

Module-4

Corrosion Control

Topics:

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.

Control of Corrosion

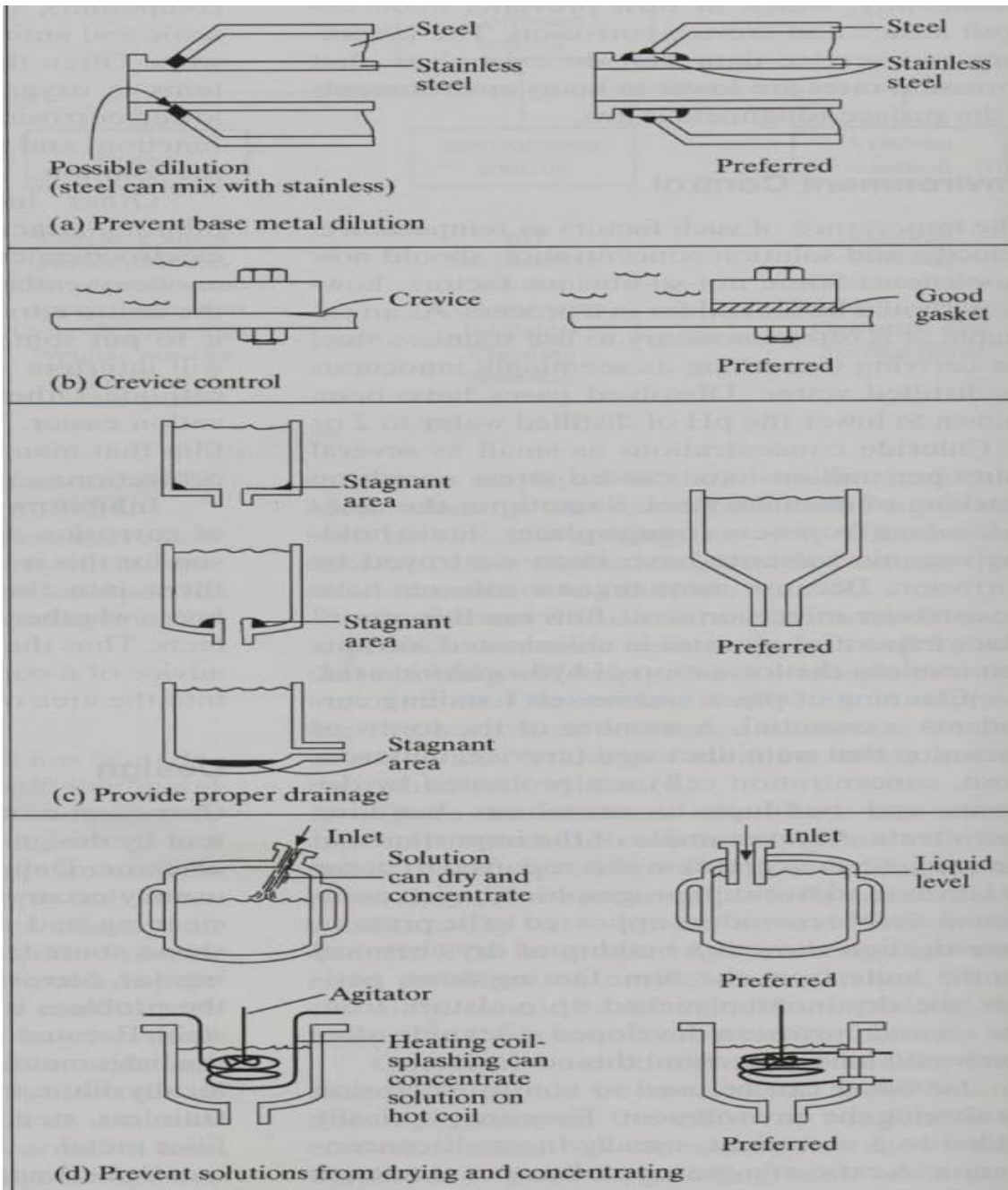
Corrosion can be controlled by:

- a) Proper designing
- b) Proper selection of metal or alloy
- c) Use of pure metals
- d) Use of alloys
- e) Cathodic protection
- f) Anodic protection
- g) Use of inhibitors
- h) Changing the environment
- i) Application of protective coatings

Design Aspects for corrosion protection

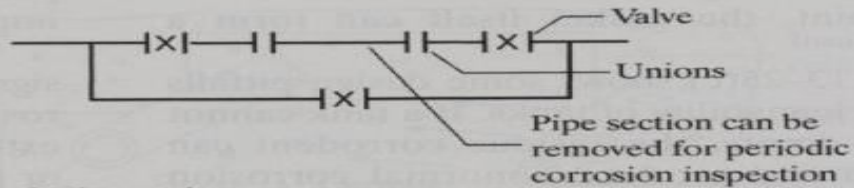
- Avoid sharp corners and sharp edges
- Avoid contact between dissimilar metals
- While working with dissimilar metals, larger anodic area and lesser cathodic area are necessary
- Insulating materials (washers, spacers) can be used when two dissimilar metals have to be put together in a fabrication
- When two dissimilar metals are together, painting or electroplating the anodic metal will help in reducing corrosion
- Weld rather than rivet
- Easy replacement of vulnerable parts
- Avoid excessive mechanical stress

DESIGN for Corrosion Protection

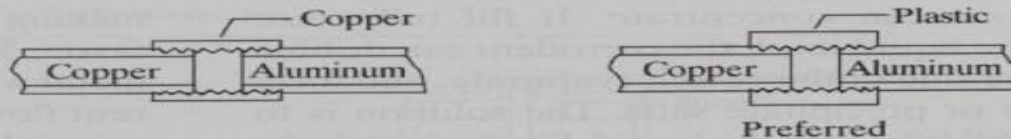


DESIGN for Corrosion Protection

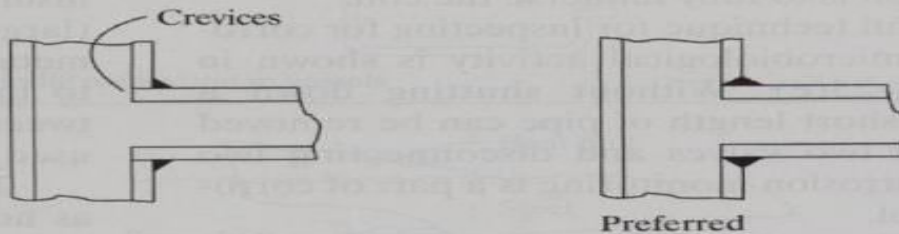
(e) Provide for inspection



(f) Prevent galvanic couples

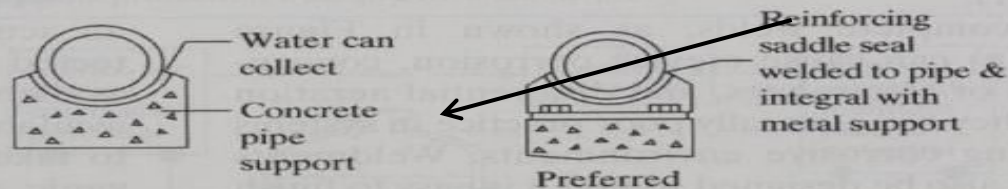


(g) Avoid incomplete weld penetration

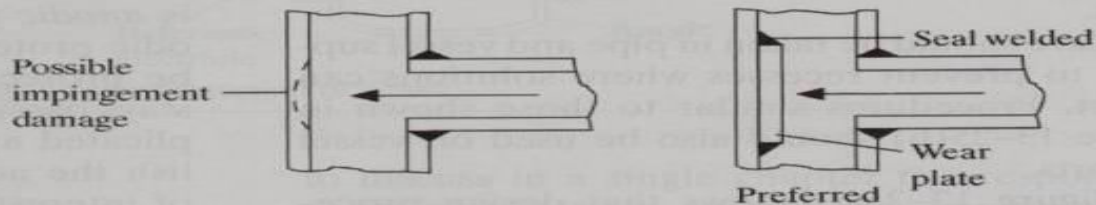


Bracket easier to replace than pipe!

