CHAPTER 1

GENERAL INTRODUCTION

Studies on Controlling Factors in Electroplating of Metals and Alloys.

1.1 General Introduction :

The electro-deposition is governed by Farady's laws of electrolysis. According to these laws, the amount deposited during electrolysis is proportional to

1) The quantity of electricity passed through the solution and
2) The equivalent weight of the metal.

In electrolysis the electrical energy is converted into chemical energy. However, this has been observed to be a universal phenomenon that this transformation is never in toto. In practice, more than one element may be deposited simultaneously or other chemical compounds formed, using a part of the electric current, a part of which is also lost due to lockages and in heat conversion and also due to short circuits.

a) Current Efficiency :

Since the purpose of electro deposition is to deposit a specific metal, the current efficiency of the process is defined as that portion of the current which is actually used to deposit that metal. In other words, the 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 Farady's laws.

$$\%\ \text{Cathode Current Efficiency} = \frac{100 \times \text{Eq.wt.of copper} \times \text{Wt.of the metal deposited.}}{\text{Eq.wt.of the metal} \times \text{wt. of copper deposited in coulometer.}}$$

It is worthwhile to note that some times the weight of the metal deposited appears to be more than that demanded by Farady's law. In such cases the metal deposited may not be in the pure form ; or it may be because of reasons other than that of electrolysis and thus the cathodic current efficiencies appear to be more than 100 % according to the above formula.

b) **Current Density :**

Current density is defined as the current per unit area of the electrode. It is generally expressed in Am/ Dm^2.

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

c) **Throwing Power :**

Throwing power is the capacity of the plationg solution by virtue of which relatively uniform deposit is obtained. It is usually expressed as the improvement in percent of the metal distribution ratio, above the primary current distribution (1).

According to the Ohm's law, the depressed parts of the cathode material, receive smaller 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, the change of current efficiency with change of current density and cathodic polarisation influence the throwing power of the solution.

d) **Polarisation:**

During electrolysis, anode dissolves, giving free ions which moves towards the cathode to get discharged and aggregate there as atoms, ultimately forming the deposit. As a result of this, the solution at the anode, tends to become stronger, because of the additional free ions from the anode; while at the cathode, it tends to become weaker, because the metal ions there give up their charges and aggregate as atoms, forming a deposit on the cathode. If the solution of the anode becomes stronger, there is less tendency for the anode to dissolve, hence it requires an increased potential or voltage to continue the passage of the current. Reverse is the case of the cathode, where the solution becomes weaker due to depletion of the metal ions, and hence there is less tendency to deposit the metal on the cathode, and hence a higher voltage is required at the cathode, due to back EMF developed by a concentration Cell. This increase in voltage at the electrodes from the normal value is called as 'concentration polarisation'. It may be anodic or cathodic as the case may be. However, this type of polarisation could be minimised by continuous uniform stirring of the plating solution. On the other hand the excess potential above the theoretical (reversible) decomposition potential, arising due to evolution of hydrogen at the cathode or oxygen at the anode is called as 'overvoltage '. In eledroplating of metals, cathodic overvoltage is of great importance.

1.2 Controlling factors in Electro plating of metals :

In view of the industrial importance of electrodeposition of metals, the influence of various factors on the physical appearance of the deposits has been the subject of much investigation. It is generally agreed that electro-deposited metals are crystalline, and the 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, the deposit will be fine grained; if the tendency is for the nuclei to grow rapidly, however, relatively large crystals will form and the deposit becomes rough in appearance. The chief 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. These are the factors controlling the nature of the deposit.

An ideal solution would be one which contains a few metal ions but plenty of dissolved metal salt to furnish a fresh supply of ions as fast as they are removed. The solution of a complex salt of the metal satisfies this condition, as the complex salt ionises in two or more stages, the metal usually being ionised 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 discharges on the cathode, the more negative metal, which in its turn precipitates the metal (positively charged), present in the complex ion. Atternatively, the metal ion concentration of any salt solution can be suppressed, though only to a limited extent, by the addition of a substance with a ' common ion ' .

The solution to be commercially useful, should have good throwing power and possess good conductivity. The stability of the solution and of course 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 paramaters is usually done.

1) Current density.
2) ~~Compo~~ Composition of bath solution.
3) Temperature.
4) Hydrogen ion concentration.
5) Cathode Material.
6) Addition agents.

