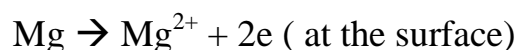


## Wagner's diffusion mechanism of Oxidation Corrosion

Let us discuss the mechanism of formation of magnesium oxide (MgO) on the surface of magnesium metal.

The various steps involved are as follows:

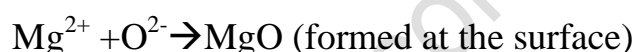
**Step-1** Metal gets oxidized to generate metal ions and electrons. It's an oxidation process.



**Step-2** Electrons so released by Mg is captured by atmospheric  $\text{O}_2$  and forms oxide anion ( $\text{O}^{2-}$ ) near the interface (metal-atmosphere). It's a reduction process.



**Step-3** The  $\text{O}^{2-}$  ions are moved towards the metal-atmosphere interface and combine with  $\text{Mg}^{2+}$  ions to form metal oxide (MgO) at the surface.



Here, MgO is a porous layer, so further oxidation occurs till whole metal is converted into oxide.

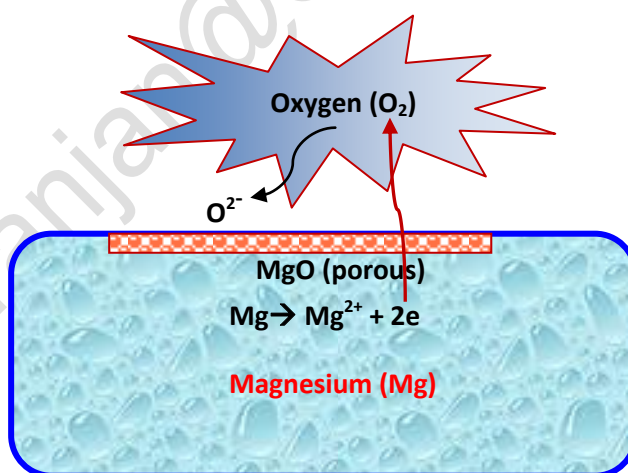


Fig. Mechanism of oxidation corrosion

But in case of Al, it forms a protective layer of  $\text{Al}_2\text{O}_3$  and hence it resists further oxidation process.

**Q. Define oxidation corrosion. Discuss its mechanism.**

**Ans.** . It is a process of loss of metal that occurs due to direct chemical interaction between the surface of metal and atmospheric O<sub>2</sub>.

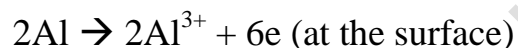


*For mechanism, refer above*

**Q. Write the mechanism of formation of aluminum oxide Al<sub>2</sub>O<sub>3</sub> on the surface of Al.**

**Ans.** The various steps involved are as follows:

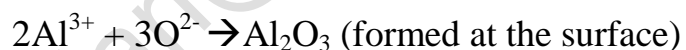
**Step-1** Al metal gets oxidized to generate metal ions and electrons. It's an oxidation process.



**Step-2** Electrons so released by Mg is captured by atmospheric O<sub>2</sub> and forms oxide anion (O<sup>2-</sup>) near the interface (metal-atmosphere). It's a reduction process.



**Step-3** The O<sup>2-</sup> ions are moved towards the metal-atmosphere interface and combine with Al<sup>3+</sup> ions to form metal oxide (Al<sub>2</sub>O<sub>3</sub>) at the surface.



As Al<sub>2</sub>O<sub>3</sub> is a non-porous layer, no further oxidation will occur.

## Electrochemical or Wet corrosion

Wet corrosion of metals occurs in aqueous solution and in humid atmosphere through formation of a large number of minute electrochemical cells. The mechanism of corrosion can be explained by *electrochemical theory*. It involves anodic dissolution (oxidation) of metal and cathodic reduction of oxidants (e.g. oxygen) present in the solution/electrolyte.