(h) Avoid water accumulation in outdoor construction



(i) Use wear plates to minimize corrosive wear



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 known are :

i) Sacrificial anodic protection

ii) Impressed current cathodic protection

i) Sacrificial anodic protection:

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

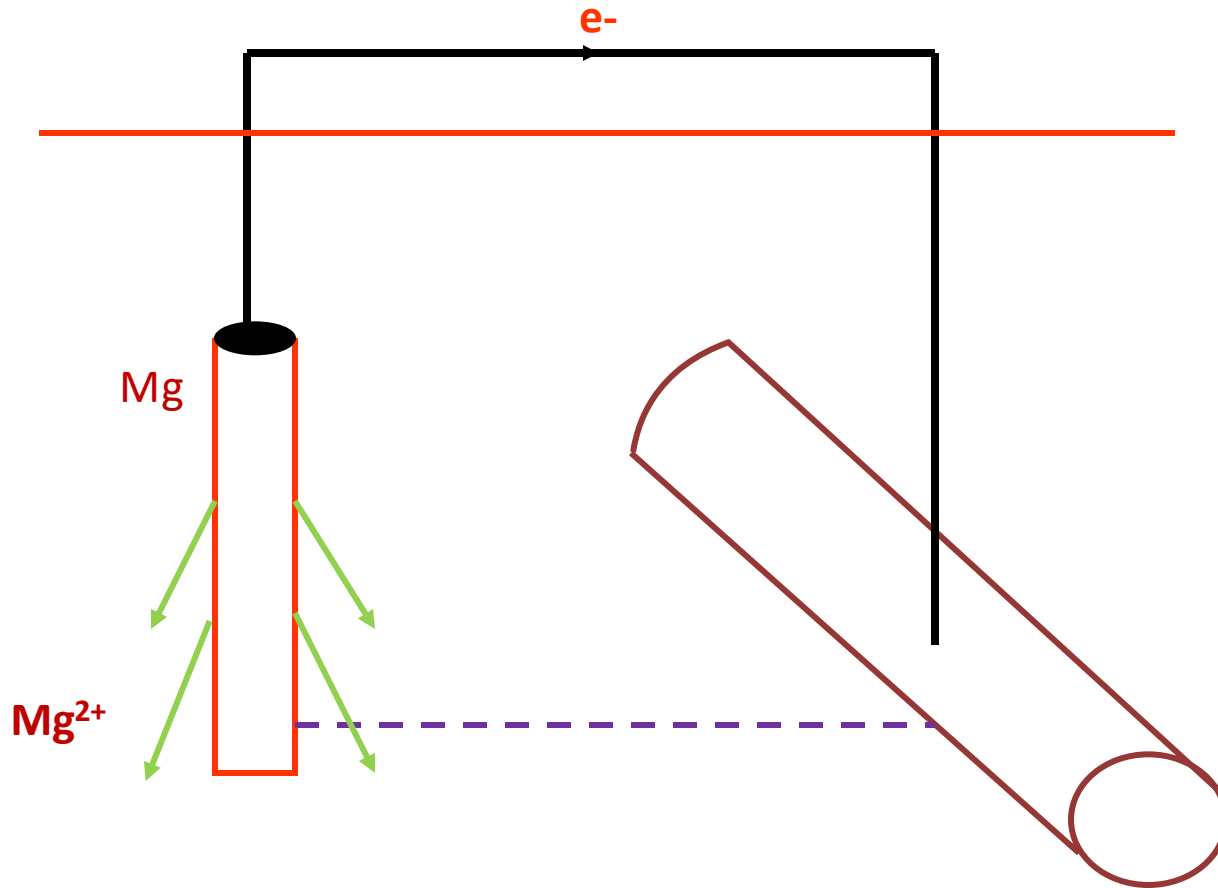
Corrosion control

ii) **Impressed current cathodic protection:**

- Impressed direct current is applied in the opposite direction to the corrosion current to nullify it.
- 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.
- The other terminal is connected to the metallic structure to be protected.
- Since the current is impressed on the metallic structure, it acts as cathode and thus gets protected.
- This method is usually used to protect underground water pipe lines, oil pipe lines, transmission lines, ships etc.

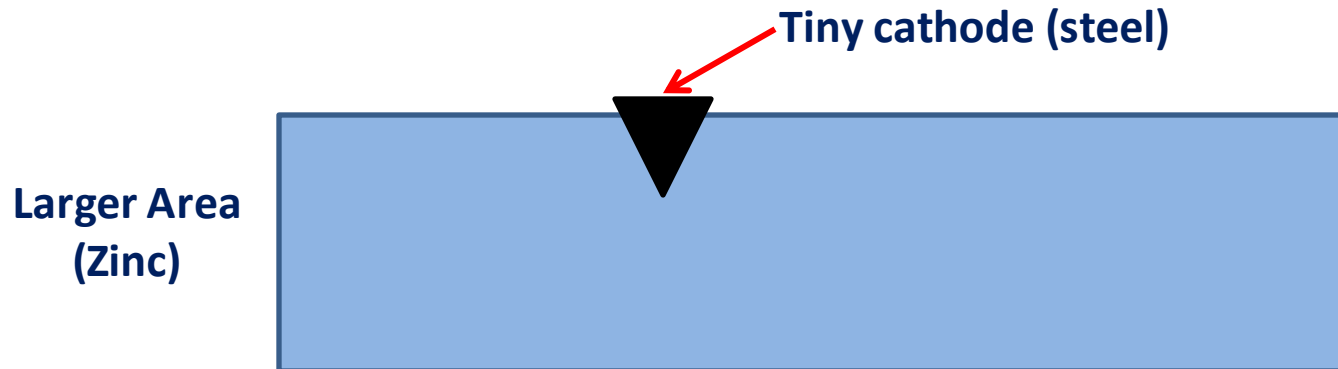
Sacrificial anodic protection

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 a unfavorable area ratio. Bad deal: huge cathode, tiny anode

Another Example

Zinc is attached to the steel hull of the vessel



Table 17.2 The Galvanic Series

| | |
|--|------------------------------------|
| | 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 |
| | [316 Stainless steel (active) |
| | [304 Stainless steel (active) |
| | [Cast iron |
| | [Iron and steel |
| | Aluminum alloys |
| | Cadmium |
| | Commercially pure aluminum |
| | Zinc |
| | Magnesium and magnesium alloys |

Increasingly inert (cathodic)



Increasingly active (anodic)

