

Module – 3 – Corrosion

- Dry and wet corrosion
- detrimental effects to buildings, machines, devices & decorative art forms, emphasizing Differential aeration, Pitting, Galvanic and Stress corrosion cracking;
- Factors that enhance corrosion and choice of parameters to mitigate corrosion.



Reference – Corrosion Engineering by Mars G. Fontana

Corrosion

Corrosion is the **deterioration** of materials/components due to **interaction** with the environment.

Types of Interaction that leads to corrosion

Physical

e.g.: Flow of liquid on a metal surface

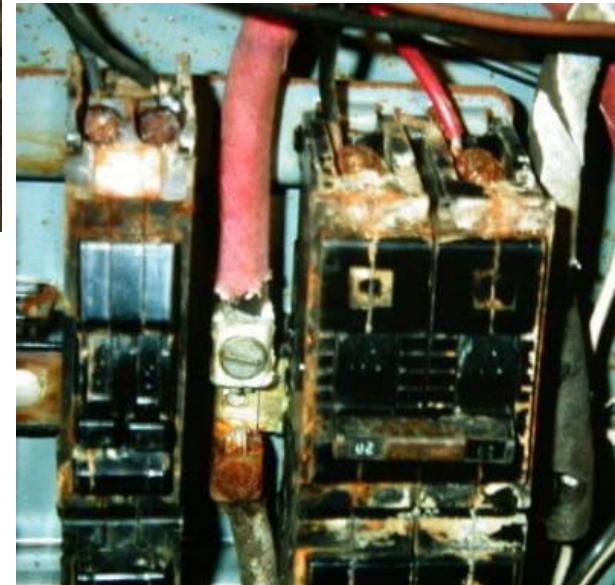
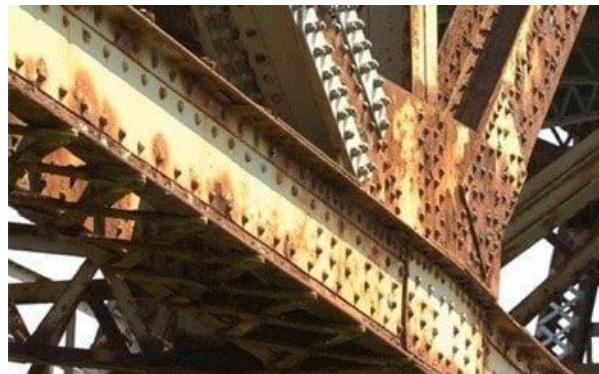
Chemical

e.g.: Iron at high temperature in air

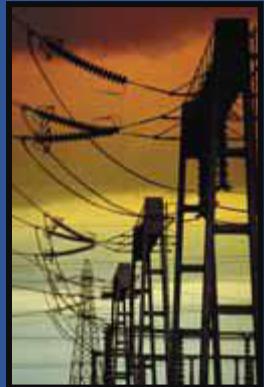
Electrochemical

e.g.: Iron in water

18.Corrosion_Module_3_(i)



Electric Power Industry



Transmission pipelines



Highway Bridges



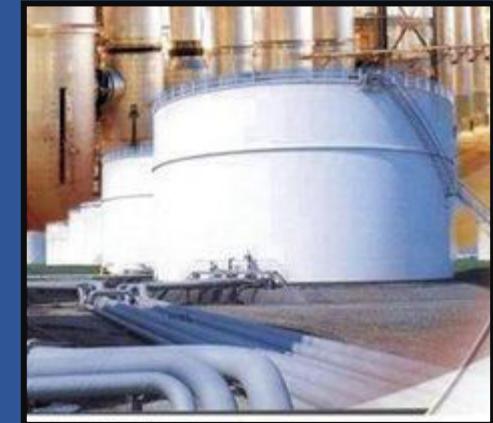
Pulp & Paper



Defense



Petrochemical Industry



***No industry
is exempted***



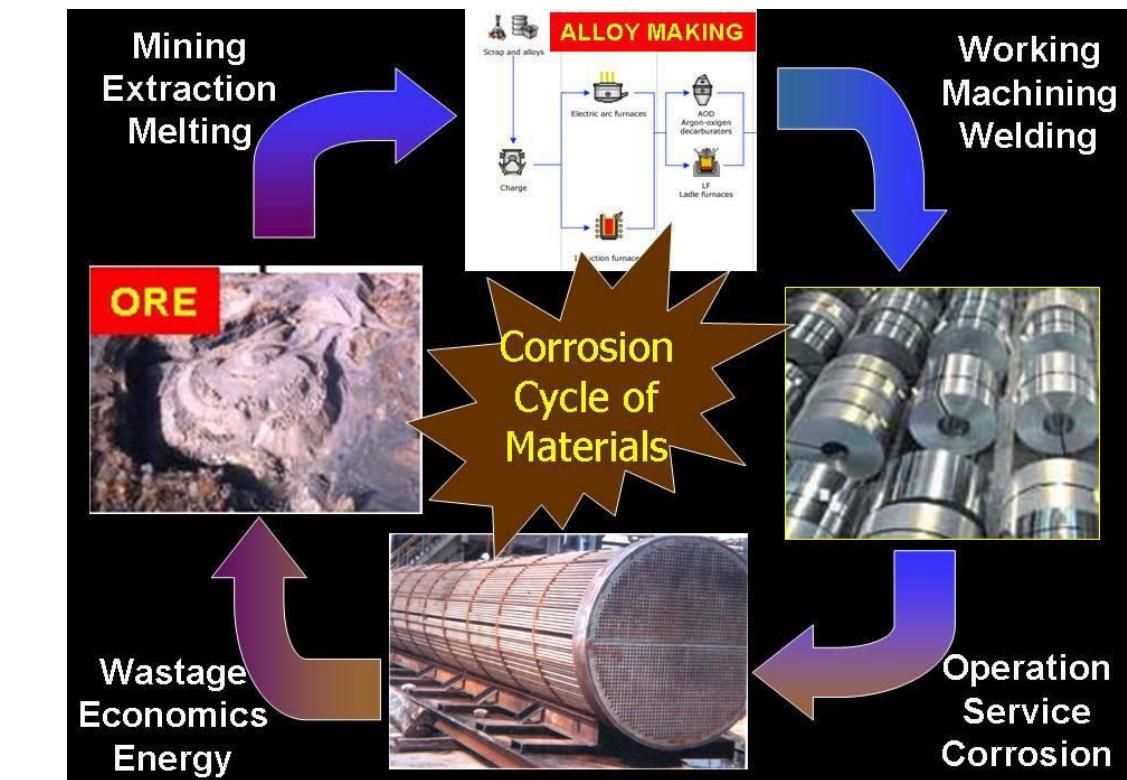
Nuclear Power Industry

Consequences of Corrosion

- Loss of aesthetic value
- Wall thinning in components, sometimes to unsafe levels
- Leaking of process fluids
- Loss of function, property or failure of components
- Economic loss
- Injury or loss of life
- Environmental damage

Why does corrosion takes place?

- Metals exist in nature as ores – stable compounds such as oxides, carbides, sulphides, carbonates, etc.
- Metals are in a higher energy state when compared to the ores – Energy has to be spent for extracting metals from ores
- Metals thus react spontaneously with the environment to revert back to the stable compounds



Types of Corrosion

Dry Corrosion / Chemical Corrosion

Involves direct attack of atmospheric gases on metal in the absence of moisture/liquid phase

Less prevalent

The corrosive media include vapours, gases, etc.

It is of various types: Oxidation corrosion, corrosion by other gases such as Cl_2 , SO_2 , H_2S , NO_x and liquid metal corrosion

Wet Corrosion / Electrochemical Corrosion

Involves electrochemical attack on metals in aqueous environments

More prevalent

The corrosive media is conducting liquid (aqueous) phase

It is of three types: differential metal corrosion, differential aeration corrosion and crevice corrosion

Dry Corrosion

- Dry corrosion occurs in the absence of a liquid phase or above the dew point of the environment. Vapors and gases are usually the corrodents.
- Dry corrosion is most often associated with high temperatures.
- e.g. Attack of Steel by furnace gases

Wet Corrosion

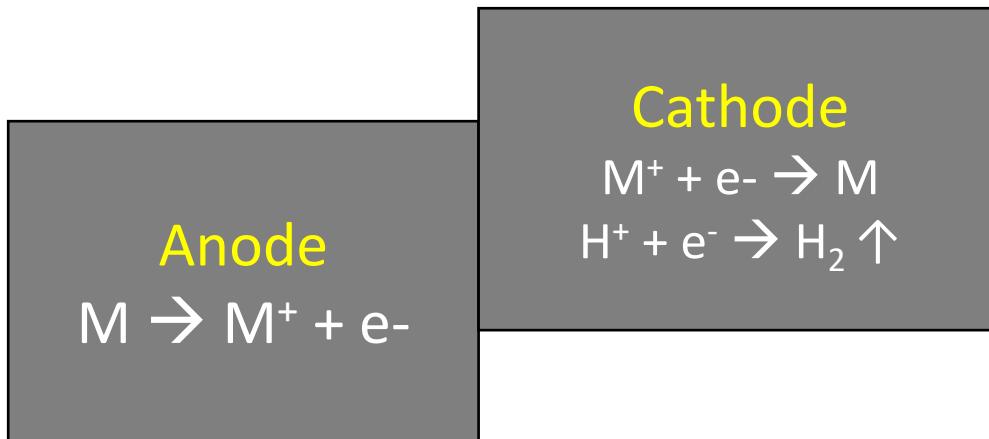
- Wet corrosion occurs when a liquid is present. This usually involves aqueous solutions or electrolytes and accounts for the greatest amount of corrosion by far.
- Types –
 - Differential metal corrosion
 - Differential aeration corrosion
 - Crevice corrosion
- e.g. Corrosion of Steel in water

Electrochemical Aspects of Corrosion

Electrochemical reaction

Oxidation takes place at anode – Metal dissolution

Reduction takes place at cathode – Gas evolution



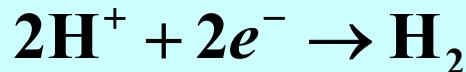
Redox reactions

Metal atoms characteristically lose up electrons in what called an **oxidation** reaction.



The site at which oxidation takes place is called the **anode**, oxidation is sometimes called an **anodic reaction**.

The electrons generated from each metal atom that is oxidized must be transferred to and become a part of another chemical species in what is termed a **reduction reaction**.

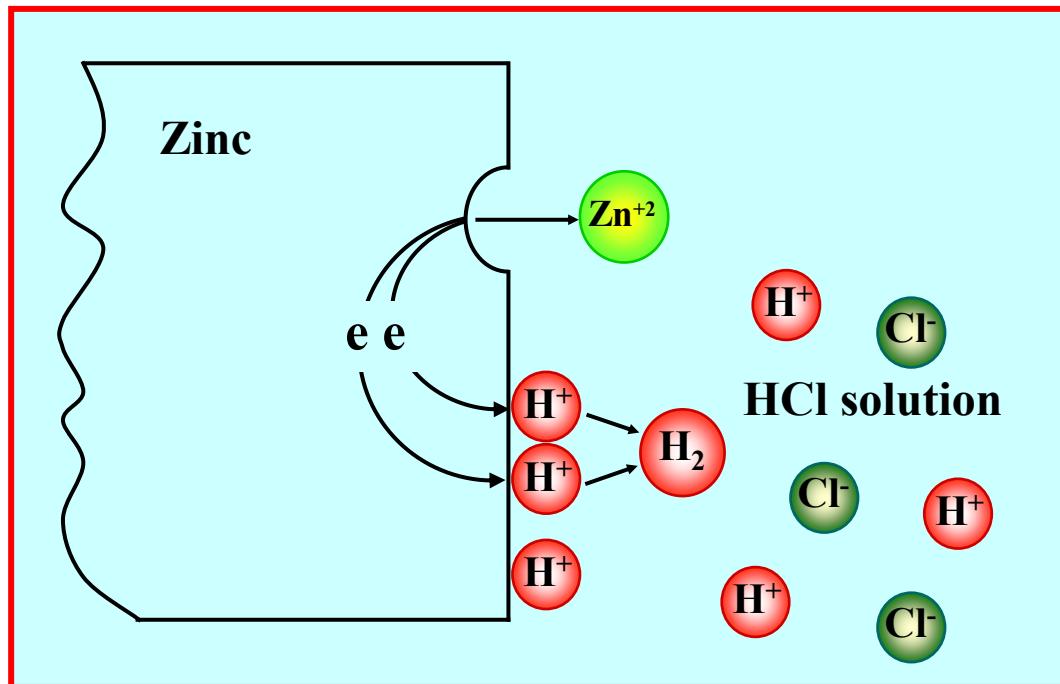


Metal Corrosion – example

Oxidation (anodic reaction)

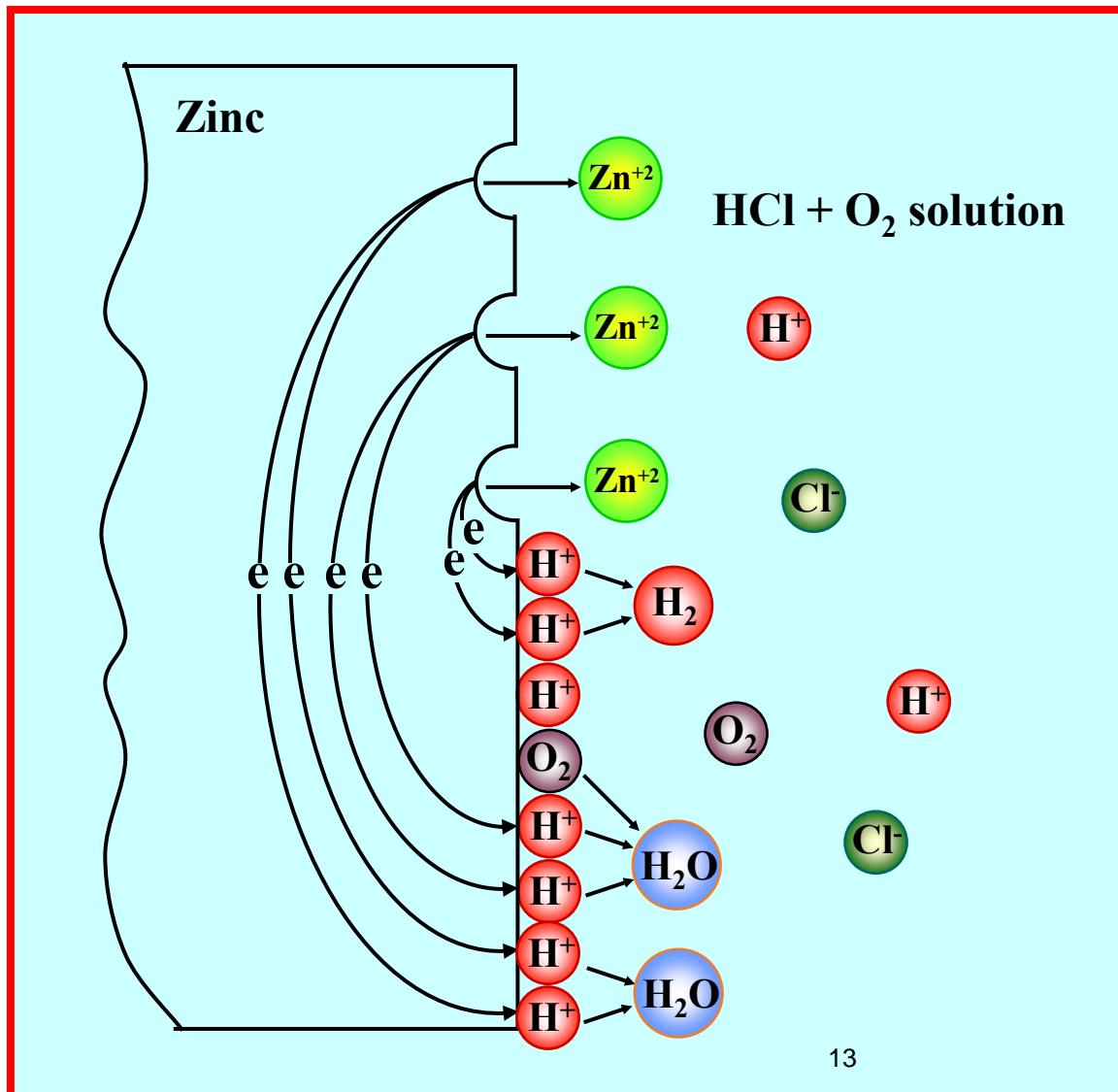


Reduction (cathodic reaction)



Electrochemical
reaction in
air free HCl

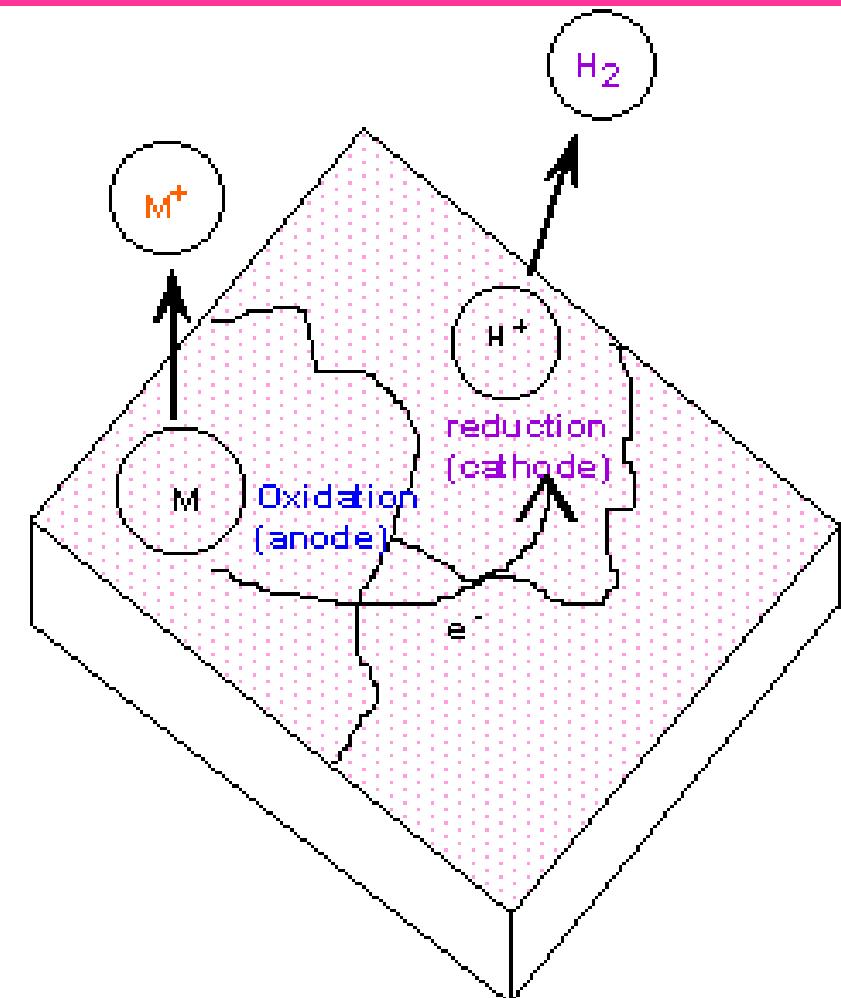
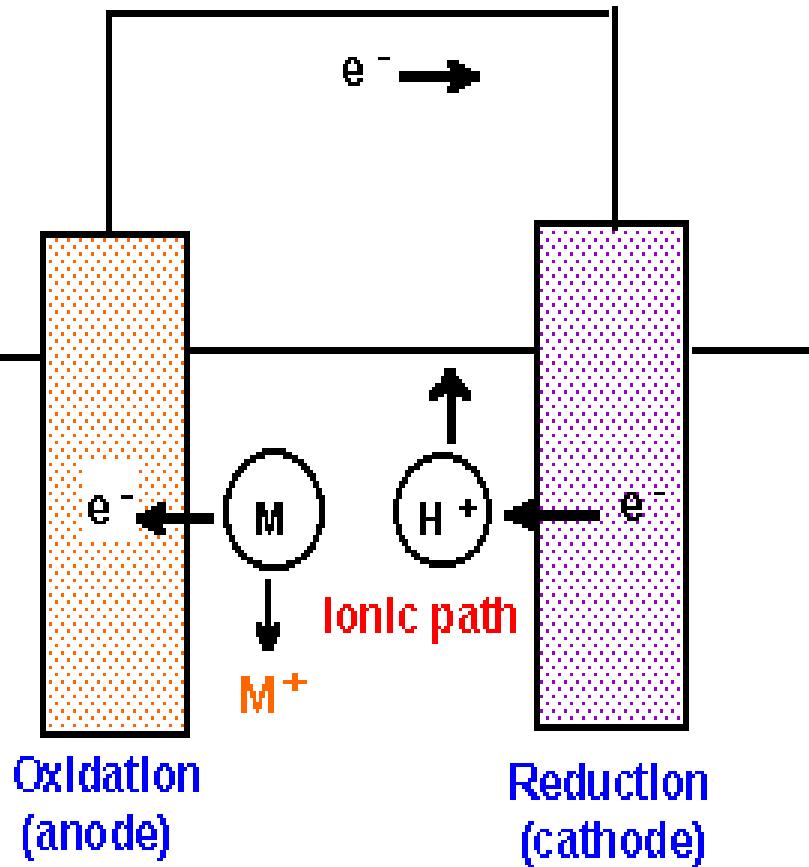
Metal Corrosion – example



