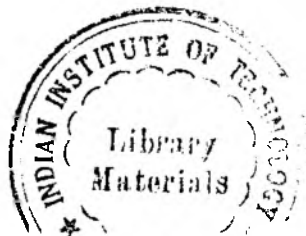


INTRODUCTION

1.1. General Introduction

Metallic coatings are often applied in art and industry to alter the characteristics of a surface with a view to providing improved appearance and protection against corrosion, imparting resistance to abrasion, and to obtain a conducting surface over a non-conducting substrate. There are various means by which such coatings may be applied, chief among them being hot dipping, vacuum metallizing and deposition from solutions. Although each of these methods has its own use depending on the circumstances and the nature of application of the coating, yet from the stand points of convenience and economy, deposition from solutions surpasses other methods and consequently has much wider applications than others.

Again among the techniques employed for the deposition of a metallic coating from solution, two distinct types may be recognized from the stand point of their technological differences. The first one is what is known as the electrodeposition of metals and takes place under the influence of an external source of current. The metal to be deposited as a coating is taken in the form of one of its simple or complex salts in solution and the substrate is made the cathode of an electrolytic cell. Thus the electrons needed for the reduction of the cations of the metal to be deposited are provided by the external source.



Under the second category come such processes as immersion deposition, and electroless (or autocatalytic) deposition. In immersion deposition, a more noble metal is usually plated on a less noble metal which is just dipped in a solution of the salt of the former. Here no external source of current is necessary and the electrons needed for reduction of the cations of the metal to be deposited are supplied by the substrate metal itself which, in the process, gets oxidized to form soluble cations that pass into the solution.

The electroless (or autocatalytic) deposition, which also does not require any external source of current, is a more complex process and its technological importance lies partly in the fact that it may also be used to provide a metallic coating on a nonmetallic substrate. Here the substrate which has a catalytic surface, owing to the very nature of the metal from which it is formed or due to some kind of special treatment (as in the case of non-metallic substrate) is dipped in the solution of a salt of the metal to be deposited in the presence of certain reducing agents. The reducing agents provide the electrons needed for the reduction process involved in the deposition of the metal. Here a further requirement is that the metal to be deposited must also be catalytic in nature in addition to the surface being catalytic in order that the deposition process continues up to the desired thickness.

Among the three processes briefly described above which are used for depositing metallic coatings from solutions, electro-deposition has, by far, attracted the attention of the chemists

and technologists most because of its versatility in the sense that a much larger number of metals and alloys, some of them having diverse characteristics can be plated by this method over a variety of metallic substrates. Further the method is amenable for use in such other industrial fields like electro-winning of metals and electroforming.

The method of electrodeposition, which originated soon after Michael Faraday formulated his classic laws of electrolysis has grown into a vast technology which has made tremendous progress during the last one and half centuries and has reached a high degree of sophistication. Barring a few, most of the metals and their alloys can be plated by this procedure. Amongst the metallic platings, nickel plating has considerable industrial use. The metal is plated for decorative purposes and as an undercoat for chromium plating which is required for protecting the basis metal from corrosion, because nickel as such tarnishes in contaminated urban atmosphere. However nickel plated from the traditional Watts bath is usually dull and has many discontinuities and pores which ultimately affect the structure of the chromium overlay, the net result being the production of a coating which provides poor protection against corrosion. These difficulties may be partly removed by buffing the dull nickel coating prior to chromium plating. The buffing operation not only brightens the dull nickel plate, making it suitable for bright chromium plating for decorative applications, but also improves its corrosion resistance by filling in pores and bridging over discontinuities. However, buffing has some disadvantages : Apart from requiring skilled labour, which is quite

costly, it inevitably causes some decrease in metal thickness and further it is necessary to clean off the buffing compounds completely from the surface prior to chromium plating. The materials used in buffing are also often costly. These reasons led to the search for addition agents that could be used in nickel plating baths to produce fully bright plates directly without the necessity of buffing. Although bright deposits can be obtained by current reversal technique (PR plating), the method of using organic brighteners in the bath to get bright deposits has been of special interest, since it often leads to production of coatings with more desirable physical and electrochemical properties owing to the incorporation of foreign substances into the coatings.