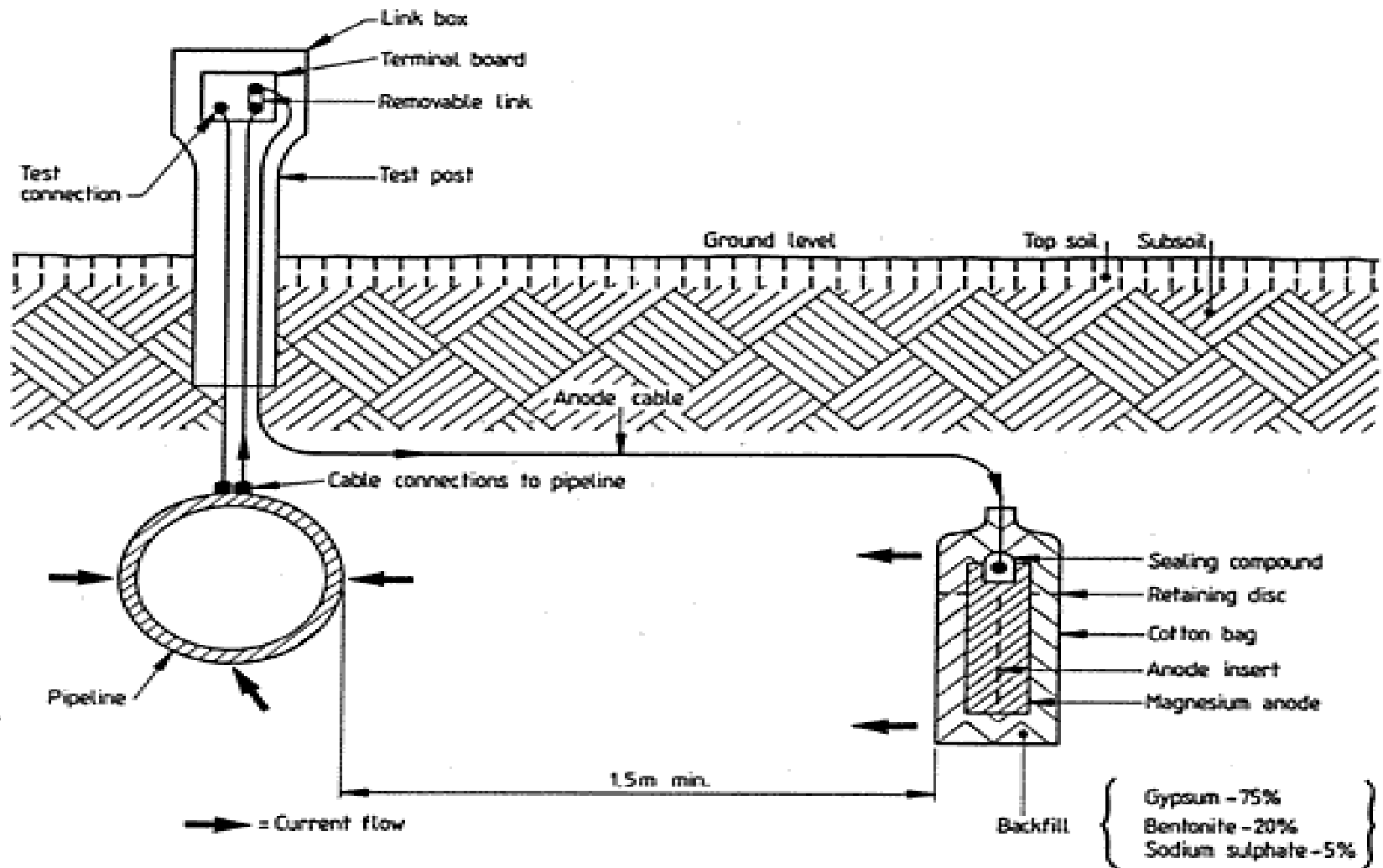


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Electrochemical Series

| Electrode | | Electrode reaction | E^0/V |
|-----------|-----------|---|---------|
| Au | Gold | $\text{Au}^{3+} + 3\text{e}^- \rightleftharpoons \text{Au}$ | +1.43 |
| Ag | Silver | $\text{Ag}^+ + \text{e}^- \rightleftharpoons \text{Ag}$ | +0.80 |
| Cu | Copper | $\text{Cu}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cu}$ | +0.34 |
| H | Hydrogen | $\text{H}^+ + \text{e}^- \rightleftharpoons \text{H}$ | 0 |
| Pb | Lead | $\text{Pb}^{2+} + 2\text{e}^- \rightleftharpoons \text{Pb}$ | -0.13 |
| Sn | Tin | $\text{Sn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Sn}$ | -0.14 |
| Ni | Nickel | $\text{Ni}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ni}$ | -0.25 |
| Cd | Cadmium | $\text{Cd}^{2+} + 2\text{e}^- \rightleftharpoons \text{Cd}$ | -0.40 |
| Fe | Iron | $\text{Fe}^{2+} + 2\text{e}^- \rightleftharpoons \text{Fe}$ | -0.44 |
| Zn | Zinc | $\text{Zn}^{2+} + 2\text{e}^- \rightleftharpoons \text{Zn}$ | -0.76 |
| Ti | Titanium | $\text{Ti}^{2+} + 2\text{e}^- \rightleftharpoons \text{Ti}$ | -1.63 |
| Al | Aluminium | $\text{Al}^{3+} + 3\text{e}^- \rightleftharpoons \text{Al}$ | -1.66 |
| Mg | Magnesium | $\text{Mg}^{2+} + 2\text{e}^- \rightleftharpoons \text{Mg}$ | -2.37 |
| Na | Sodium | $\text{Na}^+ + \text{e}^- \rightleftharpoons \text{Na}$ | -2.71 |
| K | Potassium | $\text{K}^+ + \text{e}^- \rightleftharpoons \text{K}$ | -2.93 |
| Li | Lithium | $\text{Li}^+ + \text{e}^- \rightleftharpoons \text{Li}$ | -3.05 |

Sacrificial Anode for a Pipeline



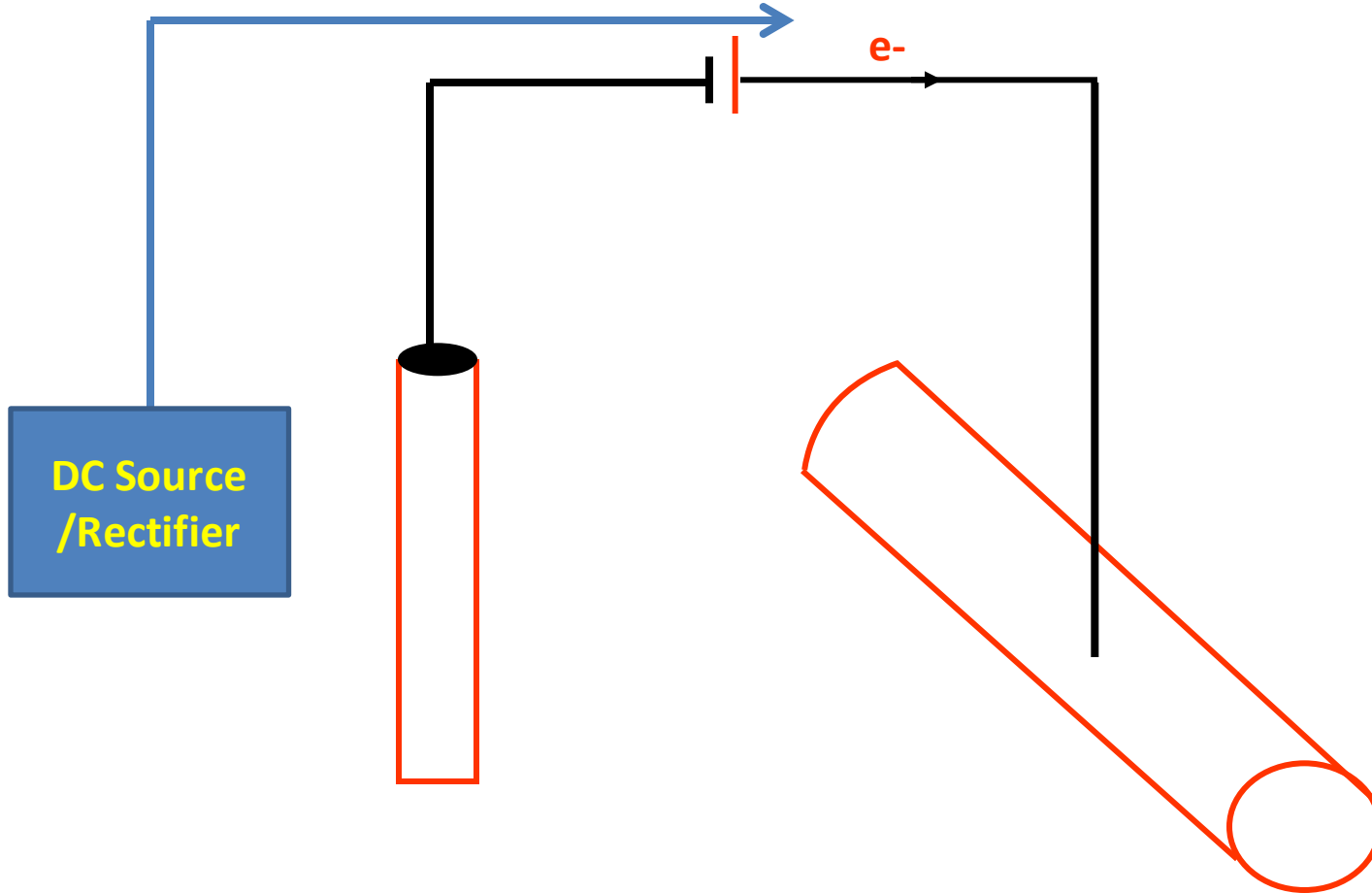


Aluminium anodes mounted on a **steel** jacket structure –
using galvanic corrosion for corrosion control! Called
cathodic protection (aka sacrificial anode)

Impressed current cathodic protection

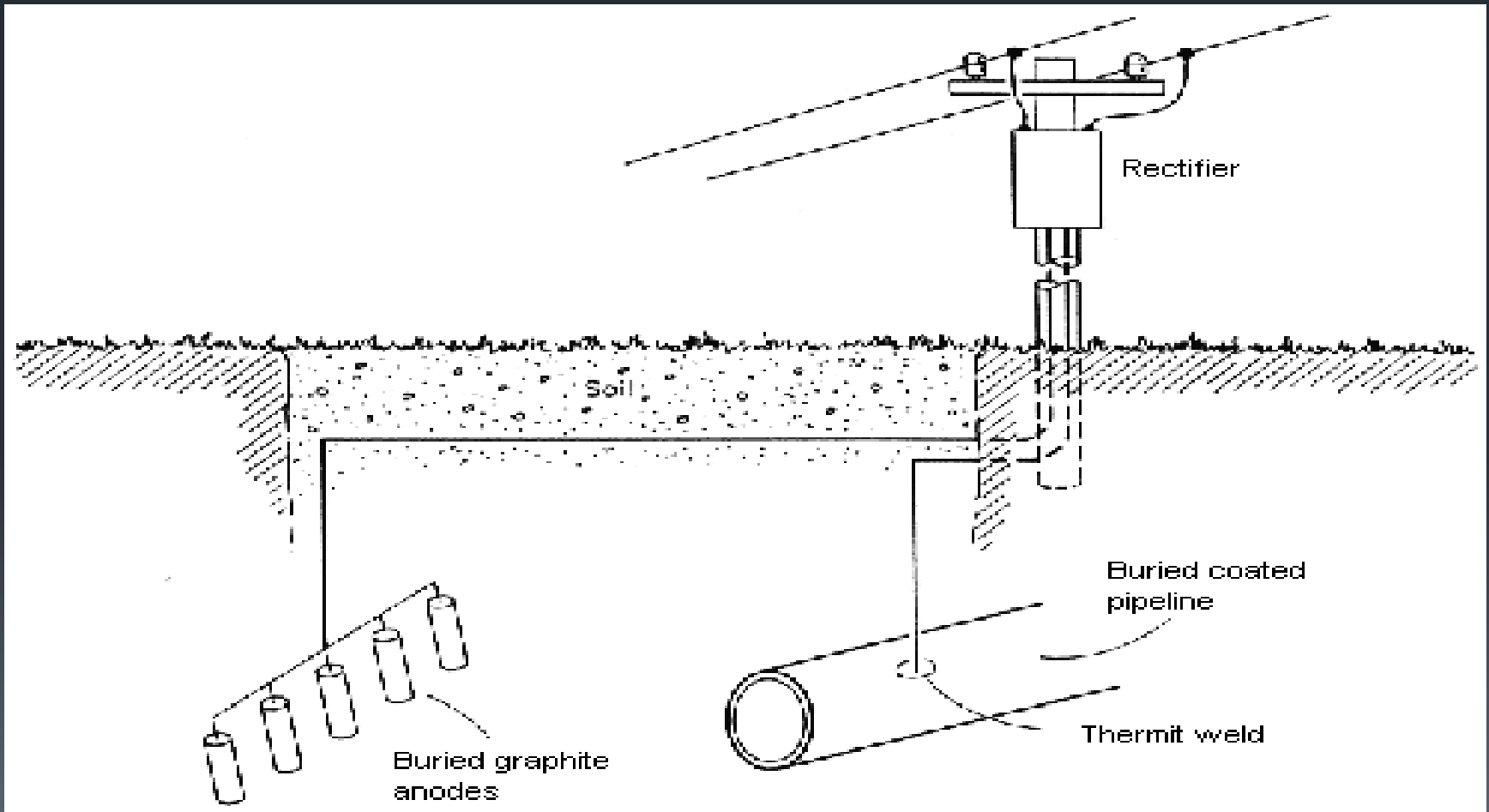
Impressed current cathodic protection - concept

