
CHAPTER-1

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1.1 Physical Nature of Electrodeposited Metals :

Electroplating or electrodeposition, a branch of electrometallurgy, is the art of depositing metals by means of an electric current.

The electrodeposition is governed by Faraday's laws of electrolysis. According to these laws, the amount of metal deposited during electrolysis is proportional to

- i) The quantity of electricity passed through the electrolyte.
- ii) The quantities of substance liberated at the electrodes are proportional to their chemical equivalents.

The mechanism of the process is explained by the theories of ionic dissociation or electrolysis. These processes and their changes which take place when a potential difference is applied by means of suitable electrodes immersed in solutions of numerous metallic salts. Such salts are appreciably ionised. The metallic ions migrate and deposit at the cathode. These are conditions which make for continued deposition. Electrodeposition occurs at cathode. In practice more than one element may be deposited simultaneously.

Electrodeposition of metals is affected by certain factors such as :

a) Current Density :

Current density is defined as the current per unit area of the electrodes. Its unit is amp per cm^2 .

$$C. D. = \frac{\text{Current (in Amps)}}{\text{Area of the electrode (in cm}^2\text{)}}$$

At low C.D. discharge of ions occurs slowly and so the rate of the growth of nuclei should exceed the rate at which new one forms, the deposits obtained under these conditions should be crystalline.

b) Current Efficiency :

Current efficiency of the process is defined as the portion of current which is actually used to deposit the specified metal or current efficiency is equal to the ratio of the theoretically used current to the current used for deposition actually.

Thus cathodic current efficiency may be defined as the ratio of the metal deposited by a given current strength to the weight of the metal that could be deposited according to the Faraday's laws.

$$\% \text{ Cathodic Current Efficiency} = \frac{100 \times \text{Equivalent weight of copper} \times \text{weight of metal deposited}}{\text{Equivalent weight of metal} \times \text{weight of copper deposited in coulometer.}}$$

It is to be noted that the weight of the metal deposited appears to be more than that demanded by Faraday's laws.

c) Throwing Power :

The property of a solution by virtue of which a relatively uniform deposit of metal may be obtained on a cathode of irregular shape is known as the throwing power.

Throwing power is favoured by high conductivity, but is best obtained by using a complex ion bath.

According to the Ohm's law, the depressed parts of the cathode material receive small current than the prominent parts and hence the former will have thinner deposits as compared to the latter. Throwing power tries to remove this defect. The conductance of the electrolyte and the change of current efficiency with change of current density and cathodic polarisation will also influence the throwing power of the solution.

If the conductance of the electrolyte is low, the current lines will tend to concentrate on the parts of the cathode nearest to the anode and throwing power will be poor. High conductance of the electrolyte improve the throwing power.

d) Polarisation :

Polarisation is indicated by the departure of the potential from the reversible value in the bath solution is relatively small. During electrolysis, metal has tendency to go into solution, i.e. it gives free ions of anode which move towards the cathode to get discharged and form atoms, ultimately give deposit. As a result of this, the solution at anode will be of greater concentration than the bulk of the solution. The result will be an increase in potential of the anode which will be greater i.e. higher than the rate at which metal dissolves.

At a cathode an opposite condition arises, the discharge of cations results in a decrease in their concentration i.e.

the solution becomes weaker due to depletion of the metal ions and hence there is less tendency to deposit the metal on the cathode due to back E.M.F. developed by a concentration cell. This increase in voltage at the electrodes from the normal value is called as concentration polarisation. The existence of concentration polarisation at an electrode can be readily detected by the fact that it is minimised by continuous uniform stirring of the plating solution, agitation of the electrolyte, increase of its concentration or raising the temperature. All these factors reduce the magnitude of concentration polarisation.

e) Over Voltage :

Over voltage is nothing but, the excess of potential above the theoretical decomposition potential, which arises due to evolution of hydrogen gas at cathode and oxygen gas at anode. (Caspari Z.Physik. Chem.30,89 1899). In electro-deposition of metals, cathodic over voltage is of great importance.

