film*** and if the thickness of the layer exceeds this value then the layer is called scale. This ***film*** may be stable, unstable, volatile or porous and such nature of the film decides the further action.

(a) Stable film : It is fine-grained in structure and can get adhered tightly to the parent metal surface. Such a film can be of impervious nature and behaves as protective coating in nature, thereby shielding the metal surface. Impervious nature means, that it cuts off penetration of attacking oxygen to the underlying metal *e.g.*, the oxide film formed on Al, Sn, Pb, Cu, Pt etc. Consequently, further oxidation corrosion is prevented in such cases.

(b) Unstable film : In this case, the oxide layer formed, decomposes back into the metal and oxygen, So, oxidation corrosion is not possible in such cases. For example, Ag and Au do not undergo oxidation corrosion.

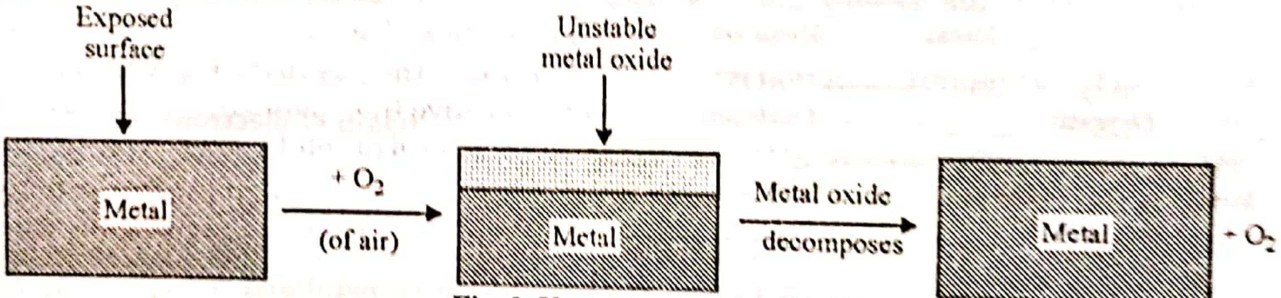

Fig. 2. Unstable oxide layer

(c) Volatile film : In such cases, the oxide layer volatilizes 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, *e.g.*, molybdenum oxide (MoO_3) is volatile.

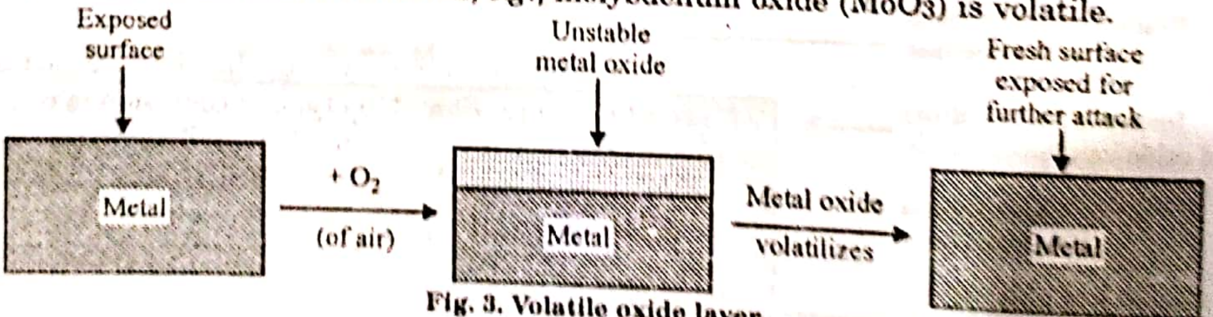

Fig. 3. Volatile oxide layer

(d) Porous film : In such cases, the oxide layer have pores or cracks and the atmospheric oxygen has an access to the underlying surface of metal, through the pores or cracks of the layers. Therefore, the corrosion continues unobstructed, till the entire metal is completely converted into its oxide.