### Condition for wet corrosion

1. Two different metals are joined and exposed to an electrolyte (**Galvanic Corrosion**)
2. A metal is exposed to different concentration of oxygen and exposed to an electrolyte (**O<sub>2</sub> concentration cell corrosion**)
3. A metal with different stress concentration and exposed to an electrolyte (**Stress corrosion**)

#### 1.6.1 *Electrochemical theory of wet corrosion:*

According to this theory, the various steps involved in wet corrosion are as follows:

**Step 1:** Formation of anodic and cathodic areas

**Step 2:** Oxidation at anodic areas results in liberation of electrons and generation of metallic ions, for example  $\text{Fe}^{2+}$  from metal Fe

**Step 3:** Generation of non-metallic anions like hydroxyl anion ( $\text{OH}^-$ ) by absorption of electrons( $e^-$ ) by oxidants like  $\text{O}_2$

**Step 4:** Formation of corrosion product near cathode

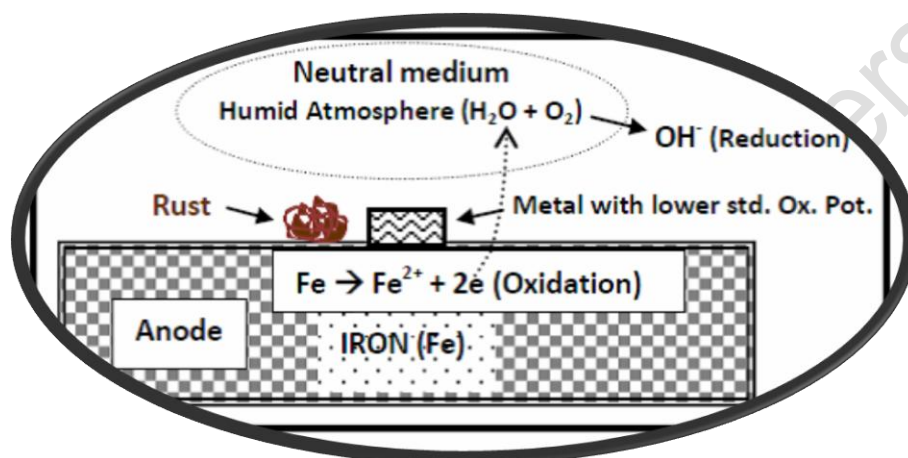
*Depending on the nature of the corrosive environment, the reaction occurs at the cathode (cathodic reaction) proceeds with either (i) absorption of oxygen or (ii) evolution of hydrogen.*

#### 1.6.2 *Mechanism of wet corrosion*

**A. Oxygen absorption mechanism in neutral medium:**

Rusting of iron (Fe) in *a neutral aqueous medium* of electrolyte (such as NaCl) with dissolved oxygen or oxygen in the atmosphere follows oxygen absorption mechanism.

Let us consider that an iron piece is exposed to a humid environment that is not acidic in nature. Also assume that a small piece of metal (nickel) with lower oxidation potential (relative to Fe) is placed on its surface. Under this situation, pure iron with higher oxidation potential acts as anode and undergoes corrosion/rusting.



**Fig. 2. Mechanism of wet corrosion by oxygen absorption.**

The mechanism of rusting of iron piece in neutral medium involves the following steps:

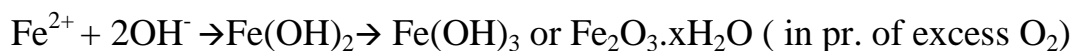
- (i) Oxidation of 'Fe' results in formation of metallic ion ( $\text{Fe}^{2+}$ ) and generation of electrons at anode of the electrochemical cell. The ions go into the solution leaving electrons on the metal. These electrons proceed towards the cathode through the metal.

**At Anode:**  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$  ----- (oxidation)

- (ii) The liberated electrons are captured by the oxidants ( $\text{O}_2$ ) at the cathode to form non-metallic ions ( $\text{OH}^-$ )

**At Cathode:**  $\frac{1}{2}\text{O}_2$  (oxidant) +  $\text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$  ----- (reduction)  
( $\text{O}_2$  absorption occurs)

- (iii) The cations  $\text{Fe}^{2+}$  and anions  $\text{OH}^-$  liberated at anode and cathode, respectively combines somewhere at the interface to form ferrous hydroxide  $\text{Fe}(\text{OH})_2$ . As ferrous hydroxide is unstable in nature, in presence of sufficient oxygen it converted into hydrated ferric oxide ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) or ferric hydroxide  $\text{Fe}(\text{OH})_3$ -a brownish product (called rust) and deposited near the cathode.



N.B.: In limited oxygen environment, ferrous hydroxide converted into a blackish oxide  $\text{Fe}_3\text{O}_4$  (Ferrous ferric oxide,  $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ )



### B. Hydrogen Evolution mechanism in acidic medium

Rusting of iron (Fe) *in an acidic medium* (such as HCl) follows **H<sub>2</sub> evolution** mechanism.