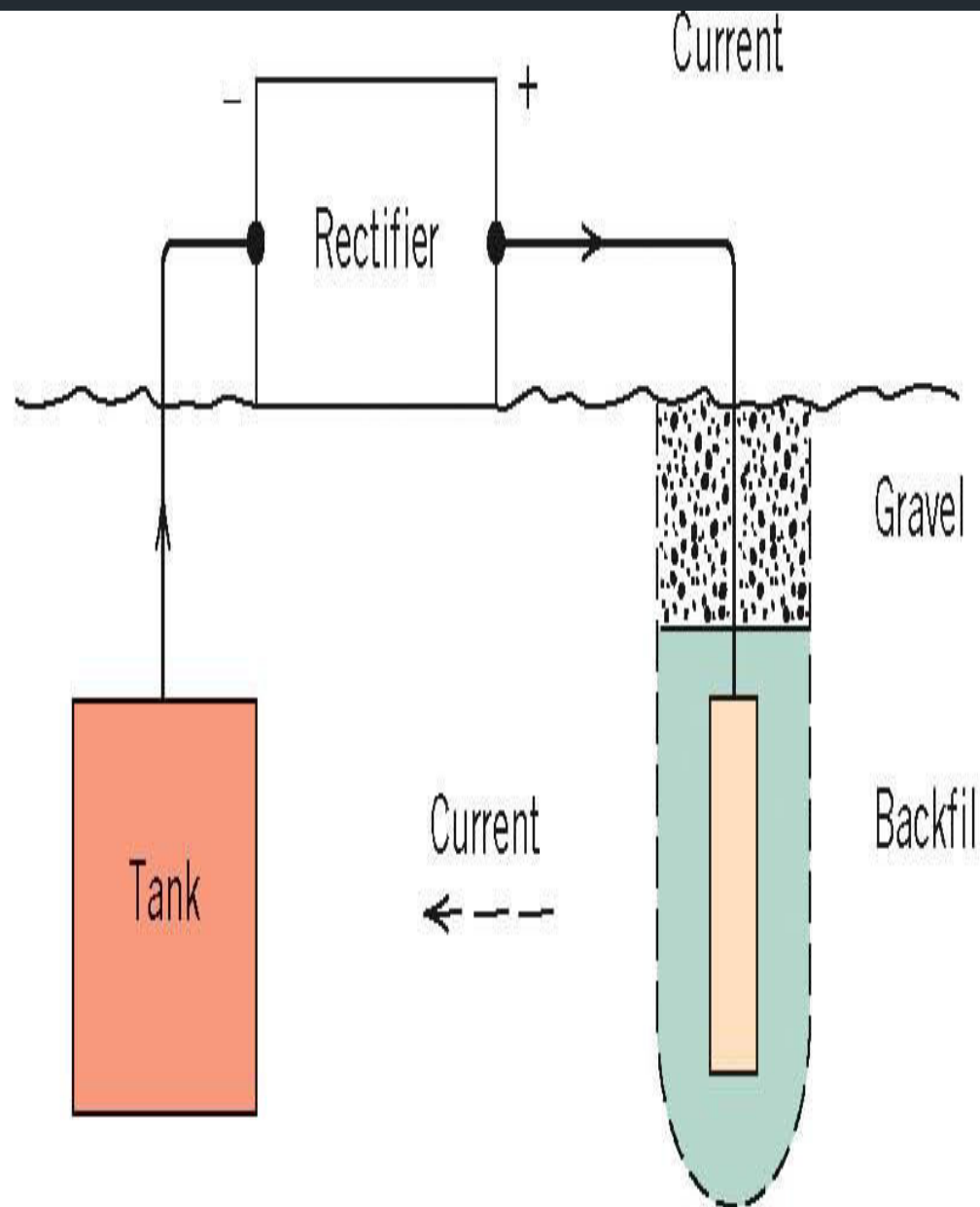
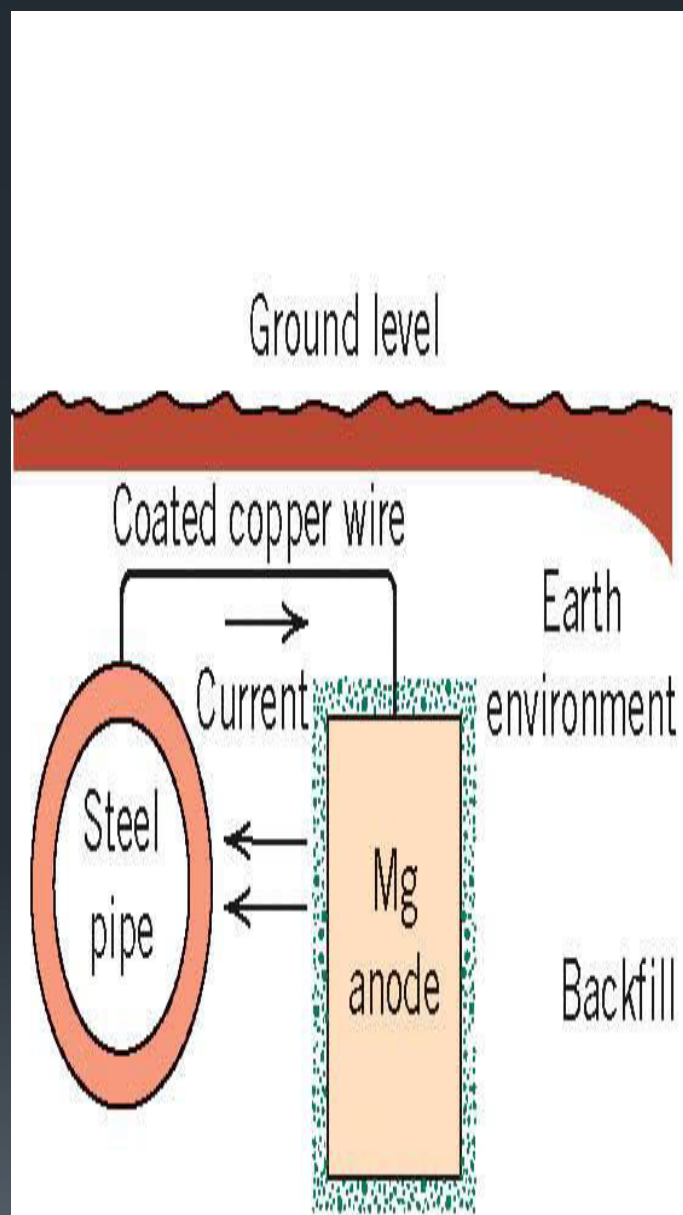
Corrosion current of equal magnitude but opposite in direction applied to nullify corrosion current

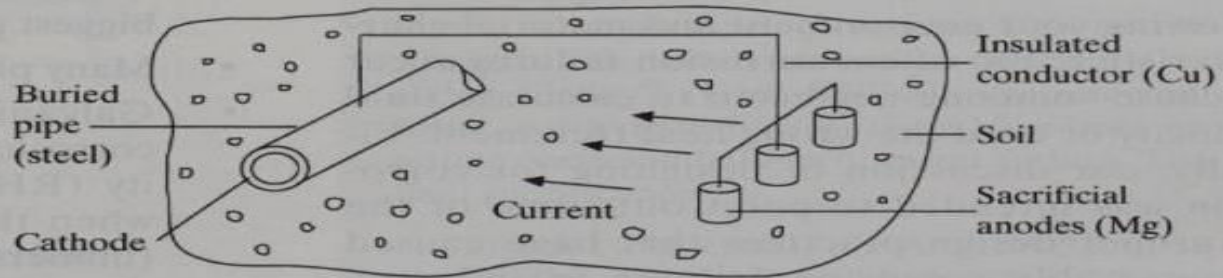


Impressed Voltage

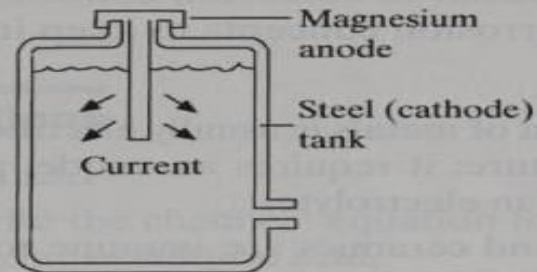
By imposing a voltage which causes electrons to flow towards the object to be protected, we make it less anodic and protect it from corrosion damage.



