

# Factors affecting corrosion

## From metal (Primary Factors):

- Position in galvanic series
- Overvoltage
- Relative area of anodic, cathodic parts
- Purity of metal
- Surface film
- Passive character
- Solubility & volatility of corrosion products

## From Environment (Secondary Factors):

- Temperature
- Humidity
- Impurities
- Suspended particles
- pH
- Nature of ions
- Formation of concentration cells
- Polarisation of electrodes

# Factors influencing corrosion

## Nature of the metal / From metal / Primary Factors:

### i) Position in the galvanic series:

- When two dissimilar metals are in contact, the more anodic metal get corrode.
- The extent of corrosion depends on how far apart are the two metals in the galvanic series.

### ii) Over voltage:

- When a metal (e.g. Zn) is dipped in 1 N sulphuric acid, the initial rate of corrosion is quite slow since hydrogen evolution takes place on Zn at 0.7V.
- If a few drops of  $\text{CuSO}_4$  are added, the hydrogen over voltage comes down to 0.33V and corrosion rate increases.
- Reduction in hydrogen over voltage increases the rate of corrosion.

# Factors influencing corrosion

## iii) Relative areas of cathode and anode:

- When two dissimilar metals are in contact, the rate of corrosion is directly proportional to the ratio of cathodic part to anodic part.
- If anodic area is small, the corrosion is rapid.

$$\text{Corrosion rate} \propto \frac{\text{Area of cathodic part}}{\text{Area of anodic part}}$$

## iv) Purity of the metal:

- Purer the metal, lesser is the rate of corrosion.
- Due to impurities, local galvanic cells are formed and anode gets corroded.

# Factors influencing corrosion

## v) Physical state of the metal:

- o The rate of corrosion depends on the physical state of the metal such as grain size, orientation of crystals, stress etc.

## vi) Nature of surface film: **(Pilling-Bedworth rule):**

- o Corrosion depends on the nature of surface film i.e. the oxide film is stable or unstable or volatile or porous or non-porous that decide the rate of corrosion of the metal.

## vii) Passive character of the metal:

- o Some metals e.g. Ti, Al, Cr, Mg, Ni and Co are passive and show resistance to corrosion.
- o They form highly protective oxide layers on their surfaces which gives the metal passive character and protects it from further corrosion.

# Factors influencing corrosion

## viii) a) Solubility of corrosion product:

- If the corrosion product is soluble in the environment in which the metal is working, then the corrosion proceeds faster.
- If the product is insoluble in the environment, then the corrosion is very slow since the corrosion product becomes a protective layer on the metallic surface. e.g.  $\text{PbSO}_4$ .

## b) Volatility of the corrosion product:

- If the corrosion product is volatile, it evaporates as soon as it is formed exposing fresh metal for corrosion and hence the corrosion becomes very rapid and the metal will disappear over a period of time.

# Factors influencing corrosion

## b) Nature of the corroding environment / Secondary Factors:

### i) Temperature:

- As temperature increases, the rate of corrosion also increases.

### ii) Humidity in environment:

- “Critical humidity” is the humidity above which the metallic corrosion rate increases sharply.
- Critical humidity depends on the nature of the metal as well as the corrosion product.
- When the humidity is higher, the gases e.g.  $\text{CO}_2$ ,  $\text{O}_2$  dissolved in the moisture and provide the conducting medium for electrochemical couple to get formed and anode corrodes.

# Factors influencing corrosion

## iii) Presence of impurities in the atmosphere:

- Gases like  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{S}$  and fumes of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$  which are present in the industrial areas provide conductive environment for enhancing the electrochemical corrosion.
- In marine environment, the  $\text{Cl}^-$  is responsible for enhanced rate of corrosion.

## iv) Presence of suspended solids in the environment:

- Particles like  $\text{NaCl}$ ,  $(\text{NH})_4\text{SO}_4$  together with moisture act as conductive electrolyte and enhance the rate of electrochemical corrosion.