Electrochemical reaction in aerated HCl

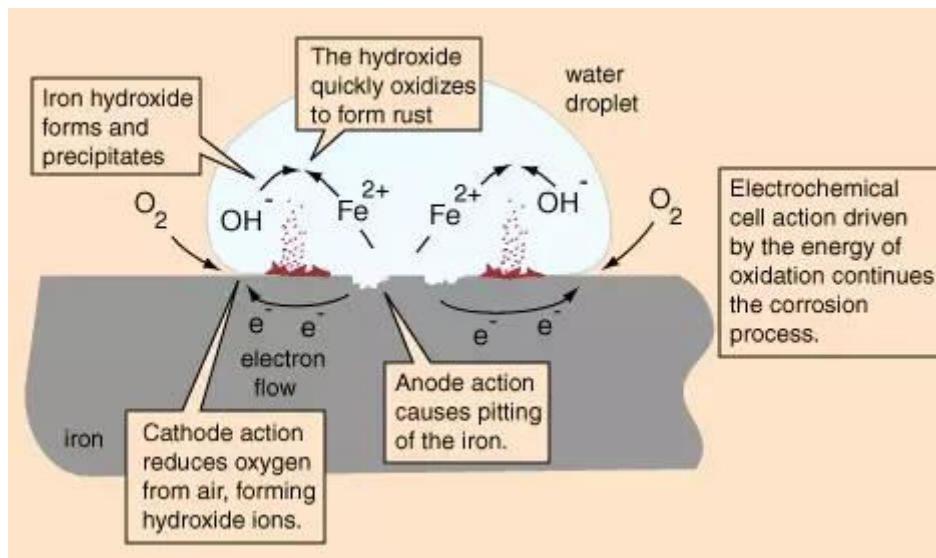
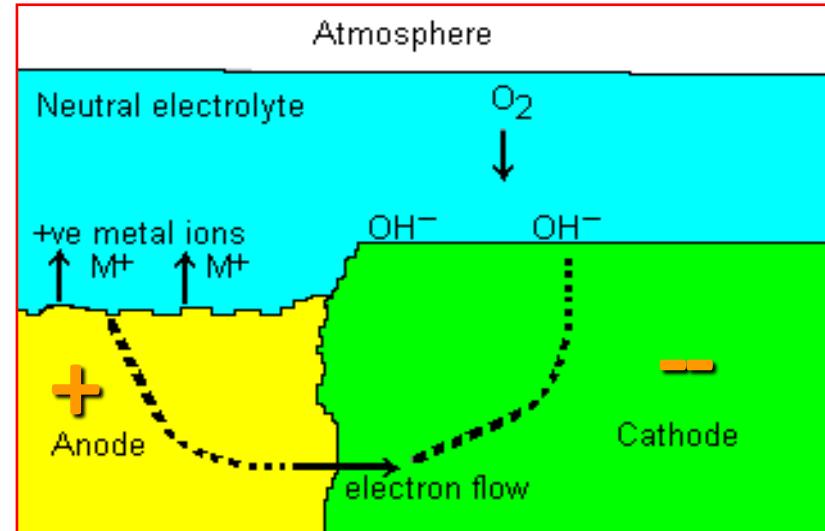
Anodic reaction same, Cathodic reaction will lead to formation of Water instead of H_2

Electronic path



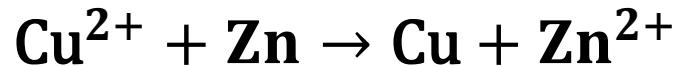
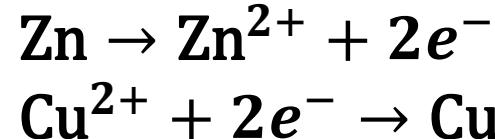
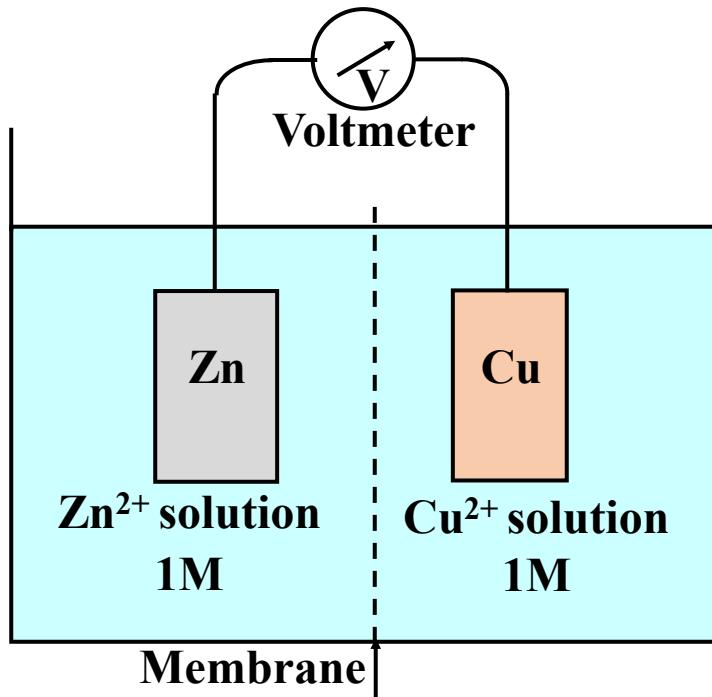
Corrosion occurs by metal dissolution (oxidation) at anode; electron released thereby is consumed by reduction of ions at cathode; Net charge is always near zero with anodic current \leftrightarrow cathodic current

Corrosion of metals and alloys



Electrode potential

Not all materials oxidize to form ions with the same degree of ease. Consider the electrochemical cell shown in the figure:



On the left-hand side is a piece of pure Zinc immersed in a solution containing Zn²⁺ ions of 1 M concentration. The other side of the cell consists of a pure copper electrode in a 1M solution of Cu²⁺ ions.

Electrode potential

- The electromotive force (emf) series is generated by coupling to the standard hydrogen electrode half-cells for various metals and ranking them according to measured voltage.

The Nernst Equation

$$E = E_0 - \frac{0.0592}{n} \log(C_{ion})$$

18.Corrosion_Module_3_(i)	Reaction	Std. Potential, V vs SHE
Noble	$\text{Au}^{3+} + 3\text{e}^- = \text{Au}$ $\text{Cl}_2 + 2\text{e}^- = 2\text{Cl}^-$ $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O}$ $\text{Pt}^{3+} + 3\text{e}^- = \text{Pt}$	+ 1.498 + 1.358 + 1.229 + 1.200
	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$ $\text{Ag}^+ + \text{e}^- = \text{Ag}$ $\text{Fe}^{3+} + \text{e}^- = \text{Fe}^{2+}$	+ 0.820 + 0.799 + 0.771
	$\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$ $\text{Sn}^{4+} + 2\text{e}^- = \text{Sn}^{2+}$ $2\text{H}^+ + 2\text{e}^- = \text{H}_2$	+ 0.337 + 0.150 0.000
	$\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$ $\text{Sn}^{2+} + 2\text{e}^- = \text{Sn}$ $\text{Ni}^{2+} + 2\text{e}^- = \text{Ni}$	- 0.126 - 0.136 - 0.250
	$\text{Co}^{2+} + 2\text{e}^- = \text{Co}$ $\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$ $\text{Cr}^{3+} + 3\text{e}^- = \text{Cr}$ $\text{Zn}^{2+} + 2\text{e}^- = \text{Zn}$	- 0.277 - 0.440 - 0.744 - 0.763
Active	$\text{Zr}^{4+} + 4\text{e}^- = \text{Zr}$ $\text{Ti}^{2+} + 2\text{e}^- = \text{Ti}$ $\text{Al}^{3+} + 3\text{e}^- = \text{Al}$ $\text{Mg}^{2+} + 2\text{e}^- = \text{Mg}$	- 1.53 - 1.63 - 1.662 - 2.363

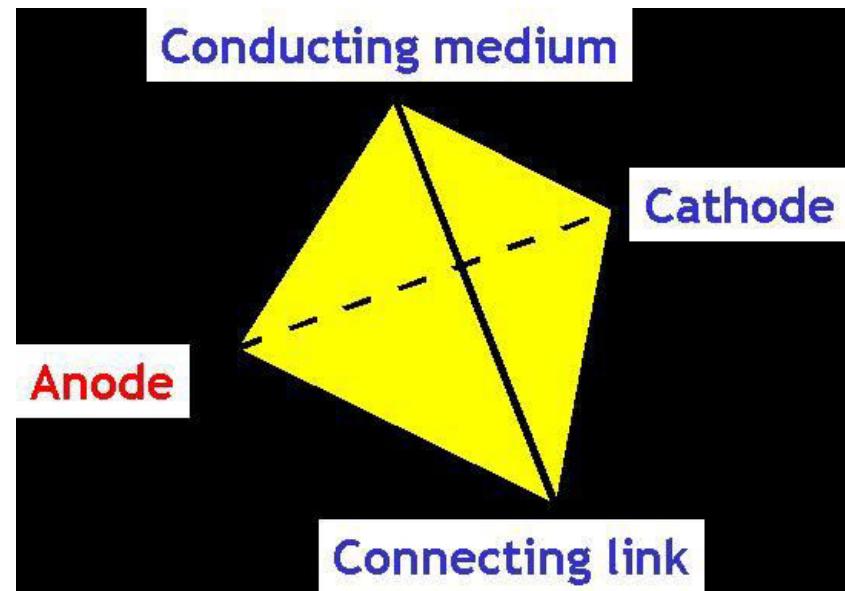
Strong Oxidizing agent

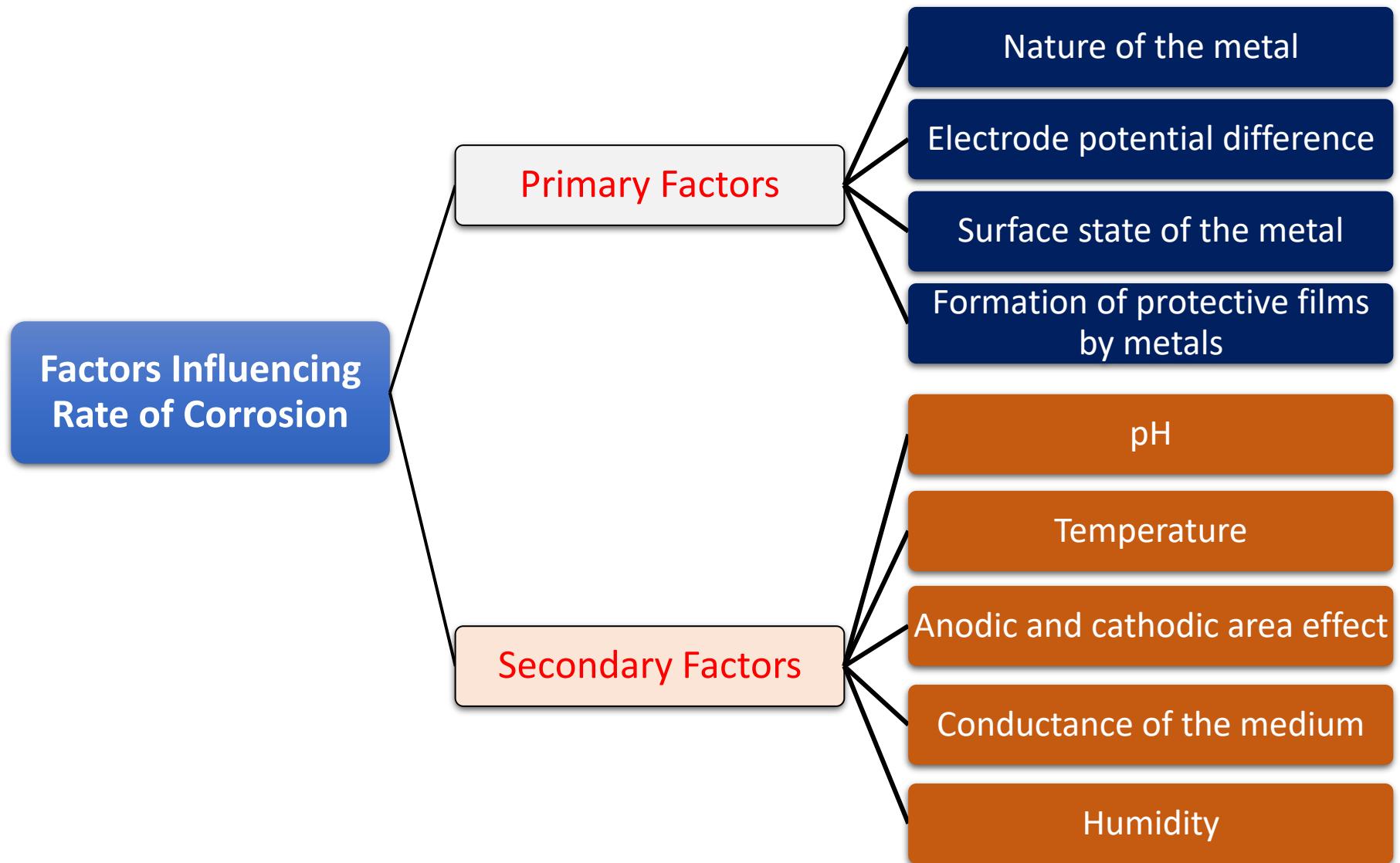
Strong Reducing agent

Corrosion mechanism

Four essential requirements for electrochemical corrosion

- **Anode** - Metal oxidation takes place releasing electrons
- **Cathode** – electrons are consumed to form reduced species
- **Electrical contact** between anode and cathode for electron transport
- **Electrolyte** for ionic transport between the electrodes





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:

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

ii) Over voltage:

- o 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.
- o If a few drops of CuSO_4 are added, the hydrogen over voltage comes down to 0.33V and corrosion rate increases.
- o Reduction in hydrogen over voltage increases the rate of corrosion.

Factors influencing corrosion

iii) Relative areas of cathode and anode:

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

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

iv) Purity of the metal:

- o Purer the metal, lesser is the rate of corrosion.
- o 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:

- o If the corrosion product is soluble in the environment in which the metal is working, then the corrosion proceeds faster.
- o 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. PbSO_4 .

b) Volatility of the corrosion product:

- o 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:

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

ii) Humidity in environment:

- o “Critical humidity” is the humidity above which the metallic corrosion rate increases sharply.
- o Critical humidity depends on the nature of the metal as well as the corrosion product.
- o When the humidity is higher, the gases e.g. CO_2 , 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:

- o Gases like CO_2 , SO_2 , H_2S and fumes of HCl , H_2SO_4 which are present in the industrial areas provide conductive environment for enhancing the electrochemical corrosion.
- o In marine environment, the Cl^- is responsible for enhanced rate of corrosion.

iv) Presence of suspended solids in the environment:

- o Particles like NaCl , $(\text{NH}_4)_2\text{SO}_4$ 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 Fe^{2+} gets oxidized to 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:

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

Types of corrosion

Dry corrosion

/ Chemical corrosion

- Oxidation corrosion (Attack of Oxygen)
- Corrosion by other gases (SO_2 , CO_2 , H_2S and NO_2)
- Liquid metal corrosion (corrosion of gold by mercury)

Wet corrosion

/ Electrochemical corrosion

- Differential metal corrosion (Galvanic corrosion)
- Differential aeration corrosion (concentration cell corrosion)
- Pitting corrosion
- Inter-granular corrosion
- Soil corrosion

Oxidation corrosion

Formation of protective layer

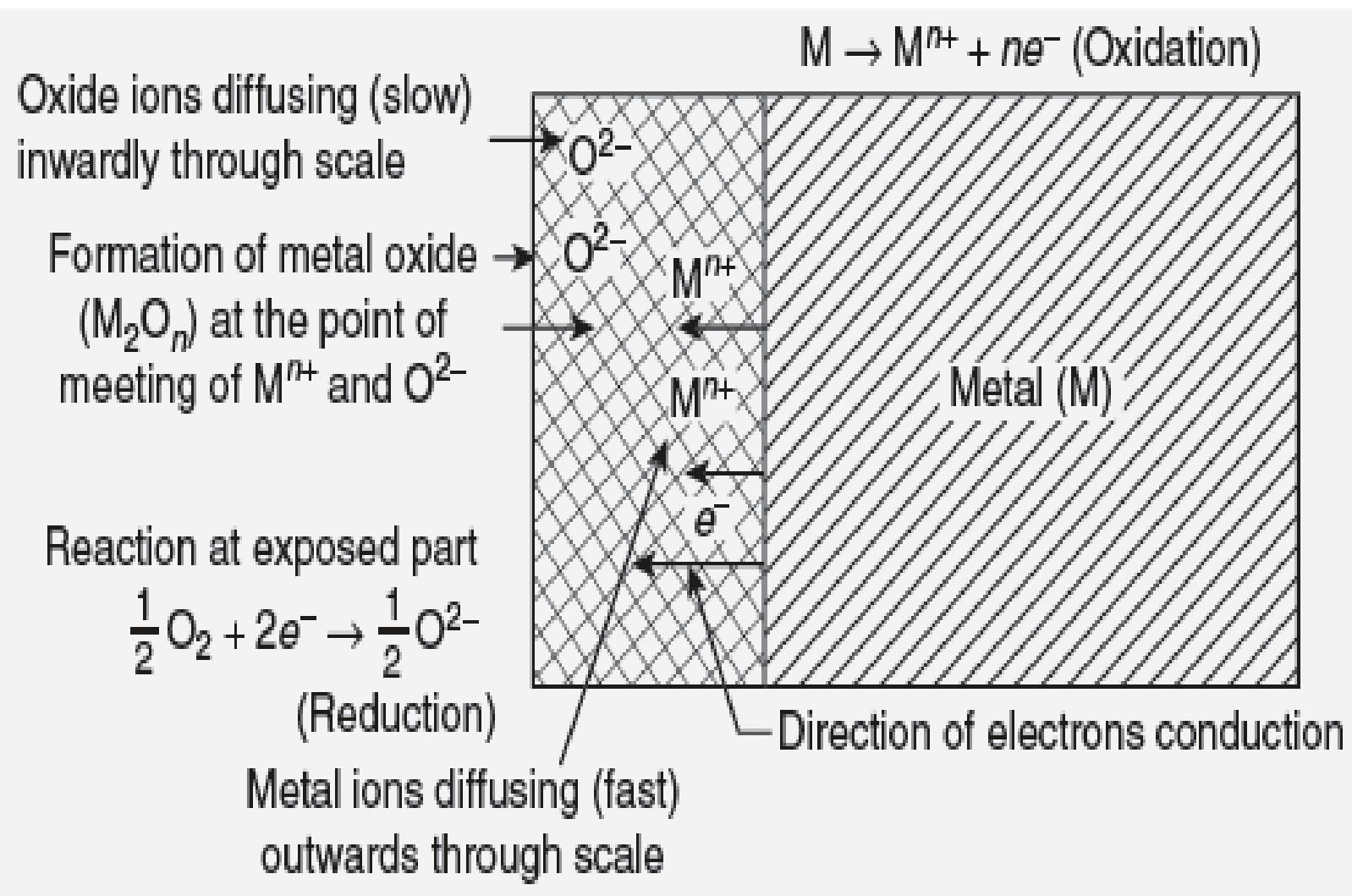
- Oxygen present in the atmosphere attacks the metal surface – formation of metal oxide layer



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

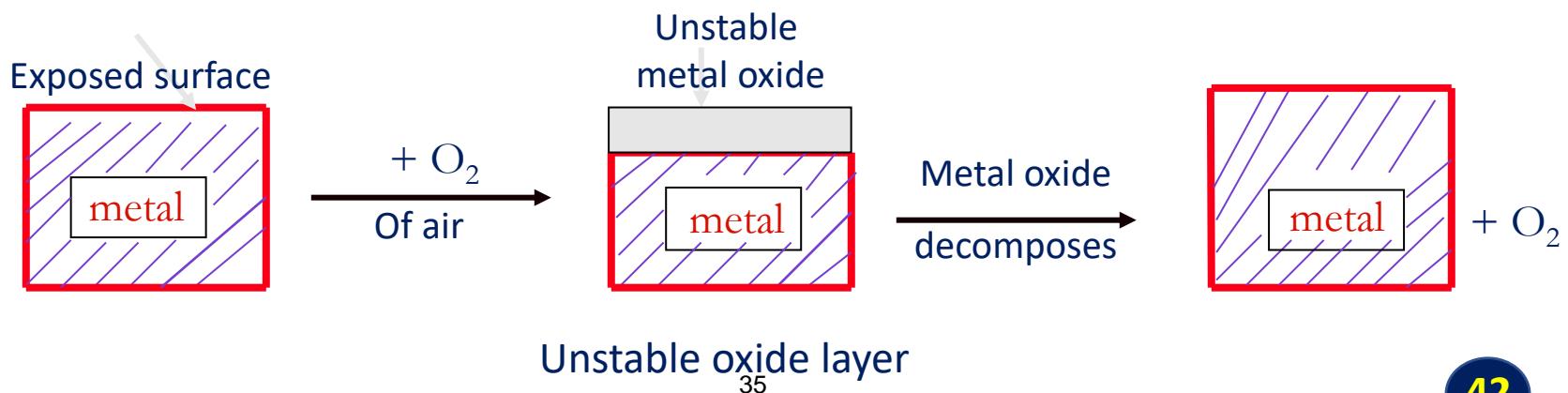
Types of Oxide layers

ii) Unstable oxide layer:

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



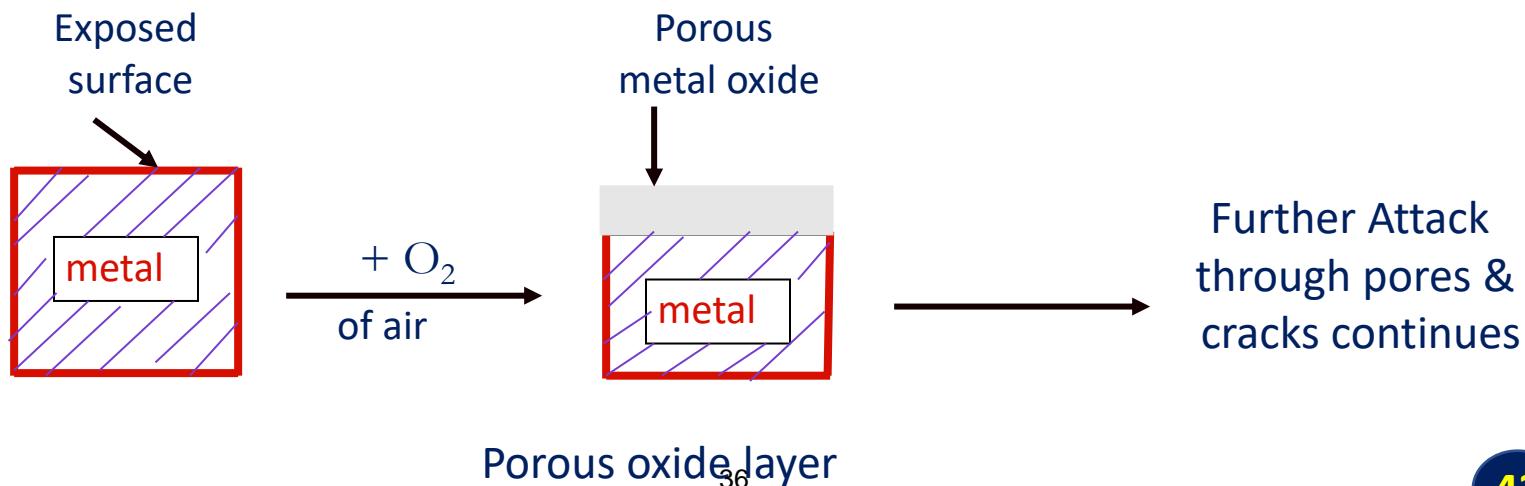
- This is formed on the surface of noble metals such as Ag, Au, Pt.
- As the metallic state is more stable than oxide, it decomposes back into the metal and oxygen
- Hence, oxidation corrosion is not possible with noble metals.