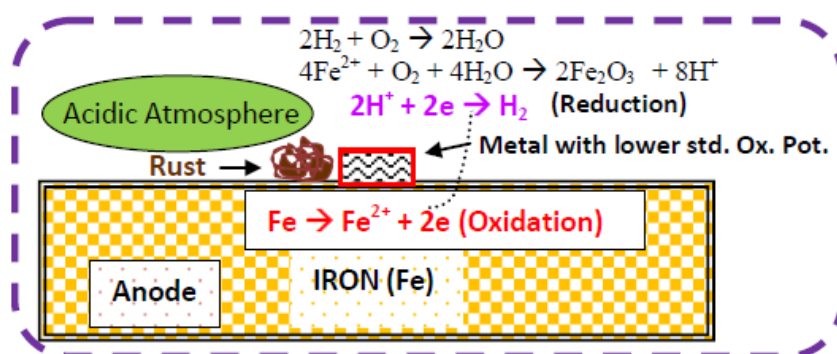


Fig. 3. Mechanism of wet corrosion by hydrogen evolution.

Let us consider that an iron piece is exposed to an acidic environment. Also assume that a small piece of metal with lower oxidation potential (relative to Fe) is placed on its surface. Under this situation, pure iron acts as anode and undergoes corrosion/rusting.

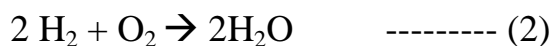
The mechanism of rusting of iron piece in an acidic environment involves the following steps:

- (i) Oxidation of 'Fe' results in formation of metallic ion ( $\text{Fe}^{2+}$ ) and generation of electrons at anode of the electrochemical cell. The ions go into the solution leaving electrons on the metal. These electrons proceed towards the cathode through the metal.

**At Anode:**  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$  (oxidation or anodic reaction)

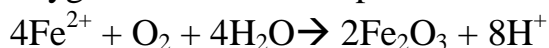
- (ii) At the cathode, the liberated electrons are captured by the hydrogen ions ( $\text{H}^+$ -ions) to form H-atoms and later form  $\text{H}_2$  molecules. The  $\text{H}_2$  molecules combine with dissolved oxygen forms water.

**At Cathode:**  $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$  (Reduction) ----- (1)  
( $\text{H}_2$  evolution occurs)



Net cathodic reaction (1) + (2) :  $4\text{H}^+ + 4\text{e}^- + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

- (iii) As the ferrous ions are unstable, they are oxidized by atmospheric oxygen to form rust as per the following reactions.



**Factors affecting the rate of rusting:** The various factors are:

- Amount of dissolved oxygen
- Presence of acid and electrolytes
- Deposition of rust on its surface
- Potential difference between iron and the metal placed on its surface
- % moisture in the atmosphere
- Conductivity of the medium

### Long Questions

**Q.1. Define wet corrosion. Discuss the mechanism of rusting of iron in a neutral or alkaline medium.**

**Ans.** Wet corrosion of metals occurs in aqueous solution and humid atmosphere through formation of a large number of minute electrochemical cells.

**Mechanism of rusting of iron: refer section 1.6.2 A**

**Q.2. Discuss the mechanism of rusting of iron in an acidic medium.**

**Ans. refer section 1.6.2 B**

### Short Questions

**Q.1 Mention the factors affecting rusting of iron.**

**Ans.** The various factors are:

- Amount of dissolved oxygen
- Presence of acid and electrolytes
- Deposition of rust on its surface

4. Potential difference between iron and the metal sat on its surface
5. % moisture in the atmosphere

**Q.2 Write the chemical reaction occurs at cathode during rusting of iron in a neutral medium.**

**Ans.**  $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^-$

**Q. 3. Write the chemical reaction occurs at cathode during rusting of iron in an acidic medium.**

**Ans. :**  $4\text{H}^+ + 4\text{e}^- + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$

**Q.4. Mention the conditions needed for a wet corrosion.**

**Ans.** The various conditions are as follows:

- 1. Two different metals are joined and exposed to an electrolyte (Galvanic Corrosion)**
- 2. A metal is exposed to different concentration of oxygen and exposed to an electrolyte (O<sub>2</sub> concentration cell corrosion)**
- 3. A metal with different stress concentration and exposed to an electrolyte (Stress corrosion)**

#### **Medium Question**

**Q.1 Discuss the electrochemical theory of wet corrosion.**

**Ans.** See section 1.6.1