

Lecture notes
on
Corrosion Engineering
for
6th Semester, Metallurgical Engineering

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Chapter – 1

Introduction to Corrosion

Corrosion – It is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Ex- Rusting of iron

Erosion – It is the destructive attack of a metal by physical causes. Ex- Destructive of dam during flood situation.

Cost of Corrosion (Corrosion losses)

Corrosion losses are of two types

1. Economic losses
 2. Conservation of available resources
1. Economic losses - Economic losses are divided into 2 types.
- (a) Direct loss
 - (b) Indirect loss

(a) Direct loss – Direct losses includes the cost of replacing corroded structures, machines or their components such as pipelines, condenser tubes, etc. including necessary labour cost.

(b) Indirect Loss – Indirect losses are more difficult to measure and announce to several billion dollars more than direct losses.

Ex. (i) Shut down – The replacement of a corroded tube in an oil refinery may cost a few hundred rupees but shut down of the unit which repair are under when may cost several thousand rupees in production loss.

(ii) Loss of products – loss of oil, gas, water, etc. occurs through a corroded pipe system until repairs are made.

(iii) Loss of efficiency – This may occur by diminished heat transfer through accumulated corrosion products or by closing the pipe which rust, necessitating increases pumping capacity. In internal combustion engines of automobiles, where piston rings and cylinders walls are continuously corroded by combustion gases and this leads to increase oil consumption.

(iv) Contamination of product – Contamination of the products by the corrosion is undesirable and may be harmful in some cases.

(v) Over design – Because in most cases corrosion rates are known equipment are often design many times heavier than is required for normal operating condition with adequate knowledge of corrosion. More reliable estimate of equipment of like can be made and design can be simplified in terms of material and labour.

- ❖ Total losses sustain in industries, military dept., municipalities, amounts to many billion dollars annually.

Following figure will give some idea about that. i.e.

USA - \$6 billion (dollar)

UK - £600 million (pounds)

Canada - £ 500 million(pounds)

Australia - \$100 million (dollar)

India – Rs. 154 Crore (rupees)

Importance of Corrosion Studies

The major corrosion research Centre in India are –

1. The National Metallurgical Laboratory, Jamshedpur (NML, Jamshedpur)
2. The Central Electrochemical Research institute, Karai Kudi.
3. Defense Research Laboratory, Kanpur
4. Central Metallurgical and Chemical Laboratory, Mumbai
5. Indian Institute of Science, Bangalore.
6. Bhaba Atomic Research Centre (BARC)
 - In addition, the research work is also carried out in different university and organization in limited fields of interest.
 - A series of investigation are being undertaken on cast iron in IIT, Roorkee.
 - The corrosion problems can be classified into the following types.
 - I. Atmospheric Corrosion
 - II. Immersed Corrosion
 - III. Buried Metal Corrosion
 - IV. Powerplant Corrosion
 - V. Mechanical And Chemical Corrosion
 - In India some aspect of corrosion research undertake are mentioned below.
 - I. Influence of galvanic contact on atmospheric corrosion of belt and wire type samples.
 - II. Detail study of ancient iron structure. Ex- Iron Pillar, Delhi
 - III. Corrosion resistance protective properties of metal and alloy.
 - IV. Evaluation of protective properties of inorganic & organic coating.
 - V. Studies of aluminum and zinc sprayed steel and galvanized steel.

Classification of Corrosion

Corrosion mainly classified in different ways-

The first method of classification

- ✓ Low Temperature Corrosion
- ✓ High Temperature Corrosion

The Second Method of Corrosion

- ✓ Chemical corrosion
- ✓ Electrochemical corrosion

The Third method of classification

- ✓ Wet corrosion
- ✓ Dry corrosion

Types of Corrosion

The Different types of Corrosion are,

- a. Atmospheric corrosion
 - b. Intergranular corrosion
 - c. Pitting corrosion
 - d. Stress corrosion cracking
 - e. Impingement corrosion
 - f. Cavitation corrosion
 - g. Fretting corrosion
 - h. High temperature oxidation corrosion
 - i. Stray current corrosion
 - j. Galvanic corrosion
- a. Atmospheric Corrosion – It is the most common type of corrosion in alloy and causes serious damage unless adequate protective natures are adopted.
 - b. Intergranular corrosion – Localized attack at the grain boundary of a metal or alloy is called intergranular corrosion.
 - c. Pitting corrosion – This is the one of the most troublesome form of corrosion and is recognized by the presence of pits or holes.
 - d. Stress corrosion cracking - Stress corrosion cracking may be described as a process of destruction of metal due to simultaneous action of corrosive environment and mechanical stress.
 - e. Impingement corrosion – This type of corrosion usually occurs in system where high velocity of fluid are encountered and failure in service may occur due to faulty design and poor selection of material.
 - f. Cavitation corrosion – It is caused by the formation of vapor bubbles or cavities on the metal surface.
 - g. Fretting corrosion - It describe corrosion occurring at contact areas between the two surfaces of any material under load subjected to slightest relative moment if small amplitudes.
 - h. Corrosion fatigue – It may be defined as the reduction of fatigue strength of material due to the presence of corrosive medium.
 - i. High temperature oxidation corrosion – The term oxidation refers to chemical reaction of a dry metal surface with an oxidizing gas which is called dry corrosion. Since every

metal and alloy reacts with air at ambient temperature oxidation resistance must be consider in most of the engineering application.

j. Galvanic Corrosion – It is an electro chemical corrosion in which the current is generated by the corrosion process when two dissimilar metals are electrically coupled together in the presence of an electrolyte.

❖ Chemical corrosion - This is a corrosion of a metal in a liquid or gases environment it may result in dissolution oxidation or selective attack. The term oxidation refers to the chemical reaction of a dry metal surface with an oxidizing gas called dry corrosion. Since, every metal and alloy react with air at ambient temperature oxidation resistance must be considered in most of the engineering application. Example - Pitting corrosion, Stress corrosion cracking.

❖ Electrochemical corrosion - the corrosion which is associated with the passage of an electric current is called electrochemical corrosion. If the current is produced by the system, it is called Galvanic corrosion. It is result from an impressed this called electrolytic corrosion. ex - rusting of iron in a Marine atmosphere

❖ Requirements for electrochemical corrosion –

1. An anode and cathode
2. Electrical connections between anode and cathode
3. An electrolyte between anode and cathode

❖ Corrosion occurs at the anode

Corrosion rate - Corrosion rate have been expressed in different way in the literature such as -

Apparent loss $\text{mg} / \text{cm}^2 / \text{day}$ and $\text{gm} / \text{inch}^2 / \text{hr}$. from an engineering point of view the rate of penetration or the thinning first structural piece can be used to predict life of a given component.