Types of Oxide layers

iii) Porous oxide layer:

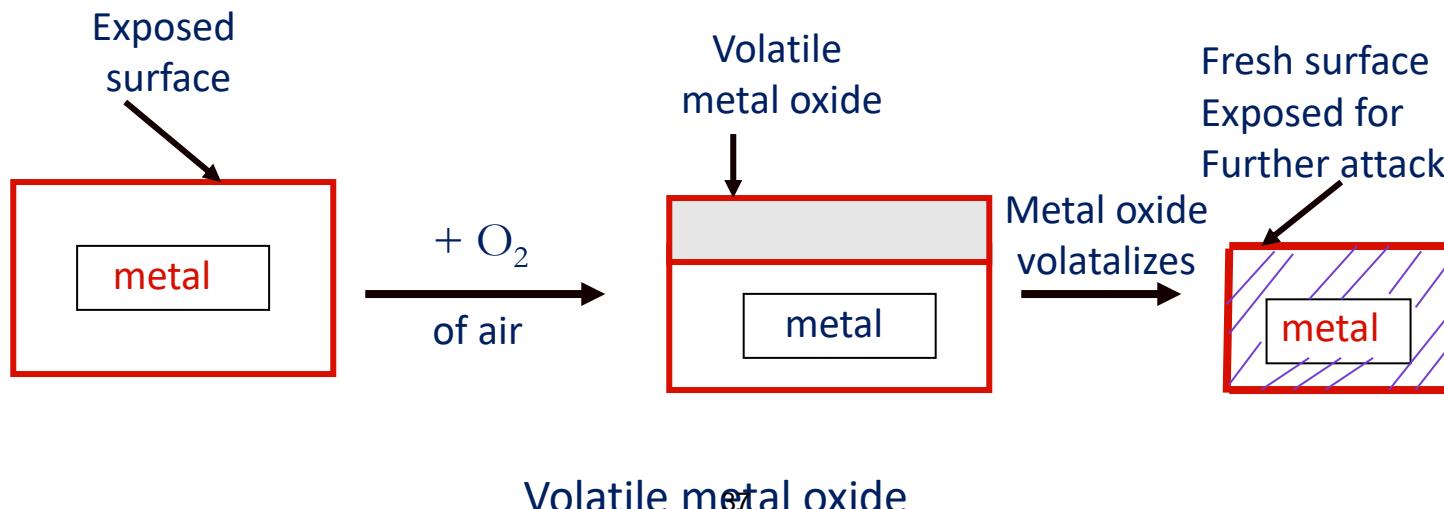
- These oxide layers have minute pores and are not impervious layers.
- Oxygen will diffuse through the pores and promote further corrosion.
- Fe is a good example of this type of corrosion.
- The layer having pores or cracks through which the atmospheric oxygen has access to the underlying surface of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



Types of Oxide layers

iv) Volatile oxide layer:

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



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:

- CO₂, Cl₂, SO₂, F₂ 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:

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



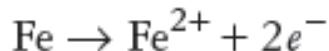
Copper plate



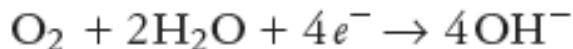
Copper amalgam

Wet / Electrochemical Corrosion

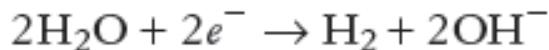
1. **Anodic reaction:** Metal undergoes oxidation (**corrosion**) with release of electrons
2. **Cathodic reactions:** These reactions are dependent on the constituents of the corrosion medium.



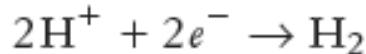
If the solution is aerated and almost neutral, oxygen is reduced in presence of H_2O to OH^- ions.



If the solution is deaerated and almost neutral, H_2 is liberated along with OH^- ions.

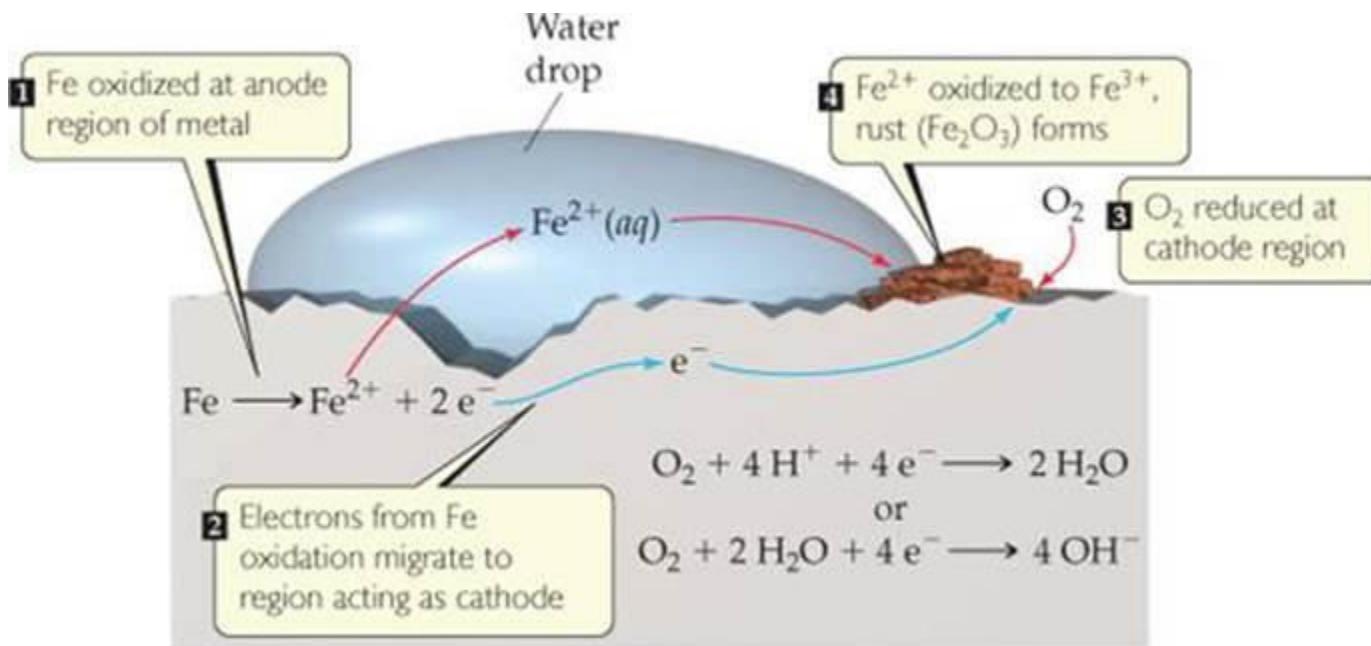


If the solution is deaerated and acidic, H^+ ions are reduced to hydrogen gas

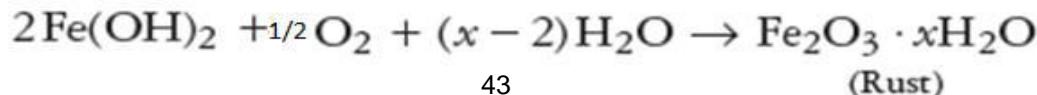
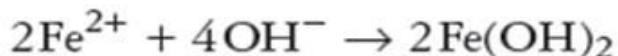


Wet corrosion (Electrochemical theory of corrosion)

- Metal comes in contact with a conducting liquid or when two dissimilar metals are immersed partly in a solution.



The metal ions formed at the anode combine with hydroxyl ions and form the corresponding metallic hydroxide Fe(OH)_2 , which further gets oxidized to hydrated ferric oxide [rust].



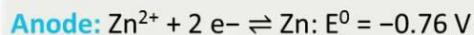
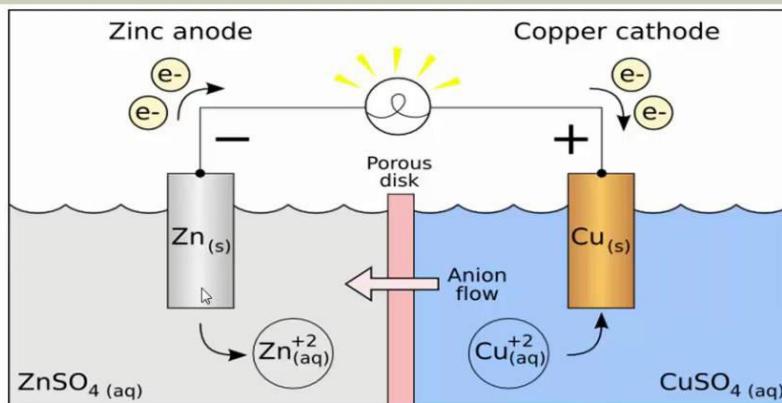
Types of Wet corrosion / Electrochemical corrosion

1. Differential metal corrosion (**Galvanic corrosion**)
2. Differential aeration corrosion (**concentration cell corrosion**
/ Water-line corrosion)
3. Pitting corrosion
4. Inter-granular corrosion
5. Soil corrosion
6. Stress corrosion cracking
7. Crevice corrosion

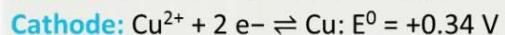
1. Differential Metal Corrosion (Galvanic Corrosion)

When two dissimilar metals are in contact in corrosive environment, metal with lesser standard reduction potential will act as anode and will undergo oxidation (corrosion). Metal with higher standard reduction potential will act as cathode and it will provide surface for reduction of oxygen.

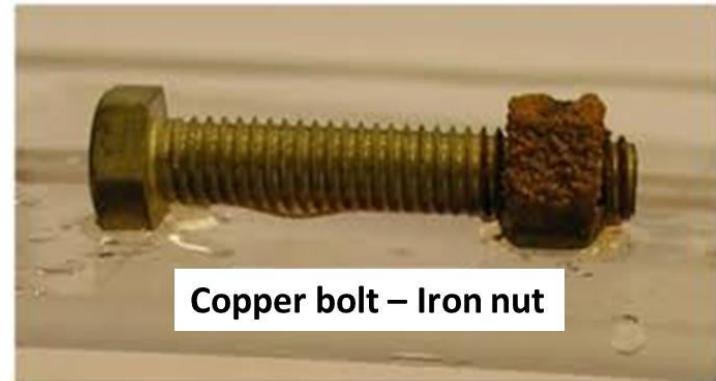
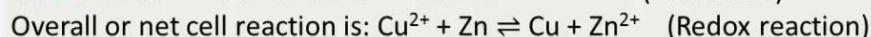
Galvanic Cell



(Oxidation)

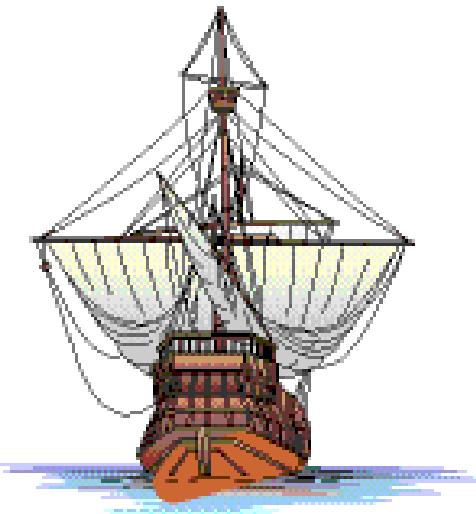


(Reduction)



Copper bolt – Iron nut

Galvanic Corrosion



One of the earliest documented incidences of serious galvanic corrosion occurred in the eighteenth century on the Royal Navy's frigate, H.M.S. Alarm. This vessel had its wooden hull covered by copper sheathing, which was in turn attached by iron nails.

One of the purposes of this copper covering was to limit marine biofouling, plaguing many materials immersed in sea water. Reduced speed and maneuverability of ships are consequences of such growths. Copper generally acts as a biocide, limiting such fouling.

Not surprisingly, the iron fasteners in contact with the copper were subject to rapid galvanic corrosion and led to detachment of some sheathing.

Other examples of differential metal corrosion (galvanic corrosion) include

1. Buried iron pipeline connected to zinc bar.
2. Steel pipe connected to copper plumbing.
3. Steel propeller shaft in bronze bearing.
4. Zinc coating on mild steel.
5. Lead–tin solder around copper wires.

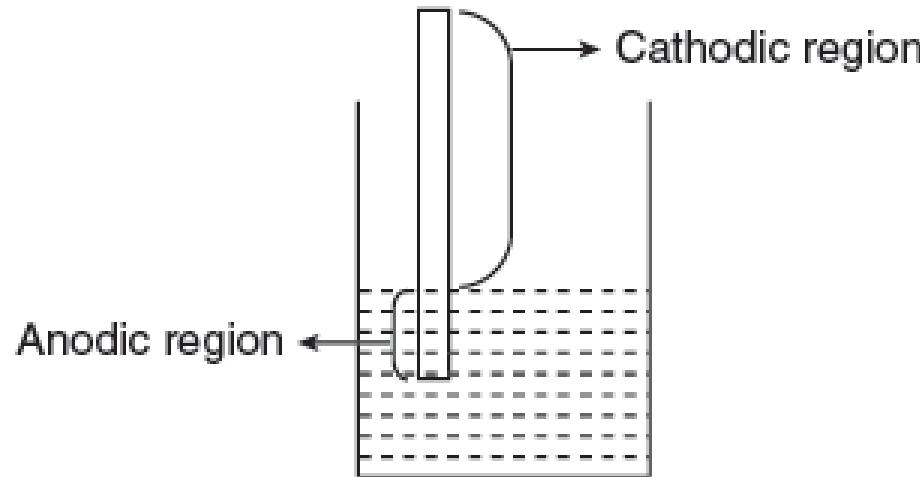
Galvanic Corrosion – prevention/control

- ✓ Selection of alloys which are similar in electrochemical behavior and/or alloy content.
- ✓ Area ratio of more actively corroding material (anode) should be large relative to the more inert material (cathode).
- ✓ Use coatings to limit cathode area.
- ✓ Insulate dissimilar metals.
- ✓ Use of effective inhibitor.



2. Differential Aeration Corrosion (Concentration Cell Corrosion) (Waterline Corrosion)

When a metal is exposed to differential air or oxygen concentration



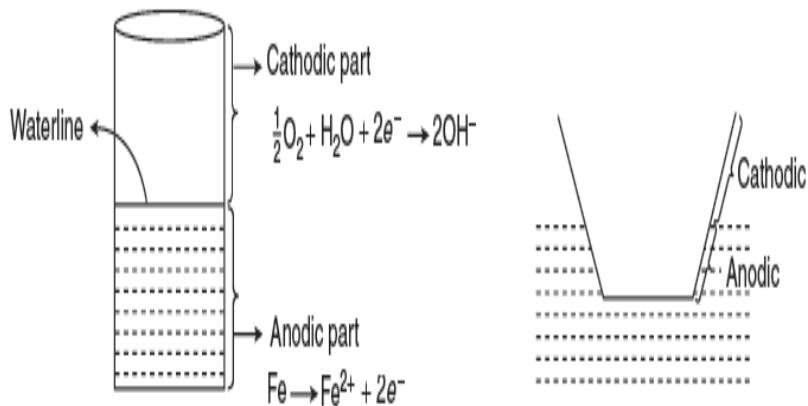
When a metal is partially dipped in an electrolyte,

- ❖ the portion dipped in the electrolyte is poor in oxygen concentration and works as an anode which gets corroded
- ❖ the portion above the electrolyte acts as cathode

The examples of differential aeration corrosion include

1. Half-immersed iron plate in aqueous solution.
2. Steel pipe carrying any liquid exposed to atmosphere.
3. Ocean going ships.
4. Steel storage tanks.

Waterline Corrosion



(a)

(b)

(c)

Waterline corrosion: (a) Water storage tank and (b) ocean going ship
 (c) Metallic pillar in water and outside

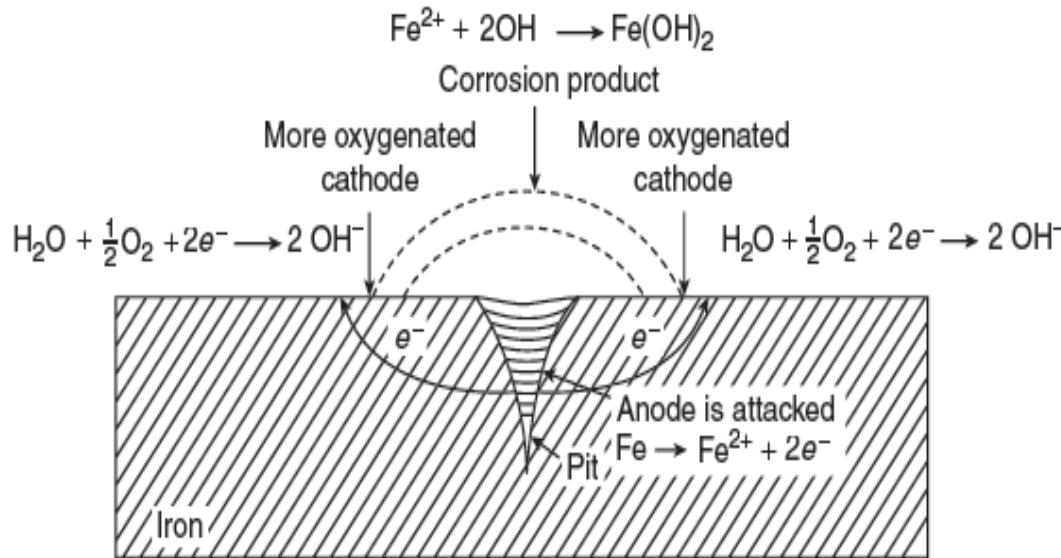
Differential Aeration Corrosion – prevention/control

- ✓ Apply a **passive coating** that prevents the contact between the electrolyte (e.g. water) and the electrode (e.g. metallic Fe)
- ✓ Use of suitable effective **inhibitor**



3. Pitting corrosion

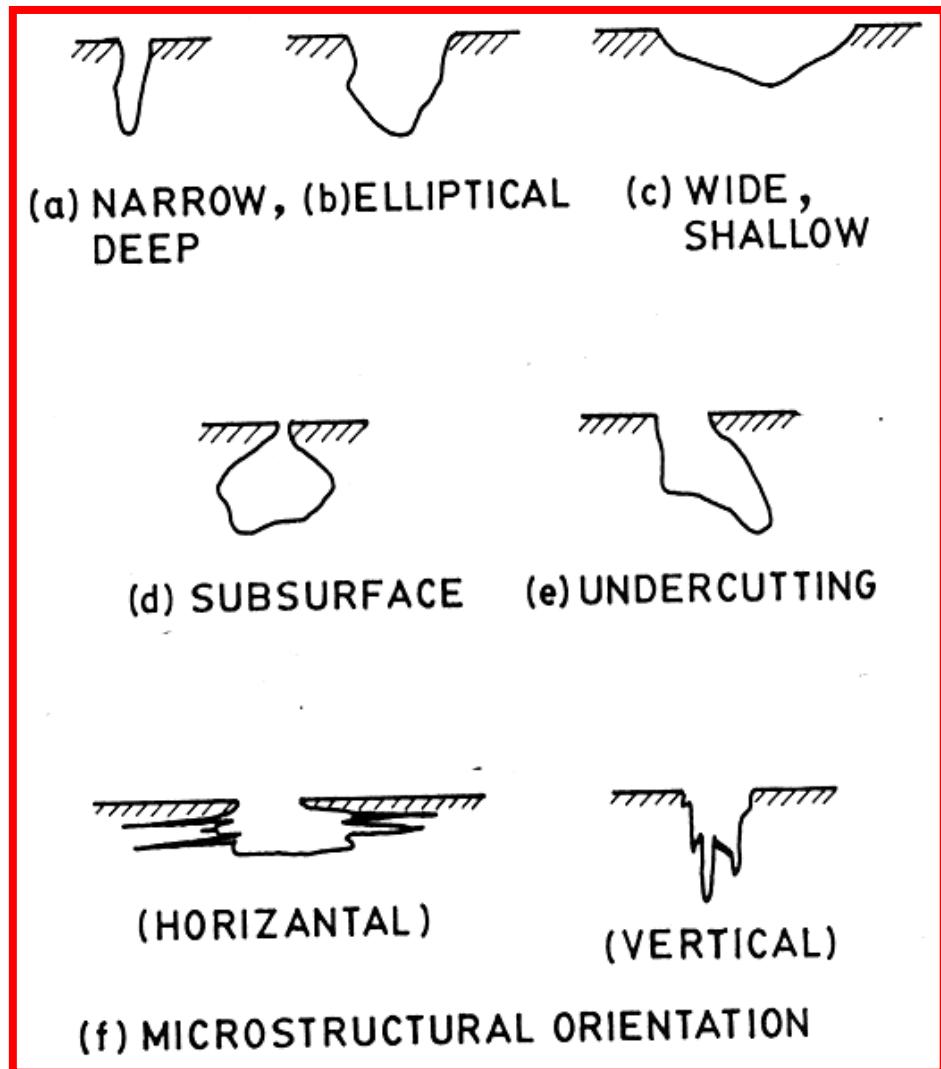
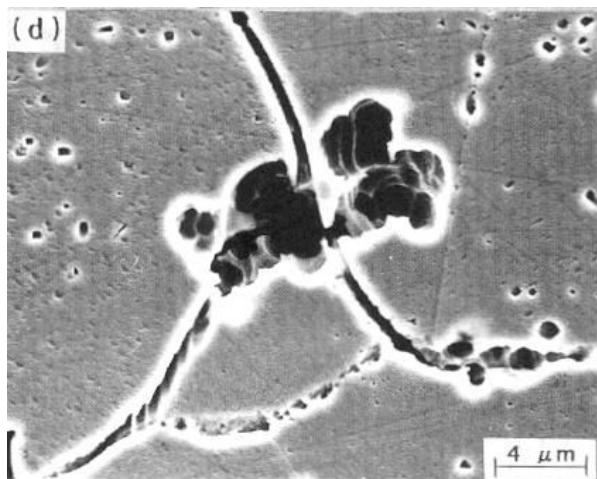
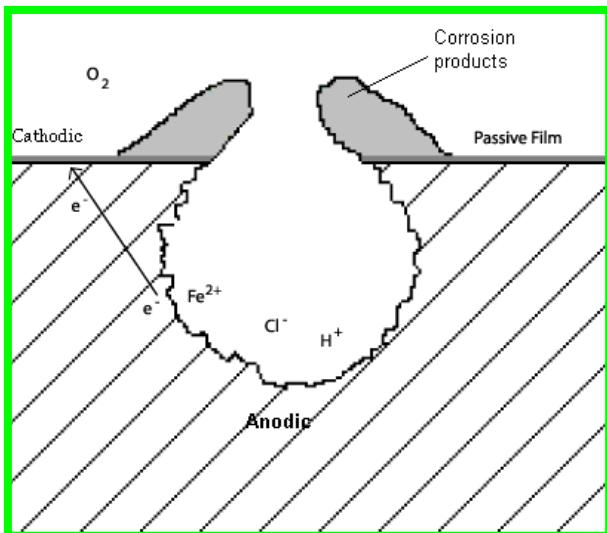
Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in the material.