The pioneering work for the development of brighteners which began around 1930 is mainly credited to Lutz et al.¹ and Schlotter² who introduced organic sulphur containing compounds for use in the nickel plating bath to obtain bright nickel platings. Since then the progress in this area has been quite rapid, as can be evidenced from the large number of patents that have appeared in this area and also from the fact that bright nickel plating in the form of duplex and triplex coatings have been now adopted as standard industrial practices and in combination with micro discontinuous chromium overlay, these have almost replaced the conventional Cu-Ni-Cr and buffed Ni-Cr coatings. The brighteners used to deposit bright nickel are usually divided into two distinct classes : The first group which is known as Class I brighteners comprises of compounds having =C - SO₂ - group (unsaturation in the α or β position to the sulphone group). They usually introduce sulphur

into the electrodeposit and do not have an upper critical concentration and consequently can be used in large amounts without affecting other properties. The second group, the so called Class II brighteners on the other hand contain unsaturated linkage like $-C=C-$, $-C\equiv C-$, $-C=N$, $-C\equiv N$, $C=O$ etc. They are used in very less quantities in combination with Class I brighteners to get very bright deposits whose brightness increases with continued plating. In addition, some of the Class II brighteners, e.g., coumarin and its derivatives also act as levelling agents, which favour metal deposition in the valleys (recesses) rather than on the peaks of an irregular surface, resulting in a levelled deposit. Although brighteners may be used in different types of nickel plating baths, including the commercial Watts bath, the latter is usually preferred since a wide variety of organic brighteners are found to function satisfactorily under conditions prevailing in such bath, i.e., at pH 3-5 and temperature 50-65°C and the electrodeposits obtained from such a bath have many desirable physical and mechanical properties.

Although the deposition of bright nickel coatings has made enormous progress as an industrial practice since 1935, the chemical and energetic processes involved in it and the structural factors responsible for brightness have not yet been fully elucidated. The main difficulty in the way of progress has been the complexity of the process. Further, the lack of a clear definition of the word 'brightness', for long, in terms of physical magnitudes has been an additional factor. The currently accepted definition of brightness as the percentage of directionally (or specularly)

reflected light to the total amount of light reflected both directionally and diffusely from a surface, originated only around 1940. Mixing up of structural and morphological characteristics of the bright deposits have also partly led to the poor understanding of the physical process. At times this has led to wrong correlations. For example, there have been attempts in the past to correlate brightness with grain size³ or with preferred orientation^{4,5} - but these have not been substantiated in the subsequent work.⁶⁻⁸ Unless the relation between structure and brightness or that of morphology with brightness are clearly understood the mechanism of functioning of organic brighteners and its relation to the formation of bright deposits will not be fully elucidated. So far as this aspect is concerned, the problem becomes much more difficult to study when more than one brightening additives are present in the bath as is the practice in the technical baths. Despite these difficulties, certain definite progress has been made to understand the phenomenon and in this connection the notable contributions made by Weil et al.⁹⁻¹⁴, Froment et al.¹⁵⁻¹⁸ and Vitakova et al.¹⁹ are worth mentioning.

It now appears that surface morphology has more to do with brightness than the structure. Bright deposits of nickel usually have no crevices, deep grain boundaries or protrusions exceeding 0.15μ from the surface plane. Contrary to many earlier views relating brightness with structure and grain size, it now appears that brightness is more related to the fraction of surface roughness below 0.15μ than to any other factor⁹. The presence of brighteners seem to promote the formation of surfaces with diminished roughness.

It has been established in some cases that the presence of brighteners inhibits the growth of fast growing crystal planes to promote the formation of three-dimensional discrete nuclei in the surface as fresh growth centres¹³. This dispersal of growth points ultimately leads to a surface morphology which is less rough. With the help of electron microscope and more recently with the advent of scanning electron microscope (SEM) which has an excellent focus depth, it is possible to study the surface topography in much detail. The Y-modulation technique of SEM is particularly quite helpful in this respect and permits quantitative estimation of surface roughness. Such studies are more desirable in the field of electrodeposition of bright nickel.

Apart from the necessity of such investigations, the need for searching new and effective combination of brighteners to suit to various kinds of baths is also there. This is rather going to be a continuing problem and an interesting area to work with.