The expression miles/ year is the most desirable way of un-expressing corrosion plate. The expression is readily calculated from the weight loss of the metal specimen during the corrosion test by the formula given below

$$\text{MPy} = 534W/\text{DAT}$$

Where, MPy = miles per year

D = density of specimen gm. per centimeter square

A = Area of the specimen square inch

T = exposure time, in/hour.

Good corrosion rate expressions should involve -

1. Familiar unit
2. Easy calculations with minimum errors
3. Ready conversations to life in years

4. Penetrations
5. Whole number

Chemical Corrosion	Electro Chemical Corrosion
<ul style="list-style-type: none"> • It occurs in dry condition. • It is due to direct chemical attack of the metal by the environment. • Even a homogeneous metal surface gets corroded. • Corrosion product accumulate at the place of corrosion. • It is a self-controlled process. • It adopt adsorption mechanism. • Ex- Formation of mild scale on iron surface. 	<ul style="list-style-type: none"> • It occurs in the presence of moisture or electrolyte. • It is due to the formation of large number of anodic and cathodic areas. • Heterogenous surface alone gets corroded. • Corrosion occurs at the anode while the product form else somewhere. • It is a continuous process. • It follows electrochemical reactions. • Ex- Rusting of iron in moist atmosphere.

Chapter 2

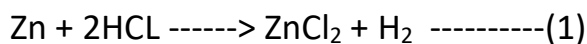
Corrosion Principles

Electrochemical principle of corrosion

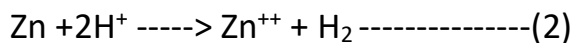
The Electrochemical nature of corrosion can be by the attack of zinc by hydrochloric acid. Therefore, the corrosion of zinc in hydrochloride acid is an electrochemical process i.e. Any reaction that can be divided into two partial reactions of oxidation and reduction. Dividing corrosion or other electrochemical reaction into partial reaction makes them simpler to understand.

Example-1

When zinc is placed in hydrochloric acid (HCl) a vigorous reaction takes place. H₂ Gas is evolved and Zinc dissolves forming a solution of ZnCl₂



If the chloride ion is not involved in the reaction this equation can be written as

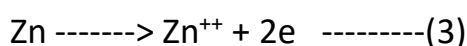


here, zinc reacts with H₂ ions of the acid solution to form zinc ions and hydrogen gas.

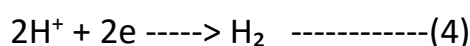
From the above equation (1) it can be seen that during the reaction zinc is oxidizes to zinc ion and H₂ ion are reduce to H₂.

Therefore equation (2) can be divided into two reactions the Oxidation reaction of Zinc and reduction reaction of H₂ ions.

Oxidation reaction (Anode reaction)



Reduction reaction Catholic reaction



An oxidation or anodic reaction is indicated by an increase in valence electron or production of electron.

Equation (3) and (4) are partial reaction must occur simultaneously and at the same rate on metal surface. This leads to one of the most important basic principle of corrosion. During metal corrosion the rate of oxidation equal to the rate of reduction. The above Concept can be illustrated by given figures.

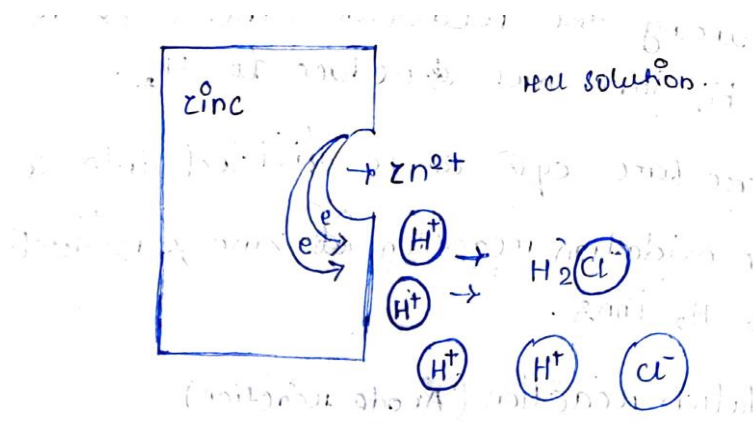
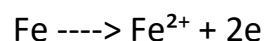


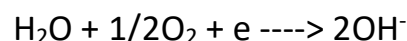
Figure- Electrochemical Reaction occurring during corrosion of HCl.

Here, zinc atom has been transferred into a zinc ion and two electrons. These electrons which remain in the metal are immediately consumed during the reduction of hydrogen ions. The verb figure shows these two processes. In some corrosion reaction the oxidation reaction occurs uniformly on the surface because in the other cases it occurs at specific area.

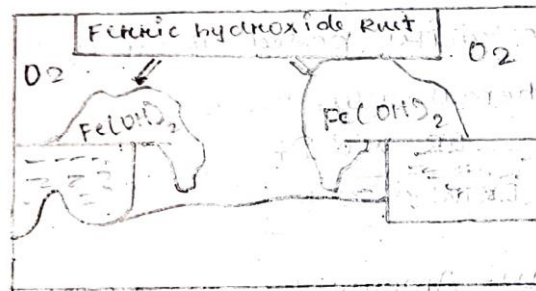
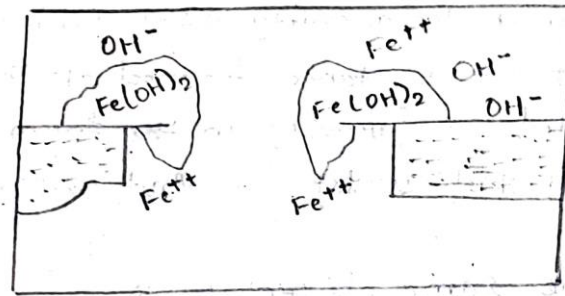
Example 2- The Electro-chemical nature of corrosion can be illustrated by considering the common example of iron rusting. The iron dissolves according to the typical anodic reaction as-



And, cathodic reaction produces hydroxyl Ion according to the reaction -



the Ferrous Hydroxide become oxidized by the dissolved oxygen and converted to ferric Hydroxide which iron rust.



Electrolysis:

Electrolysis may be defined as the process in which the chemical reaction is brought on the electrodes in contact with an electrolyte in contact with an electrolyte. By means of external electromotive force.

