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CORROSION

INTRODUCTION

- Corrosion is a process of formation of the compound of pure metal by the chemical reaction between metallic surface and its environment.
- It is an oxidation process. It causes loss of metal.
- Hence, disintegration of a metal by its surrounding chemicals through a chemical reaction on the surface of the metal is called corrosion.

- Example: Formation of rust on the surface of iron, formation of green film on the surface of copper.
- The responsible factors for the corrosion of a metal are the metal itself, the environmental chemicals, temperature and the design.

DIFFERENT THEORIES OF CORROSION

There are three theories of corrosion:

- (1) acid theory,
- (2) dry or chemical corrosion and
- (3) galvanic or electrochemical

(I) ACID THEORY

- This theory suggests that corrosion of a metal (iron) is due to the presence of acids surrounding it.

- According to this theory, iron is corroded by atmospheric carbon di-oxide, moisture and oxygen. The corrosion products are the mixture of $Fe(HCO_3)_2$, $Fe(OH)CO_3$ and $Fe(OH)_3$.

The chemical reactions suggested are given below

$$Fe + 2CO_2 + H_2O + \frac{1}{2}O_2 \longrightarrow Fe(HCO_3)_2$$

$$2Fe(HCO_3)_2 + H_2O + \frac{1}{2}O_2 \longrightarrow 2Fe(OH)CO_3 + 2CO_2 + 2H_2O$$

$$2Fe(OH)CO_3 + 2H_2O \longrightarrow 2Fe(OH)_3 + 2CO_2$$

(2) CHEMICAL THEORY OF CORROSION

- According to this theory, corrosion on the surface of a metal is due to direct reaction of atmospheric gases like oxygen, halogens, oxides of sulphur, oxides of nitrogen, hydrogen sulphide and fumes of chemicals with metal.
- The extent of corrosion of a particular metal depends on the chemical affinity of the metal towards reactive gas.
- Oxygen is mainly responsible for the corrosion of most metallic substances when compared to other gases and chemicals.

There are main three types of chemical corrosion.

- (i) Oxidation corrosion (*Reaction with oxygen)*
- (ii) Corrosion by other gases
- (iii) Liquid metal corrosion

(i) Oxidation corrosion (Reaction with oxygen)

- Some of the metals directly react with oxygen in the absence of moisture.

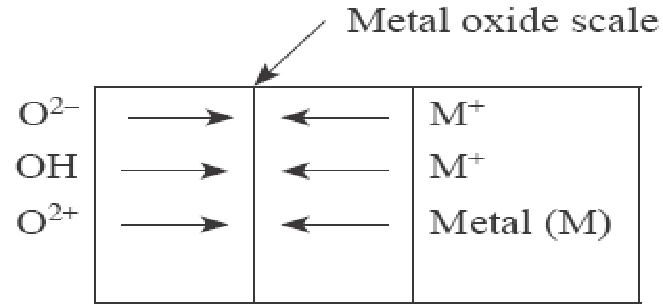
- Alkali and alkaline earth metals react with oxygen at room temperature and form corresponding oxides, while some metals react with oxygen at higher temperature.

- Metals like Ag, Au and Pt are not oxidized as they are noble metals.

$$M \longrightarrow M^{n+} + ne^- \quad (\text{if } n = 1)$$

$$\frac{1}{2} O_2 + 2e^- \longrightarrow O^- \quad \text{for alkali metals.}$$

$$2M + \frac{1}{2} O_2 \longrightarrow M_2O$$



- During oxidation of a metal, metal oxide is formed as a thin film on the metallic surface which protects the metal from further corrosion.

- If diffusion of either oxygen or metal is across this layer, further corrosion is possible. Thus, the layer of metal oxide plays an important role in the process of corrosion..

- Oxides of Pb, Al and Sn are stable and hence inhibit further corrosion. They form a stable, tightly adhering oxide film.
- In case of porous oxide film, atmospheric gases pass through the pores and react with the metal and the process of corrosion continues to occur till the entire metal is converted into oxide.
- Porous oxide layer is formed by al- kali and alkaline earth metals. Molybdenum forms a volatile oxide film of MoO3 which accelerates corrosion.
- Au, Ag, Pt form unstable oxide layer which decomposes soon after the formation, thereby preventing further corrosion.