Due to crack on the surface of a metal,

- ❖ there is a formation of a **local galvanic cell**.
- ❖ The **crack portion acts as anode** and the rest of the metal surface acts as cathode.
- ❖ It is the anodic area which is corroded and the **formation of a pit** is observed.

Pitting corrosion



Pitting Corrosion – prevention/control

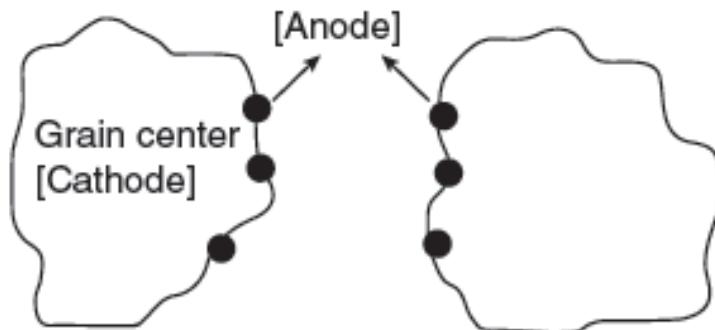
- ✓ Proper selection of materials with known resistance to the service environment
- ✓ Control pH, chloride concentration and temperature
- ✓ Cathodic protection and/or Anodic Protection
- ✓ Selection of alloy with higher alloy content (e.g. in stainless alloys-higher Cr, Mo and N) for increased resistance to pitting corrosion

4. Intergranular Corrosion:

- Generally observed in alloys, this corrosion involves an attack on the grain boundaries of a metal or alloys, where the formation of corrosion products takes place (like carbides in steel).
- Externally not visible and there is a sudden failure of material due to this corrosion

Example

- During the welding of stainless steel (an alloy of Fe, C and Cr), chromium carbide is precipitated at the grain boundaries which causes depletion of chromium composition in the adjacent regions.
- This become anode with respect to the region within the grains richer in chromium.



Cathode: Chromium –rich grain centers

Anode: Grain Boundary – Chromium depleted regions

Intra granular Corrosion – prevention/control

- ✓ Rapid quenching after heat treatment of a metal is the remedy of inter-granular corrosion

Consider organic coating

- ✓ Paint, ceramic, chrome, etc. (Danger if it gets scratched)

Consider cathodic protection

- ✓ Such as zinc (or galvanized) plating on steel
- ✓ Mg sacrificial anode on steel boat exterior

5. Soil corrosion:

Underground pipes, cables, tank bottoms, etc., get corroded due to

- moisture
- pH of soil
- ionic species like chlorides
- micro-organisms like bacteria

It is further enhanced by differential aeration of various parts of the soil



Soil Corrosion – prevention/control

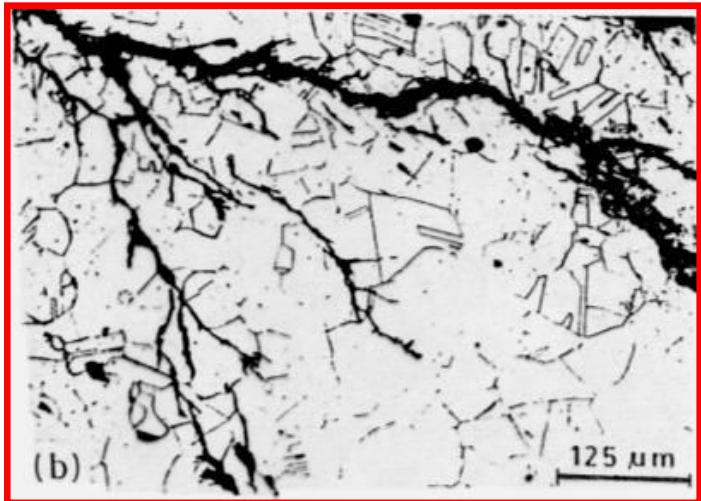
- ✓ Using organic and inorganic coatings
- ✓ Applying metallic coatings
- ✓ Alteration of soil
- ✓ Cathodic protection

6. Stress corrosion cracking:

- In a metallic structure, if there is a portion under stress, it acts as anode and rest part of the structure acts as cathode
- This small anodic region undergoes corrosion

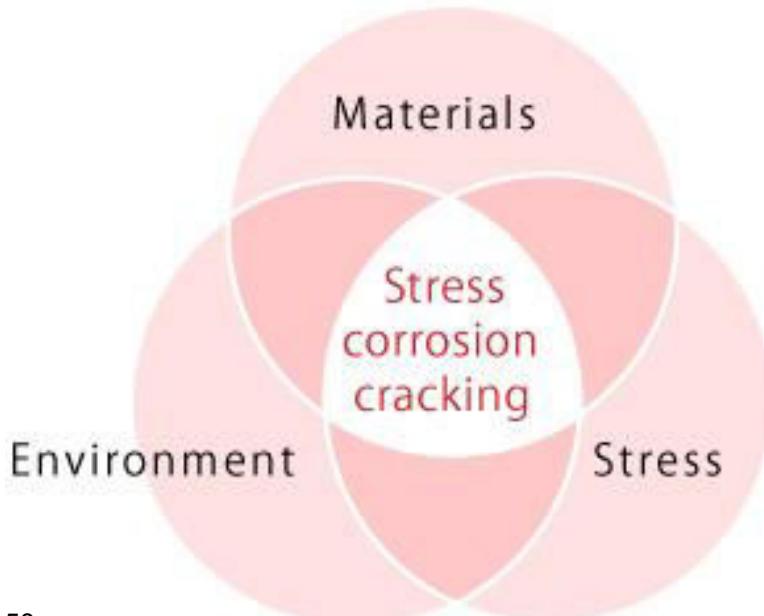
Example

- Caustic embrittlement is a type of stress corrosion occurring in boiler at high temperature and in alkaline medium



Stress Corrosion Cracking

[Causes of stress corrosion cracking]



Stress Corrosion Cracking – prevention/control

- ✓ Choosing a material that is not susceptible to Stress Corrosion Cracking in the service environment

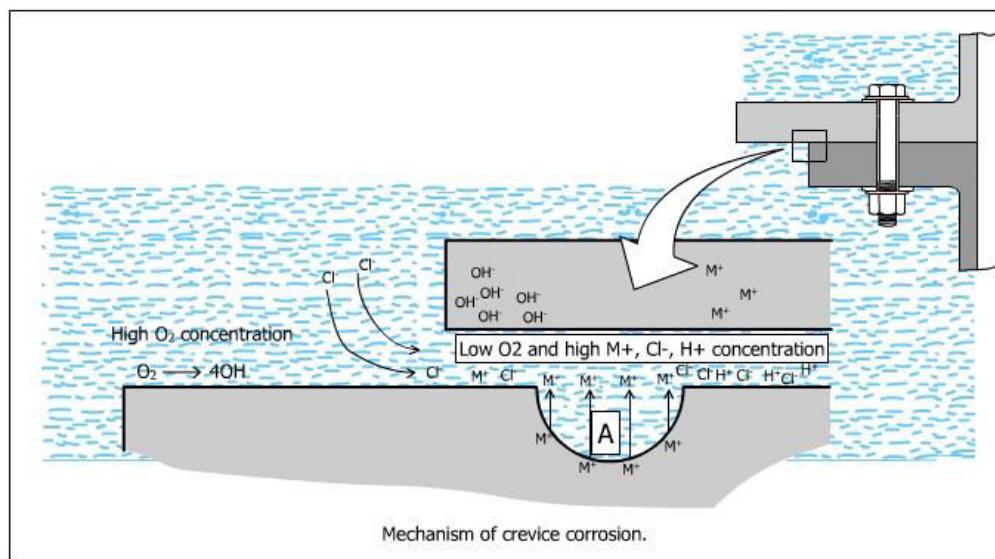
- ✓ Residual stresses can be relieved by annealing

- ✓ Neutralizing the environment whenever possible. For e.g. reducing chloride ion concentration

- Crevice corrosion occurs when two components are joined close together to form a crevice
- Corrosion occurs as the crevice accumulates water.

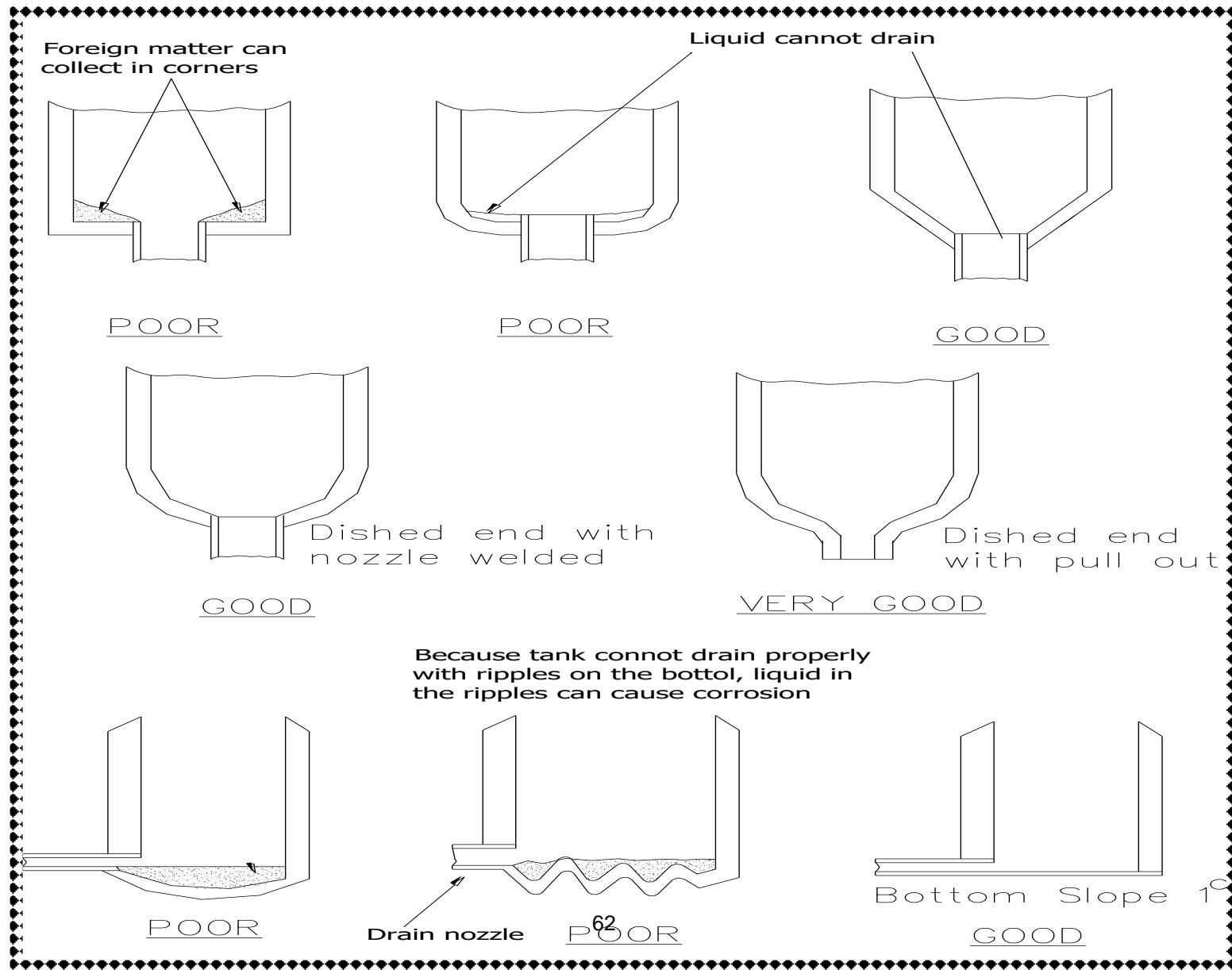
Gap → wide enough to liquid to enter, narrow enough to make it stagnant

- When this happens the base of the crevice becomes anodic to the upper region.



Crevice corrosion often occurs under bolts, rivet heads, etc.

Design against Corrosion



Crevice Corrosion –prevention/control

- Design vessels for complete drainage; avoid sharp comers and stagnant areas. Complete draining facilitates washing and cleaning and tends to prevent solids from settling on the bottom of the vessel.
- Inspect equipment and remove deposits frequently
- Use "solid," non-absorbent gaskets, such as Teflon, wherever possible.

Module – 4 – Corrosion Control

- Corrosion protection - cathodic protection – sacrificial anodic and impressed current protection methods; Advanced protective coatings: electroplating and electroless plating, PVD and CVD.
- Alloying for corrosion protection – Basic concepts of Eutectic composition and Eutectic mixtures - Selected examples – Ferrous and non-ferrous alloys.



Reference – Corrosion Engineering by Mars G. Fontana

Corrosion Protection/Control

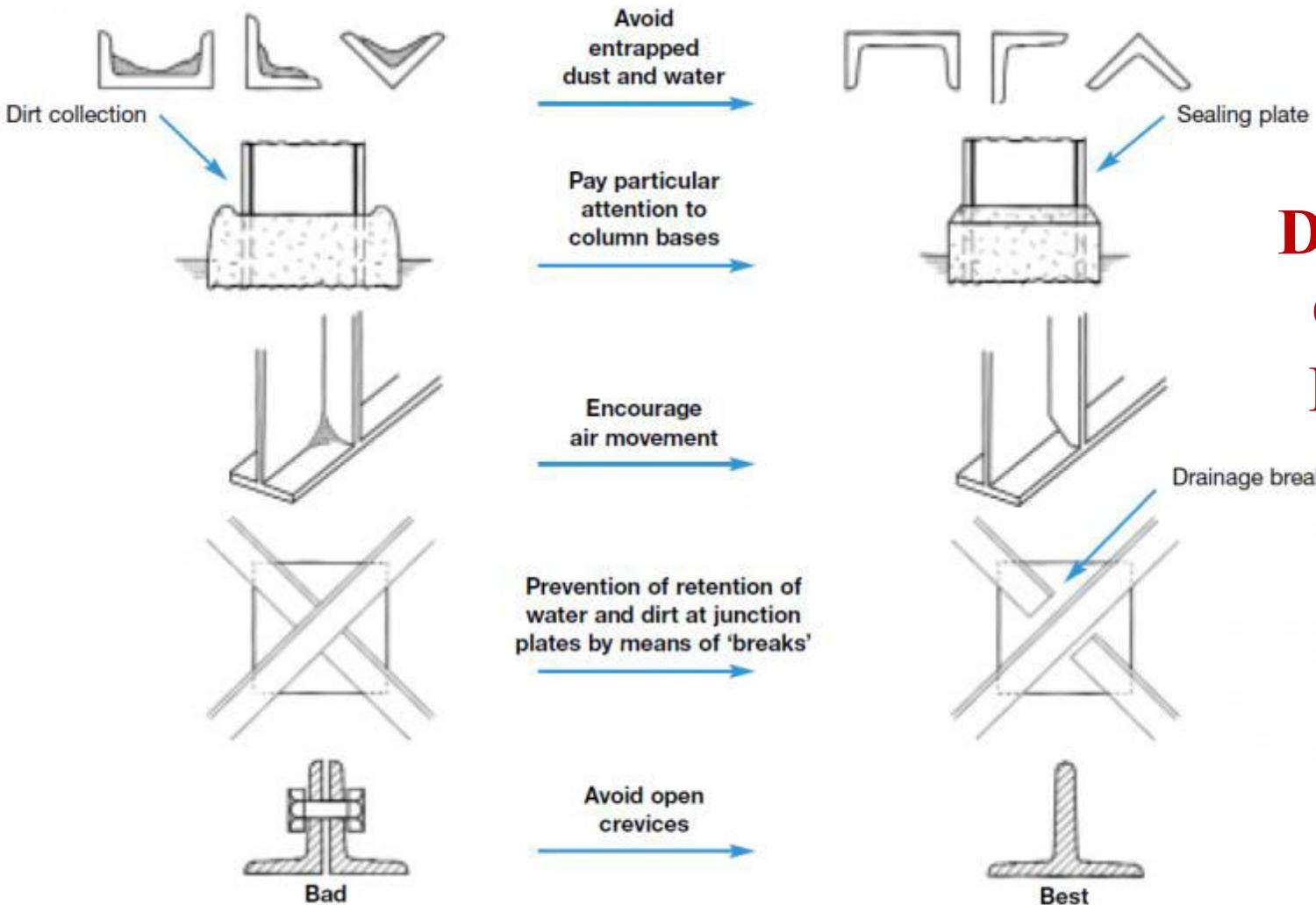
- 1. Proper Designing**
- 2. Using pure metal**
- 3. Using metal alloys**
- 4. Cathodic protection**
 - a. Sacrificial anodic protection
 - b. Impressed current cathodic protection
- 5. Modifying the environment**
- 6. Corrosion inhibitors**
 - a. Anodic inhibitors
 - b. Cathodic inhibitors
- 7. Protective coatings**
 - a. Anodic coatings
 - b. Cathodic coatings

Corrosion Protection/Control

1. Proper Designing

- Avoid contact of dissimilar metals
- Dissimilar metals should be as close as possible in Galvanic series
- Anodic material should be large
- Insulating fitting between dissimilar metals
- Prevent inhomogeneities
- No sharp edges or corners & crevices in joints
- Free circulation of air
- Uniform flow of liquids
- Prevent some areas of structure to stress

1. Proper Designing



DESIGN for Corrosion Protection

Corrosion Protection/Control

2. Using pure metal (impurity causes corrosion)

- 100% pure metal does not undergo corrosion

3. Using metal alloys (should be homogeneous)

- Alloys may change the metal structure to stable form
- Alloys may act as a protective coating

4. Cathodic Protection

Cathodic protection:

Principle is to make the base metal to be protected as cathode by connecting to a highly anodic metallic plate.

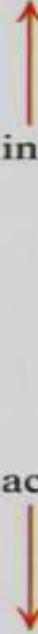
Two methods of cathodic protection are known:

- i) Sacrificial anodic protection
- ii) Impressed current cathodic protection

i) Sacrificial anodic protection:

- o The metallic structure to be protected is connected through a metal wire to a more anodic metal.
- o This will induce corrosion at the anodic metal.
- o Thus the more anodic metal sacrifices itself and gets corroded protecting the metallic structure.
- o Sacrificial anodes known are Zn, Mg, Al and their alloys.
- o Applications are: protection of underground pipelines, ship hulls and other marine devices, water tanks.

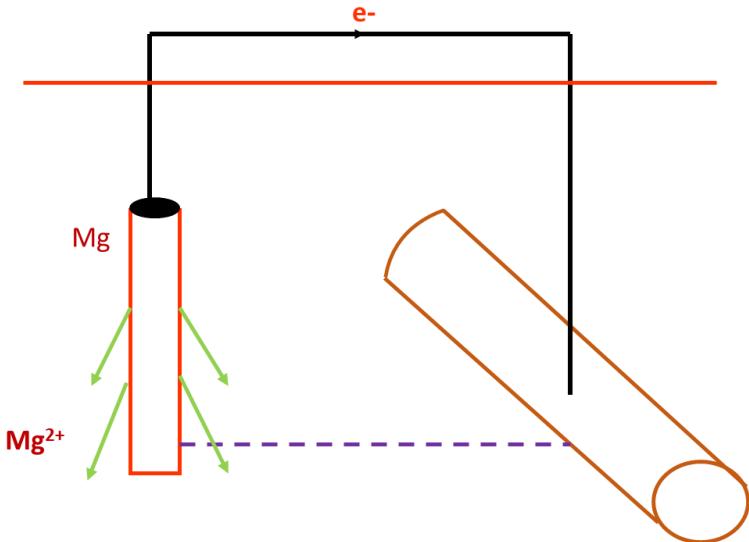
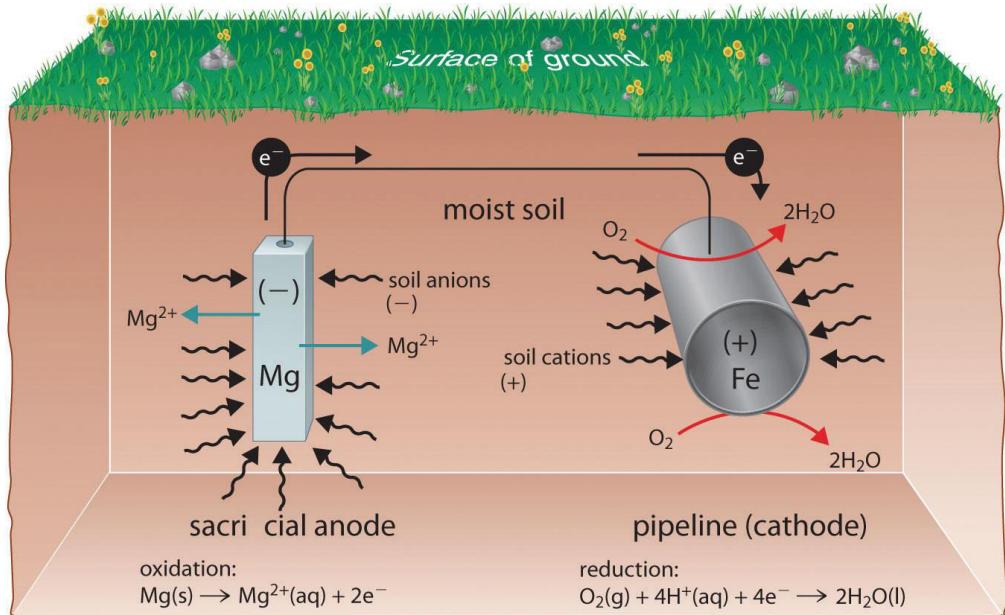
Table 17.1**The Galvanic Series**

 <p>Increasingly inert (cathodic)</p>	Platinum Gold Graphite Titanium Silver 316 Stainless steel (passive) 304 Stainless steel (passive) Inconel (80Ni–13Cr–7Fe) (passive) Nickel (passive) Monel (70Ni–30Cu) Copper–nickel alloys Bronzes (Cu–Sn alloys) Copper Brasses (Cu–Zn alloys) Inconel (active) Nickel (active) Tin Lead
 <p>Increasingly active (anodic)</p>	316 Stainless steel (active) 304 Stainless steel (active) Cast iron Iron and steel Aluminum alloys Cadmium Commercially pure aluminum Zinc Magnesium and magnesium alloys

Source: M. G. Fontana, *Corrosion Engineering*, 3rd edition. Copyright 1986 by McGraw-Hill Book Company. Reprinted with permission.

