DRY (or) CHEMICAL CORROSION

Dry corrosion is due to the attack of metal surfaces by the atmospheric gases such as oxygen, hydrogen sulphide, sulphur dioxide, nitrogen, etc. in the absence of moisture.

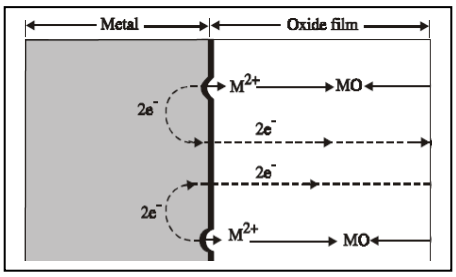
There are 3 main types of dry corrosion.

1. Oxidation corrosion (or) corrosion by oxygen.
2. Corrosion by hydrogen.
3. Liquid-metal corrosion.

Oxidation Corrosion (or) Corrosion by Oxygen

- Oxidation corrosion is brought about by the direct attack of oxygen at low or high temperatures on metal surface in the absence of moisture
- Alkali metals (Li, Na, K, etc.) and Alkaline-earth metals (Mg, Ca, Sn, etc.) are rapidly oxidised at low temperature
- At high temperature, almost all metals (Except, Ag, Au and Pt) are oxidised.

Mechanism of Dry Corrosion



(i)Oxidation occurs first at the surface of the metal resulting in the formation of metal ions (M^{2+}), which occurs at the metal /oxide interface.

$$\mathbf{M \longrightarrow M^{2+} + 2e^-}$$

(ii) Oxygen changes to ionic form (O^{2-}) due to the transfer of electron from metal, which occurs at the oxides film / environment interface

$$\tfrac{1}{2} O_2 + 2e^- \longrightarrow O^{2-}$$

(iii) Oxide ions reacts with the metal ion to form the metal-oxide film

$$M + \tfrac{1}{2} O_2 \longrightarrow M^{2+} + O^{2-} \equiv MO \quad \text{(Metal-oxide film)}$$

Once the metal surface is converted to a monolayer of metal-oxide, for further corrosion (oxidation) to occur, the metal ion diffuses outward through the metal-oxide barrier.

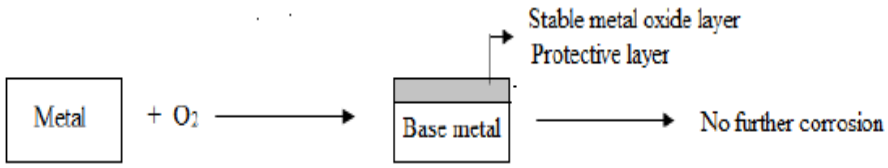
Thus the growth of oxide film commences perpendicular to the metal surface.

Nature of Oxide Film

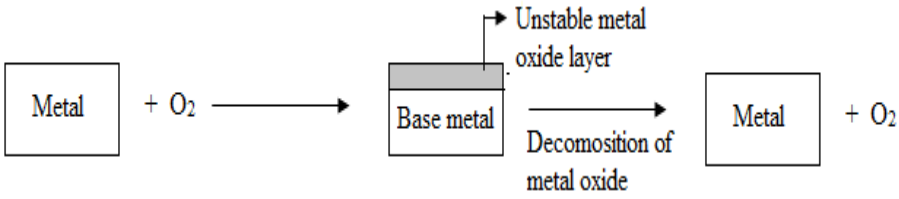
The nature of oxide film formed on the metal surface plays an important role in oxidation corrosion

(i) Stable Oxide Layer

If the metal oxide is stable, it behaves has a protective layer which prevents further corrosion. e.g., The oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.



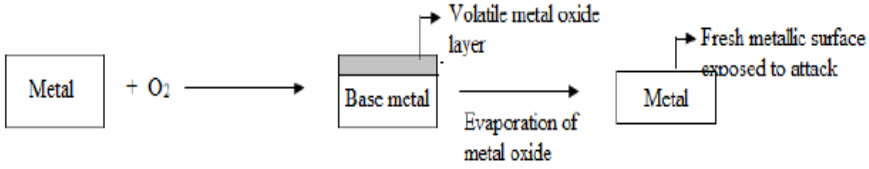
(ii) Unstable Oxide Layer



Unstable oxide layer is mainly produced on the surface of noble metals, which decomposes back into the metal and oxygen

EX: *Oxides of Pt, Ag, etc., are unstable oxide layers.*

(iii) Volatile Oxide Layer



The oxide layer volatilizes as soon as it is formed, leaving the metal surface for further corrosion

EX: Molybdenum oxide (MoO_3) is volatile.

Pilling-Bedworth Ratio

The ratio of the volume of the oxide formed to the volume of the metal consumed is called “Pilling-Bedworth ratio”

E.g: (a) According to Pilling-Bedworth rule, if the volume of the oxide layer formed is less than the volume of the metal, the oxide layer is porous and non-protective.

The volume of oxides of alkali and alkaline earth metals such as Na, Mg, Ca, etc., is less than the volume of the metal consumed. Hence the oxide layer formed is porous and non-protective.

b) On the other hand, if the volume of the oxide layer formed is greater than the volume of the metal, the oxide layer is non-porous and protective.

E.g The volume of oxides of heavy metals such as Pb, Sn, etc., is greater than the volume of the metal. Hence the oxide layer formed is non-porous and protective.