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

- 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 (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:**

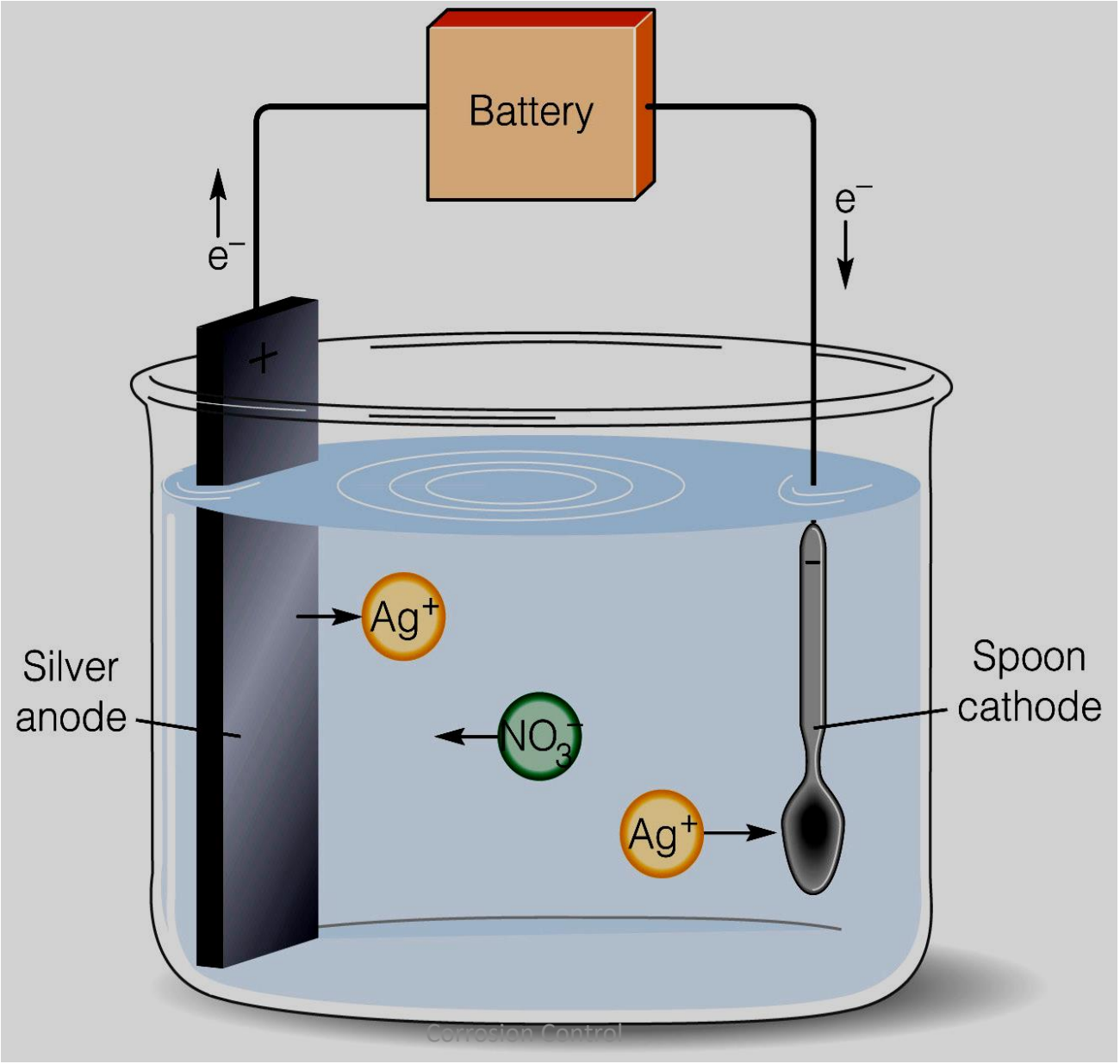
  - Method depends upon the type of metal to be electroplated, the size and type of article to be electroplated.

  - Its main objectives and economics are also considered.