A second area of metal deposition from solution which has some practical applications, though not to the same extent as electrodeposition, is the immersion deposition. Although the coatings obtained by this method are porous, such a process is however simple and economical as it neither requires any external source of electrical energy nor any reducing agent. The immersion coatings are applied for either decorative or functional purposes. The important industrial uses are the so called liquor finish on steel wires as a drawing lubricant, and the immersion tinning of aluminium alloy pistons for internal combustion engines and aircraft pistons²⁰. Apart from these functional needs, immersion coatings

are also applied on pins, paper clips, buttons etc. for decorative purposes and also as an undercoat for electrodeposition of other metals.²¹

In a developing country like India which has an abundant supply of aluminium compared with other nonferrous metals, immersion deposition has some practical significance. Aluminium has now extensively replaced copper as the material for electrical conductors. With a view to improving the surface conductivity of aluminium conductors, it is often necessary to coat it with a layer of electrolytic copper but this requires an immersion layer of zinc as an undercoat to improve adhesion because as is well known electrolytic copper does not adhere well to aluminium surfaces. Although immersion deposition of copper on aluminium does not take place readily yet there have been some recent reports^{22,23} of such deposition on aluminium. Provided adherent deposits are possible, such a technique is likely to be more useful as it would obviate the necessity of zinc immersion deposition and provide a surface on which not only copper, but a large variety of other metals and alloys can be directly electroplated. It was therefore felt necessary to study this problem from a practical angle with a view to developing some solutions from which copper could be readily deposited on aluminium.

The purpose of the present thesis is to present the results of our studies relating to some problems falling in these two areas, namely, the electrodeposition of bright nickel in the presence of some organic additives and immersion deposition of copper on aluminium.

1.2. Fundamental principles of metal deposition processes

(a) Electrodeposition of metals :

(i) Faraday's laws :

Electrodeposition is the process of depositing metals using an external source of current. In this process the article on which the metal is to be deposited is made the cathode of an electrolytic cell, the electrolyte of which contains the soluble ions of the metal as one of the constituents. The anode may be made of either the metal itself or some other insoluble conducting material. On passing the current, the metal gets deposited on the cathode obeying Faraday's laws of electrolysis, which state that, the amount of chemical change produced by the electric current is proportional to the quantity of electricity and the amounts of different substances liberated by a given quantity of electricity are proportional to their chemical equivalent weights. The quantity of electricity required to deposit one gram equivalent of a metal is equal to $96,490 \pm 2.4$ coulombs or 1 faraday.

Faraday's laws have been confirmed without any exceptions. Apparent exceptions are due to our failure to take into account all the chemical reactions involved, or the partially nonelectrolytic nature of the reaction as in the case of the excess weight loss of zinc anode. In the case of codeposition of another metal or hydrogen, Faraday's laws apply to the total number of equivalents of all the substances produced, irrespective of their proportions.

When a soluble anode is used, the same number of equivalents of the metal, as deposited on the cathode, dissolves from the anode if there is no other side reaction occurring on both the electrodes. Thus the concentration of the bath is maintained as the electrolysis is continued. In the case of insoluble anode, the anodic reaction in the aqueous electrolytic solutions will be the evolution of oxygen. So in order to keep up the composition of the bath, metal salts should be added to the bath periodically.

(ii) The electrolytic baths :

Electrolytic solutions or the so called 'baths' can be aqueous or nonaqueous solutions containing the simple salts or complexes of the metal to be deposited. The bath solutions may also contain compounds and additives for a variety of purposes such as, to improve the conductivity of the bath, to maintain its pH, to get levelled and bright electrodeposits, and to produce anti-pitting effect, i.e., ^{to} reduce the adherence of hydrogen bubbles that cause pitting.

(iii) The effect of electrode potential :

A metal electrode dipping into an electrolyte containing its ions establishes an equilibrium potential which is dependent on the nature of the metal and on the activity of the metal ion in the solution. For example, a copper electrode dipping into a solution containing Cu(II) ions at unit activity has the potential + 0.345 V. If this potential is lowered to + 0.340 V by applying an external potential, the rate of the anodic reaction, i.e., the dissolution of copper is decreased by the additional supply of

electrons which bind the copper ions more firmly to the metal lattice; at the same time, the added electrons in the metal increase the attraction for hydrated copper(II) ions in the solution and thus increase the rate of cathodic reaction. However to attain significant rates of deposition, greater potential difference is required. When the potential of the electrode is raised to + 0.350 or more, the effects are reversed.

At the cathode, the reaction requiring the least negative potential will take place exclusively if the deposition potential of any alternative process is much more negative. For example, the reduction of hydrogen ions in a copper sulphate solutions of pH 4 which requires a cathode potential $-0.240V$, does not take place along with copper deposition. Another factor which retards the reduction of hydrogen ions, is the high hydrogen overpotential of some metals. If the cathode potential is made sufficiently more negative to produce a second reaction, that reaction may occur simultaneously as in the case of electrodeposition of alloys where simultaneous reduction of two or more metal ions takes place.