1.2 Controlling Factors :

In view of the industrial importance of electrodeposition of metals, the influence of various factors on the physical appearance of the deposit has been the subject of much investigation. Electrodeposited metals are crystalline. Their external appearance depends mainly on the rate at which the crystals grow and on the rate of formation of fresh nuclei. If the conditions are such as to favour the rapid formation of crystal nuclei, then deposit will be fine grained. The main

factors influencing the appearance of the electro deposited metals are, (1) The current density of deposition, (2) Concentration of the electrolyte, (3) Temperature (4) Presence of colloidal matter (5) Nature of the electrolyte, (6) Nature of the basis metal.

An ideal solution is one which contains few metal ions and plenty of dissolved metal salt. The solution of a complex salt of the metal satisfies this condition. The complex salt ionises in two or more stages. The metal usually ionises at the last stage and to a limited extent. According to another theory, fine grained deposits are obtained from the complex salt solution because the current first discharge on the cathode. The more negative metal which in its turn precipitates the metal present in the complex ion. Alternatively, the metal ion concentration of any salt solution can be suppressed, though only to a limited extent by the addition of a substance with "common ion".

The solution to be commercially useful, should have good throwing power and possess good conductivity. The stability of the solution and the cost of the chemicals employed should also be taken into consideration to establish optimum conditions for obtaining a fine grained adherent and shining deposit, a careful study of the following parameters is usually done :

- a) Current density
- b) Composition of both solution
- c) Temperature
- d) Hydrogen ion concentration
- e) Cathode material
- f) Addition agents.

a) Current density :

It is the measurement of the current on a specific area and is usually expressed in terms of amp. per sq. dm. At low current density the distribution of the deposit is more uniform. Increasing the current density, upto a certain limit increases the fineness of the crystals of the deposited metals. At higher current density the deposit becomes loose because the metal ions near the cathode are removed so fast that the migration and diffusion of the ions do not supply fresh ions in sufficient quantities. Hence at cathode there will be impoverishment of metal ions and yields rough, porous or spongy deposit. The character of the deposit, its distribution and the current efficiency depends on the current density.

b) Composition of Bath Solution :

The solution should be such that

- i) It contains a large proportion of metal ions.
- ii) It is stable to the action of air
- iii) It has good throwing power
- iv) It has simple composition and so capable of easy analysis.
- v) It has a good conductance.

To increase the conductivity of the solution, conducting salt and mineral acids are added to the solution. In the case of acid baths of nickel, zinc, iron and cobalt neutral salts like the sulphates of sodium, ammonium and potassium have been used. Good conductance reduces the voltage required for a given current density and also reduces the tendency of rough deposit.

When fine grained deposits are desired, a low metal ion concentration is beneficial. This is achieved by using a complex salt, as in case of electrodeposition of copper, silver, gold, zinc and cadmium from cyanide baths. The complex ion which dissociates to a very small extent to form metal ions, which get reduced at cathode during electrolysis. Thus fine grained, uniform and adherent deposit is produced.

Then metal-ion concentration can be reduced by the following methods :

- i) Use of dilute solution : A dilute solution will reduce the number of ions in the electrolyte. But after the passage of current there should be an impoverishment of ions at the cathode, hence a burnt or spongy deposit would result. Hence this is not a practical method of reducing the metal-ion concentration.
- ii) Use of Complex Salt : This is an ideal condition. There is low metal-ion concentration, but there will be no depletion

of these ions, since they are formed as fast as they are removed,

iii) Use of common ion : The metal-ion concentration can be reduced by the addition of a compound with common ion.

C) Temperature :

Increasing the temperature of the bath increases the coarseness of the crystals on the cathode. Since most plated work is expected to develop a fine deposit and high polish, generally electroplating solutions would be used cold or slightly above the room temperature. But in certain cases warmed baths are used because of some advantages e.g. hot solutions cause (i) an increase in the solubility of the salt which helps in using high concentrations and high current density, (ii) an increase in conductance which reduces the tendency of treeing, lowers the cost of electricity.

d) Hydrogen-ion concentration (pH) :

In nickel or zinc plating a high acid content and therefore a low pH value causes a fine and bright deposit. But such bright deposit may serve as a warning that the solution is near the danger point at which cracked or curled deposits may occur.