# Factors influencing corrosion

## v) Effect of pH:

- Acid medium facilitates corrosion than neutral and basic media as a general rule.
- The corrosion rate of Fe in oxygen free water is very slow up to pH 5.0 but in the presence of oxygen, the corrosion at pH 5.0 enhances greatly.
- At pH 4.0, the corrosion rate of Fe is very high since  $\text{Fe}^{2+}$  gets oxidized to  $\text{Fe}^{3+}$ .
- Zinc corrodes rapidly in acidic solutions but the rate of corrosion is low in alkaline medium (pH 11.0).
- Aluminium corrodes less at pH 5.5 but the rate of corrosion is very high in pH 8.5.

# Factors influencing corrosion

---

## vi) Nature of ions present:

- Anions like silicates form insoluble salts in the medium and inhibit further corrosion.
- But,  $\text{Cl}^-$  present in the atmosphere destroy the protective oxide film and enhance rate of corrosion.

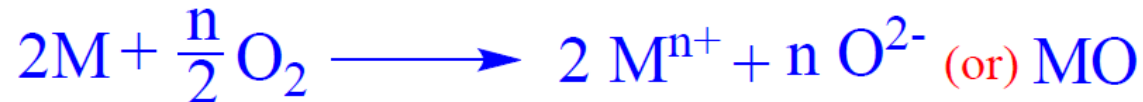
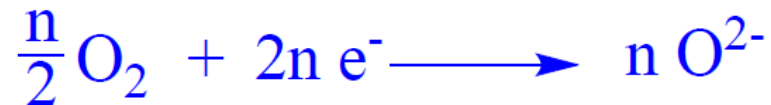
# Types of corrosion

<b>Dry corrosion</b> <b>/ Chemical corrosion</b>	<b>Wet corrosion</b> <b>/ Electrochemical corrosion</b>
<ul style="list-style-type: none"><li><input type="checkbox"/> Oxidation corrosion (Attack of Oxygen)</li><li><input type="checkbox"/> Corrosion by other gases (<math>\text{SO}_2</math>, <math>\text{CO}_2</math>, <math>\text{H}_2\text{S}</math> and <math>\text{NO}_2</math>)</li><li><input type="checkbox"/> Liquid metal corrosion (corrosion of gold by mercury)</li></ul>	<ul style="list-style-type: none"><li><input type="checkbox"/> Differential metal corrosion (Galvanic corrosion)</li><li><input type="checkbox"/> Differential aeration corrosion (concentration cell corrosion)</li><li><input type="checkbox"/> Pitting corrosion</li><li><input type="checkbox"/> Inter-granular corrosion</li><li><input type="checkbox"/> Soil corrosion</li></ul>