Sometimes the anode becomes coated with a film of oxide or a compound of the metal which prevents the dissolution of the metal anode. Thus the anode becomes passive. These anodic films may be insulators or ionic conductors and they require a higher voltage difference to allow the passage of current. The potential of passive anode increases until it reaches the potential at which oxygen evolution reaction can take place or to produce ions in some higher valence state as in the case of tin anodes in an alkaline stannate solution.

The deposition of metals proceeds less readily when the metal ions are complexed, since the deposition potential is shifted towards more negative values. Sometimes complexing of metal ions brings about a change in the relative position of the deposition potentials of metals to allow the codeposition of two or more metals. The electrodeposition of brass from a zinc and copper cyanide complex bath is an example of this codeposition. Complexing the metal ions in the bath produces some favourable effect on the quality of the metal deposit although it does not lead to good microthrowing power and high current efficiency. The macrothrowing of complex bath is good and very smooth deposits are obtained from complex baths.

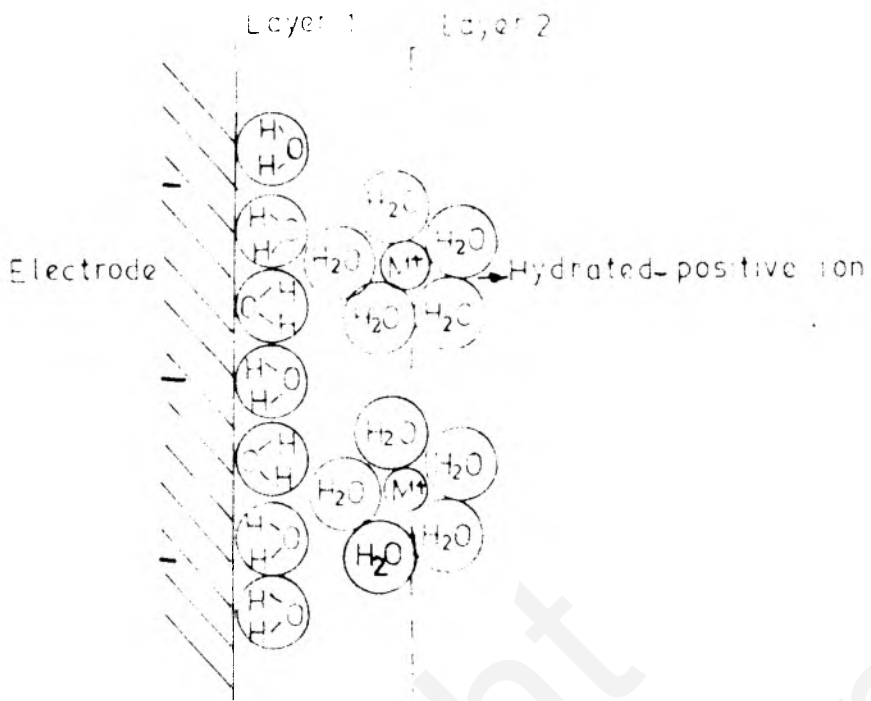
(iv) The role of electrical double layer at the electrode :

A metal crystal or grain consists of ions of the metal (along with the core electrons) located in regular lattice positions, and other electrons, required to render the mass of metal electrical neutral, exist as indefinite cloud of negative charge, so that these electrons are not specifically identified with a particular ion. The ionic charges are statistically neutralized by the electron cloud over a period of time. The high conductivity of most of the metals is due to the free movement of this electron cloud under the influence of an applied potential.