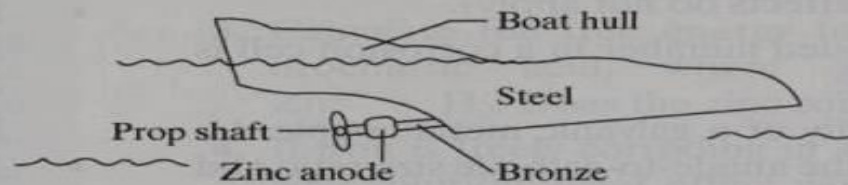




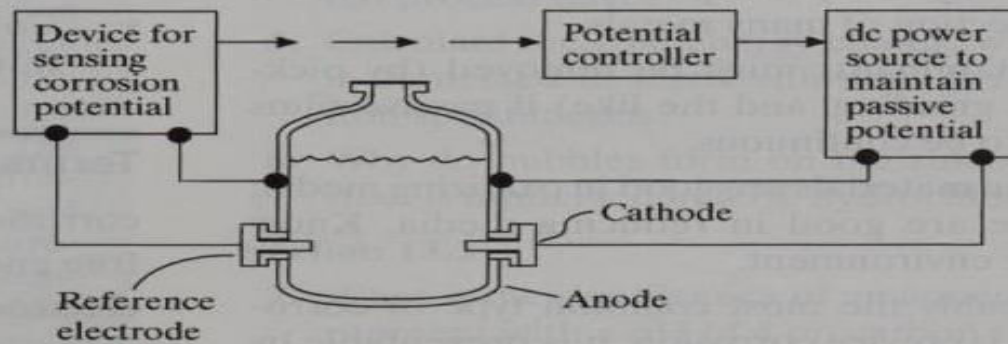
(a) Cathodic protection in soil



(b) Cathodic protection in vessels



(c) Galvanic protection with an active anode metal



(d) Anodic protection of a tank

Passivation of the anode

- We have two examples already. Stainless and aluminum.
- A thin oxide layer forms on the surface and isolates the metal from the environment.
- Zn, Mg, Cu and Ti are also capable of passivation under normal conditions of operation.
- Steel will also passivate in the presence of an alkaline environment, such as rebar in concrete.
- Corrosion inhibitors. Some of these, such as the chromates, are capable of coating a steel and passivating it.
- Coatings, paints, etc.

Corrosion control

Changing 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).
- Neutralisation of acidic environment containing H_2S , SO_2 , HCl , CO_2 etc., can be done by introducing alkaline neutralisers like ammonia gas, lime, naphthionic soaps, caustic etc., (Used in refinery to protect the equipment).

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 article.
- 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

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

- Surface preparation is a process to remove rust, oxide scales, oil, grease, dust etc.
- If these materials are not removed, the protective coating will not be smooth, uniform, cohesive and will not adhere to the metallic surface.
- Hence, mechanical and electrical methods are used to prepare the surface of the metallic article to be coated clean and free of these impurities.
- 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:

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

Protective coatings

b) Sandblasting:

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

c) Solvent cleaning:

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

Protective coatings

d) Alkali cleaning:

- 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.
- After alkali cleaning, washing is done with 1% chromic acid solution.

e) Acid pickling and etching:

- Base metal is dipped inside the acid solution at higher temperature for long periods of time.
- This treatment ensures cleaning of the base metal surface free from all kinds of impurities including oils, greases, rust etc.,
- 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 *galvanisation*.

Protective coatings

Cathodic coatings:

- Cathodic coatings are given on anodic metals using metals which are more cathodic.
- Coating of tin, chromium, nickel on iron surface are cathodic coatings.
- If there is a discontinuity in the coating, then galvanic couple will form with base metal as anode and the coated metal as cathode.
- Then the process of corrosion will start by the base metal ions going into solution and the metal deteriorating.
- 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) Metal cladding
- c) Electroplating
- d) Electrolessplating
- e) PVD
- f) CVD

a) Hot dipping:

Two types of hot dipping techniques 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

- 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.
- Electroplating is done for improving
 - a) corrosion resistance
 - b) wear resistance
 - c) chemical resistance
 - d) surface hardness
 - e) appearance
- Both ferrous and non-ferrous metals are plated with Ni, Cr, Cu, Zn, Pb, Al, Ag, Au, Sn etc.
- 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**
 - 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.

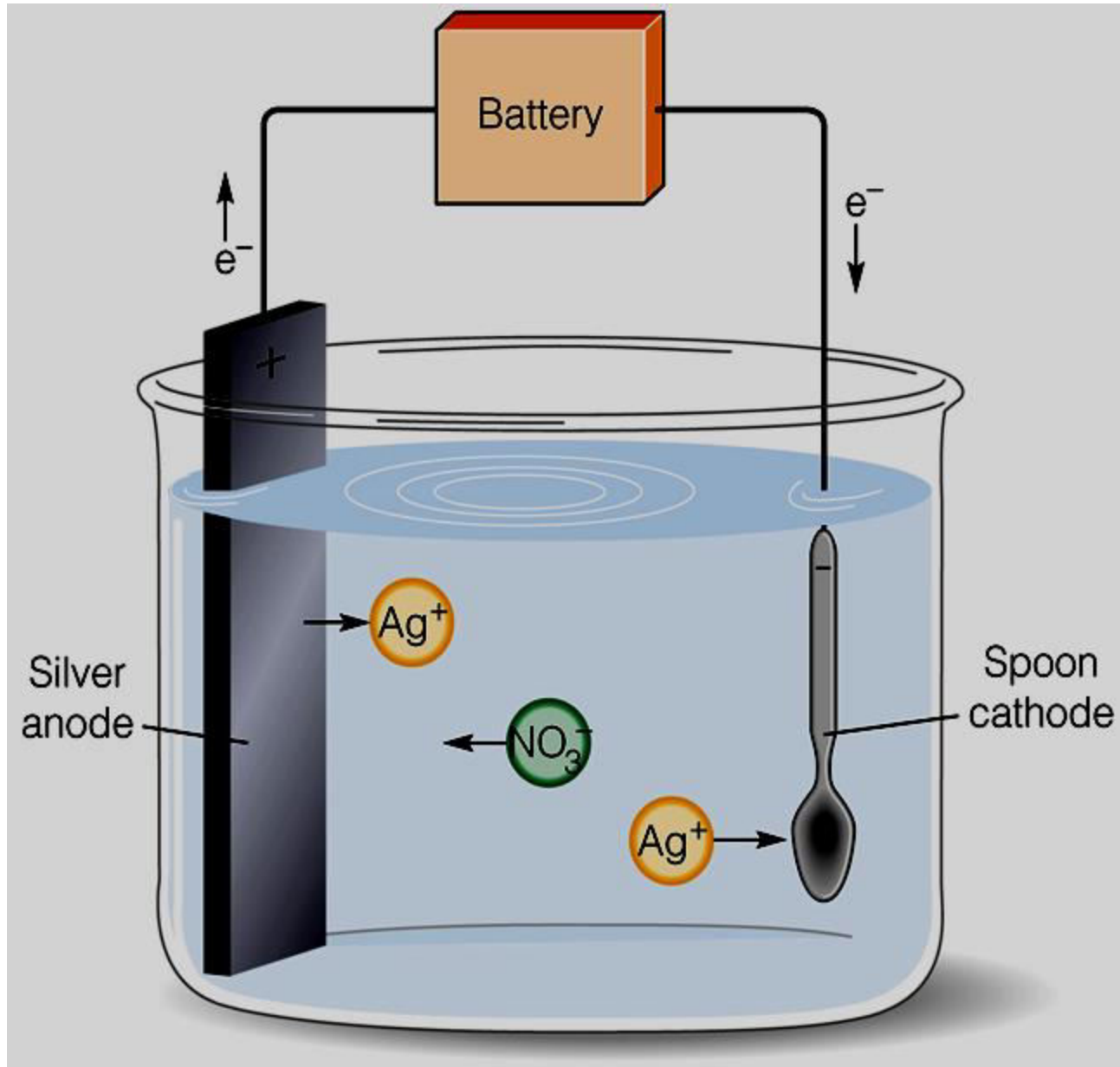
○ Method of Electroplating:

- 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.