# Oxidation corrosion

## Formation of protective layer

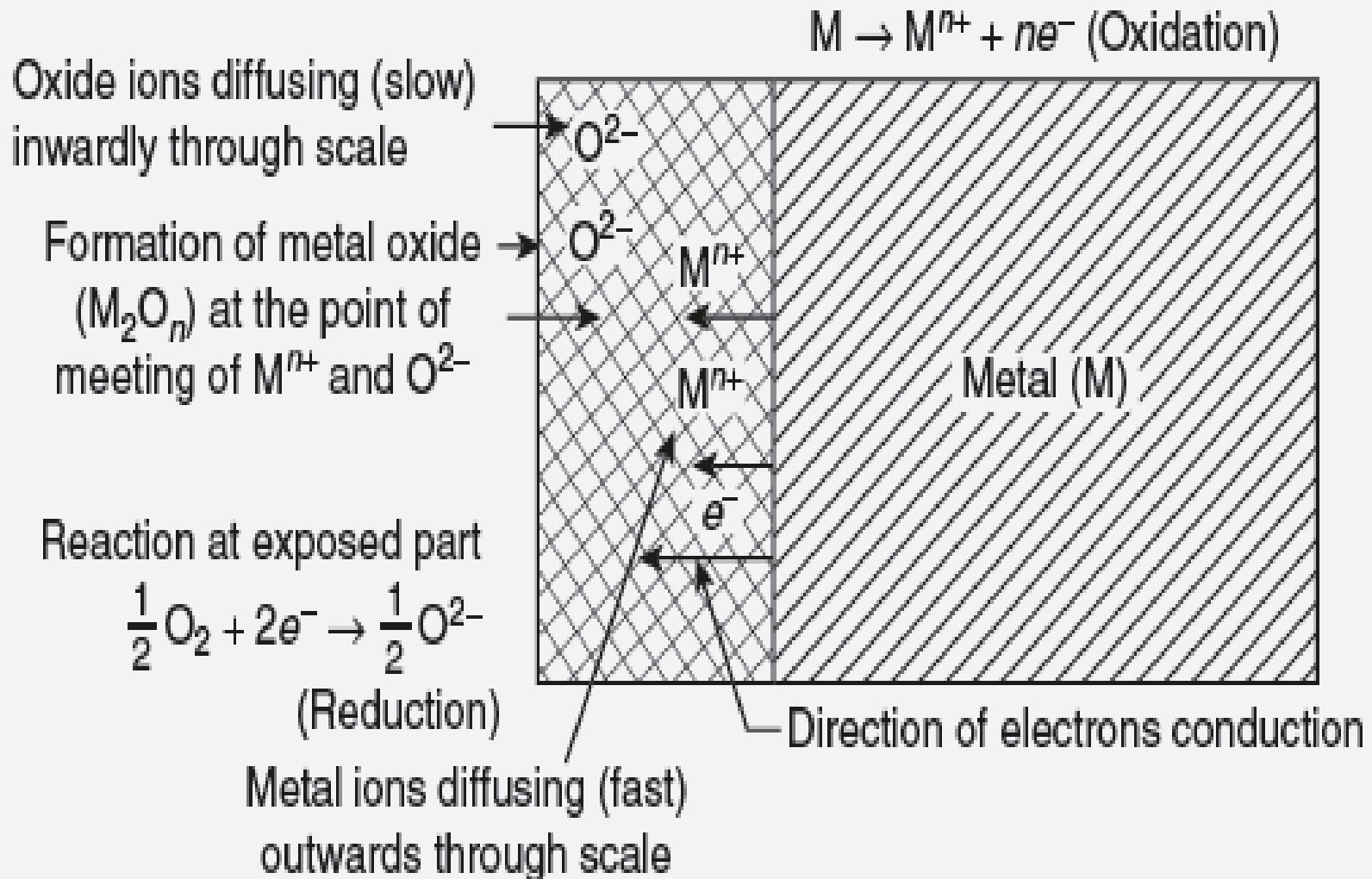
- Oxygen present in the atmosphere attacks the metal surface – formation of metal oxide layer



When oxidation starts, a thin layer of oxide film forms on the surface and the nature of the film decides the further action

# Mechanism of Dry Corrosion

## Mechanism for oxidation corrosion



# Oxidation corrosion

---

## Types of Oxide layers

- i) Stable oxide layer
- ii) Unstable oxide layer
- iii) Porous oxide layer
- iv) Volatile oxide layer

Pilling-Bedworth rule

# Oxidation corrosion - Types of Oxide layers

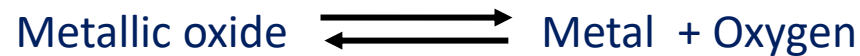
## i) Stable oxide layer:

- It is a fine grain of oxide layer which is non-porous and adheres strongly to the metal.
- Oxides of Al, Sn, Cu forms such impervious layers which prevents oxygen from diffusing through the metal and hence further attack is stopped.
- such layer can be of impervious nature (i.e., which cuts-off penetration of attaching oxygen to the underlying metal). Such a film behaves as protective coating in nature, thereby shielding the metal surface.
- The oxide films on Al, Sn, Pb, Cu, Pt, etc., are stable, tightly adhering and impervious in nature