1) Current density :

Increase in current density increases the proportion of the less noble metal in the alloy deposit. At higher current density the deposit becomes loose, especially at the edge, owing probably to the decrease in metal ion concentration near the cathode and evolution of hydrogen. There is tendency to produce rough or treed deposits. A still further increase in current density yields spongy or burnt deposits. The darkening of the deposit at high current density may be atributed to the more alkalinity produced near the cathode due to evolution of hydrogen and subsequent formation and inclusion in the deposit of hydrousoxides and basic salts. Current density is a very important variable in all electroplating operations ; the character of the deposit, its distribution, the current efficiency and perhaps even whether a deposit forms at all may depend on the current density employed. Illustrations of these statements will be found in subsequent places.

2) Composition of Bath Solution :

The solution should be such that -

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

To increase the conductivity of the solution, conducting salts which comprise freely dissociating salts 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 to treeing of the 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 cynide baths. For, the complex ion dissociates to a very small extent to form positive metal ions, which get reduced at the cathode during electrolysis. Thus a fine grained, uniform and adherent deposit is produced.

The metal ion concentration may be brought down in the case of single or simple salt plating electrolytes by adding a compound with a common ion viz. addition of sodium chloride in tin chloride bath, in the electrodeposition of tin. A reduced metal ion concentration in the solution increases its throwing power (2).

Other salts are sometimes added to aid the anode corrosion, like chlorides and fluorides. To prevent the solution from getting too much acidic or alkaline " buffering agents " are added like boric acid (3). Glycine is used in nickel chromium alloy deposition, as it helps to maintain the pH and prevents pitting (4). Thus bath composition is also an important factor and the chemical balance should be kept at optimum range.

3) Temperature :

Increase of temperature on one hand favours diffusion and tends to produce a fine grained, uniform deposit, but on the other, it increases the rate of crystal growth, decreases the hydrogen overvoltage, favouring evolution of the gas. The influence of temperature is caused by a greater solubility and dissociation of the metal salt, which in turn, leads to a higher conductivity of the solution. The higher current density counteracts the effect of the higher temperature.

Increase in temperature usually increases the proportion of the nobel metal in the deposit. The effect is complicated, since temperature change may also alter the degree of dissociation of complexes and have various effects on polarisation factors.

4) Hydrogen ion concentration :

Metals below hydrogen in EMF series, can be easily plated out from solutions of high acidity, that is low pH which cause bright deposits; moreover, it prevents the precipitation of the basic salts. The pH of the cathode film tends to be higher than that of the body of solution, if the cathode efficiency is less than 100 percent. The pH reached in the cathode film under uniform conditions depends upon the pH in the body solution.

In general the use of a low pH in the bath will result in a lower pH in the cathode film than in a bath with higher pH. A low pH in the bath permits the use of higher current densities in the bath to produce a sound deposit at a relatively high efficiency (5). In one of the few papers (6) on the pH of cynide baths, it was shown that the effects of pH on anode and cathode efficiencies are highly specific.

5) <u>Cathode material</u> :

The structure of the cathode material plays an important role in electrodeposition of metals. Hogaboom and others have demonstrated the influence of cathode material. In practically 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 basis metal is more marked with a thin than that with a thick deposit. Deposits from baths with good covering power or from those containing addition agents may cover over and smooth up small scratches or defects in the basis metal (7). There is evidence (8) that alloy deposits, because of differences in deposition potentials can give complete coverage of all crystal faces by the first few atomic layers of plate, whereas single metals give " selective " deposition on some crystal faces only, until appreciable plate thickness is reached.

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

6) Addition agents :

In electrodeposition, of a metal or an alloy, it is customary to add some foreign substances, in traces, which have a remarkable influence on the structure of the resulting deposits. No complete 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 od 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, or for one which prossesses a permanent or induced dipole (9). 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 then the water dipoles or ions on the metal surface are most easily displaced (10.,11).

Addition agents are generally consumed in the deposition process. They may be decomposed (12) and the products in part incorporated into the deposit (eg. sulfur, carbon or both)(13;14). or released back into electrolyte. As a rule, they affect the internal stresses in the deposits, either positively or negatively, common of the addition agents are glucose, glue, gelatine, quinine, gum, olive oil, pyrogallol, glycerine, oil of clove etc. Many of the newer addition agents are not colloidal.

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 and finally (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 obtain an optimum conditon 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 prim 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.

General Applications of Electroplating :

Many metals used in manufacturing operations lack 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 nobler metals. It is often desirable to reproduce metal surfaces in copper and other metals; for example, the processes of electroplating as carried out for printing purposes or for artistic effects. Machine parts which are [illegible] worn, require their dimensions increased. This is accomplished by the deposition of a suitable metal coating which also supplies the required wearing properties. 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 smelting 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.