(ii) Corrosion by other gases (Cl_2, SO_2, H_2S, NO_x)

- In dry atmosphere, these gases react with metal and form corrosion products which may be protective or non-protective.

- Dry Cl_2 reacts with Ag and forms AgCl which is a protective layer, while $SnCl_4$ is volatile.

- In petroleum industries at high temperatures, H_2S attacks steel forming FeS scale which is porous and interferes with normal operations.

(iii) Liquid - metal corrosion

- In several industries, molten metal passes through metallic pipes and causes corrosion due to dissolution or due to internal penetration.

- For example, liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.

(3) Wet or electrochemical theory of corrosion

- It is a common type of corrosion of metal in aqueous corrosive environment. This type of corrosion occurs when the metal comes in contact with a conducting liquid or when two dissimilar metals are immersed or dipped partly in a solution.
- According to this theory, there is the formation of a galvanic cell on the surface of metals. Some parts of the metal surface act as anode and rest act as cathode.

- The chemical in the environment and humidity acts as an electrolyte.
- Oxidation of anodic part takes place and it results in corrosion at anode, while reduction takes place at cathode.
- The corrosion product is formed on the surface of the metal between anode and cathode.

Differences between dry and wet corrosion

Dry corrosion	Wet corrosion
• Corrosion occurs in the absence of moisture.	• Corrosion occurs in presence of conducting medium.
• It involves direct attack of chemicals on the metal surface.	• It involves formation of electrochemical cells.
• The process is slow.	• It is a rapid process.
• Corrosion products are produced at the site of corrosion.	• Corrosion occurs at anode but rust is deposited at cathode.
• The process of corrosion is uniform.	• It depends on the size of the anodic part of metal.

Factors Influencing Corrosion

- The nature and extent of corrosion depend on the metal and the environment. The important factors which may influence the corrosion process are
- (i) Nature of the metal
- (ii) Environment
- (iii)Concentration of electrolyte
- (iv) Temperature
- (v) Electrode potential and
- (vi) Hydrogen over voltage

TYEPS OF CORROSION

- There are basically eight types of corrosion

I. Uniform corrosion
II. Pitting corrosion
III. Transgranular and Intergranular (Intercrystalline) corrosion
IV. Exfoliation corrosion
V. Stress corrosion
VI. Crevice corrosion
VII. Galvanic corrosion
VIII. Erosion

I. Uniform corrosion

- This type of corrosion develops as pits of very small diameter, in the order of a micrometer, and results in a uniform and continuous decrease in thickness over the entire surface area of the metal.

- The rate of uniform corrosion can be easily determined by measuring the mass loss, or the quantity of released hydrogen

II. Pitting corrosion

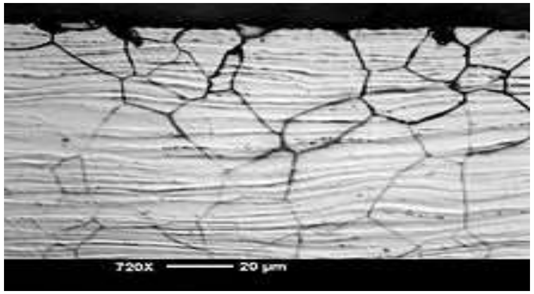
- This localized form of corrosion is characterized by the formation of irregularly shaped cavities on the surface of the metal. Their diameter and depth depend on several parameters related to the metal, the medium and service conditions.

- Unlike uniform corrosion, the intensity and rate of pitting corrosion can be assessed neither by determining the mass loss nor by measuring released hydrogen.

- Pitting corrosion can be assessed using three criteria : the density, i.e. the number of pits per unit area, the rate of deepening and the probability of pitting.

- In fact, these measurements do not make sense because a very deep and isolated pit results only in a small mass loss, where as a very large number of superficial pits can lead to a larger mass loss.