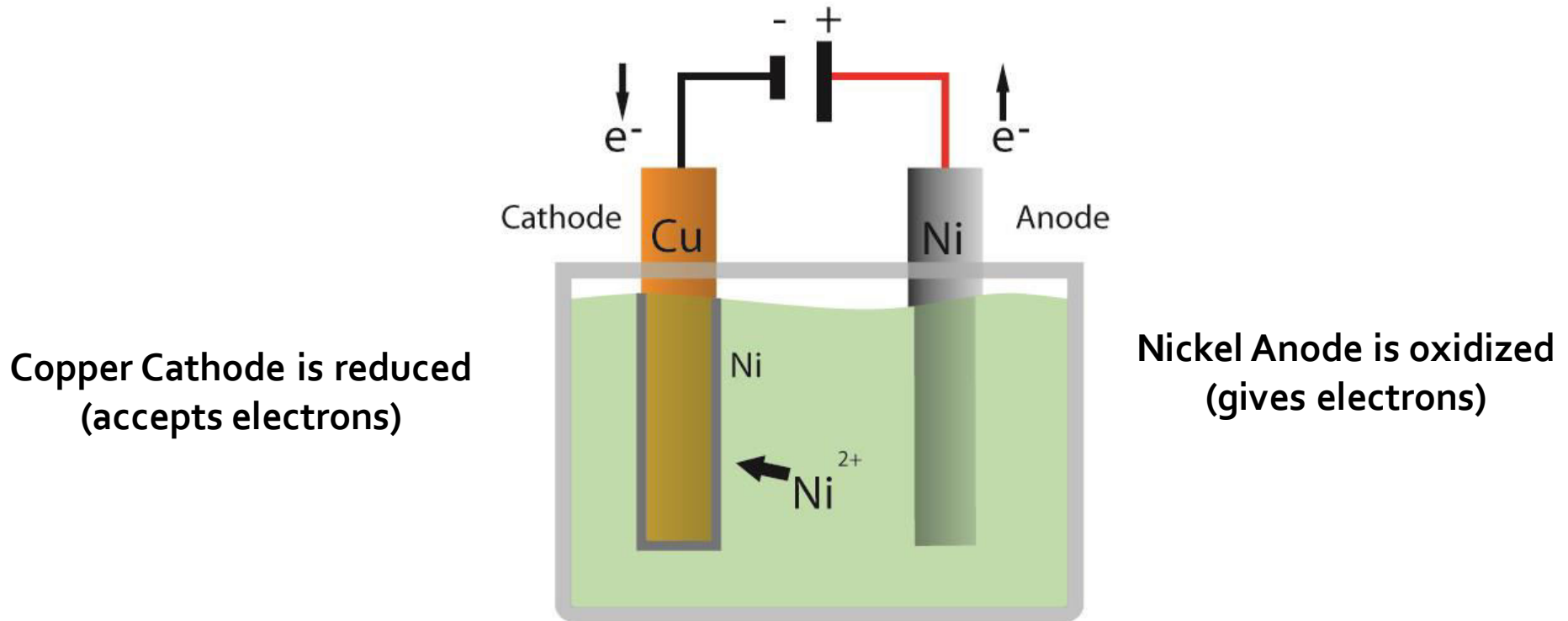
Plating bath solution

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

Electroplating



Electroplating with **Nickel** on **Copper**



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

Electroless plating

Electroless plating, also known as chemical or auto-[catalytic](#) plating, is a [non-galvanic](#) plating method that involves several simultaneous reactions in an [aqueous solution](#), which occur without the use of external electrical power.

The process is a chemical reaction and is autocatalytic.

It is mainly different from [electroplating](#) by not using external electrical power.

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.

Typically nickel and copper are used in electroless platings.

In the case of nickel, the deposits are dense, relatively hard and brittle.

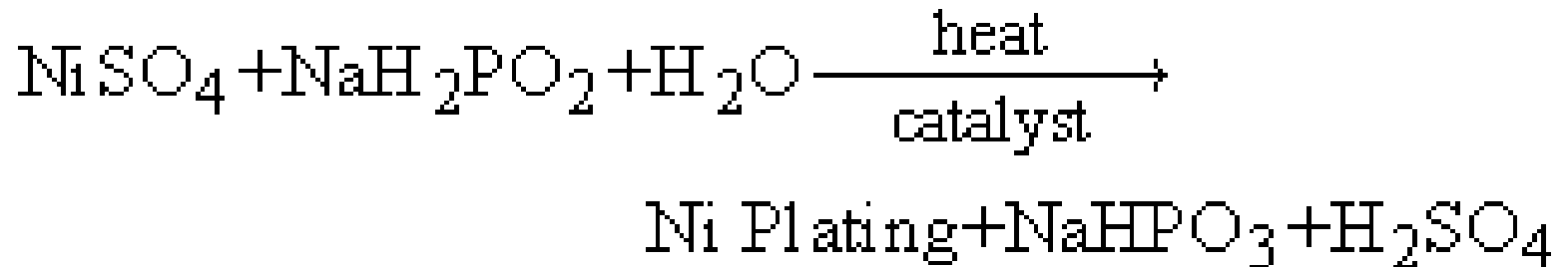
Electroless Nickel is not as bright as electroplated, easy to solder and braze, but difficult to weld.

Autocatalytic platings 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 Platings

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

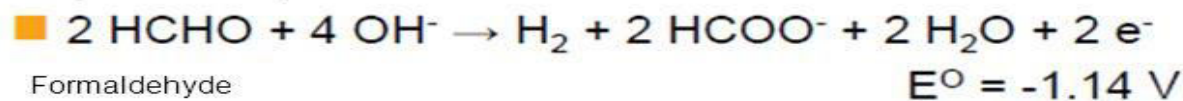
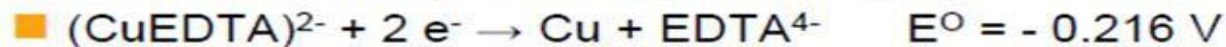
The electroless plating involving a nickel sulfate bath has the following reaction:



Copper electroless deposition

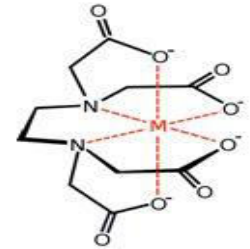
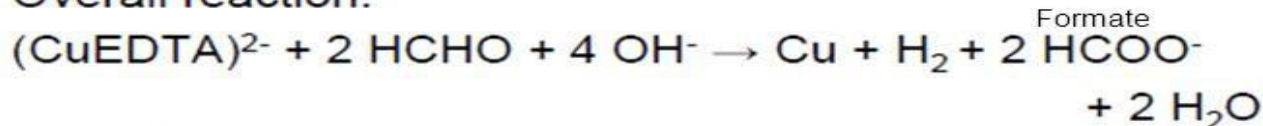
Ethylenediaminetetraacetic acid, EDTA

Two subreactions (reduction and oxidation):



Formaldehyde

Overall reaction:

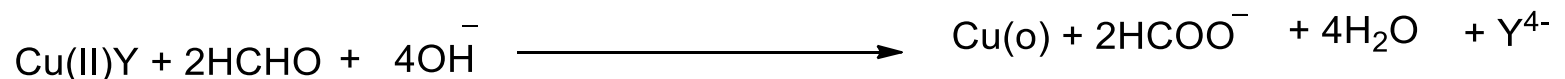


$$E^\circ = E^\circ(\text{reduction}) - E^\circ(\text{oxidation}) = -0.216 \text{ V} - (-1.14 \text{ V}) = 0.924 \text{ V}$$

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

- 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.



Electroless Plating

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

Electroplating

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

Galvanising and Tinning

Hot dipping is also a technique of metallic coating

Two types of hot dipping techniques are known

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

Eg. Galvanised iron pipes used for water lines

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

Eg. Tin coated steel containers for storage of food stuff such as Fruit pulp etc.

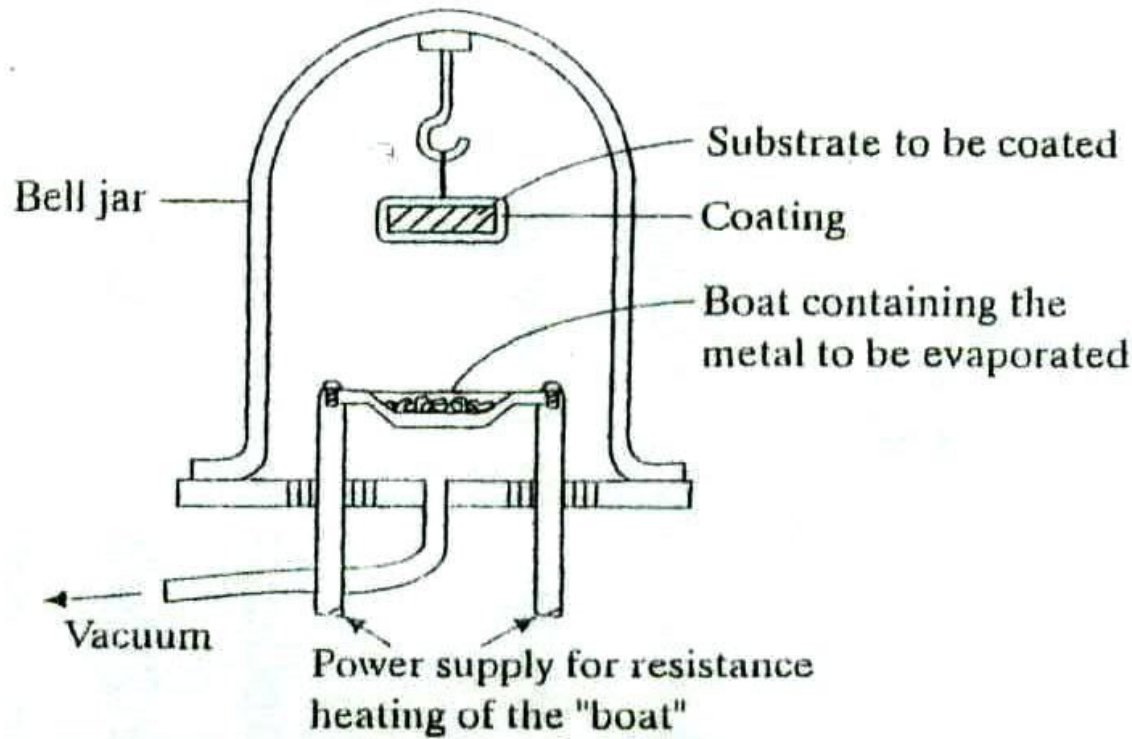
Physical Vapour Deposition

- This is a process of depositing some material by atom by atom or molecule by molecule or ion by ion.