During electrolysis the passage of current is accompanied by migration of ions. Positively charged electrodes and negatively charged ion are attached towards positively charged electrodes. Positively charged ion are called cations and negatively charged ion are called anions.

Positively charged electrodes are called anode, negatively charged electrodes are called cathode.

FARADAY'S LAW: -

The relations between the quantity of electricity passed and the amount of substance formed at the electrodes has been formulated by Faraday in the form of two independent laws that is 1st law and 2nd law.

1st LAW: - For the same electrolytes the amounts of substance liberated is directly proportional to the quantity of electricity passed through the solution.

Mathematically, $W \propto Q$

OR $W \propto IT$

OR $W = ZIT$

Where, W = amount of substance liberated at the electrode

I = Electric current

t = time

z = constant called electro chemical equivalent

Q = It is the total charge passed

Electrochemical equivalent: -

The electrochemical equivalent of a substance is the mass of substance which is liberated during electrolysis by the passage of current of one ampere for one second.

The unit of electricity OR charge is coulomb.

2nd LAW: -

The weight of various substances deposited by 1 and same quantity of electricity are proportional to their respective equivalent weight.

Mathematically, $W \propto E$

Where, W = Weight of the substance deposited by the passage of certain quantity of electricity.

E = Equivalent weight = atomic weight /valency

Equivalent weight may be defined as the = atomic weight/valency

That is $E = A/n$

Where, E = Equivalent Weight

A = Atomic Weight

n = Valency

From the 2nd law it follows that same amount of electricity is required to liberate 1gm equivalent of substance from any electrolyte. This quantity is called Faraday and is denoted by F. If the reaction of electro deposition, then weight in gms of deposit may be calculated from Faraday's law as follow – combine from of equation of Faraday's 1st law and 2nd law.

From Faraday's 2nd law 1gm equivalent of substance will be deposited by 96,500 coulombs. Thus A/n gm of substance will be deposited by 96,500 coulomb Wgm of substance will be deposited by $F \cdot W / (A/n)$ coulomb, as we know quantity of electricity - $Q = I \cdot t$

$$W = I \cdot t \cdot A / F \cdot n$$

$$\frac{F \times W}{(A/n)} \text{ coulomb, As we know quantity of}$$

$$\text{electricity} - Q = I \cdot t$$

$$\Rightarrow \frac{F \times W}{(A/n)} = I \times t$$

$$\Rightarrow \boxed{W = \frac{I \times t \times A}{F \times n}}$$

The no. of ions in one mole of any substance is known as Avogadro Number. It is denoted by capital N = 6.032×10^{23}

PROBLEM-1

Q. 100 ml of copper sulphate solution was deposited 1.2 Amp current was maintained for 1 hr. drying the electrolysis calculate the weight of copper deposited during electrolysis.

Ans- Given –

100 ml of copper sulphate solution

$$W = I \cdot t \cdot A / F \cdot n$$

$$W = 1.2 \cdot 60 \cdot 60 \cdot 63.54 / 96,500 \cdot 2$$

$$W = 137246.4 / 96,500$$

$$= 1.422.$$

Deviation of Faraday's law: -

Faraday's law is applicable to both aqueous and fused electrolyte. However, when faradays law are tested experimentally, the apparent deviation from there law are observed experimentally with both fused and aqueous electrolyte. These deviations increase with temperature therefore deviations are more in case of fused electrolyte, deviations are due to the following reasons.

- I. Discharge of other ions
- II. The formation of compound at the electrodes
- III. The dissolution of the electrodes
- IV. Recombination of primary products
- V. Mechanical losses
- VI. Evaporation losses

Discharge of other ions

Current loss occurs due to the discharge of ions of impurities or even necessary components of electrolyte at the electrodes.

Formation of compound at the electrodes

It has been shown in certain cases that formation of compounds at electrodes results in current loss.

Dissolution of electrodes

Current loss can be attributed to the dissolution of electrodes in electrolyte. This factor is mainly present in case of fused salt. Dissolution continues unless saturation reached of dissolved ions near electrode surface. The following are the factor governing the solubility of dissolution.

- a) Solubility or dissolution of metal increases with increase in temperature with electrolyte.'
- b) In general, highest solubility of a metal is absorbed in its own salt.

Recombination of Primary product

The possibility of recombination is more incase of fused salt electrolyte due to their high temperature. This factor can be avoided by using the salt mixer which melts below the melting point of pure salt.

Mechanical losses

There can be mechanical loss of the substance form at the electrode depending upon the structure of the deposits.

Evaporation losses

This is present only on salts of metals having high vapour pressure.

Chapter 3

Types of Electrochemical Cells

An electrochemical cell is one which chemical reaction generate electricity. The essential components of an electrochemical cell are electrolyte, anode, cathode & electronic conductor. In electrochemical cell cathode is one where reduction reaction occurs & anode is one where oxidation reaction occurs.

- Electrochemical cells can be reversible or irreversible.
- ➔ The cell is reversible when chemical reaction at the electrodes are same but reverse in direction, when the direction of the flow of the current is reversed.
- ➔ The cell is irreversible when different reaction occurs at one or both the electrodes, when the direction of current is reversed.

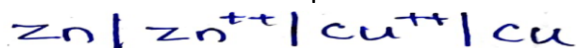
Use of Electrochemical cells

- ➔ Electrochemical cells are valuable in the calculation of thermodynamic properties of certain aqueous & fused electrolyte.
- ➔ In understanding the mechanism of corrosion & protection of metals & production of electric power.

Schematic Representation of cell

Short notation are used to simplify the desc of cells. The single vertical line represents the phase boundary between electrode & electrolyte adjacent to the electrode.

The double vertical lines represent salt bridge between two solutions in contact with each other. For Example: Daniel cell can be represented by



Simialrly,

A cell with saltbridge is represented by

$$\text{Zn} | \text{Zn}^{2+} || \text{Cd}^{2+} | \text{Cd}$$

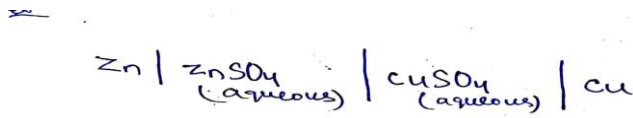
Galvanic Cell

In galvanic cell emf arises due to chemical reaction within the cell & exchange of electrical charges takes place in chemical reactions in which ions are involved. Galvanic cell is also called voltaic cell.