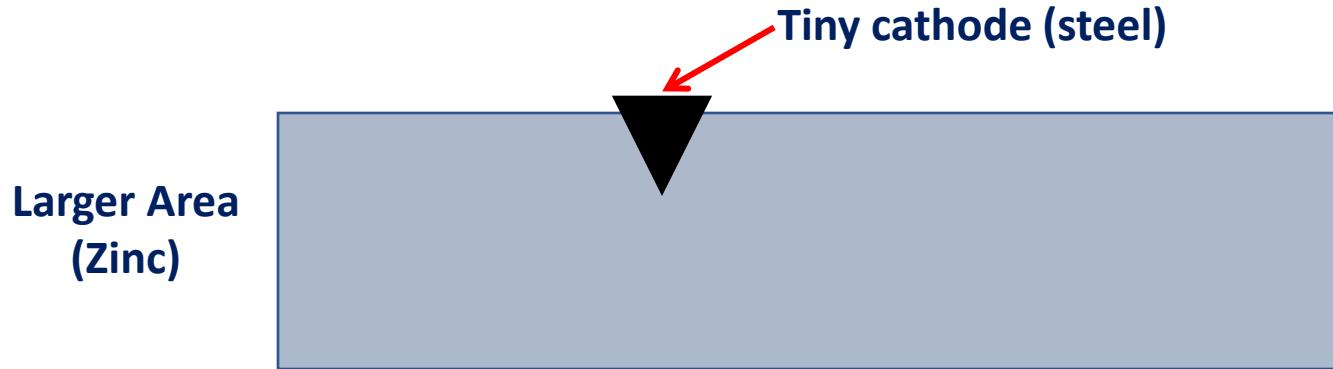
Sacrificial anodic protection

Sacrificial anodic protection - concept



Sacrificial Anodes

- Galvanization of Steel
- Dip steel sheet in molten zinc. Get a pretty thin coating.
- Zinc will be anode. Steel exposed by crack is the cathode. Since we have a huge anode having to be served by a small cathode, corrosion rate will be slow.



An example of an unfavorable area ratio. Bad deal: huge cathode, tiny anode

Another Example

Zinc is attached to the steel hull of the vessel



Corrosion control

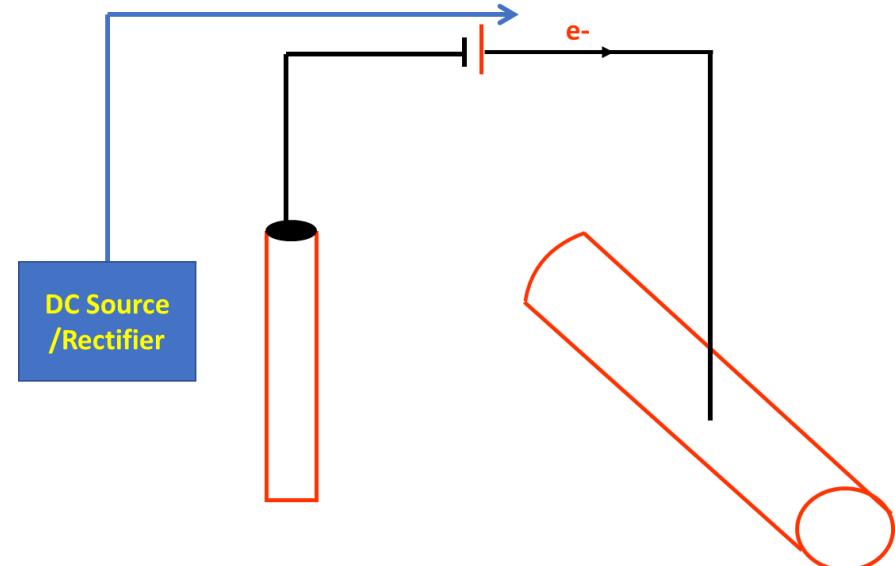
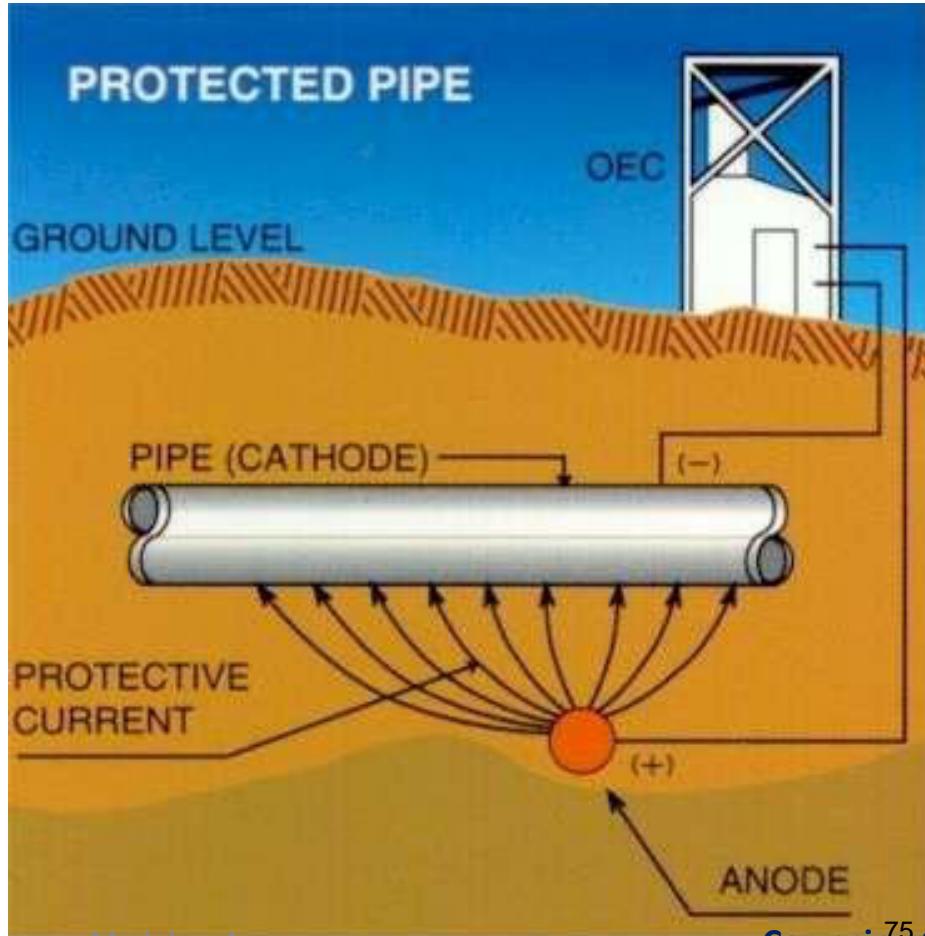
ii) Impressed current cathodic protection:

- o Impressed direct current is applied in the opposite direction to the corrosion current to nullify it.
- o Usually, one terminal of a battery is connected with an insoluble anode e.g. graphite electrode is immersed in black fill containing coke, gypsum, bentonite and sodium sulphate for good electrical conductivity.
- o The other terminal is connected to the metallic structure to be protected.
- o Since the current is impressed on the metallic structure, it acts as cathode and thus gets protected.
- o This method is usually used to protect underground water pipe lines, oil pipe lines, transmission lines, ships etc.

Impressed current cathodic protection

Impressed current cathodic protection - concept

Corrosion current of equal magnitude but opposite in direction applied to nullify corrosion current



Corrosion control

5. Modifying the environment

- Certain changes in the environment can be made to reduce acidic, oxygen or humidity which will reduce corrosion.
- Oxygen can be removed by mechanical agitation or by addition of hydrazine or sodium sulphite.



- Dehumidification is carried out by introducing certain substances like dehydrated alumina, anhydrous silica gel etc. (suitable for closed areas).
- Neutralization of acidic environment containing H_2S , SO_2 , HCl , CO_2 etc., can be done by introducing alkaline neutralizers like ammonia gas, lime, naphthionic soaps, caustic etc., (Used in refinery to protect the equipment).

Corrosion Protection/Control

6. Corrosion inhibitors (Reduce the rate of corrosion)

- Two types – anodic and Cathodic inhibitors
 - ✓ **Anodic inhibitors** – form sparingly soluble products which are adsorbed on the surface of metal, protect from corrosion
 - e.g. Phosphate, chromate and tungstate
 - ✓ **Cathodic inhibitors** – Delay reduction reaction occurs at cathode
 - e.g. organic amines, mercaptans, thiourea and substituted urea

7. Protective coatings

Protective coating provide a physical barrier between the metal and the environment.

- They not only give corrosion protection but also add to the decorative value of the system.
- Coatings are broadly divided as:
 - a) Inorganic coatings : metallic and chemical conversion coatings
 - b) Organic coatings : paints, varnishes, enamels, lacquers
- Protective coatings are classified as:
 - I. metallic coatings
 - II. chemical conversion coatings
 - III. organic coatings and linings
 - IV. ceramic protective coatings

Protective coatings (Surface preparation)

The most important step before protective coatings are applied to metals is *surface preparation*.

- o Surface preparation is a process to remove rust, oxide scales, oil, grease, dust etc.
- o If these materials are not removed, the protective coating will not be smooth, uniform, cohesive and will not adhere to the metallic surface.
- o Hence, mechanical and electrical methods are used to prepare the surface of the metallic article to be coated clean and free of these impurities.
- o Mechanical cleaning, sandblasting, solvent cleaning, alkali cleaning, acid pickling and etching are normal processes followed for surface preparation of the article to be coated.

a) Mechanical cleaning:

- o Useful for removing loose scales and rust.
- o Hammering, wire brushing, grinding, pneumatic blasting, polishing are the methods commonly used.

Protective coatings

b) Sand blasting:

- o Fine sand or abrasive material along with air stream at a pressure of 25-100 atm. is impinged on the metal surface.
- o This will produce enough roughness for good adherence of the protective coating.
- o Though the method is expensive, it is quite fast and useful.



Protective coatings

c) Solvent cleaning:

- o Solvent cleaning is mainly used to remove oil, grease and rust from the base metal.
- o Alcohols, xylene, toluene, chlorinated hydrocarbons are used.
- o Hot water cleaning is followed after solvent cleaning is done.



Protective coatings

d) Alkali cleaning:

- o Cleaning of the base metal with sodium hydroxide, trisodium phosphate, sodium silicate, soda ash etc., is carried out to remove old paint coatings soluble in alkaline medium.
- o After alkali cleaning, washing is done with 1% chromic acid solution.

e) Acid pickling and etching:

- o Base metal is dipped inside the acid solution at higher temperature for long periods of time.
- o This treatment ensures cleaning of the base metal surface free from all kinds of impurities including oils, greases, rust etc.,
- o H_2SO_4 , HCl , HF , H_3PO_4 , HNO_3 are the acids commonly used for pickling and etching.

Protective coatings

Metallic coatings:

- a) Anodic coatings
- b) Cathodic coatings

a) Anodic coatings:

- o Anodic coatings are given on cathodic metals using metals which are more anodic.
- o Zinc, aluminium, cadmium coatings on iron are anodic coatings.
- o If the coating breaks, then a galvanic couple is set up and corrosion rate gets enhanced.
- o During this process, the anodic coating gets disintegrated, but it protects the cathodic base metal.
- o Hence, the anodic metal sacrifices itself to protect the base metal.
- o This type of coating is known as *galvanization*.

Protective coatings

Cathodic inhibitors/coatings:

- o Cathodic coatings are given on anodic metals using metals which are more cathodic.
- o Coating of tin, chromium, nickel on iron surface are cathodic coatings.
- o If there is a discontinuity in the coating, then galvanic couple will form with base metal as anode and the coated metal as cathode.
- o Then the process of corrosion will start by the base metal ions going into solution and the metal deteriorating.
- o To avoid this, the article is checked and re-plated periodically so that there is no discontinuity in the coating.

Protective coatings

Methods of metallic coatings:

- a) Hot dipping
- b) Electroplating
- c) Electroless plating
- d) Metal cladding
- e) PVD
- f) CVD

Protective coatings

Methods of metallic coatings:

- a) Hot dipping
- b) Electroplating
- c) Electroless plating
- d) Metal cladding
- e) PVD
- f) CVD

a) Hot dipping:

Two types of hot dipping techniques to protect iron metal are known:

- i) **Galvanizing:** Dipping the base metal iron in molten zinc metal solution
- ii) **Tinning** : Dipping the base metal iron in molten tin metal solution.

Electroplating

- o It is a process by which a coating metal is deposited on the base metal by passing direct current through an electrolytic solution, containing the soluble salt of the coating metal.
- o Electroplating is done for improving
 - a) corrosion resistance
 - b) wear resistance
 - c) chemical resistance
 - d) surface hardness
 - e) appearance
- o Both ferrous and non-ferrous metals are plated with Ni, Cr, Cu, Zn, Pb, Al, Ag, Au, Sn etc.
- o Electroplating is mainly used in automobile, aircraft, refrigerator, chemical and electrical appliances etc.

Important Factors of electroplating

- **Cleaning of the article is essential for strong adherence of the electroplating:**
 - Scraping, grinding, sand blasting, wire brushing, solvent cleaning and acid pickling are used for surface cleaning.
 - A well cleaned and properly pre treated surface of any material to be electroplated is necessary for obtaining the coating of long life.
- **Concentration of the electrolyte is another important factor:**
 - Low concentration of metal ions will give uniform coherent deposition.
 - To maintain low conc. of metal ions, complexing agents are added to the electrolyte.
- **Thickness of the deposition should be optimised to get a strong and adherent deposition:**
 - For corrosion protection multiple coatings are given to get impervious coating without any discontinuity.
 - For decorative purpose, thin coating is given.
- **Current density (C.D.)**
 - Current density is the current per unit area of the article being plated (amps cm^{-2}).
 - The C.D. should be maintained at optimal level to get uniform and adherent deposition.

Important Factors of electroplating

- **Additives to electrolytic bath**

- Additives to electrolyte are added in small quantities to get strong adherent deposition.
- Commonly used additives are gelatin, glue, glycine, boric acid etc. and brighteners for bright plating.

- **pH of the bath:**

- For a good electrodeposit, the pH of the bath must be properly maintained. For most plating baths, pH ranges from 4 to 8.

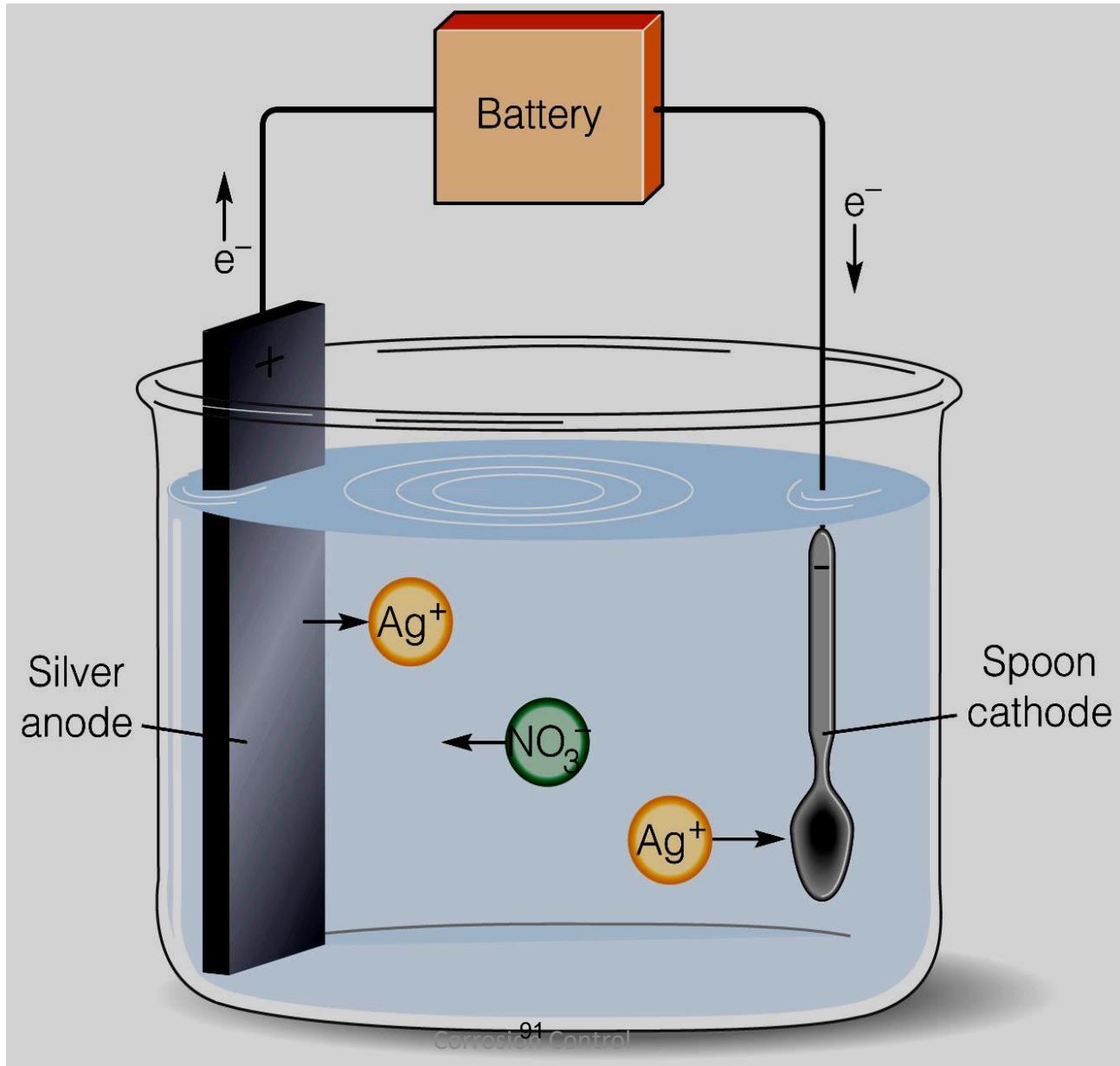
- **Method of Electroplating:**

- Method depends upon the type of metal to be electroplated, the size and type of article to be electroplated.
- Its main objectives and economics are also considered.

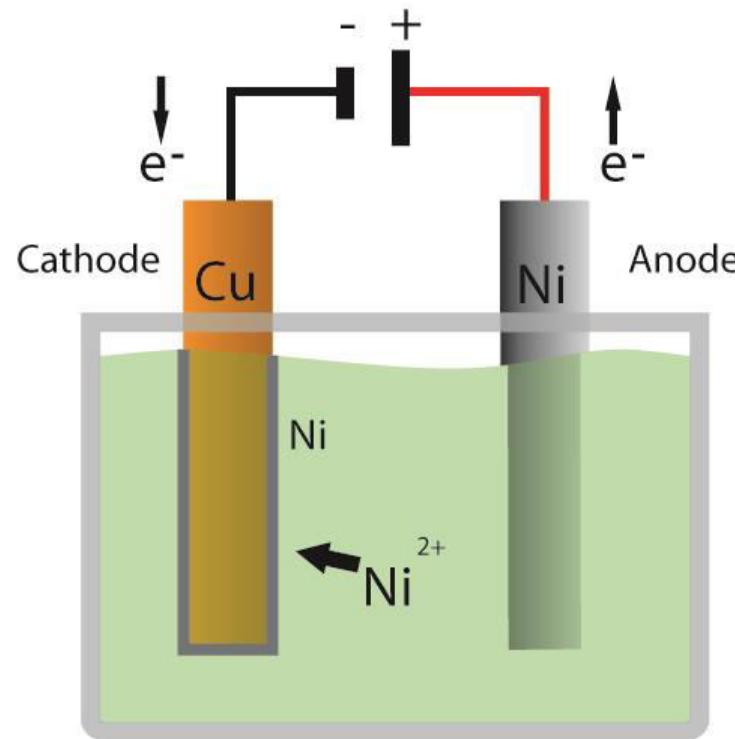
Plating bath solution

- o It is a highly conducting salt solution of the metal which is to be plated.
- o However, non-participating electrolytes are added to the bath solution to increase the conductivity and the throwing power.
- o The level of the plating bath should cover completely the cathode and sufficient area of anode.
- o Heating if required is provided by heating coils or hot gases.
- o Air sparger or nitrogen sparger is employed to introduce convection current in the plating bath solution.
- o It should possess sufficient throwing power. Hence mixture of two or more electrolytes is used for preparing electrolytic bath.
- o It should be good conductor and highly soluble.
- o It should not undergo hydrolysis, oxidation, reduction and other chemical changes.

Electroplating



Electroplating with Nickel on Copper



Copper Cathode is reduced
(accepts electrons)

Nickel Anode is oxidized
(gives electrons)

Ni^{2+} ions within solution become attracted
to Copper cathode

Electroless plating

Otherwise known as,

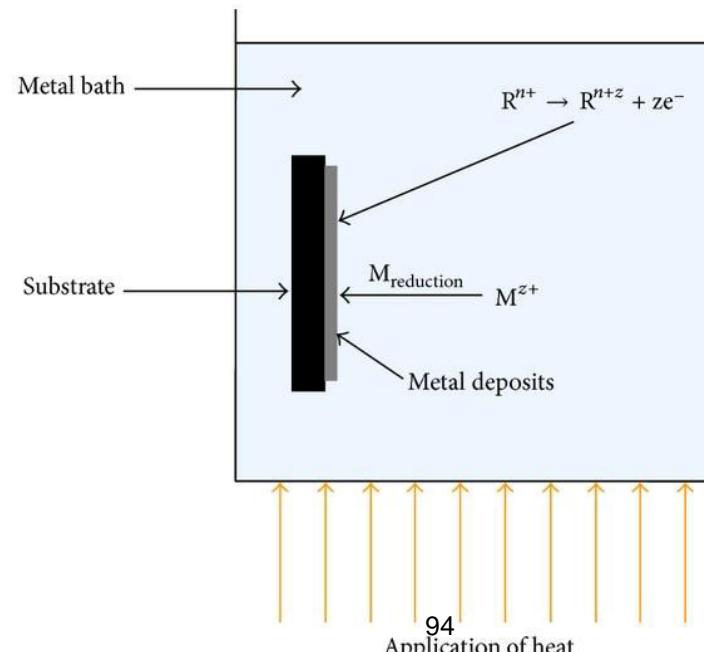
- Chemical plating
- Auto-catalytic plating
- Non-galvanic plating

Electroless plating method

- Involves several simultaneous reactions in an aqueous solution, which occur **without the use of external electrical power.**
- The process is an **autocatalytic chemical reaction.**
- The deposition rate is normally **12.5 – 25 μm (.0005 – .001 in).**
- The plating **thickness tends to be uniform** compared to electroplating due to the absence of electric fields and the associated problems in making them uniform.