III. Transgranular and Intergranular (Intercrystalline) corrosion



- Within the metal, at the level of the grain, corrosion may propagate in two different ways :

(i) It spreads in all directions, corrosion indifferently affects all the metallurgical constituents; there is no selective corrosion. This is called transgranular or transcrystalline corrosion because it propagates within the grains.

(ii) It follows preferential paths: corrosion propagates at grain boundaries. Unlike transgranular corrosion, these forms of intercrystalline corrosion consumes only a very small amount of metal, which is why mass loss is not a significant parameter for assessment of this type of corrosion.

- It is not detectable which naked eye but requires microscopic observation, typically at a magnification of 50. When penetrating into the bulk of the metal, intercrystalline corrosion may lead to a reduction of mechanical properties and even lead to the rupture of components.

IV. Exfoliation Corrosion

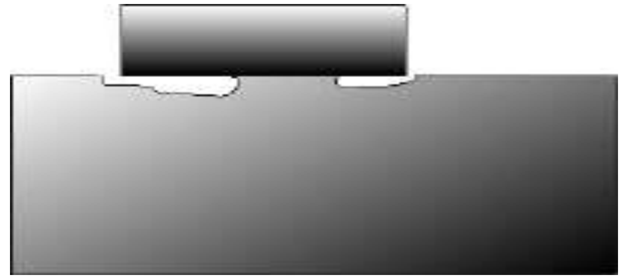
- Exfoliation corrosion is a type of selective corrosion that propagates along a large number of planes running parallel to the direction of rolling or extrusion.
- Between these planes are very thin sheets of sound metal that are not attacked, but gradually pushed away by the swelling of corrosion products, peeling off like pages in a book; hence the term exfoliation corrosion.
- The metal will swell, which results in the spectacular aspect of this form of corrosion.

V. Stress corrosion

- This type of corrosion results from the combine action of a mechanical stress (bending, tension) and a corrosive environment.

- Each of these parameters alone would not have such a significant effect on the resistance of the metal or would have no effect at all.

VI. Crevice corrosion



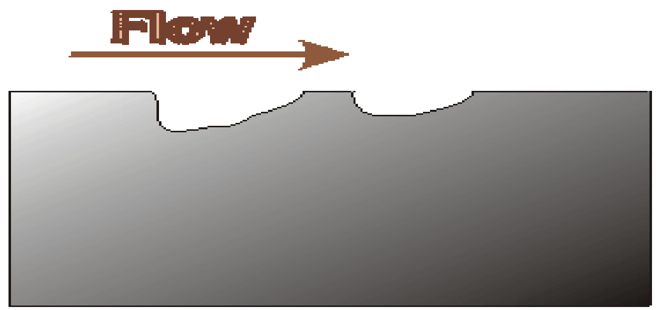
- Crevice corrosion is a localized corrosion in recesses :
- overlapping zones for riveting, bolting or welding, zones under joints and under various deposits. These zones also called crevices, are very tiny and difficult to access for the aqueous liquid that is covering the rest of the readily accessible surfaces.
- This type of corrosion is also known as deposit attack.

VII. Galvanic corrosion

- When two dissimilar metals are in direct contact in a conducting liquid, experience shows that one of the two may corrode. This is called galvanic corrosion. The other metal will not corrode; it may even be protected in this way.
- This corrosion is different in its kind and intensity from the one that would occur if they were placed separately in the same liquid.

- Unlike other types of structural corrosion, galvanic corrosion does not depend on the metal's texture, temper, etc.
- Galvanic corrosion may occur with any metal, as soon as two are in contact in a conductive liquid. It works like a battery.
- The appearance of galvanic corrosion is very characteristic. It is not dispersed like pitting corrosion, but highly localized in contact zone with the other metal.
- The zone affected by galvanic corrosion often has a shinier aspect than the rest of the surface.

VIII. Erosion



- Corrosion by erosion occurs in moving media. This type of corrosion is related to the flow speed of the fluid.

- It leads to local thinning of the metal, which results in scratches, gullies, and undulations, which are always oriented in the same direction, namely the flow direction.

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