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

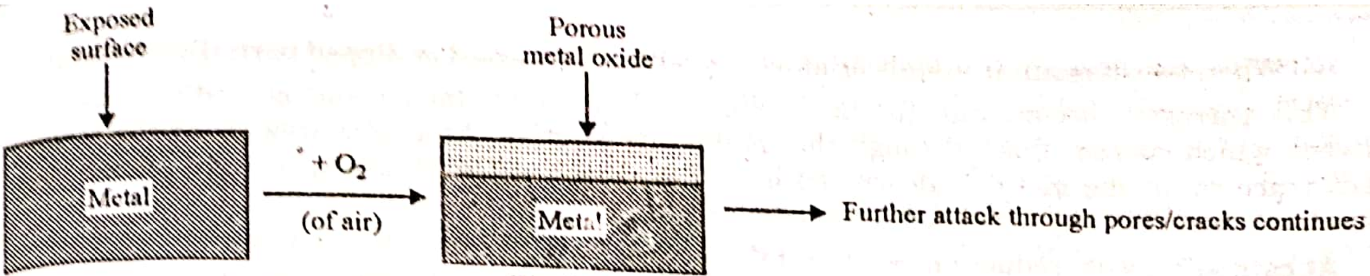

Fig.4. Porous oxide layer

For example, alkali and alkaline earth metals generally form oxides of volume less than the volume of metals from which they are formed and consequently the volume of oxide formed is not sufficient enough to cover the comparatively large surface area of the metal and hence the oxide layer faces stress and strains. As a result, pores and cracks are developed and porous oxide scale permits the diffusion of oxygen into the underlying metal and this causes unobstructed and serious corrosion.

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

(B) Corrosion by other gases : There are certain other dry gases except oxygen such as CO_2, SO_2, Cl_2, H_2S, F_2 etc. which also cause corrosion of metals. The extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack in such cases also depends upon the formation of protective (non-porous) or non protective (porous) films on the surface of metal as in the case of oxidation corrosion by oxygen or air.

(i) If the film formed is protective or non porous, the intensity or extent of attack decreases, because the film formed protects the metal from further attack, *e.g.*, AgCl film resulting from the attack of Cl_2 on Ag.

(ii) If the film formed is non-protective or porous, the surface of the whole metal is gradually destroyed. For example, dry Cl_2 gas attacks on tin forming volatile $SnCl_4$ (which volatilizes immediately), thereby leaving fresh metal surface for further attack. Similarly, in petroleum industry, H_2S at high temperature attacks steel forming a FeS scale, which is porous and interferes with the normal operations.

(C) Liquid metal corrosion : Such type of corrosion occurs due to the chemical action of flowing liquid metal at high temperature on solid metal or alloy. This type of corrosion is common in devices used for nuclear power. The corrosion reaction involves one of the following :

(i) Dissolution of a solid metal by a liquid metal.

(ii) Internal penetration of the liquid metal into the solid metal.

In both the cases, the solid metal becomes weak.

- **(2) The Electrochemical Theory or Wet Corrosion**

This theory is based on Nernst's theory according to which all metals have a tendency to pass into solution. This theory explains the indirect corrosion and is also known as **immersed corrosion.** The tendency of a metal to pass into solution when immersed in a solution of its own salt is measured in terms of its electrode potential. The standard electrode potentials of various metals have been determined in comparison with the standard electrode potential of hydrogen taken as zero.

Electrochemical corrosion occurs under one of the following conditions :

(i) When a conducting liquid is in contact with metal.

(ii) When two dissimilar metals or alloys are either immersed or dipped partially in a solution.

This corrosion occurs due to the existence of separate anodic and cathodic areas/parts, between which current flows through the conducting solution. At anodic area, oxidation reaction takes place so anodic metal is destroyed by either dissolving or obtaining it in combined state. Therefore, corrosion always occurs at anodic areas.