Chemical reaction involve release or acceptance of electrons when two dissimilar metal are in contact with electrolyte containing their ion, thus cells are represented by

Anode / Anode electrolyte / cathode electrolyte / cathode .

Ex

Types of Galvanic cell

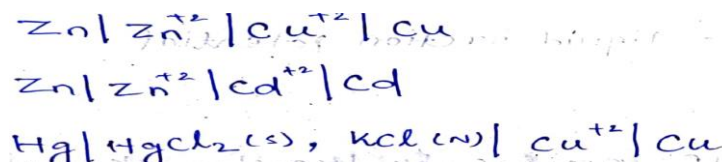
It is of 2 types

- i) Galvanic cells with transference
- ii) Galvanic cell without transference

→ Galvanic cell with transference

These cells are characterized by the appearance of a liquid junction potential between two electrolyte solution of different concentration & composition.

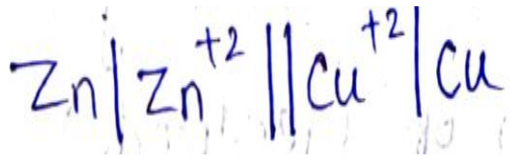
Ex



→ Galvanic cell without transference

This type of cells are characterized by the absence of liquid junction potential different at the phase boundary between two different solution.

Ex



The electromotive force of the galvanic cell is due to the potential difference between various combinations of metal. Galvanic cell consists of two compartments each of them is called a half cell. The half cell with more negative potential is called anode & other is called cathode. At anode oxidation reaction occurs & at cathode reduction reaction occurs.

The EMF of galvanic cell without transference is given by the sum of the EMF of two half cells reaction. (oxidation & reduction reaction)

$$E_{\text{cell}} = E_1 + E_2$$

The EMF of galvanic cell with transference is given by,

$$E_{\text{cell}} = E_1 + E_2 + E_j$$

Where, E_j = liquid junction potential

Concentration Cell

The cell where EMF arises by transfer of material from one electrode to the other electrode due to concentration gradient is known as concentration cell. The concentration gradient may be due to any of the following reasons:

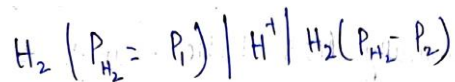
- (i) Concentration cell without transference
- (ii) Concentration cell with transference

Types of concentration cell

→ Concentration cell without transference

This type of cells are characterized by the absence of liquid junction potential.

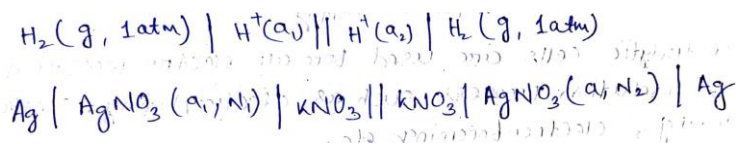
Ex



→ Concentration cell with transference

This type of cells are characterized by the appearance of liquid junction potential between the two solution.

Ex



In concentration cell the value of E^0 is 0.

EMF of the concentration cell without transference is given by the equation:

$$E_{cell} = -\frac{RT}{nF} \ln \frac{a_2}{a_1}$$

EMF of the concentration cell with transference is given by

$$E_{cell} = -\frac{RT}{nF} \ln \frac{a_2}{a_1} + E_j$$

E_j = liquid junction potential

↳ It depends on the concentration of solution.

R = const. T = temp. F = Faraday constant

E = EMF of the cell, a_2, a_1 = concentration

ELECTROLYTIC CELL

Electrolytic cell is just reverse of electrochemical cell. Current is supplied from external source to bring about the chemical reaction whose product are thermodynamically less stable than the reaction like electrochemical cells the electrolytic cell consists of following components:

- I) Anode
- II) Cathode
- III) Electrolyte
- IV) External power supply

Electrolytic cells are used for all electro-deposition & dissolution process such as electroplating, electro-wining, electroforming, etc.

An electrolytic cell should be designed to meet the following requirements:

- It should consume little energy per unit weight of the metal.
- It should have a high output for a small volume & working area.
- It should be easy to operate without any danger to safety.
- It should provide complete recovery of desired electrolysis product.
- It should be corrosion resistance to the electrolyte.
- It should be resistant to heat, if it is operated in higher temperature.

The nature of reaction of electrolytic cell is non-spontaneous. When the surface of metal & electrolyte are homogeneous to such a degree that no cathodic & anodic area are developed even in the presence of energy from external source can develop cathodic & anodic area.

CHAPTER – 4

Electrode Potential

In an electro chemical cell oxidation occurs at 1 electrode and reduction occurs at the other electrode. In other words, one electrode has the tendency to loose electrons and the other electrode has the tendency to gain electrode. The tendency of an electrode to loose or gain electrons is called electrode potential.

The electrode potential is further called oxidation potential if oxidation takes place at the electrode. The electrode potential is called reduction potential if reduction take place at the electrode.

If in the half cell the electrode is suspended in a solution of one molar concentration and the temperature is kept at 25°C the electrode potential is called standard electrolyte potential. It is represented by E° .

❖ Determination of Electrode Potential: -

The absolute value of electrode potential can't be determined because neither oxidation nor reduction take place independent. Therefore, with respect to standard electrode, the electrode potential of an electrode changes with the change in concentration of ions in solution in contact with metals. In simple words, reduction potential of an electrode is proportional to concentration of ions whereas oxidation potential of an electrode is inversely proportional to the concentration of ions.

❖ Single Electrode Potential: -

The single electrode potential cannot be measured experimentally unless it is connected by another half cell so that potential difference between the two electrodes can be measured thus, we can determine only relative value of single electrode potential with respect to another electrode which is called reference electrode.

❖ Reference Electrode: -


It is nothing but standard hydrogen electrode whose potential is set at 0. The conditions are: -

1. Concentration of hydrogen ion solution is 1.
2. Partial pressure of hydrogen is 1 atmosphere.
3. The temperature is fixed at 25°C.