Electroless plating

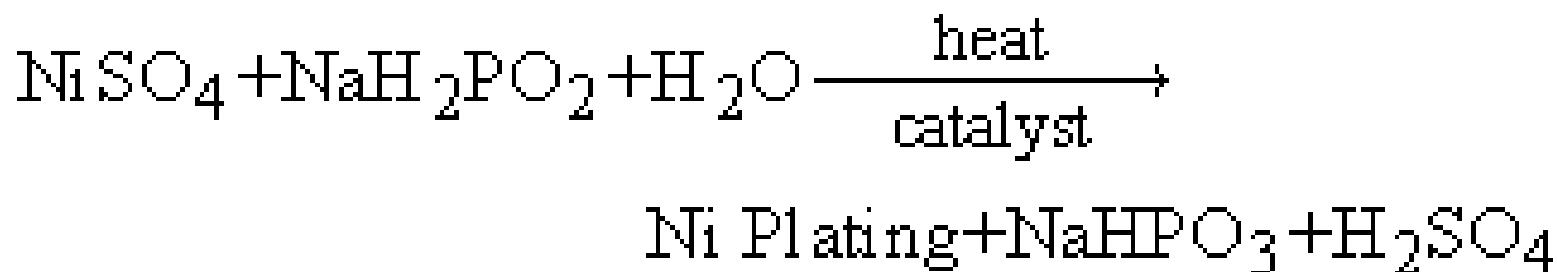
- Typically nickel and copper are used in electroless plating.
- In the case of nickel, the deposits are dense, relatively hard and brittle.
- Electroless nickel is not as bright as electroplated, easy to solder and braze, but difficult to weld.
- Autocatalytic plating are widely used for machine frames, base plates, fixtures, some machine parts where metal-to-metal wear applications are needed and the conventional oils and greases can not be used.



Theory of Autocatalytic Plating

In autocatalytic plating, the metal ion is reduced to a metal only on a specific surface, which must have a catalyst present before the reaction can begin.

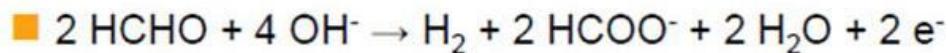
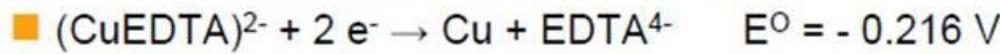
The electroless plating involving a nickel sulfate bath has the following reaction:



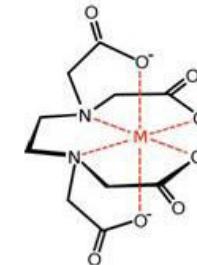
Copper electroless deposition

Ethylenediaminetetraacetic acid, EDTA

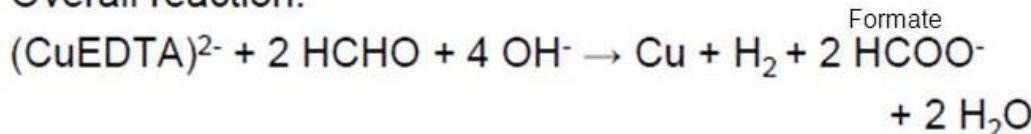
Two subreactions (reduction and oxidation):



Formaldehyde



Overall reaction:



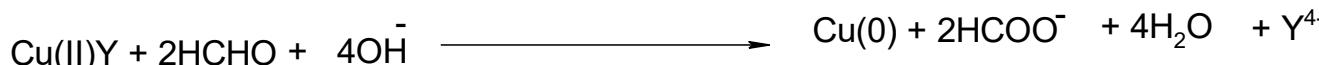
$$E^\circ = E^\circ(\text{reduction}) - E^\circ(\text{oxidation}) =$$

$$-0.216 \text{ V} - -1.14 \text{ V} = 0.924 \text{ V}$$

$$\rightarrow \Delta G^\circ = -zFE^\circ < 0$$

- the process is spontaneous and the solution metastable
- homogeneous precipitation is kinetically inhibited
- the heterogeneous deposition reaction is catalyzed

Copper electroless deposition is done by reduction of alkaline solution containing copper(II) ion Stabilized by EDTA. Here formaldehyde acts as reducing agent.



Difference between Electroplating and Electroless plating

Electroplating

- External current source
- Non catalytic process
- Suitable only for conducting materials
- Difficult for hollow parts
- Thickness may vary

Electroless Plating

- No external current source
- Catalytic process
- Suitable for conducting and Insulating materials
- OK for hollow parts and blind holes
- Constant thickness

Physical Vapor Deposition

Physical ejection of material (atoms, ions) and condensation and nucleation on top of material to be coated

Physical ejection by

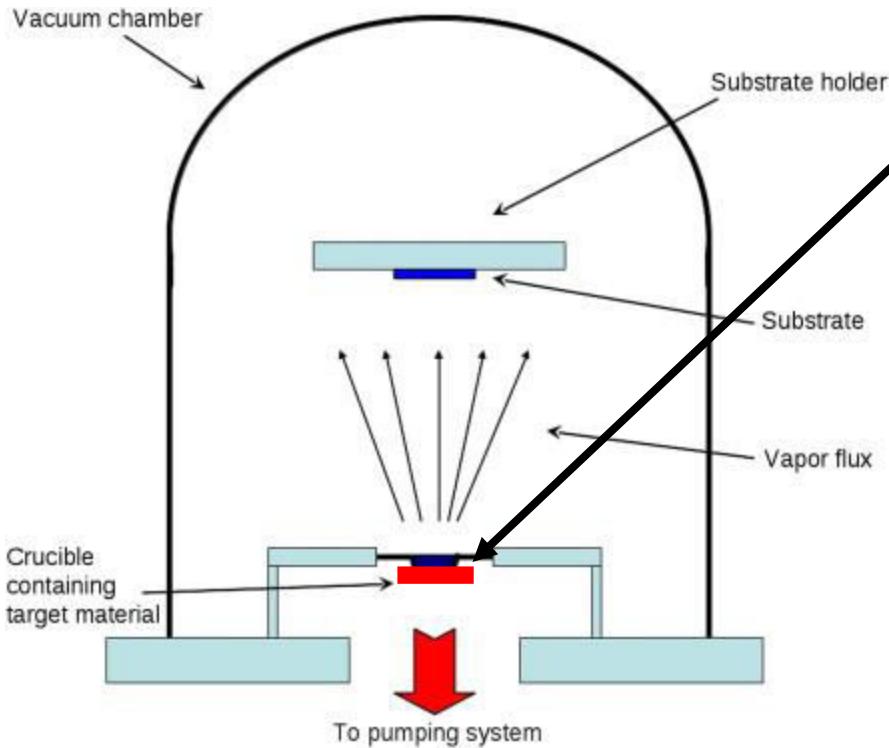
- Heating – Thermal, E-beam
- Sputtering – RF, DC
- Ion implantation

Chemical reaction is possible by maintaining reactive gas atmosphere

Applications

1. This process is widely used to produce decorative coatings on **plastic parts those are resembling shiny metal.**
2. Many automobile parts are plastic with a PVD coating of aluminium.
3. A lacquer coating is applied over the decorative coating to provide corrosion protection.
4. This process is also used to apply relatively **thick (1mm) coatings** of heat resistant materials on jet engine parts, A special alloy of chromium, aluminium and yttrium is used for this type of coating.

Thermal Evaporation



Heating by

- Direct resistive heating
- In-direct Resistive heating
- Induction heating
- Laser Ablation

Evaporated material in vapor form is condensed on top of substrate (surface to be coated)
Vacuum is maintained to avoid unnecessary reactions

1-100 µm thick coating

Eg. Metal evaporated in vacuum leads to metal coating,
Metal evaporated with particular oxygen atmosphere leads to metal oxide coating (Reactive Thermal Evaporation)

Thermal Evaporation

- Requirement – coating materials should have **low melting point, high vapor pressure** in given temperature e.g. Al, Au can be coated
- W, Ti cannot be coated → higher melting point (low vapor pressure)
- Purity ==> source materials purity and vacuum

Advantages

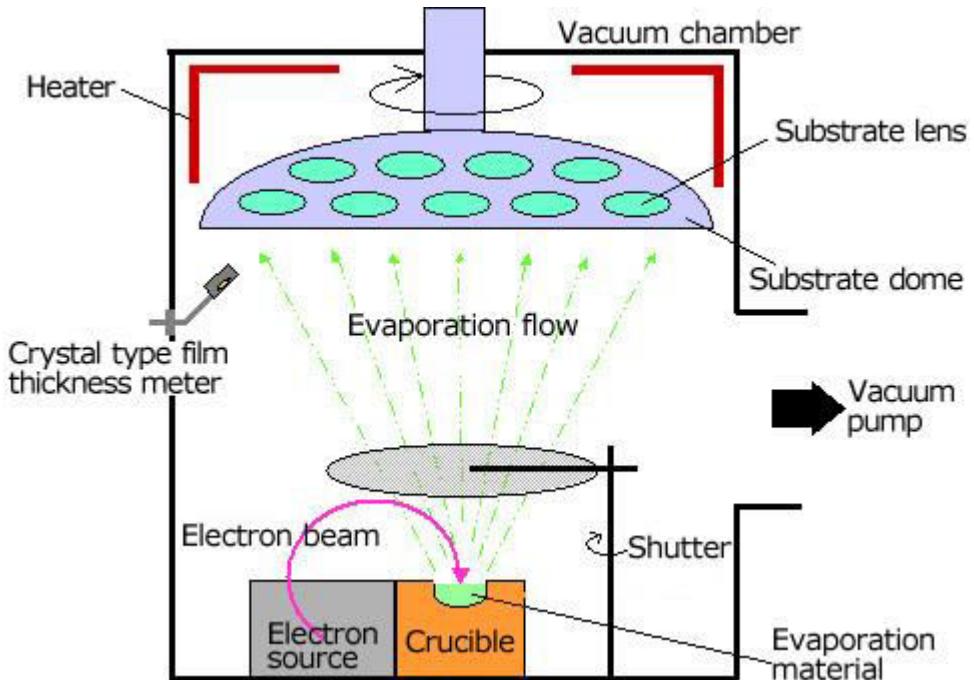
Simple and cheap, excellent purity, less surface damage on the substrate

Disadvantages

Limited to materials with low melting point, filament limits the materials that can be deposited (temperature)

E-beam evaporation

- Target anode is bombarded with electron beam – charge tungsten filament under high vacuum
- Atoms transformed to gaseous phase due to the electron beam and deposited on top of heated substrate (materials to be coated)



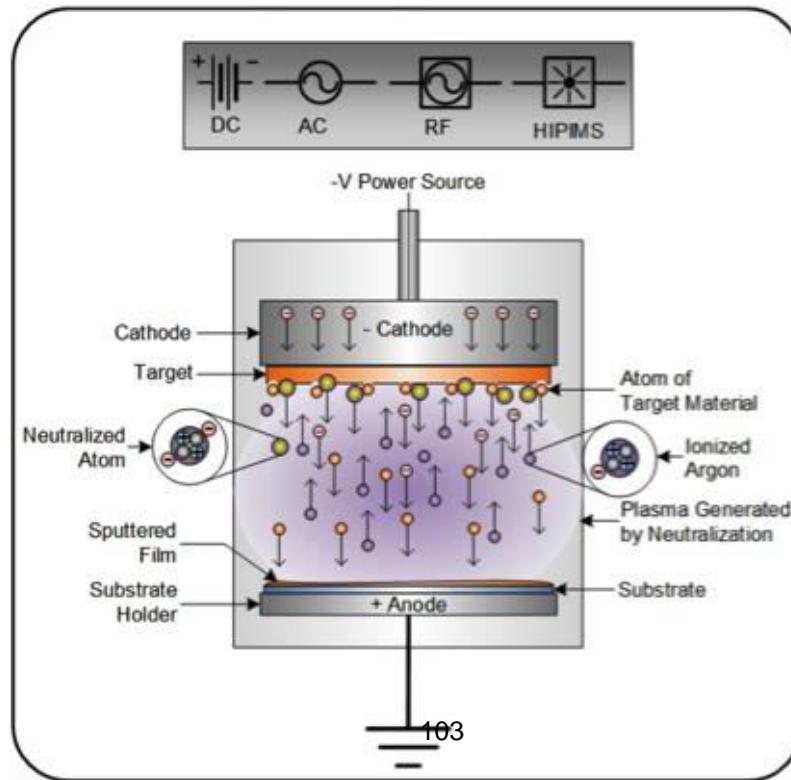
Advantages – higher deposition rate
 Disadvantages – Filament degradation due to non uniform evaporation of the material

Sputtering

A popular **method for adhering thin films on to a substrate**.

Sputtering is done by bombarding a target material with a charged gas (typically argon) which releases atoms in the target that coats the nearby substrate.

It all takes place inside vacuum chamber under low pressure.



Applications

- Sputtering is used extensively in the semiconductor industry to deposit thin films of various materials in integrated circuit processing.
- Thin anti reflection coatings on glass for optical applications are also deposited by sputtering.
- An important advantage of sputter deposition is that even materials with very high melting points are easily sputtered.
- Deposited films have a composition close to that of the source material.

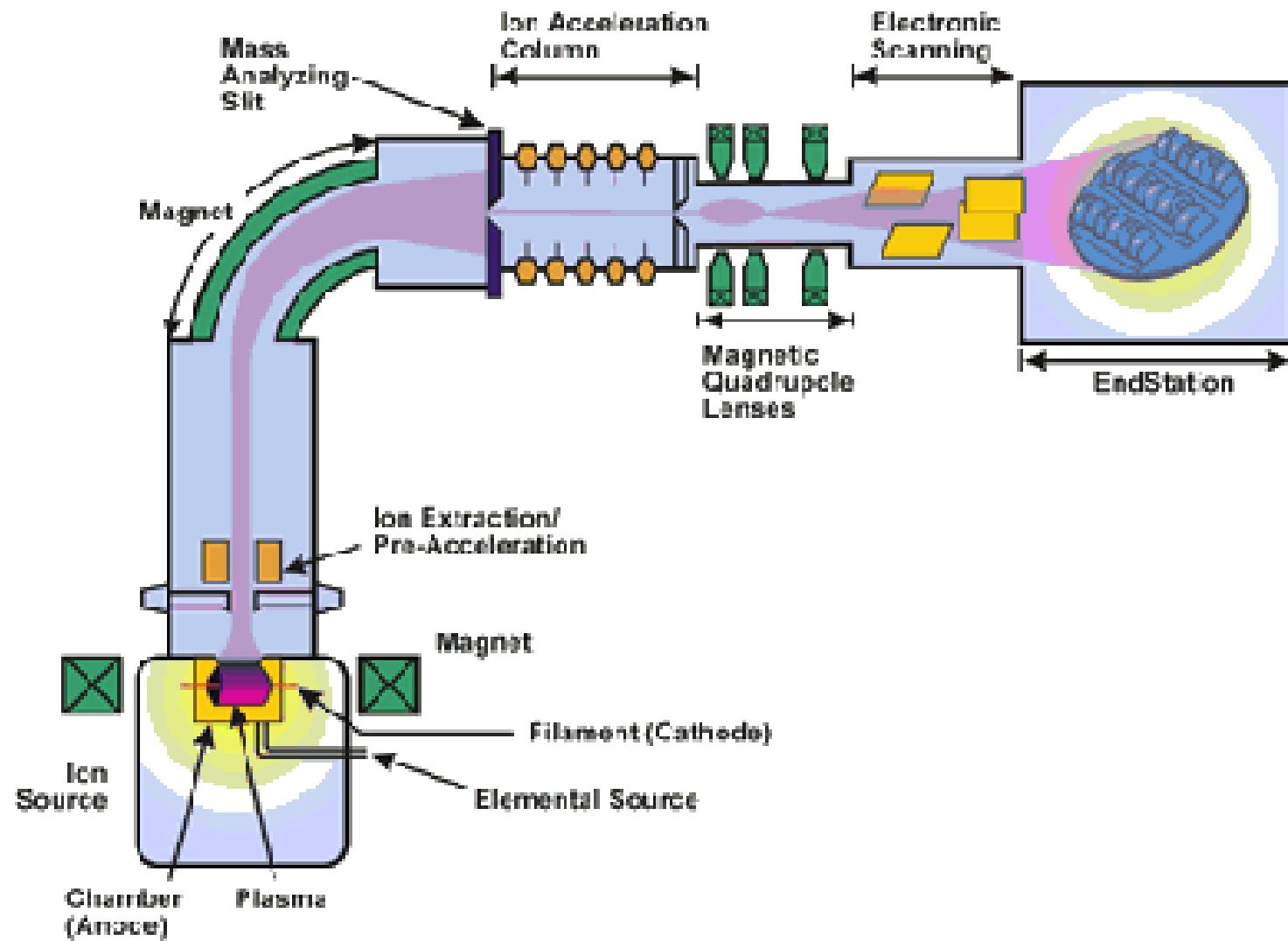
Ion Implantation Method

- 1.A third variation of the **PVD process** is **ion implantation** .
- 2.Metal is evaporated thermally and plasma is established to ionize the evaporating species
- 3.Evaporant ions bombard the substrate with energy
- 4.They physically implant into the **substrate to produce an extremely strong coating bond.**
- 5.Sputter and ion plated coatings are used in **design for very thin films for electrical, optical and wear-resistant applications.**
- 6.The wear properties of tools are **widely enhanced by hard thin film coatings.**

Ion Implantation

1. The common systems in use are ion implantation, laser treatment and electron beam treatment.
2. In ion implantation ions of specific element with sufficient energy are impinged on the surface of a material with sufficient energy.
3. The ions so impinged are embedded into the atomic lattice of substrate. This process is performed in a vacuum chamber.
4. Usually ion gun produce the ions. It is done by passing the gas through an electron beam or plasma. The gas atoms on collision with the electron beam or with the species in plasma become ions.
5. The ions are accelerated by an applied magnetic field. These ions impinge on the work surface. The surface of the metal is hardened by creating atomic defects or misfits by the impinged ions.
6. The depth of implantation is usually about $0.1\mu\text{m}$. However, the sphere of influence is much deeper, may be a micrometer.

Ion Implantation



PVD applications

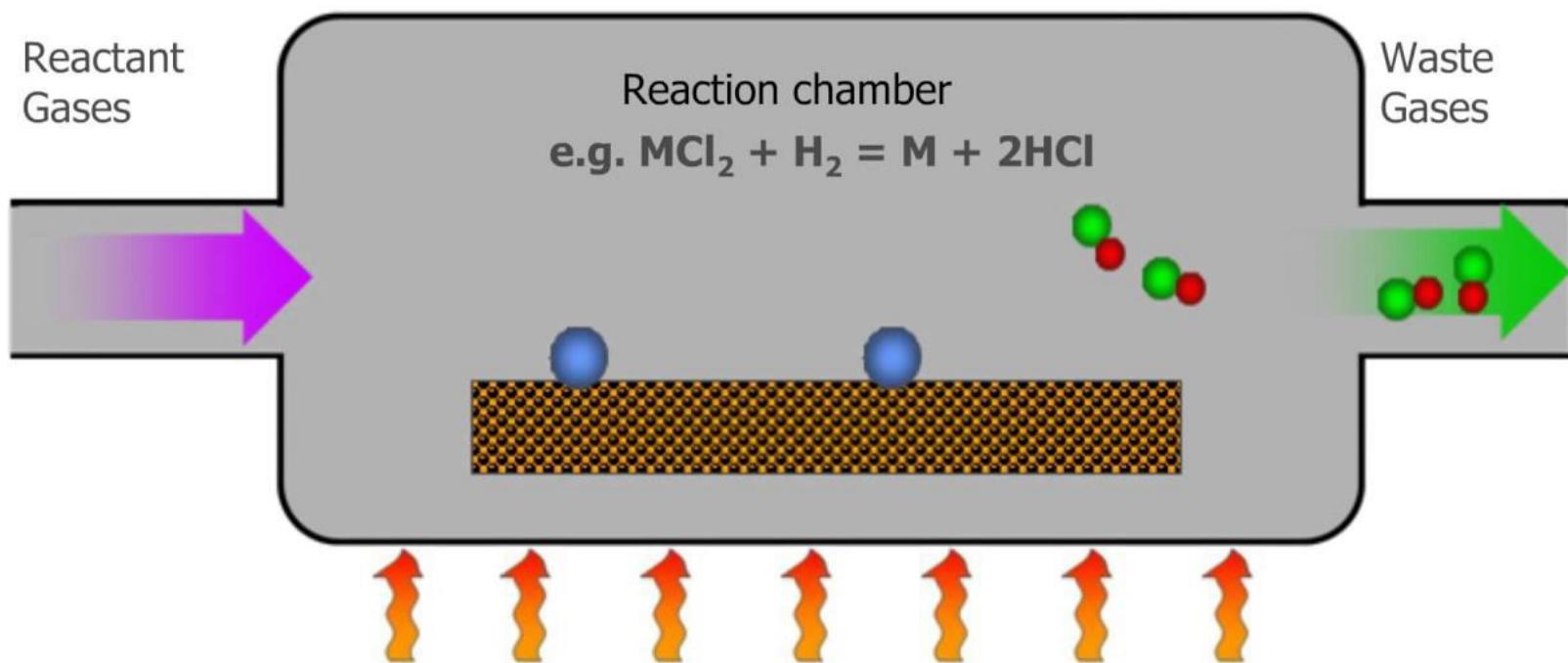
Coating	Hardness (HV)	Colour
Titanium nitride	2900	gold
Zirconium nitride	2800	gold
Titanium aluminum nitride	2600	brown
Titanium carbonitride	4000	silver
Chromium nitride	2500	silver
Amorphous diamond like carbon	1000 – 5000	black

Chemical Vapor Deposition (CVD)