At cathodic areas, reduction reaction takes place. Usually, cathode reactions do not affect the cathode, since most metals cannot be further reduced. So, at cathodic areas, dissolved constituents in the conducting medium accept the electrons to form some ions.

The metallic ions (at anodic part) and non-metallic ions (formed at cathodic part) diffuse towards each other through a conducting medium and forms a corrosion product somewhere between anode and cathode. Thus, the essential requirements of electrochemical corrosion are :

(a) Formation of anodic and cathodic areas.

(b) Electrical contact between the cathodic and anodic parts to enable the conduction of electrons.

(c) An electrolyte through which the ions can diffuse or migrate. This is usually provided by moisture.

Mechanism : Electrochemical corrosion involves flow of electron-current between the anodic and cathodic areas.

(i) Anodic reactions : At the anode, the metal atoms lose their electrons to the environment and pass into the solution in the form of positive ions (oxidation), *i.e.*,

$$M(s) \longrightarrow M^{n+}(aq) + ne^- \text{ (Oxidation)}$$

This continues as long as the electrons and ions are removed from the environment. In case they are not removed, the corrosion will not proceed further. Therefore, the extent of corrosion of the metal anode depends upon the reactions at the cathode which *'mop up'* electrons flowing from the anode and convert the metal ions formed at the anode into insoluble corrosion product. For example,

$$Fe(s) \longrightarrow Fe^{++}(aq) + 2e^- \text{ (Oxidation at anode)}$$

$$Fe^{++}(aq) + 2OH^-(aq) \longrightarrow Fe(OH)_2$$

(ii) Cathodic reactions : The electrons released at the anode are conducted to the cathode and are responsible for the various cathodic reactions as mentioned below.

(a) Electroplating : The metal ions at the cathode collect the electrons and deposit on the cathode surface, *e.g.*,

$$Cu^{++}(aq) + 2e^- \longrightarrow Cu(s)$$

(b) Liberation of hydrogen : In acid solution, (in the absence of oxygen) hydrogen ions acquire electrons and hydrogen gas is formed.

$$2H_3O^+(aq) + 2e^- \longrightarrow H_2(g) + 2H_2O(l)$$

In neutral and alkaline media and in the absence of oxygen, the reaction taking place will be:

$$2H_2O + 2e^- \longrightarrow H_2\uparrow + 2OH^-$$

Such type of corrosion in which hydrogen is evolved is called ***hydrogen type corrosion***.

(c) Formation of hydroxyl ion : (i) In presence of dissolved oxygen and in neutral or alkaline medium, the reaction is :

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$

(ii) In presence of dissolved oxygen and in acid medium, the reactions is :

$$4H^+ + O_2 + 4e^- \longrightarrow 2H_2O$$

Such type of corrosion involving oxygen is called ***oxygen type corrosion.***

The above mentioned reactions only represent the predominent reactions. In many cases, many of these reactions may take place simultaneously.

3. The Acid Theory

According to this theory, corrosion occurs in presence of an acid. This theory is particularly applicable to rusting of iron in the atmosphere. Rusting of iron is due to the continued action of oxygen, carbon dioxide and moisture, converting the metal into a soluble ferrous bicarbonate which is further oxidised to basic ferric carbonate and finally to hydrated ferric oxide.

$$Fe + O + 2CO_2 + H_2O \longrightarrow Fe(HCO_3)_2$$

$$2Fe(HCO_3)_2 + H_2O + O \longrightarrow 2Fe(OH)CO_3 + 2CO_2 + 2H_2O$$

$$2Fe(OH)CO_3 + 2H_2O \longrightarrow 2Fe(OH)_3 + 2CO_2O$$

This theory is supported by the following facts :

(i) Rust analysis generally shows the presence of ferrous and ferric carbonates along with hydrated ferric oxide.

(ii) Retardation of rusting in presence of added lime or NaOH to the water in which iron is immersed.