The metals at the top of the emf series are more active than those lower in series, it would appear that they would plate out the solution with more difficulty.

With special reference to hydrogen, if H^+ ions are present in the electrolytic bath, they should plate out more easily than the ions of any metal above hydrogen. The overvoltage of hydrogen on zinc is sufficiently high to permit zinc to be plated out unless H^+ ions are relatively in large number.

e) Cathode Material :

The structure of the cathode material plays an important role in the electrodeposition of metals. Hogaboom and others have demonstrated the influence of cathode material. Practically in all cases, a given deposit produced on a rough surface will be less smooth than that on the fine grained or smooth surface. The effect of basic metal is more marked. Deposits from baths with good covering power or from those containing addition agents may cover over and smoothen up small scratches or defects in the basic metal. There is evidence that alloy deposits, because of differences in deposition potentials can give complex coverage all crystal faces by the first few atomic layers of plates. Single metal gives "selective" deposition on some crystal faces only, until appreciable plate thickness is reached.

Another effect of the basic metals that any nonmetallic or poorly conducting particles on the surface are likely to prevent or retard deposition at those points and hence to cause pores in the deposit.

f) Addition agents :

In electrodeposition, of a metal or an alloy, it is customary to add some foreign substances, in traces, which have a remarkable or satisfactory explanation of their behaviour was developed. Although it was generally assumed that the addition agents or products derived from them were colloidal and hence under favourable conditions, migrated to the cathode, where they increased the polarisation and were adsorbed into deposits. This theory of migration and adsorption is supported by the fact that almost all metals deposited in the presence of addition agents, contain appreciable quantities of organic matter. Adsorption of addition agents may result from electrical attraction of the charge at the cathode for an ionic agent. Some addition agents are chemisorbed, that is, held by specific chemical bonding, especially when the cathode potential is near the point of zero charge, for them the water dipoles or ions on the metal surface are most easily displaced.

Addition agents are generally consumed in the deposition process. They may be decomposed and the products in part incorporated into the deposit (eg. sulphur, carbon or both) or released back into electrolyte. As a rule, they affect the internal stresses in the deposits, either positively or negatively. Common addition agents are glucose, glue, gelatine, gum, olive oil, pyrogallol, glycerine, oil of clove, etc.

1:3 The equipment for the work of Electrodeposition :

The work of electrodeposition of metals requires the following essentials :

- i) The electrolyte which is a good conductor of electricity and contains essentially a salt of the metal to be plated.
- ii) The electrodes comprising an anode usually of the metal to be deposited and a cathode plate which is the object to be plated.
- iii) A source of current to set up the necessary potential in the plating cell.

A systematic study of electrodeposition of the metal from a particular bath solution makes it possible to attain an optimum condition. For a smooth, uniform, fine grained and adherent deposit, with a characteristic pleasing colour, particular to the metal in question. Though the quality of the work produced is of prime importance in electroplating, the detailed quantitative study is necessary in a scientific research of the problem. Hence with an adjustment between the quality of the deposit and the high cathode current efficiency it is possible to obtain a state of mutual co-operation between an electroplater and a chemist.

1.4 General Applications of Electroplating :

Many metals used in manufacturing operations are with lack of pleasing colour. Coatings of other metals considerably add to their appearance. Many industrial metals lack resistance to the corrosive conditions of the atmosphere and the surrounding

industrial localities. Such metals are well protected against corrosion by depositing them electrolytically with the noble metals. It is often desirable to reproduce metal surface in copper and other metals, for example, the presence of electroplating as carried out for printing purpose or for artistic effects. Machine parts which are worn, require of a suitable metal coating. Again, principles of electrodeposition are also employed in electro-refining of metals, in which, metals are highly refined by electrodeposition from suitable solutions, the deposited metals, being usually much more pure than those obtained by melting processes.

Of these different processes mentioned above, we are here mainly concerned with those in which electrodeposition is carried out for the purpose of applying coatings which are relatively thin and are required for protective and decorative purposes. In such cases the deposits obtained are required to adhere firmly to the base metal to which they are applied and which provide the required strength for the finished product.