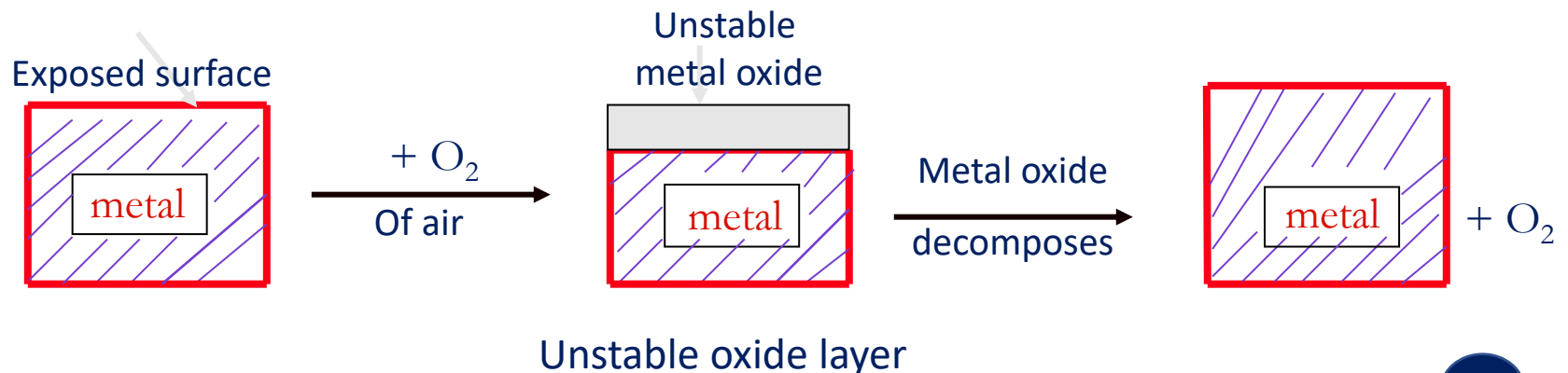
# Types of Oxide layers

## ii) Unstable oxide layer:

- These are produced on noble metal surfaces and these oxide layers decompose back to the metal.



- This is formed on the surface of noble metals such as Ag, Au, Pt.
- As the metallic state is more stable than oxide, it decomposes back into the metal and oxygen
- Hence, oxidation corrosion is not possible with noble metals.