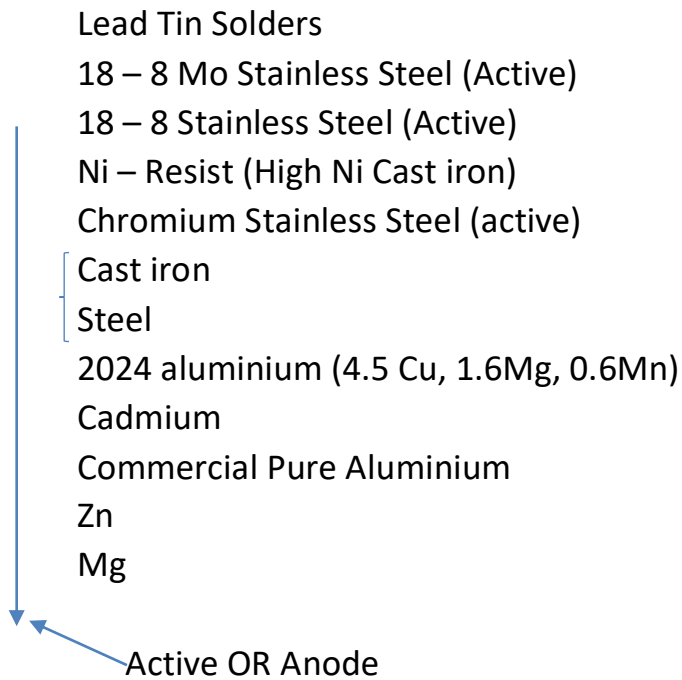
❖ **Galvanic cell and Galvanic Series:** -

These cells are formed due to 2 dissimilar metals in contact in the presence of an electrolyte in which one metal becomes anodic and gets corroded. For example – Iron pipe, carrying water is anodic to copper pipe. The questions arise as to which metal will be anode OR cathode. This can be predicted from galvanic series by taking pairs of metal and alloy in a given medium such as sea water and observing which become the anode. We can prepare a series known as the Galvanic series.

The galvanic series of many metals and alloys are given in the table.



Platinum
 Gold
 Graphite
 Titanium
 Silver
 Chlorimint -3 (62 Ni, 18 Cr, 18 Mo)
 Haste alloy C (62 Ni, 17 Cr, 15 Mo)
 18 – 8 Mo stainless Steel (Passive)
 18 – 8 Stainless steels (Passive)
 Chromium Stainless Steel (Passive)
 Inconel (80 Ni, 13 Cr, 7 Fe) (Passive)
 Nickel (Passive)
 Silver Solder
 Monel (70 Ni, 80 Cr)
 Cupro Nickels (60 – 90W, 40 – 10 Ni)
 Bronets (Cu – Sn)
 Copper
 Brasses (Cu - Zn)
 Chlorimint – 2(66 Ni, 20 Mo, 1 Fe)
 Haste Alloy B (60 Ni, 30 Mo, 6 Fe, 1 Mn)
 Inconel (Active)
 Nickel (Passive)
 Tin
 Lead



The following inference can be made from the Galvanic Series-

1. The metals and alloys at the top of the series are less corroded while the metal at the bottom is highly corroded.
2. The farther the metals and alloys in the series the greater is the potential generated. Therefore, metals and alloys which are farther apart in the series should not be coupled together.
3. When metals and alloys of the same group are coupled together there is little danger of corrosion.
4. Same metal achieved different positions in the series. For Example – Stainless Steel in passive state occupy more noble position as compared to active cell.
5. Galvanic cell may also be formed in the same metal consisting of dissimilar sections the dissimilarity may be due to any of the reason given below.
 - a) Different Thermal Treatment
 - b) Scratches and Abrasions
 - c) Differential Strain
 - d) Differential Grains
 - e) Grain Boundary
 - f) Differential Grain Size
 - g) Surface Condition

CHAPTER 5

Different Forms of Corrosion

The various types of corrosion are-

1. Atmospheric Corrosion
2. Inter-Granular Corrosion
3. Pitting Corrosion
4. Corrosion Fatigue
5. Galvanic Corrosion
6. Stress Corrosion Cracking
7. Cavitation Corrosion
8. Fretting Corrosion
9. High Temperature Oxidation Corrosion
10. Stray Current Corrosion
11. Impeachment Corrosion

❖ **Inter-Granular Corrosion: -**

Localised attack at the grain boundaries of a metal or alloy is called inter-granular corrosion. Ex- 1. The corrosion in aluminium copper Alloy
2. Corrosion in stainless steel

❖ **Causes of Inter-Granular Corrosion: -**

1. This is caused by impurity at the grain boundaries.
2. Enrichment of one of the alloying elements or depletion of one of the elements in the grain boundary area.
3. Small amounts of iron in aluminium can cause inter-granular corrosion.
4. Depletion of chromium in the grain boundary region results in inter-granular corrosion of stainless steel.
5. Number of failures of 18's stainless steel has occurred because of inter-granular corrosion.

❖ **Method of Prevention of Inter-Granular corrosion: -**

3 methods are used to control or minimize the inter-granular corrosion of austenitic stainless steel are given below-

1. Employing High Temperature. Solution heat treatment known as solution quenching.
2. Adding elements that are strong carbide formers.
3. Lowering the carbon content to below 0.03%.

❖ **Corrosion Fatigue: -**

This is defined as the reduction of fatigue strength of material due to the presence of corrosive medium.

Corrosion environment reduces the fatigue life considerably. For corrosion fatigue failure even mild corrosive environment is sufficient. Corrosive fatigue result in the appearance of cracks having the following characteristics-

1. Corrosion Fatigue cracks appears on the surface of the metal these cracks have blunt edges.
2. These cracks occur usually in groups.
3. These cracks are trans crystalline.

Example – The Failure due to corrosion fatigue are-
Boiler, Turbine, Propeller, Shaft, etc.

❖ **Mechanism of Corrosion Fatigue: -**

The real mechanism of corrosion fatigue is not yet established but the scientist Eben has given electro-chemical mechanism according to which failure occurs in two stages. In the first stage the pits of various depth are formed on surface of metal as a result of corrosion in the second stage, there is an appearance of crack and development of cracks.

❖ **Factors Affecting Corrosion Fatigue: -**

1. Environmental Factors strongly influence corrosion fatigue behaviour.
2. Stress cycle frequency influence the fatigue testing machine.
3. Corrosion Fatigue is most pronounced at low stress frequency.
4. Corrosion Fatigue is also influenced by the corrosive medium to which the metal is exposed.
5. Oxygen content influence corrosion fatigue.
6. Temperature influences the corrosion fatigue.
7. pH influence corrosion fatigue.
8. Corrosion fatigue is influenced by solution composition.

❖ **Method of Prevention of Corrosion Fatigue: -**

1. Increase in the tensile strength of a metal OR Alloy increases the fatigue strength.
2. Corrosion Fatigue can be eliminated OR reduced by reducing the stress on the component.
3. Corrosion inhibitors are also effective in reducing or eliminating the effect of Corrosion fatigue.