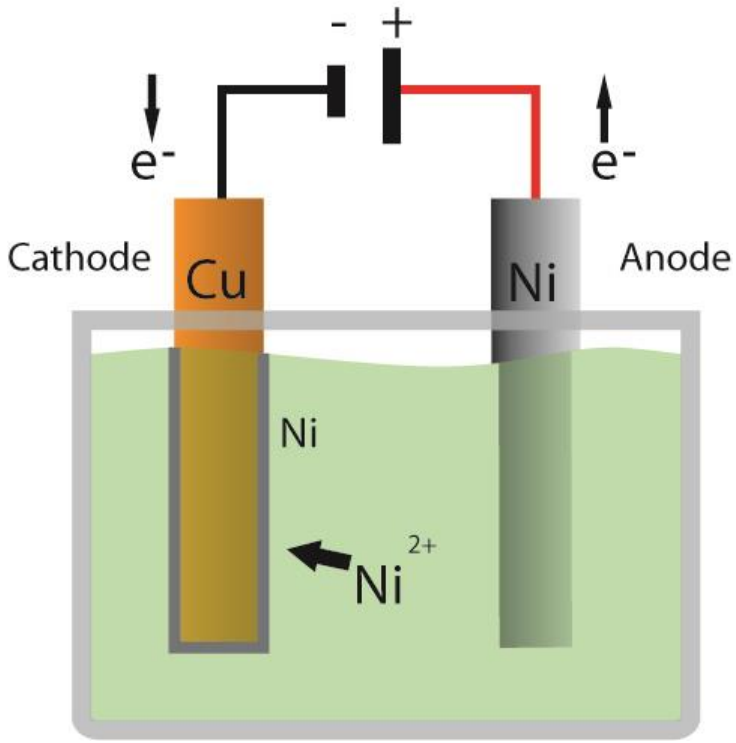
Plating bath solution

- 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**



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,

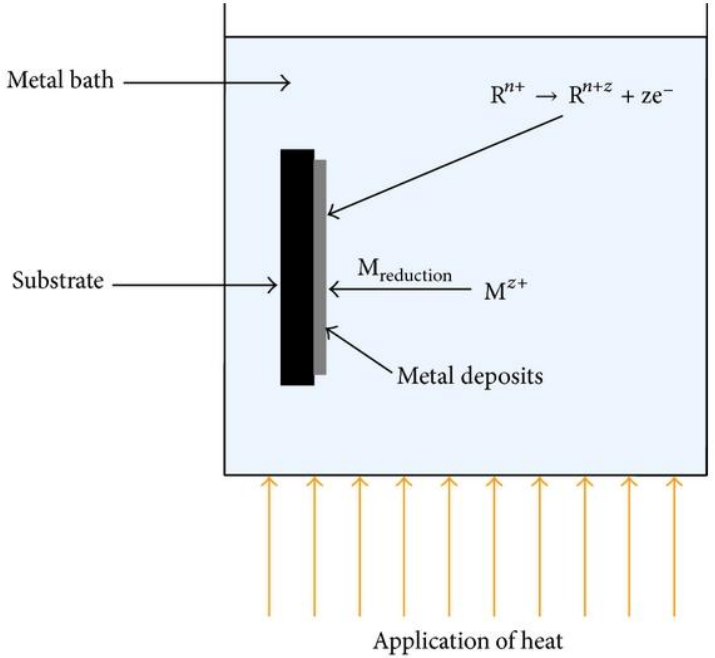
- Chemical plating
- Auto-catalytic plating
- Non-galvanic plating

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

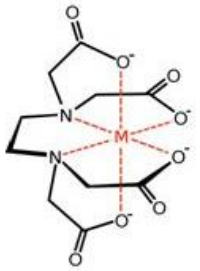
In autocatalytic plating, the metal ion is reduced to a metal only on a specific surface, which must have a catalyst present before the reaction can begin.

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

$$NiSO_4 + NaH_2PO_2 + H_2O \xrightarrow[\text{catalyst}]{\text{heat}} Ni\ Plating + NaHPO_3 + H_2SO_4$$

Copper electroless deposition

Ethylenediaminetetraacetic acid, EDTA



Two subreactions (reduction and oxidation):

- $(CuEDTA)^{2-} + 2\ e^- \rightarrow Cu + EDTA^{4-}$ $\quad E^O = -0.216$ V
- $2\ HCHO + 4\ OH^- \rightarrow H_2 + 2\ HCOO^- + 2\ H_2O + 2\ e^-$ $\quad E^O = -1.14$ V

Formaldehyde

Overall reaction:

Formate

$(CuEDTA)^{2-} + 2\ HCHO + 4\ OH^- \rightarrow Cu + H_2 + 2\ HCOO^- + 2\ H_2O$

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

$-0.216\ V - -1.14\ V = 0.924\ V$

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

→ 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.

$$Cu(II)Y + 2HCHO + 4OH^- \longrightarrow Cu(0) + 2HCOO^- + 4H_2O + Y^{4-}$$

Ref: Langmuir, 1990, 6, 1709

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