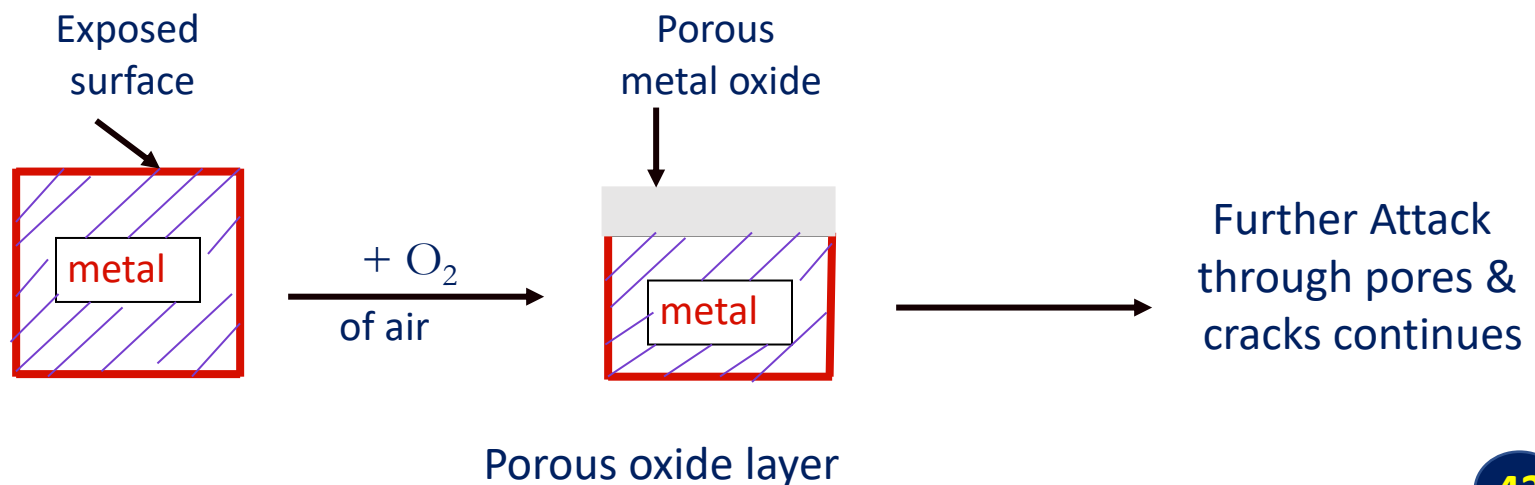




# Types of Oxide layers

## iii) Porous oxide layer:

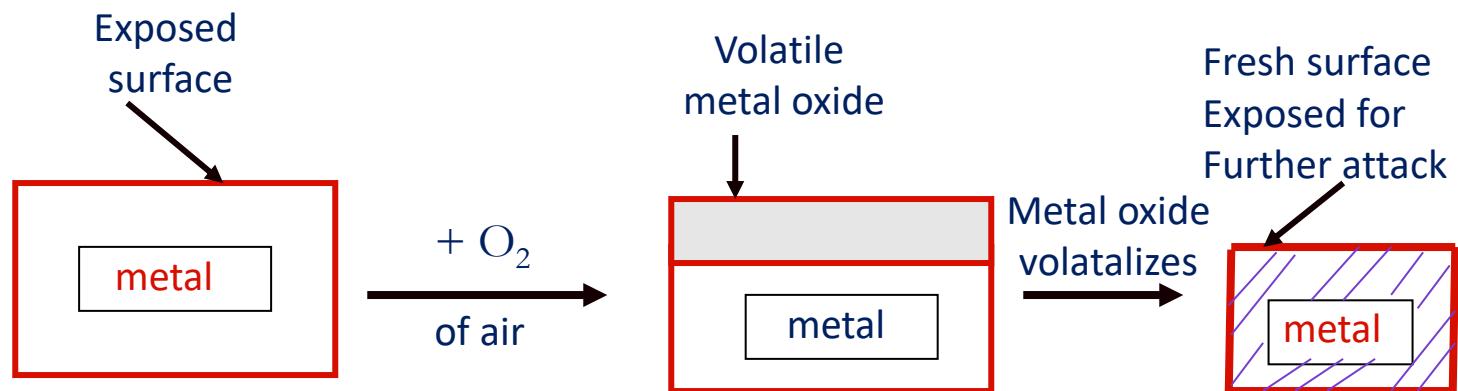
- These oxide layers have minute pores and are not impervious layers.
- Oxygen will diffuse through the pores and promote further corrosion.
- Fe is a good example of this type of corrosion.
- The layer having pores or cracks through which the atmospheric oxygen has access to the underlying surface of metal, thereby corrosion continues unobstructed, till the entire metal is completely converted into its oxide.



# Types of Oxide layers

## iv) Volatile oxide layer:

- These are oxide layers which evaporate as soon as they are formed and hence further corrosion is facilitated.
- After some time the metal itself will disappear.
- Molybdenum is an example of volatile oxide layer corrosion.



Volatile metal oxide

# Pilling – Bedworth rule

- If the **volume of the metallic oxide is equal or greater** in volume to the metal surface – Metal surface is compact, non-porous and **protective**. e.g. Al, Cu, Ni, Cr
- If the **volume of the metallic oxide is less** than the volume of the metal surface – Oxide layer is porous and **non-protective**. e.g. Mg, K

$$R_{PB} = \frac{V_{\text{Oxide}}}{V_{\text{Metal}}}$$

$R_{PB} < 1$  – Tensile stress in oxide film – brittle oxide cracks

$R_{PB} > 1$  – Compressive stress – uniformly covers & Protective

$R_{PB} \gg 1$  – Too much compressive stress and – Oxide cracks



# Pilling-Bedworth Ratio

Pilling-Bedworth ratio for some oxides

$K_2O$	$Na_2O$	$MgO$	$Al_2O_3$	$NiO$	$Cu_2O$	$Cr_2O_3$	$Fe_2O_3$
0.41	0.58	0.79	1.38	1.60	1.71	2.03	2.16

Stainless steel – Corrosion resistant material → addition of ~11 % Cr in Fe, leads to formation of Passive  $Cr_2O_3$  layer



# Other corrosion processes

## ii) corrosion by other gases:

- CO<sub>2</sub>, Cl<sub>2</sub>, SO<sub>2</sub>, F<sub>2</sub> etc. are gases which can attack the metal and corrode



- Extent of corrosion depends on the affinity of the metal to the gas.
- These gases chemically react with the metal forming either porous or non-porous layers of films.
- Hydrogen corrosion: Hydrogen gas attacks the metal to make them brittle (Hydrogen embrittlement)



# Other corrosion processes

## iii) liquid metal corrosion:

- Flowing liquid metal (Hg) can penetrate through another metal to corrode.
- Gold (Au) can be corroded by mercury (Hg).
- Such corrosion is found in nuclear devices
  - For example, liquid metal mercury dissolves most metals by forming amalgams, thereby corroding them.



Copper plate



Copper amalgam