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.

PVD: – 1. Thermal Evaporation Method

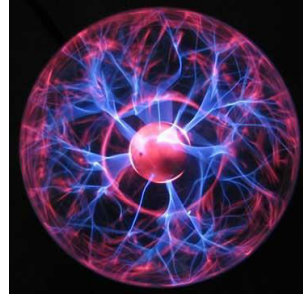


Al and Au are quite usable in thermal evaporation system with heated crucible, for they can be melt in crucible and generate enough quantity of vapours.

However, W and Ti are not suitable for their low vapour pressure.

Typical deposition rates in industry is around $0.5 \mu\text{m}/\text{min}$ ($\sim 8 \text{ nm}/\text{s}$, for Al)

PVD: 2 – Sputtering Method



Sputtering :

A popular **method for adhering thin films onto 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 a magnetron vacuum chamber under low pressure.

1. High technology coatings such as *ceramics, metal alloys and organic and inorganic compounds* are applied by sputtering.
2. The substance to be coated is connected to a high voltage DC power supply.
3. When the vacuum chamber has been pumped down, a controlled amount of argon or another gas is introduced to *establish a pressure of about 10^{-2} to 10^{-3} torr.*
4. On energizing current supply, plasma is established between the work and the material to be coated.
5. The sputtering gas is often an inert gas such as argon. For efficient momentum transfer, the atomic weight of the sputtering gas should be close to the atomic weight of the target, so for sputtering light elements neon is preferable, while for heavy elements krypton or xenon are used. Reactive gases can also be used to sputter compounds.

PVD: 2 – Sputtering Method

Sputtering is a process whereby particles are ejected from a solid target material due to bombardment of the target by energetic particles.

Sputtering is done either using DC voltage (DC sputtering) for **metals** or using AC voltage (RF sputtering) for **dielectric materials and polymers**.

The gas atoms are ionized and they bombard the material to be coated.

The energy of imposing ions cause atoms of the target material to be sputtered off and they are transported through the plasma to form a coating.

Direct current sputtering is used when the *target is electrically conductive*.

Radio-frequency sputtering, which uses a RF power supply is used when *the target is a non conductor such as polymer*.

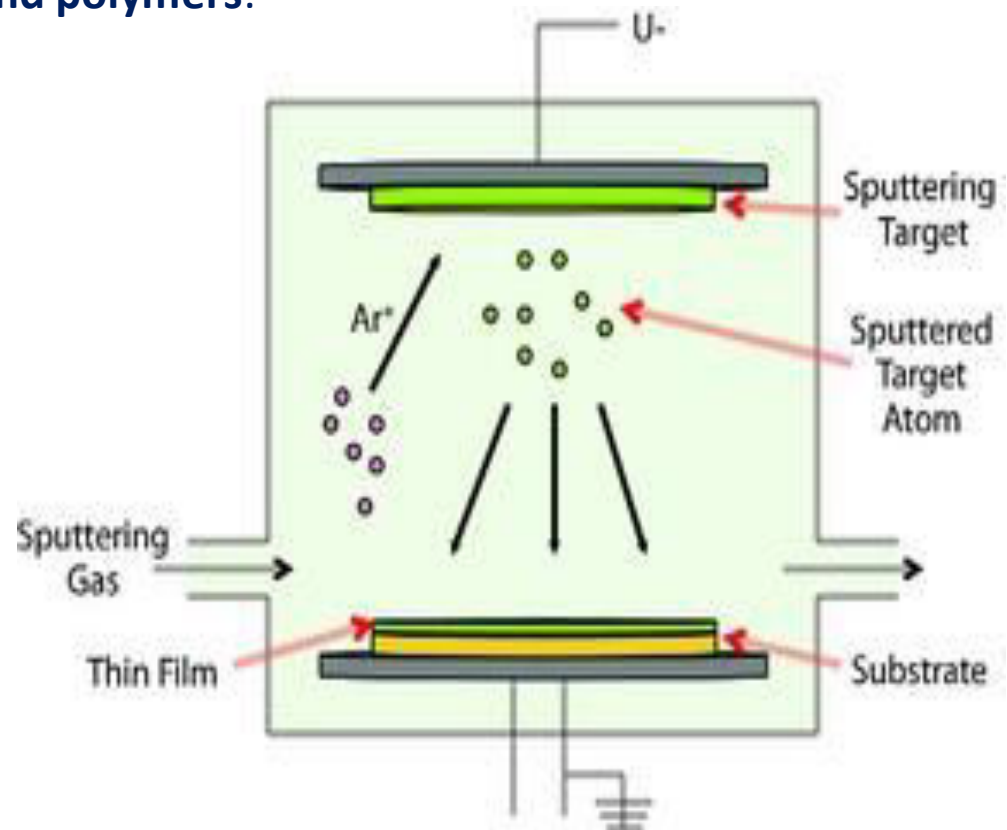


Figure : PVD by sputtering process₄₂

PVD: 2 – Sputtering Method

Plasma is a “[state of matter](#) similar to gas in which a certain portion of the particles are [ionized](#)”

- The main principle is to build a vacuum chamber and fill with Argon
- *By adding a high voltage, the argon will arc to plasma state*
- The argon ion (Ar^+) will move toward to cathode with high speed and sputter the target material (use target as cathode).
- The target atom or molecular will be hit to substrate surface and condense as a film.
- Instead of heat melting in evaporation method, the plasma Ar^+ ion hit and sputter the target is the main mechanism in plasma sputtering method.
- The target atom is knocked out by Ar^+ ion, the knock force is so big and can accelerate target atom a high speed. With such velocity, the target atom can hit and attach to substrate surface deeply.
- **The film density is good compared to thermal evaporation.**

PVD: 2 – Sputtering Method

Applications of Sputtering method:

- This method is used in VLSI fabrication

(Very-large-scale integration (VLSI) is the process of creating an integrated circuit (IC) by combining hundreds of thousands of transistors or devices into a single chip)

- Sputtering is used extensively in the semiconductor industry to deposit thin films of various materials in integrated circuit processing.
- Thin antireflection coatings (MgF_2 and Fluoropolymers; mesoporous silica materials; titanium nitride and niobium nitride) 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 while evaporation of these materials in a resistance evaporator or Knudsen cell is problematic or impossible. Sputter deposited films have a composition close to that of the source material.

Sputtering offers the following advantages over other PVD methods used in VLSI fabrication:

- 1) Sputtering can be achieved from **large-size targets**, simplifying the deposition of films with **uniform thickness** over large wafers;
- 2) Film **thickness is easily controlled** by fixing the operating parameters and simply adjusting the deposition time;
- 3) **Control of the alloy composition**, as well as other film properties such as step coverage and grain structure, is more easily accomplished than by deposition through evaporation;
- 4) **Sputter-cleaning of the substrate** in vacuum prior to film deposition can be done;
- 5) **Device damage from X-rays generated by electron beam evaporation is avoided.**

Sputtering, however, has the following disadvantages too:

- 1) High capital **expenses** are required;
- 2) The rates of deposition of some materials (such as SiO₂) are **relatively low**;
- 3) Some materials such as organic solids are easily **degraded** by ionic bombardment;
- 4) Sputtering has a greater tendency to **introduce impurities** in the substrate than deposition by evaporation because the former operates under a lesser vacuum range than the latter.

PVD – 3 - Ion Implantation Method

1. A third variation of the **PVD process is ion implantation method**
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