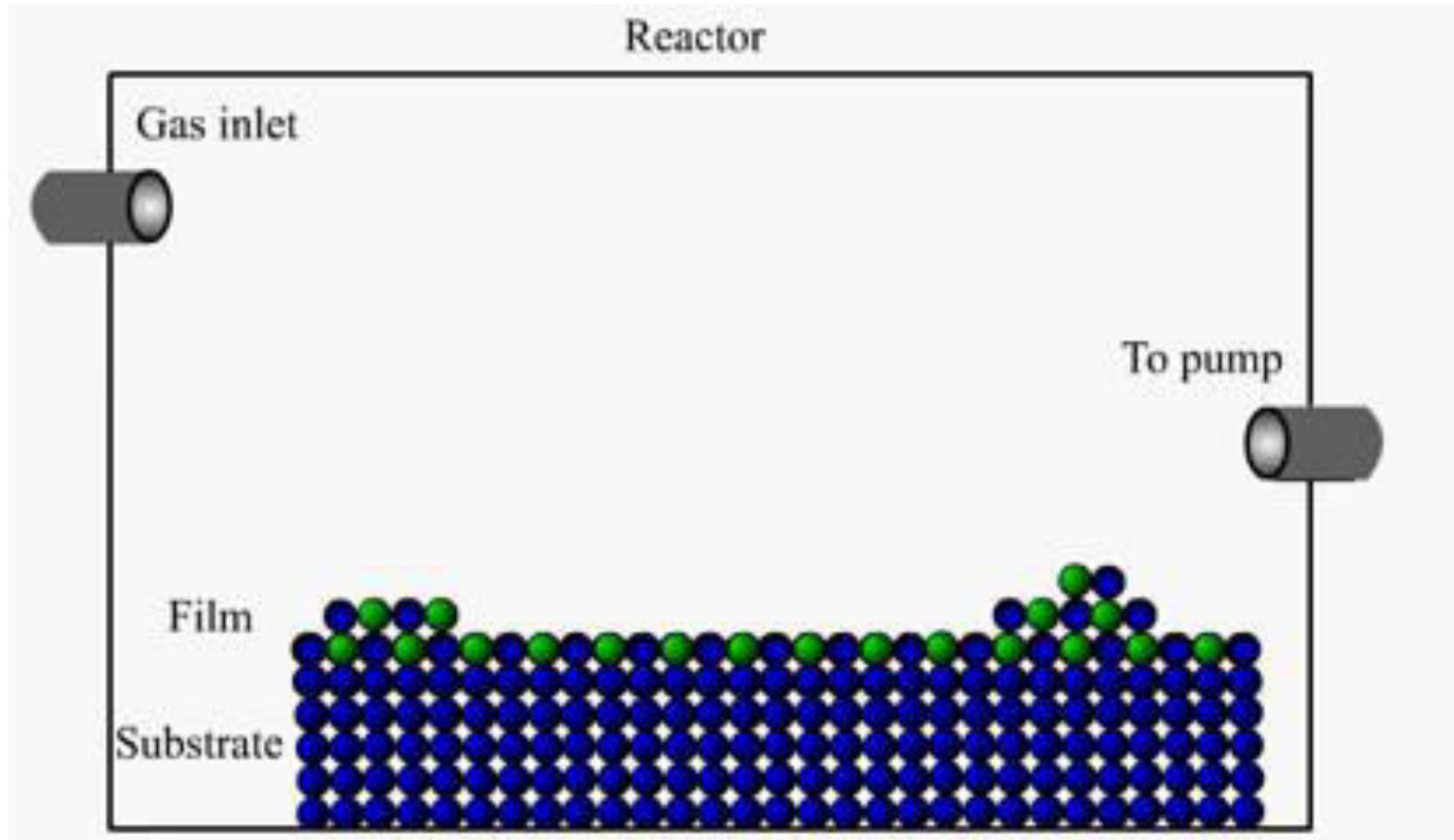
- Chemical vapour deposition or CVD is a process whereby a solid material is deposited from a vapor by a chemical reaction occurring on or in the vicinity of a normally heated substrate surface.
- The solid material is obtained as a coating, a powder, or as single crystal
- By varying the experimental conditions such as
 - substrate material
 - substrate temperature
 - composition of the reaction gas mixture
 - total pressure gas flows, etc.materials with different properties can be grown
- CVD is an example for solid-vapor reaction

Chemical Vapor Deposition (CVD)

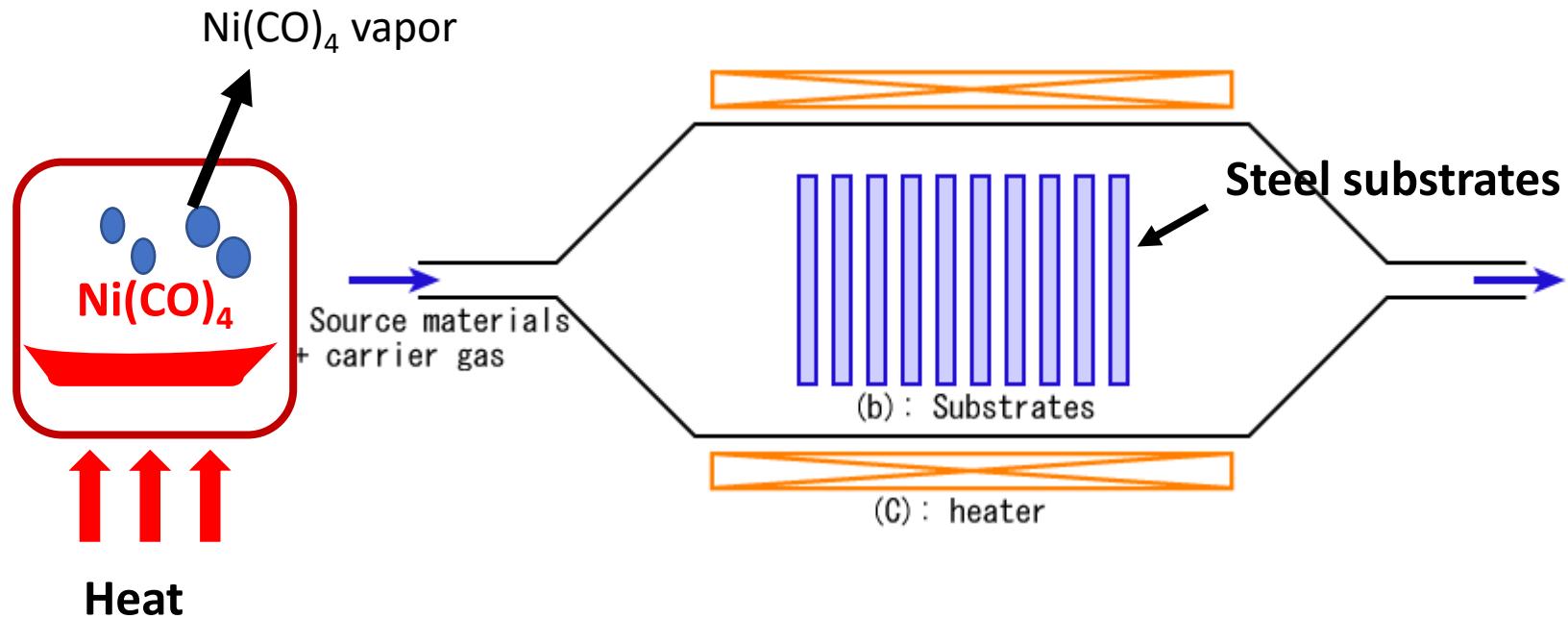
"CVD is a process where gaseous precursors react to form a solid coating on a heated substrate"



Chemical Vapor Deposition (CVD)



Nickel Coating on top of Steel



Nickel Carbonyl vapor decomposes on top of heated steel substrate to form nickel coating and gaseous by-products

Optimized Temperature and flow rate

Chemical Vapor Deposition (CVD)

CVD Apparatus

A CVD apparatus consist of several basic components

➤ Gas delivery system	– For the supply of precursors to the reactor chamber
➤ Reactor chamber	– Chamber within which deposition takes place
➤ Substrate loading mechanism	– A system for introducing and removing substrates, mandrels etc.
➤ Energy source	– Provide the energy/heat that is required to get the precursors to react/decompose.
➤ Vacuum system	– A system for removal of all other gaseous species other than those required for the reaction/deposition.

Chemical Vapor Deposition (CVD)

- **Exhaust system** – System for removal of volatile by-products from the reaction chamber.
- **Exhaust treatment systems** – In some instances, exhaust gases may not be suitable for release into the atmosphere and may require treatment or conversion to safe/harmless compounds.
- ***Process control equipment*** – Gauges, controls etc to monitor process parameters such as pressure, temperature and time. Alarms and safety devices would also be included in this category

This coating finds application on glass containers to make explosion or shatter resistant glasses.

Advantages of CVD over PVD

- ✓ **CVD films are generally quite conformal**, i.e. the ability of a film to uniformly coat a topographically complex substrate
- ✓ **Versatile** – any element or compound can be deposited
- ✓ **High purity** can be obtained
- ✓ **High density** – nearly 100% of theoretical value
- ✓ **CVD films are harder** than similar materials produced using conventional ceramic fabrication process
- ✓ **Material formation well below the melting point**
- ✓ **Economical in production**, since many parts can be coated at the time

Disadvantages of CVD

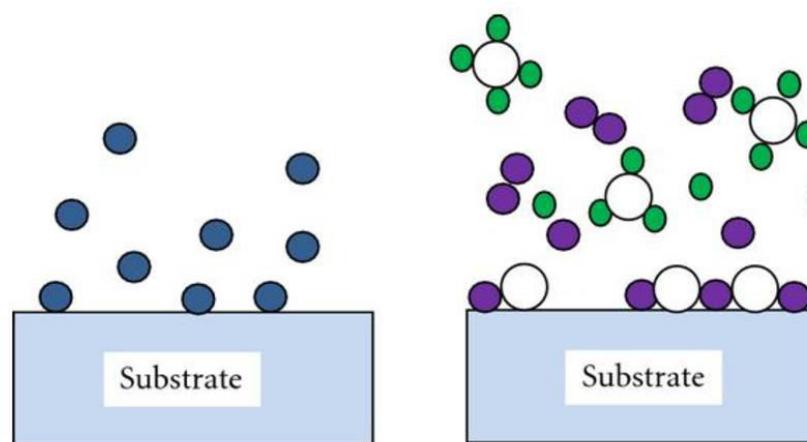
- ✗ Need to have precursors – volatile near room temperature.
- ✗ Most of the precursors are toxic or corrosive.
- ✗ Some precursors are very costly.
- ✗ Deposition at elevated temperatures has restrictions on substrates used.
- ✗ All surfaces in the reaction chamber get coated.
- ✗ Separate process and reaction must be developed for each coating.
- ✗ Some of the gases are toxic and dangerous.

CVD applications

- **Coatings** – Coatings for a variety of applications such as wear resistance, corrosion resistance, high temperature protection
- **Semiconductors and related devices** – Integrated circuits, sensors and optoelectronic devices
- **Fiber optics** – for telecommunication
- **Used in the microelectronics industry** to make films serving as dielectrics, conductors, passivation layers, oxidation batteries and epitaxial layers

VD vs CVD

PVD	-	CVD
Low temperature process (500 °C)	-	High temperature process (1000 °C)
Thin coatings	-	Thick and thin coatings
Non-uniform coatings	-	Uniform coatings
Sharp cutting edges possible	-	Larger honing radius needed
Tough cutting edges	-	Wear resistant coatings

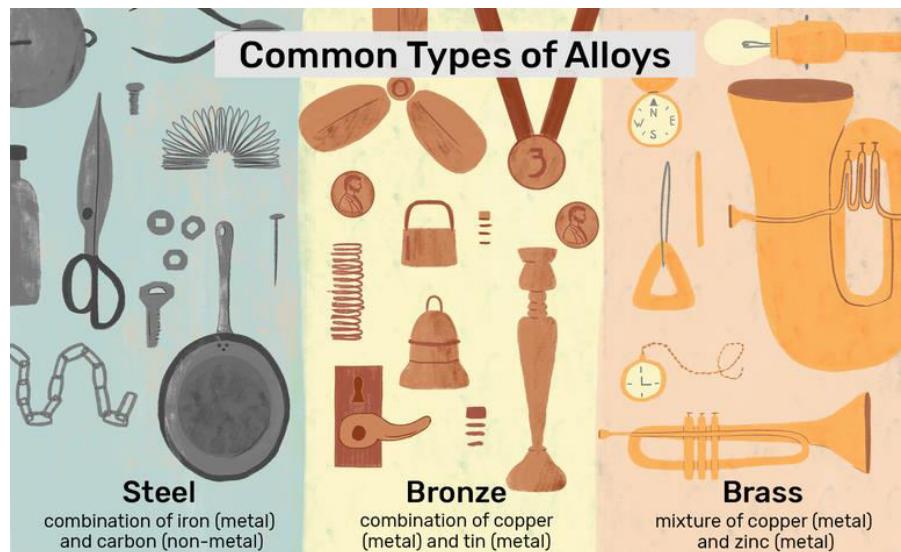
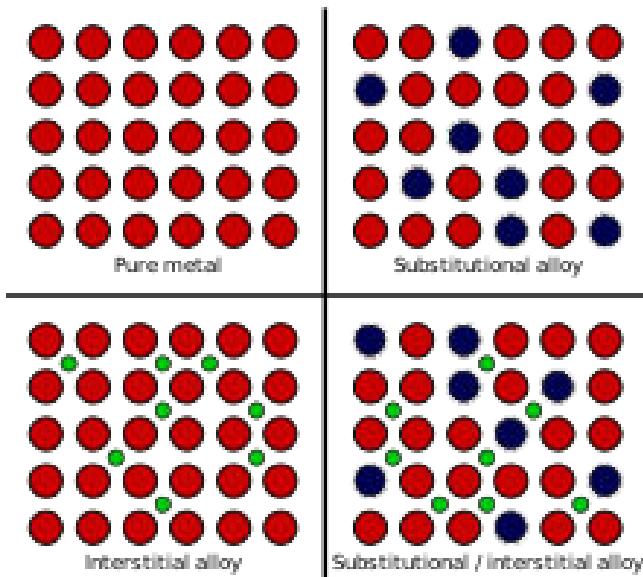


Alloys

Alloy is a homogeneous substance formed by mixing two or more elements, at least one of them being a metal.

Alloys are of three types:

- Alloys which are formed by **two or more metals**; e.g. Cu-Zn (Brass)
- Alloys which are formed between **a metal and a non-metal**; e.g. Steel
- Alloys which are formed between **mercury and another metal**; e.g. Zinc amalgam



Purpose of alloying is to get

- a) Increased mechanical strength
- b) Reduced chemical reactivity
- c) Improved corrosion resistance
- d) Better hardenability
- e) Increased/Reduced electrical conductivity
- f) Increased/Reduced temperature stability
- g) Grain size control
- h) Improved machine ability
- i) Improved ductility
- j) Better wear resistance

Characteristics of alloys

- a) **Hardness and tensile strength** of the alloy is **higher** than its constituents
 - *Tensile strength of iron is increased by 10 fold by alloying with 1% Carbon*
- b) **Melting points of alloys** is generally **lower** than the melting points of the constituents
 - *Solder melts at 183°C while its constituents Pb melts at 327°C and Sn melts at 232°C*
- c) **Alloys are less conductive** than pure metals
 - *Small quantity of impurities in copper will reduce its conductivity*
- d) **Colour of alloy gets modified** as compared to the individual metals
 - *Red coloured copper and Silver white Zinc will get modified to Yellowish brown in brass*
- e) **Chemical Properties are modified** i.e. either enhanced or depressed
 - *Dissolution of alloy in HCl is lower compared to its constituent metals*
- f) **Corrosion:**
 - The most useful property of alloying is its ability to resist corrosion.
 - Generally alloys are more resistant to corrosion than pure metals.
e.g. Stainless steel (an alloy of Fe, C, Ni and Cr) is not corroded by atmospheric conditions though pure Fe corrodes heavily in moist environment.
- g) **Solidification character** of an alloy is more suitable for making a casting.

Significance of Alloying

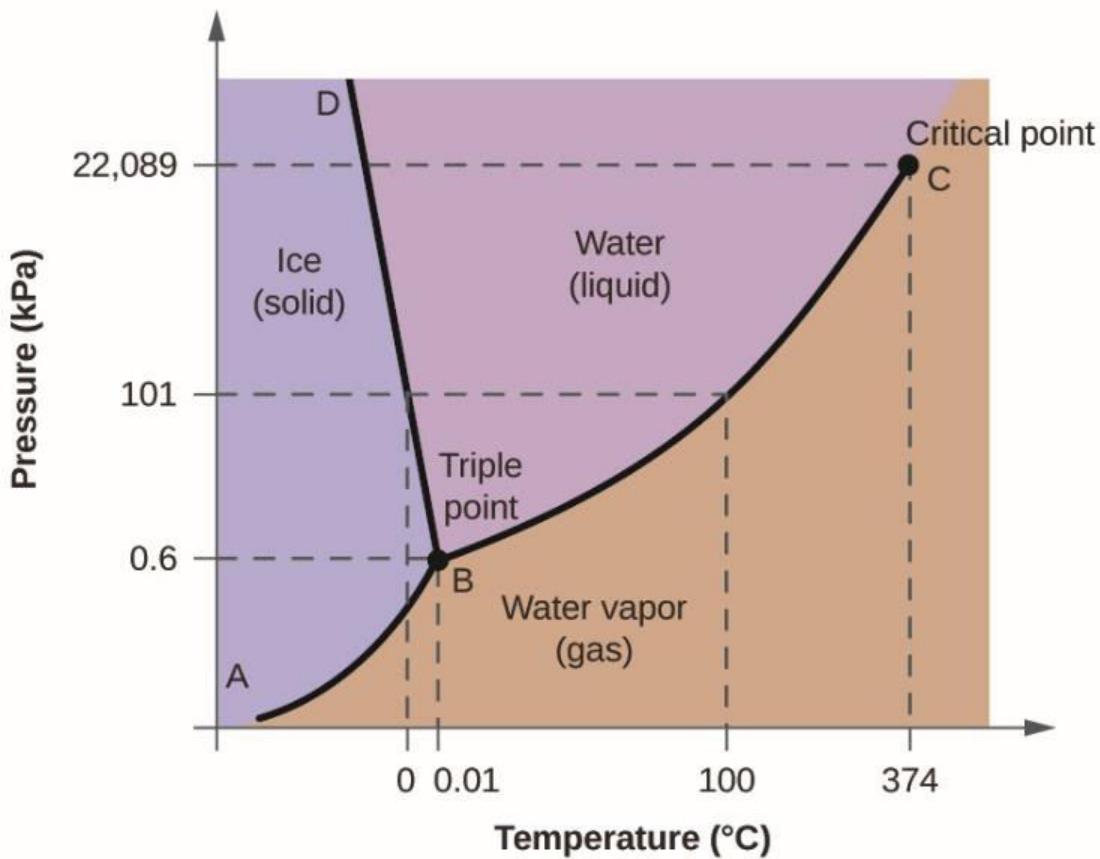
The alloy coatings bring **quality, reliability** and **durability** for process vessel linings and pipe linings along with the surface protection of components and equipment **against extreme conditions such as high temperature, higher abrasion or high acidity surroundings.**

Examples

- **Lead-Tin** alloys are used for **soldering purpose**
- **Nickel alloys** are known for **resistance to extreme corrosion** and **high temperature requirements.**
- **Copper-nickel** alloys are used for **anti-fouling.**
- **Iron-nickel alloys** show **low thermal expansion.**
- **Nickel-titanium alloys (Nitinol)** exhibit **shape memory.**

Phase Diagram

Phase diagram is a graphical representation of the physical states of a substance under different conditions of temperature and pressure.



One
component
system

Phase diagram of water

Alloying Phase Diagram

Composition Vs Temperature diagram

Physical and chemical state of elements at different temperatures and concentrations

Along blue line, Composition of metal α and β is fixed

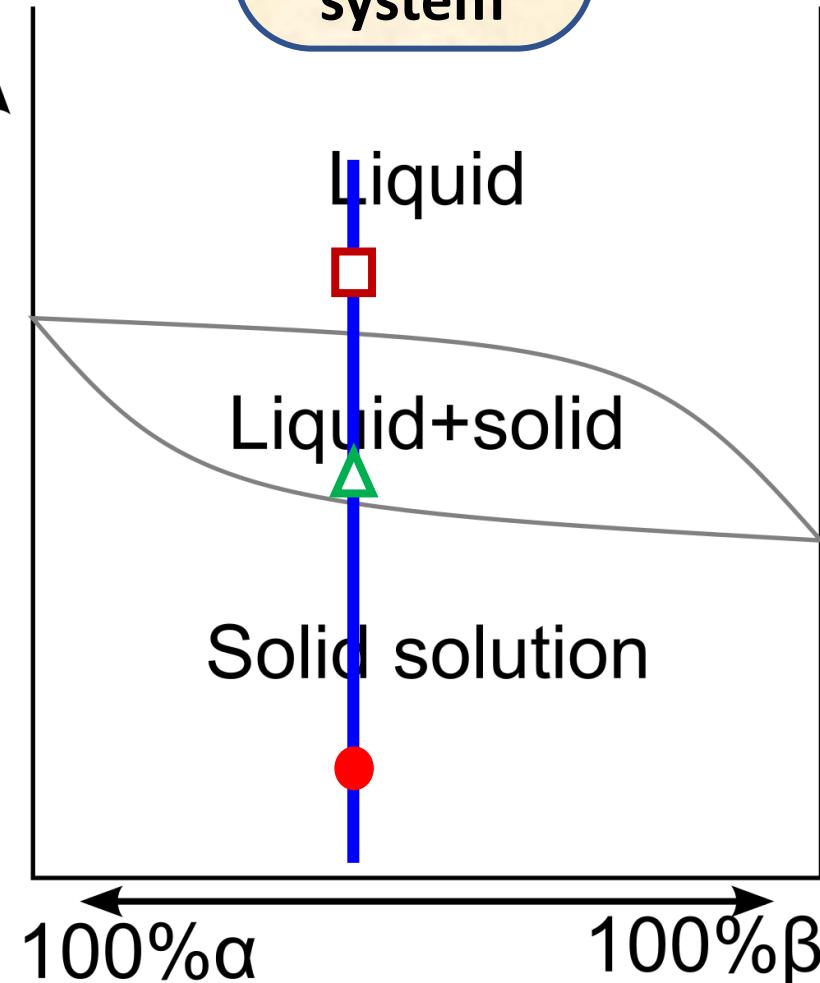
Points

A - • - **Solid solution** of metal α and β
 (Solid state solution, crystal structure of major component remains unchanged, single homogeneous phase)

B - Δ - **Liquid + Solid**

C - \square - both the metals are in **liquid** state

Two component system



Phase Diagram of alloys

- Phase diagrams of alloys can be used to predict the phase changes in an alloy which exposes to a particular heat treatment process.
- This is important because the properties of a metal component depend on the phases present in the metal.
- Phase diagrams are useful for selection of alloys with a specific composition.
- They are also used to troubleshoot quality problems.