4. Corrosion fatigue resistance can be improved by using coatings such as- Electro-Deposited Zinc, Chromium, Nickel.

❖ **Cavitation Corrosion: -**

Cavitation Corrosion is caused by the formation and collapsed of paper bubbles or cavities on the metal surface. Cavitation corrosion occurs in system which are subjected to alternative ranges of pressure liquid bubbles are formed during the low-pressure cycle and collapse occurs in high pressure cycles. The collapse produces high strength impact which gradually removes particles of the surface and is responsible for cavitation damage. For example – Hydraulic Turbine, Diesel engine Cylinder.

❖ **Mechanism: -**

Cavitation corrosion is a result of both mechanical and chemical action. The impact by the collapse of the bubbles can cause cavitation damage due to any of the following reasons-

1. Destruction of the protective film on the metal surface.
2. Formation of bubbles on protective film.
3. The newly expose metal surface corrode and the film is reformed.
4. The bubble collapse and destroy the film.
5. Fatigue crack of metal occurs if the collapse of the bubble produces cyclic stresses.

❖ **Method of Prevention: -**

1. To prevent cavitation corrosion materials with better resistance should be used.
2. The design should be perfect.
3. Addition of inhibitors are effective methods for preventing cavitation corrosion.
4. Applying coating of various kinds that produces a barrier between the metal and its environment are sometime utilized for prevention of cavitation corrosion.
5. Cathodic protection is utilised for prevention of cavitation corrosion.

❖ **Pitting Corrosion: -**

This is the one of the most trouble some form of corrosion and is recognised by the presence of pits or holes.

The following characteristics of pitting corrosion can be identified-

1. Corrosion attack is confined to very small area of metal surface.
2. Pits are formed randomly on the surface.
3. Active metals are more successively to this form of attack.

4. They depend on formation upon irregularities in the passivation oxide layer.
5. The potential inside the pit is within the active region while the outside is within the passive region.
6. The electro polish in the pit keeps the current density constant.

❖ **Factors Affecting Pitting Corrosion: -**

1. Effect of Alloying
 2. Heat Treatment
 3. Cold Work
 4. Surface Finish
 5. Solution Composition
1. Effect of Alloys: - Stainless steel are affected by effect of alloying.
 2. Heat Treatment: - Pitting Corrosion can be increase depending upon the type of heat treatment. Ex- Pitting corrosion decreases in type 304 and 316 steel.
 3. Cold Work: - Cold working is found to increase the pitting attack.
 4. Surface Finish: - Surface finish has a greater effect on heating resistance. Pitting Corrosion are less likely to occur on polishing surface than rough surface.
 5. Solution Composition: - The agents which are most active in chromium and solution of oxidised salt.

❖ **Mechanism: -**

There are several theories and mechanism of pitting corrosion, they are-

1. Imperfection Theory
2. Penetration Theory
3. Acid Theory
4. Ion exchange Theory
5. Adsorption Theory
6. Magnetic Theory

❖ **Methods of Prevention: -**

1. Used folded butt joints instead of rebated joints in equipment.
2. Design vessels for complete drainage.
3. Avoid sharp corners.
4. Inspect equipment and remove deposits frequently.
5. Provide uniform environment.
6. Remove Solids in suspension.
7. Weld instead of rolling in tube sheets.

❖ **Stress Corrosion Cracking: -**

Stress corrosion cracking refers to cracking caused by simultaneous presence of tensile stress and a specific corrosive medium in other way it may be defined as a process of destruction of metal due to simultaneous action of corrosive environment and mechanical stress. For example – Season Cracking of Brass.

❖ **Characteristics of Brass: -**

1. These cracks appear on the surface of the metal subjected to simultaneous action of corrosive environment and stress.
 2. This crack propagates in a direction perpendicular to the stress.
 3. These cracks propagate at relatively low speed.
 4. These cracks are narrow during early stages of cracking and wider during the later stages of cracking.
 5. These cracks can be three types: -
 - I. Inter-granular
 - II. Trans-granular
 - III. Combination of both
- ❖ Intergranular proceeds along the grain boundaries, this is found in aluminium alloy and mild steel.
- ❖ Trans-granular crack propagation shows no preferences for grain boundaries. This is found in austenitic stain-less steel cast iron and brass. In both case, inter-granular and trans-granular cracking may occur in the same alloy depending on the metal structure and environment.

In stress corrosion cracking the basic requirement is come joint action of mechanical stress and environment. That is failure of material is much quicker than under the action of corrosion alone and also under the action of stress alone. The stress must satisfy the true condition: -

- I. Stress should be static
- II. Stress should be tensile
- III. Stress should be insufficient magnitude.

❖ **Factors affecting stress corrosion cracking: -**

1. Nature of Stress
2. Temperature
3. Solution Composition
4. Metal Composition
5. Metal Structure

6. Plastic Deformation
7. Influence of Alloying Elements
8. Size Factor
9. Influence of Stress

1. Nature of Stress: -

Charging may be takes place only during the action of tensile stress. The stress corrosion cracks are formed always normal to the plane of action tensile stress.

2. Temperature: -

From the data given for various metals and corrosive environment are different temperature it can be easily concluded that the rate of corrosion increases with increase in temperature of environment.

3. Influence of size Factor: -

The decrease of area to volume ratio in stress corroding specimen gives rise to a shaft decrease of the rate of stress corrosion cracking.

4. Influence of Alloying Elements: -

The degree of influence of alloying elements a stress corrosion cracking depends on the nature of alloying element and environment. For example- Stress corrosion rate increase as carbon content in steel increases up to 0.75%.

5. Influence of stress: -

It is dependent on the nature of corrosive environment stresses irrespective of their nature increase the rate of corrosion in acid environment and there is a linear relationship between the increase of rate of corrosion and increase of stress.

❖ Method of Prevention: -

1. Lowering the stress below the threshold value. This may be done by annealing in case of residual stress.
2. Eliminating the critical environmental species by degasification and distillation.
3. Changing the Alloy.
4. Applying cathodic protection to the structure with an external power supply.
5. Adding inhibitors to the system.
6. Coatings are sometimes used.