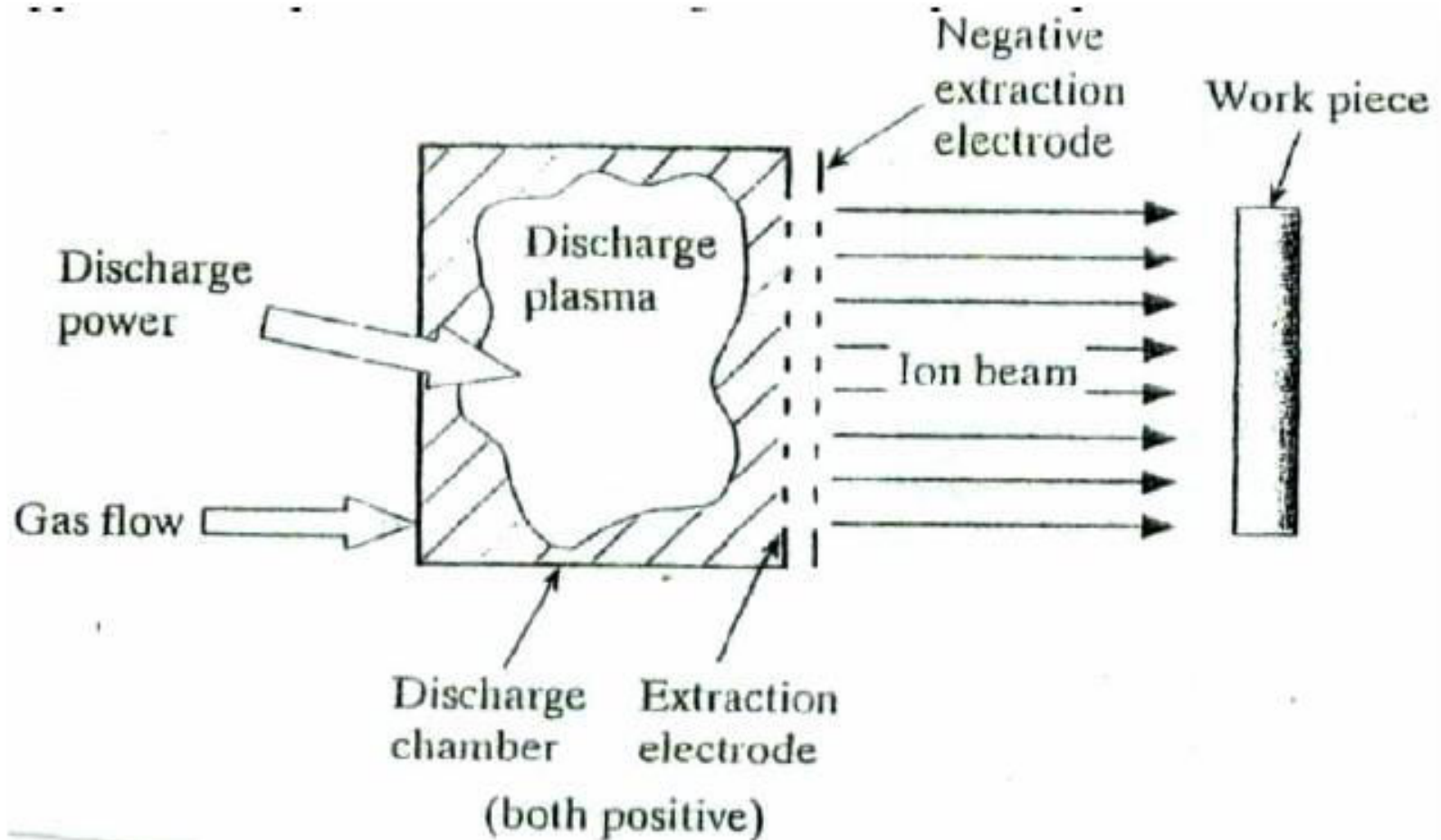


Fig.13 Ion implantation

Applications of PVD

| 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 |

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 polish 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.

Chemical vapour deposition

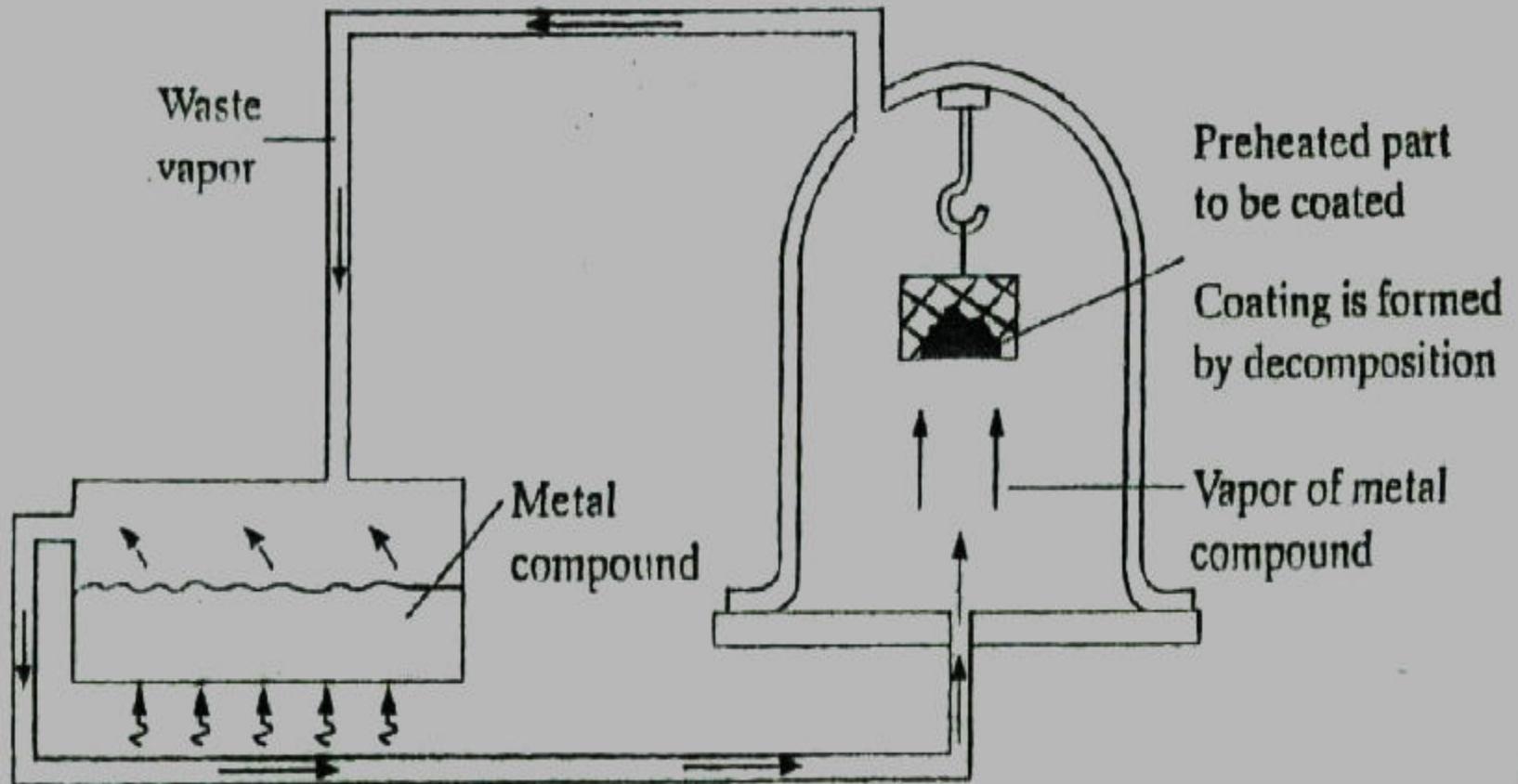
Chemical vapour deposition or CVD is a generic name for a group of processes that involve depositing a solid material from a gaseous phase and is similar in some respects to physical vapour deposition (PVD).

PVD differs in that the precursors are solid, with the material to be deposited being vaporised from a solid target and deposited onto the substrate

Precursor gases (often diluted in carrier gases) are delivered into the reaction chamber at approximately ambient temperatures. As they pass over or come into contact with a heated substrate, they react or decompose forming a solid phase which and are deposited onto the substrate. The substrate temperature is critical and can influence what reactions will take place.

Eg. Ni(CO)_4 for the deposition of Ni

Chemical Vapour Deposition



CVD Apparatus

A CVD apparatus will 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.

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

Advantages of CVD over PVD:

One of the primary advantages is that **CVD films are generally quite conformal**, i.e., that the film thickness on the sidewalls of features is comparable to the thickness on the top.

In, contrast, physical vapor deposition (PVD) techniques, such as sputtering or evaporation, generally require a line-of-sight between the surface to be coated and the source

Another advantage of CVD is that, in **addition to the wide variety of materials that can be deposited**, they can be deposited with very high purity.

This results from the relative ease with which impurities are removed from gaseous precursors using distillation techniques.

Other advantages include **relatively high deposition rates**, and the fact that CVD often **doesn't require as high a vacuum** as PVD processes

CVD also has a number of disadvantages:

1. The precursors need to be volatile at near-room temperatures.
 2. CVD precursors can also be highly toxic (Ni(CO)_4), explosive (B_2H_6), or corrosive (SiCl_4).
 3. The byproducts of CVD reactions can also be hazardous (CO, H_2 , or HF).
-
1. Some of these precursors, especially the metal-organic precursors, can also be quite costly.
 1. The other major disadvantage is the fact that the films are usually deposited at elevated temperatures. This puts some restrictions on the kind of substrates that can be coated.
 1. More importantly, it leads to stresses in films deposited on materials with different thermal expansion coefficients, which can cause mechanical instabilities in the deposited films.
 1. All surfaces in the reaction chamber get coated.
 1. Separate process and reaction must be developed for each coating. Some of the gases are toxic and dangerous.

Applications of CVD

1. A newer process known as **plasma assisted chemical vapour deposition**. This process is used **to apply diamond and diamond like carbon** coatings.
2. used largely in the production of semiconductors
3. **Silicon carbide** barrier coatings are applied **on plastic films** and **semiconductors**.
4. **Chemical Vapour Deposition is used to produce bulk shapes of high purity silicon carbide**. Reactants are deposited on a chamber wall to a thickness in terms of millimeters.
5. Thin-film coatings are key to the manufacture of many electronic devices. They involve the application of dopant, sealant and other microelectronic paste.
6. Thermal evaporation is a low cost process, but all these processes are normally batch processes because of vacuum chamber requirements.
7. CVD is also used to produce ***synthetic diamonds***.