Binary phase diagram

1. Isomorphous phase diagrams
2. Eutectic phase diagrams (& Basic concepts)

Specific examples of

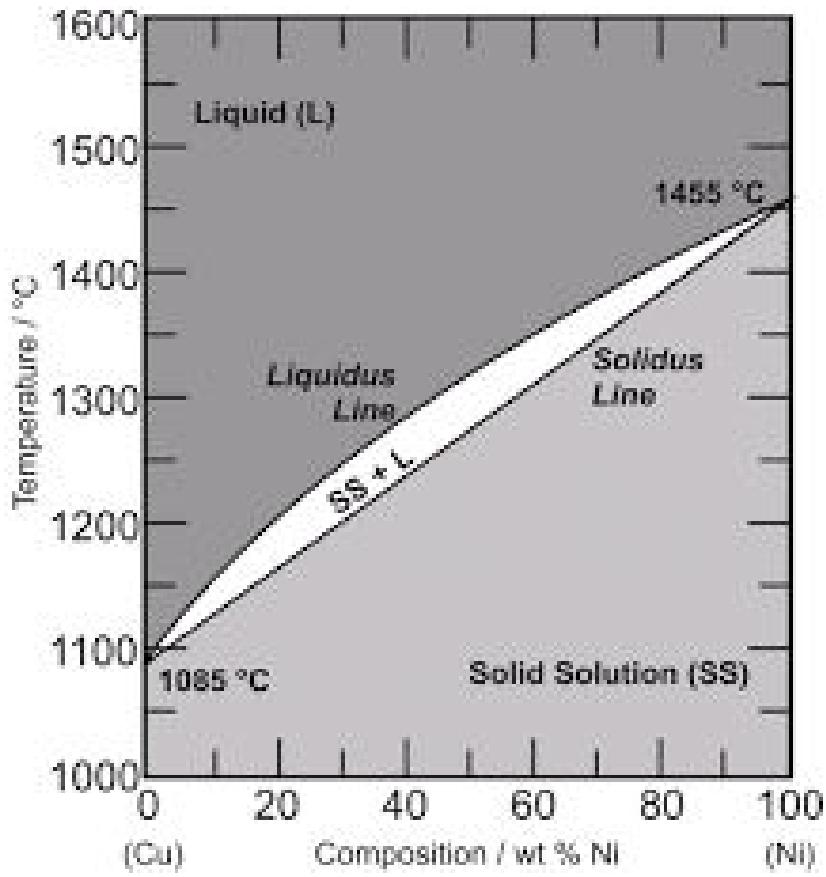
1. Ferrous alloys
2. Non-Ferrous alloys

Binary Phase Diagrams

1. Isomorphous phase diagrams

Complete solubility of one component in another

Example: Cu-Ni Alloys follow Hume-Rothery rules

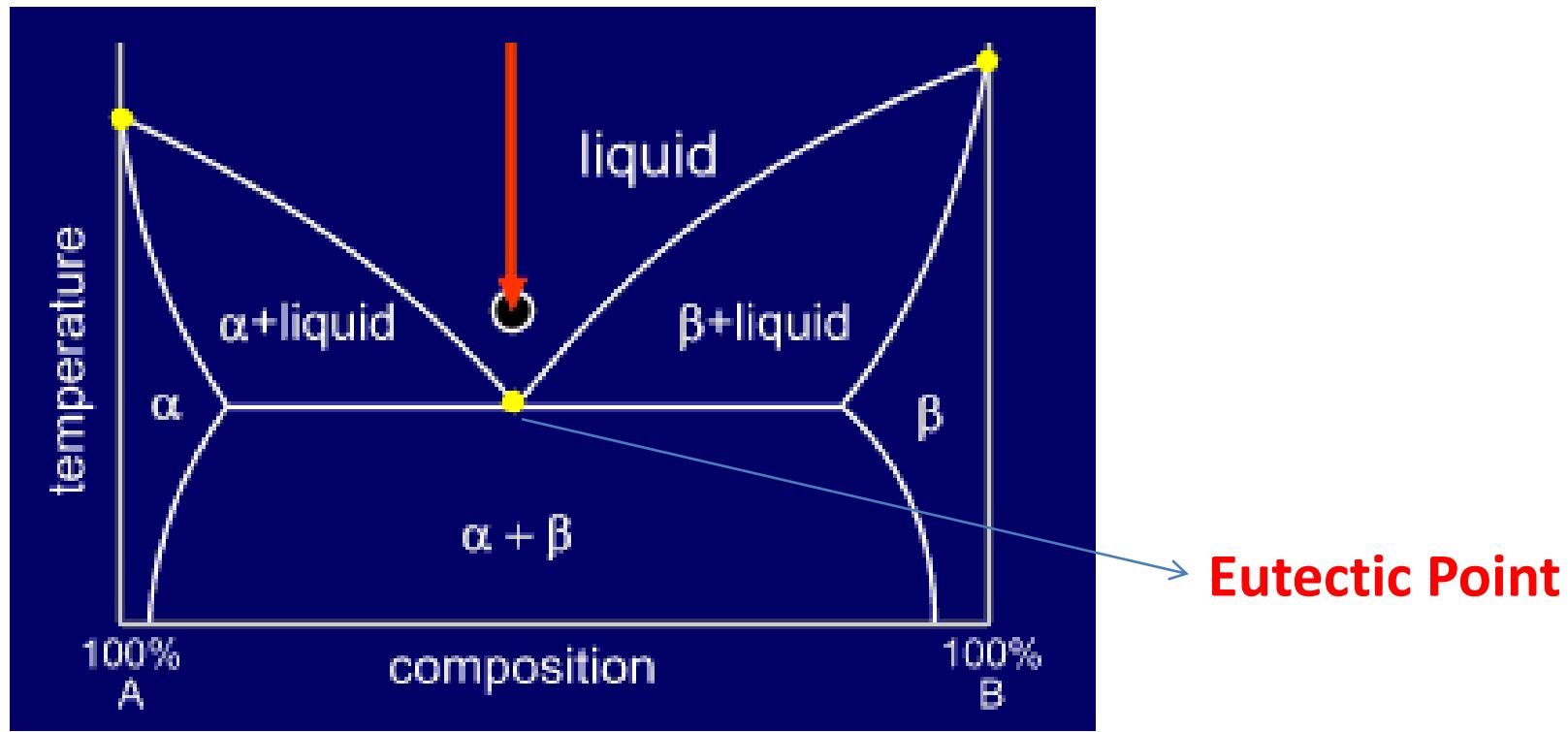


Hume-Rothery rules for solid solutions

1. The atomic radius of the solute and solvent atoms must differ by no more than 15%.
2. The crystal structures of solute and solvent must be similar.
3. Complete solubility occurs when the solvent and solute have the same valency. (A metal of higher valency is more likely to dissolve in a metal with lower valency).
4. The solute and solvent should have similar electronegativity (If the electronegativity difference is too great, the metals tend to form intermetallic compounds instead of solid solutions).

2. Eutectic phase diagrams

- The binary eutectic phase diagram explains the chemical behaviour of two immiscible (unmixable) crystals from a completely miscible (mixable) melt.



A (α) and **B** (β) are two different metals.

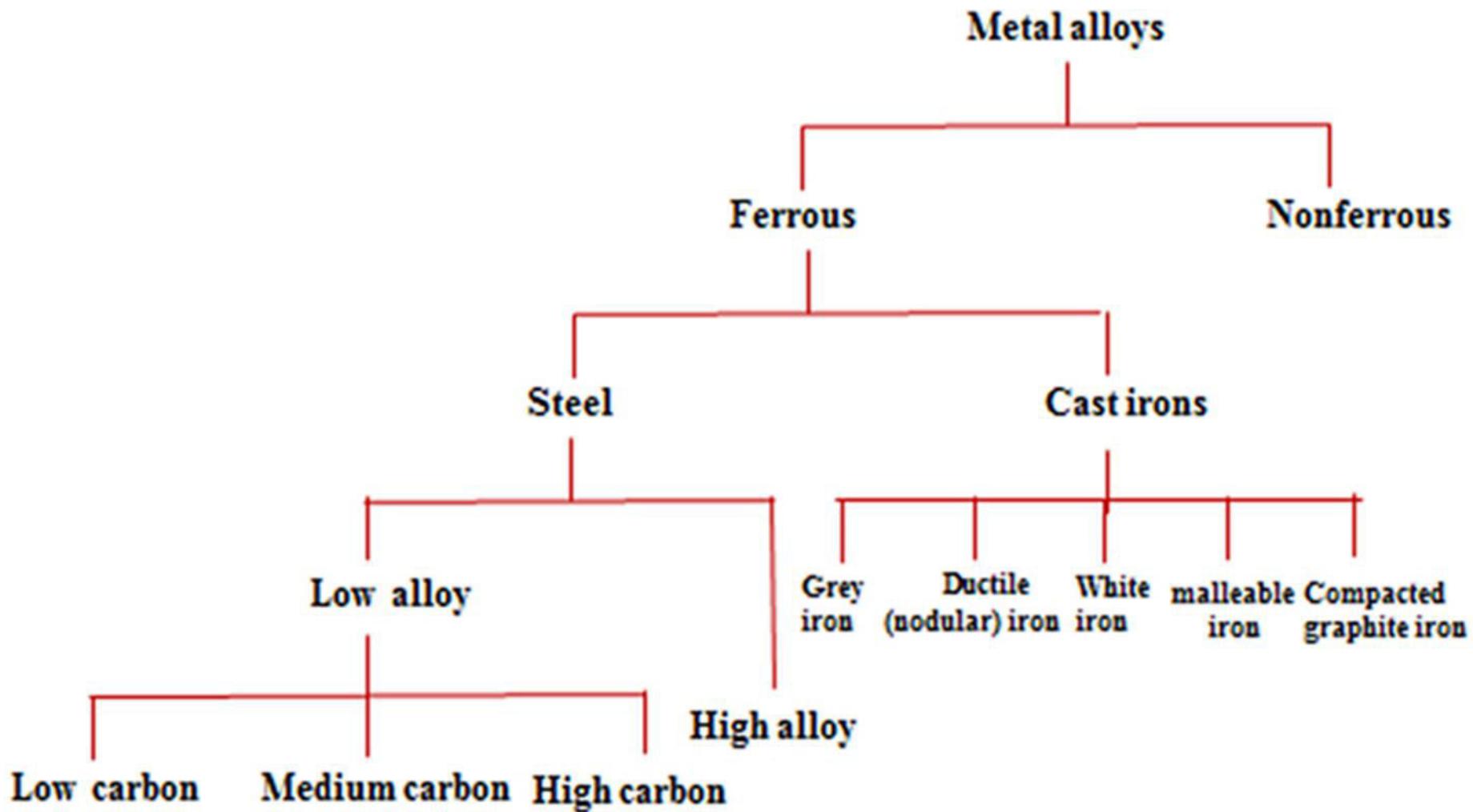
Basic concepts of Eutectic composition

The melting point of the **eutectic alloy** is lower than that of the components (eutectic = easy to melt in Greek).

Eutectic mixture. A **mixture** of two or more substances which melts at the lowest freezing point of any **mixture** of the components. This temperature is the **eutectic** point. The liquid melt has the same composition as the solid.

- **Eutectic alloys** have two or more materials and have a **eutectic composition**.
- When a well-mixed **eutectic** alloy melts, it does so at a single and sharp temperature.
- Conversely, when a **non-eutectic** alloy solidifies, its components solidify at different temperatures.

Alloys classification

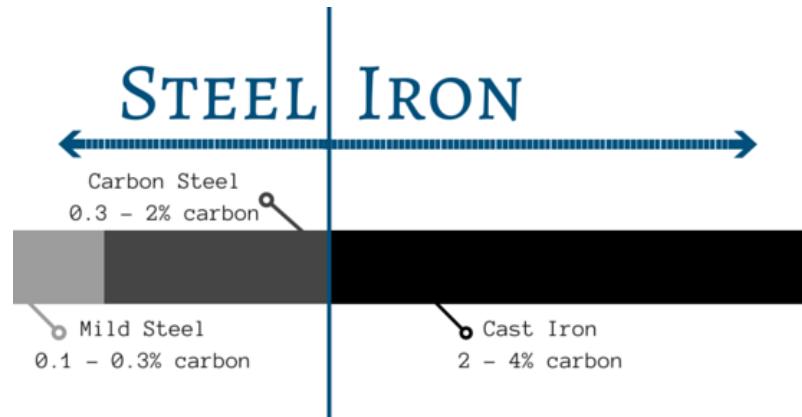


(a) Ferrous Alloys

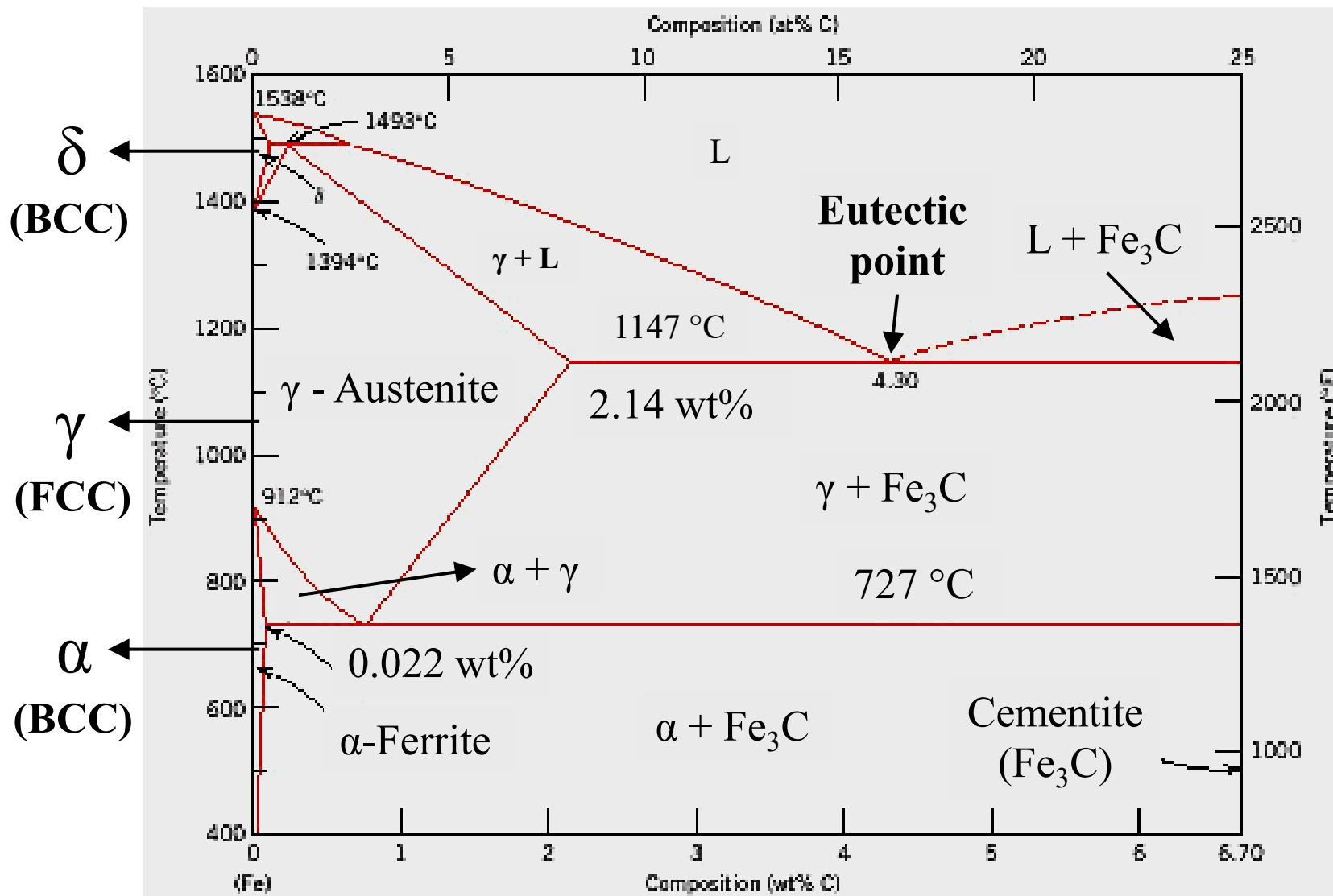
- Ferrous alloys contain *Iron* as the major component.
- They have small amounts of other metals or elements added, to give the required properties.
- Generally, the Ferrous alloys are magnetic and give little resistance to corrosion.

Some examples of the ferrous alloys are:

- Mild steel
- Carbon steel
- Cast iron

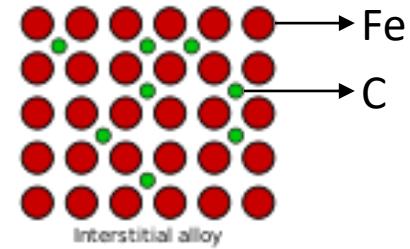


The Iron (Fe) - Iron Carbide (Fe_3C) Phase Diagram



Comments on Fe–Fe₃C system

- Carbon is an interstitial impurity in Fe.
- It forms a solid solution with α , γ , δ phases of iron
- Maximum solubility in BCC α -ferrites 0.022 wt% at 727 °C.
- BCC: relatively small interstitial positions
- Maximum solubility in FCC austenite is 2.14 wt% at 1147 °C
- FCC has larger interstitial positions
- Mechanical properties: Cementite(Fe₃C) is hard and brittle: strengthens steels).
- Mechanical properties also depend on microstructure: how ferrite and cementite are mixed.
- Magnetic properties: α -ferrite is magnetic below 768 °C, austenite is non-magnetic



Applications of Ferrous alloys

- Ferrous steel is produced as sheet for automobiles, appliances, and containers.
- As plates for ships, boilers and bridges, as a structural member (such as I-beams).
- Bar products for leaf springs, gears axles, crank shaft and railroad rails.
- As stock for tools and dies.
- As music wire and as fasteners such as bolts, rivets and nuts.
- Ferrous materials comprise 70% to 85% by weight of virtually all structural members and mechanical components.
- Carbon steels are least expensive.

(b) Non-Ferrous Alloys

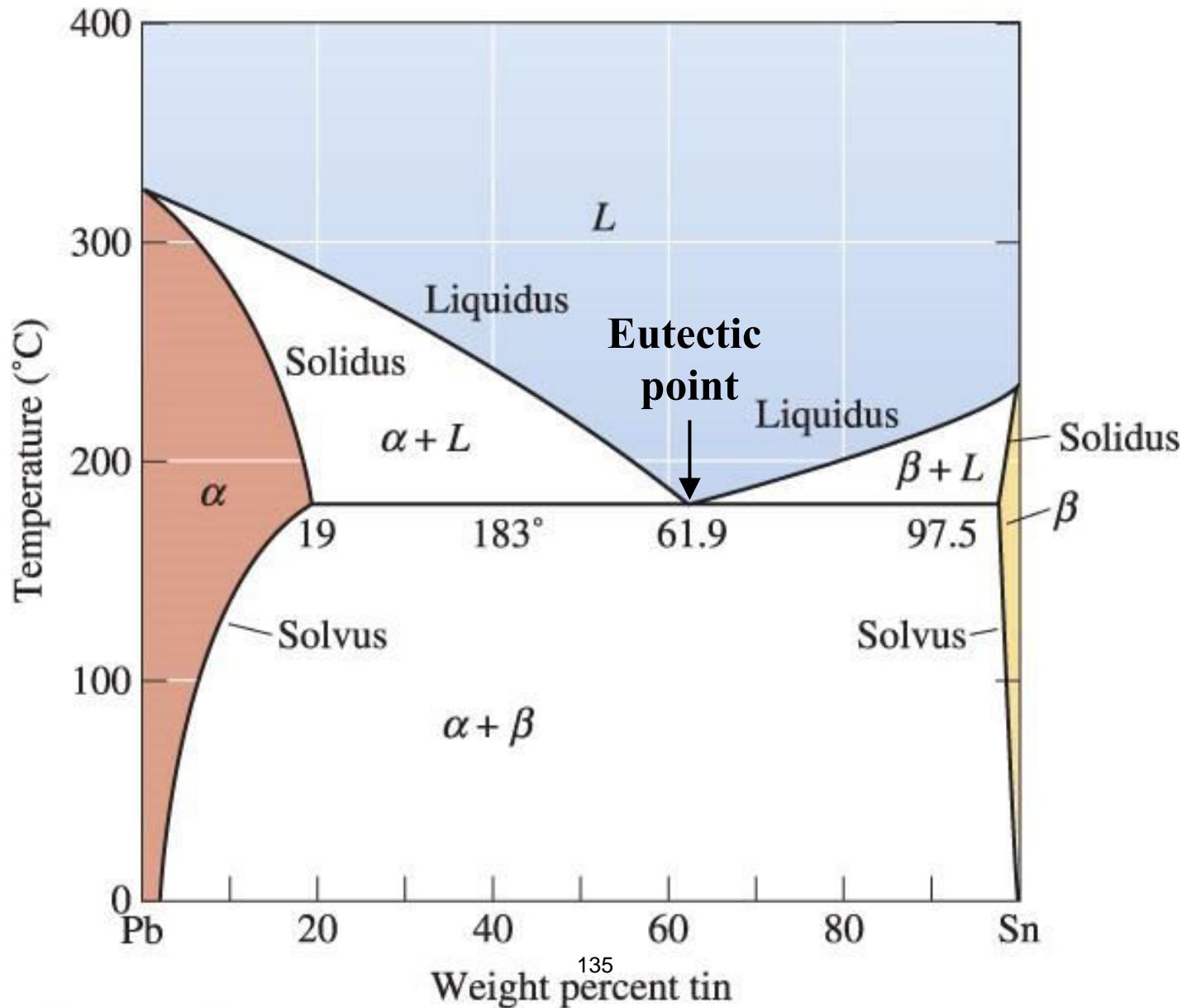
Non-Ferrous alloys are not iron based.

Some examples of **Non-Ferrous alloys** are:

- **Lead-Tin alloy for solder**
- Aluminium Alloys
- Copper Alloys
- Magnesium Alloys
- Beryllium Alloys
- Nickel and Cobalt Alloys
- Titanium Alloys



Lead (Pb) – Tin (Sn) alloy



Some applications of non-ferrous alloys

Copper Alloys:

- One of the largest uses of Cu is probably in coins.
- The various Euro coins are made of Cu-Ni, Cu-Zn-Ni or Cu-Al-Zn-Sn alloys.
- Brasses and Bronzes are most commonly used alloys of Cu.
- Brass is an alloy with Zn. Bronzes contain tin, aluminium, silicon or beryllium.
- Other copper alloy families include copper-nickels and nickel silvers.
- More than 400 copper-base alloys are recognized.

Magnesium Alloys:

- Aerospace industry
- High speed machinery
- Transportation and materials handling equipment

Nickel Alloys:

- Corrosion resistant parts: Valves, pumps, vanes Heat exchangers, shafts, impellers
- Heat treatment equipment, Gas turbines, Chemical reactor components