❖ **Fretting Corrosion: -**

This corrosion occurs at contact areas between the two surfaces of any material under load the basic requirement for the occurrence of fretting corrosion are-

1. Surface in contact must be under load.
2. Repeated motion between the two surfaces must be copper.
3. The load and the interface must be sufficient to produce deformation on the surface. Ex – (i). Riveted Joints
(II). Machine Parts

❖ **Factors Affecting Fretting Corrosion: -**

1. Amount of relative motion
 2. Temperature
 3. Environment
 4. Metallurgical factors
- I. Amount of Relative- The fretting corrosion increases in amount of relative motion.
 - II. Temperature – damage due to fretting corrosion decreases with decrease in temperature.
 - III. Environment – Fretting corrosion is more in dry condition and less in wet condition.
 - IV. Metallurgical Factors – Soft materials are generally more attracted to fretting than hard materials.

❖ **Mechanism of Fretting corrosion: -**

There are two mechanism to explain the damage cost by fretting corrosion:-

1. Wear Oxidation Mechanism
2. Oxidation Wear Mechanism

1. Wear Oxidation Mechanism: - The two surfaces make contact at only small numbers of high points.
Cold working due to apply load these contact point are rupture during subsequent relative motion.
2. Oxidation wear Mechanism: - According to this mechanism metal surfaces are protective from atmospheric oxidation by the oxide film. When the metals are placed in contact under load and

subjected to repeated subsequent motion of the oxide layer rupture the high points.

❖ **Methods of Prevention: -**

1. Increase the hardness of one or both of the contacting materials.
2. Increase the friction between the two parts.
3. Increase load to reduce slip between the two surfaces.
4. If possible, increase the relative motion between the two parts to reduce the attack.

❖ **Stray Current Corrosion: -**

This is a corrosion based on electrolytic corrosion and it is caused by stray electric current.

Causes: - A common cause is a bad earth return on electrical appliance giving rise to high leakage current through metal parts which are in contact with water. For Ex – Ship Equipment.

❖ **Atmosphere Corrosion: -**

This is a corrosion found in alloy and it causes serious damage unless adequate protection measurement is adopted. For ex – rusting of iron.

Causes: -

Atmospheric corrosion is due to the combined effect of film formation and film breakdown the formation of protective film occurs due to oxidizing action of air on a metal surface. The film breakdown is the result of electro-chemical action and thus can occur only in the presence of an electrolyte. The presence of moisture on the metal surface is necessary for film breakdown.

❖ **Factors Affecting Atmospheric corrosion: -**

1. Degree of Humidity
2. Contents of the Atmosphere.

1. Degree of Humidity: -

The rate of atmospheric corrosion of metals depends upon the moisture content in the atmosphere. For metal there is usually a critical humidity above which the rate of corrosion increases sharply. For example – Rusting of iron is very less below 60% relative humidity while rusting occurs severely if humidity is above 85%. The value of critical humidity is different for different metals and depends on the following factors.

- i. Physical characteristics of metal
- ii. Type of corrosion products.

2. Contents of the Atmosphere: -

The corrosion is primarily due to moisture and O_2 . but it is greatly affected by the presence of other contaminate in the atmosphere.

Ex- 1. Presence of Sulphur dioxide atmosphere may get contaminated with sulphur dioxide arising for burning of fuels in the industrial area.

2.The sulphur dioxide and moisture form sulphuric acid and sulphurous acid, which are both corrosive and there, for increasing corrosion rate.

(2) **Presence of chloride:** - localized corrosion is initiated by chlorides on the surface of aluminium and chromium resulting in the formation of heat which become responsible for corrosion attack.

❖ **Galvanic corrosion** – A potential difference usually exist between two dissimilar metals when they are emerged in corrosive medium or solution. If these metals are placed in contact these potential difference produces electron flow between them. Corrosion of the less corrosion resistant metal is usually increased and attack of the more resistant material is decreased as compared with the behaviour of these metals when they are not in contact. The less resistant metal becomes anodic and the mole resistant metal become cathodic. Because of the electric current and dissimilar metal involved this form of corrosion is called galvanic corrosion. It is an electro chemical corrosion type.

Galvanic corrosion something occurs in unexpected area this is also occurs in the atmosphere these depends upon the type and amount of moisture present in the atmosphere.

For example – Corrosion is greater near the sea shore than day atmosphere.

❖ **Factors affecting:** -

1. Environment Effect
2. Distance Effect
3. Area Effect

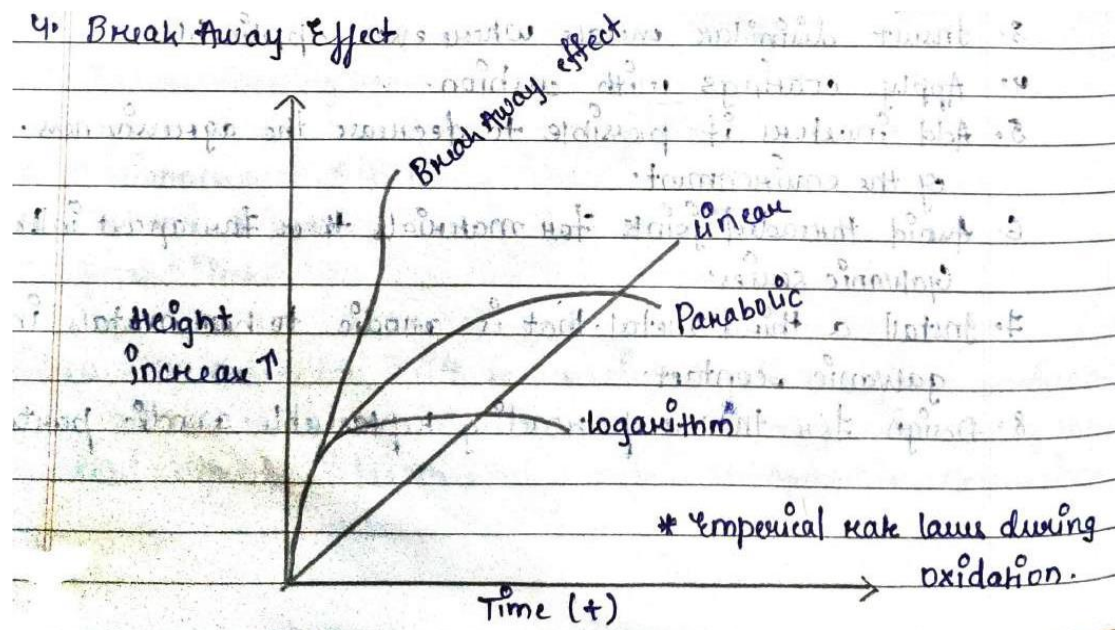
- ❖ Usually, the metal with less resistance to the given environment becomes anodic the nature and aggressive of the environment determine the degree of galvanic corrosion.
- ❖ Accelerated corrosion due to Galvanic effect usually greatest near the junction with corrosion attack decreasing with increasing distance from that point. The distance affected depends on the conductivity of the solution.
- ❖ Another important factor in galvanic corrosion is the area effect or the ratio of the cathodic to anodic area an unfavourable area ratio consists of a large cathode and a small anode for a given current flow in the cell the current density is greater for a small electrode than large electrode. The greater the current density at an anodic area the greater in the corrosion rate.
- ❖ **Prevention: -**
 1. Select combination of metals are flows together as possible in the galvanic series.
 2. Avoid the unfavourable area effect of a small anode and large cathode.
 3. Insult dissimilar metals where ever applicable.
 4. Apply coatings with cushion.
 5. Add investors, if possible, to decrease the aggressiveness of the environment.
 6. Avoid threaded joints for materials far apart in the galvanic series.
 7. Install a third metal that is anodic to both metal in the galvanic contact.
 8. Design for the use of readily replaceable anodic parts.

