DRY (OR) CHEMICAL CORROSION

The dry chemical corrosion is defined as the direct chemical reaction on the metals surfaces by the atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide or anhy inorganic acid, vapours etc., present in the environment. This is most often associated with high temperature. Examples (i) Silver undergoes corrosion by atmospheric H_2S gas.

(ii) Iron undergoes corrosion by HCl.

Types of dry corrosion

There are three types of chemical corrosion.

- Oxidation corrosion or corrosion by oxygen.
- Corrosion by Hydrogen.
- Liquid – metal corrosion.

Oxidation Corrosion or Corrosion by Oxygen

Oxidation corrosion is caused by the direct attack of oxygen on the metal surface in the absence of moisture at low or higher temperature. Examples: Alkali metals (Li, Na, K, etc.,) and alkaline earth metals (Mg, Ca, etc.) are rapidly oxidized at low temperature. At high temperature, almost all the metals (except Ag, Au and Pt) are oxidized.

Mechanism

The mechanism of oxidation corrosion

i) Oxidation occurs first at the surface of metal and forming metal ions

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

ii) Atmospheric oxygen changes to ionic form (O^{2-}) by receiving electron from metal.

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

iii) Oxide ion reacts with the metal ion to form the metal – oxide film.

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

Once the metal surface is converted to metal – oxide film, the metal ion diffuses outward through the metal oxide barrier which leads to further corrosion. Thus, the growth of oxide film commences perpendicular to the metal surface (Fig.1. 2).

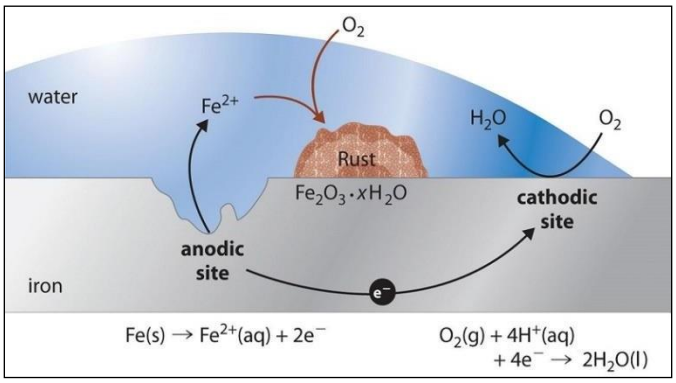

Fig.1.2. Mechanism of oxidation corrosion

Nature of the Oxide Film

Nature of the oxide film formed on the metal surface plays an important role in oxidation corrosion. Different types of oxide films formed on the surface of the metals are explained as follow:

i) Stable Oxide Layer

A stable oxide film is a fine-grained structure and gets adsorbed tightly on the metal surface. This film is impervious in nature and prevents further attack of oxygen and acts as a protective coating and shielding the metal surface from corrosion. Examples Oxide film of Al, Sn, Pb, Cu, etc.,

ii) Unstable Oxide Layer

The unstable oxide layer formed is immediately decomposed back into metal and oxygen. Consequently, oxidation corrosion is not possible. Examples: Oxides of Ag, Au, Pt, etc.,

Metal oxide ⟷ Metal + oxygen

iii) Volatile Oxide Layer

The oxide layer volatilizes as soon as it is formed, leaving the fresh metal surface for further corrosion. This causes rapid and continuous corrosion. Example: MoO_3 molybdenum oxide is volatile.

iv) Protective or Non-Protective Oxide Film (Pilling – Bedworth Rule) or PB Ratio

The ratio between the volume of metal oxide and volume of metal consumed is called **"Pilling Bedworth"** rule or ratio.

Pilling Bedworth ratio = Volume of metal oxide/Volume of metal consumed

- **If the volume of oxide layer formed is less than the volume of metal consumed then the oxide layer is porous and non–protective.**

  Examples: Alkali and alkaline earth metal oxides (Na, Mg, Ca, etc.)

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

  Examples: Heavy metal oxides (Pb, Al, Cu, Sn, etc.)