❖ **High Temperature Oxidation Corrosion: -**

The term oxidation refers to the chemical reaction of a dry metal surface with an oxidising gas. It is also called dry corrosion since heavy metal and alloy reacts with air at ambient temperature. Oxidation resistant must be considered in most of the engineering application. Oxidation limits the use of metals in high temperature power plant as temperature increases the importance of metal oxidation increases. For example – Oxidation should be considered in design of gas turbines, rocket engine and temperature Petro-chemical process.

The most important parameter of metal oxidation is the reaction rate. The various empirical rate loss observe during oxidation are given the figure.

1. Linear law
2. Logarithmic law
3. Parabolic law
4. Break Away Effect



1. **Linear law:** - The linear law applies to the initial stages of oxidation. It is the characteristics of metals for which a porous or crack scales are formed. The scale doesn't represent a diffusion barrier between the two reactants. For example – Sodium, Potassium Oxide linearly here, $x \propto t$
2. **Logarithmic law:** - Logarithmic law applies to highly protective thin film formed at low temperature. For example – Aluminium copper, Iron and some other metal oxides in this manner.
3. **Parabolic law:** - The Parabolic law is widely obey at temperature which is known as intermediate temperature. For ex- Iron oxides in this manner the temperature is 200°C to 400°C
4. **Break Away Effect:** - Break away effect are observed when something happens to the films such as cracking which reduces its thickness the plasticity of oxide at high temperature is important because it helps to prevent cracking when the oxide is brittle the discontinuous break away cause is obtained. For ex- the oxidation rate for of copper at 500°C

CHAPTER – 6

Corrosion Prevention

The various protective methods that are commonly in use can be classified under the following headings.

1. Control of the physical, Chemical and mechanical characteristics of metals and alloys.
2. Control of environment.
3. Control of external source of electric potential.

❖ **Control of Physical, Chemical and mechanical characteristics of metals and Alloys.**

The various method based on the above principle are given below-

1. Protective coatings
2. Purification
3. Heat Treatment
4. Alloying
5. Change in Design

1. **Protective coating:** - The protective coating applied to prevent corrosion can be either metallic or non-metallic. Both metallic or non-metallic coating applied to the metals for the prevention of corrosion should have the following characteristics-
 1. Good corrosion resistance against medium with which it comes in contact.
 2. Perfect adherence to the underlying metal.
 3. Continuous so as to cover the surface completely.
2. **Metallic Coating:** - The metal film coated on the surface of the metal may prevent the corrosion of the base metal in two ways-
 - i. Cathodic
 - ii. Anodic
 - i. **Cathodic Coating:** - Cathodic coating provides a physical barrier between the base metal and the corrosion media. For ex – Coating of Gold, Aluminium, Chromium on Iron.

- ii. **Anodic Coating:** - It provides an anodic surface between the base metal and corrosion media. Ex- Coating of Zinc, Aluminium, Cadmium on steel

❖ **Advantages of Metallic Coating: -**

1. Metallic coating is more durable than the non-metallic coating.
2. Metallic coating is more decorative than other coatings.
3. Metallic coating acts as shielding material against corrosion.

❖ **Methods of Applying Metallic Coating: -**

There are two methods by which metallic coating can be employed.

1. Mechanical Method
2. Electrolytic Method

❖ **Mechanical Method** – There are several techniques applied in mechanical method as-

- i. Hot Dipping
- ii. Spraying
- iii. Mechanical Cladding
- iv. Cementation
- v. Colourisation

- i. Hot dipping: - In this method the object is dip into the molten both of the metal to be portended.
- ii. Spraying: - In this method the liquid metal is sprayed over the object.
- iii. Mechanical Cladding: - This method is used for porting copper on steel plates.
- iv. Cementation: - In this method the object is heated to a sufficient high temperature so that the coating metal diffuses into heat to form a layer of alloy on the surface.
- v. Colourisation: - This is a special technique adopted for aluminium coating.
- vi. Electrolytic Method: - It is a very commonly used method of coating metals this method can be used to pored almost every metal.

❖ **Properties of coating metals: -**

- i. Nickel – It has very good wear and corrosion resistant properties.
- ii. It is the most resistant to alkaline.
- iii. Nickel coating is cathodic to iron and brass.

• Uses:-

1. Nickel coating is used for protection of iron steel and brass.
2. It is also used for decoration purpose.

❖ **Chromium: -**

Chromium has a very good corrosion resistant property.

- Uses: - Chromium coating is used on house hold object and large basin parts.

❖ **Tin** – Tin has a very good corrosion resistant property and it is also a alkaline resistant metal.

- Uses – Tin coating can be applied in extremely thin layer. It is used in the protection of tin plates.

❖ **Zinc** – it is a anodic metal in the steel.

- Uses – 1. Zinc is coated on iron plates.
2. zinc coating provides protection to steal under sea water.

❖ **Cadmium: -** It is better resistant to alkali. It is easy to Shoulder. It can be used as a plating material.

- Uses – 1. It is used for decorative purpose.
2. It is used in steel plant
3. Used in Refrigerator.

❖ **Copper** – 1. It is a corrosion resistant metal.
2. Good resistant atmosphere.

- Uses – Copper plating usually done nickel or chromium

❖ **Aluminium** – 1. It is a very good ductile metal.
2. Very good electro-chemical properties.

- Uses – Used for coating of iron or steel.

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