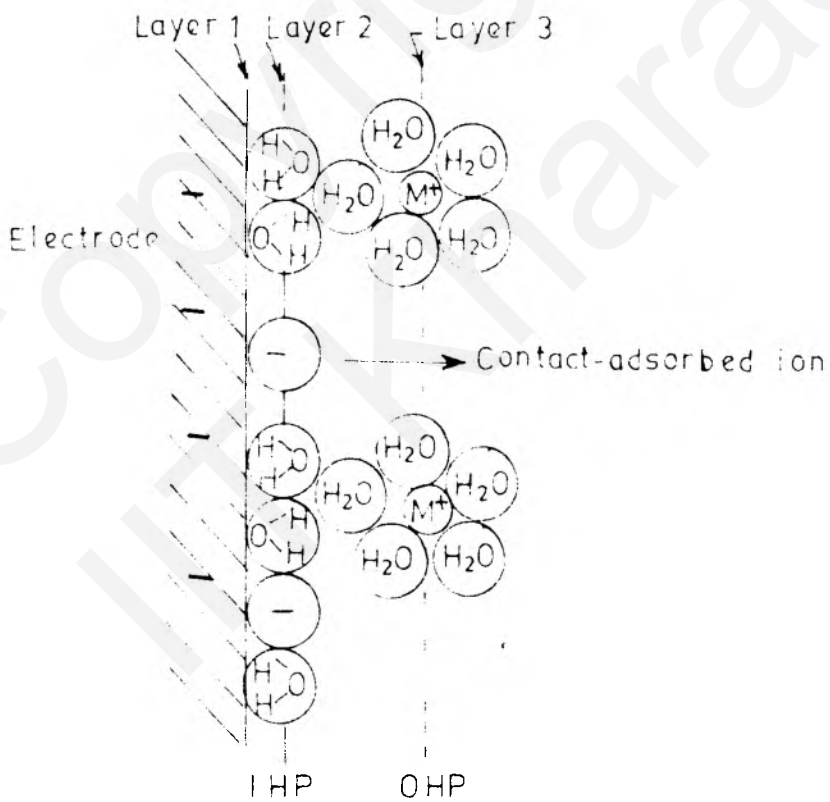
When a metal electrode is dipped in a solution containing its salt, some of the metal ions in the electrode have the tendency to leave their lattice positions, become hydrated and pass into the solution. Similarly some of the hydrated metal ions present in the

solution lose their water molecules and occupy some of the vacant lattice positions. A dynamic equilibrium is reached between these two opposing reactions, as a result of which the metal electrode becomes either negatively or positively charged with respect to the solution side and thus an electrical double layer is formed at the interface. The electrical double layer in its wake produces several effects and also gets modified structurally. First of all in an aqueous medium, the charged electrode attracts water molecules which are dipoles. They orient according to the charge on the metal. Two types of possible orientations are the flop-down configuration, in which the water dipole orients the two hydrogen atoms towards the electrode surface and the flip-up configuration in which the water dipole orients its oxygen atom towards the electrode. In addition to polar water molecules, neutral organic molecules, e.g., organic additives also often get adsorbed on the electrode surface and form a part of the double layer structure.

The charged electrode also attracts ions carrying an opposite charge (or the same charge as in the case of contact adsorption) and these ions are held near the metal surface by the electrostatic forces. Thus an electric double layer²⁴ is formed (Fig. 1a) which has the characteristics of a capacitor. Actually the so called double layer is not a double layer, but a triple layer because beyond the first layer formed by the immobile adsorbed ions and solvent molecules, there may be another loosely bound and relatively mobile layer which is formed by the hydrated metal ions as shown in Fig. 1b. The first immobile layer is called



(a) DOUBLE LAYER



(b) TRIPLE LAYER

FIG. 1. AN ELECTRICAL DOUBLE LAYER AND AN ELECTRICAL TRIPLE LAYER

the **inner** Helmholtz layer. The second layer formed by the hydrated metal ions is called the outer Helmholtz layer and the imaginary plane passing through the centre of the hydrated metal ions is called the outer Helmholtz plane or OHP. Thus the double layer at the interface contains three layers of charges and they behave like two capacitors connected in series.

The potential difference across the double layer under equilibrium conditions is called the reversible electrode potential or the single electrode potential. Since the single electrode potential cannot be measured directly, the electrode is coupled with a reference electrode to form a cell and the potential of the test electrode with respect to reference electrode is measured. For this purpose, normal hydrogen electrode ($\text{Pt}, \text{H}_2 (1 \text{ atm}) / \text{H}^+_{a=1}$) or some other secondary reference electrode like calomel or silver-silver chloride electrode whose potential with respect to the hydrogen electrode is known is used as the reference electrode.

The magnitude of the electrode potential is related to the difference in the free energy of metal ion in two phases, i.e., in the metal lattice and in the solution. The metal ions in the solution are bound to solvent molecules or the complexing agent. This process lowers the energy of the metal ions in the solution although the energy of hydration or coordination partly depends on the activities of the reacting species. The metal ions in the metal, which are energetically more stable than the free ions in gaseous state, are bound by the lattice energy which depends on the nature or type of the lattice plane which the ion occupies.

Thus the single electrode potential depends on the sum of lattice energy and hydration energy of the ions.

The dependence of the equilibrium electrode potential on the concentration of metal ion in the solution is given by the Nernst equation,

$$E = E_{M^{n+}}^{\circ} + \frac{RT}{nF} \ln a_{M^{n+}}$$

where E is the electrode potential, $E_{M^{n+}}^{\circ}$ is the standard reduction potential for unit activity of the metal ion, M^{n+} , R is the gas constant, T is the absolute temperature, F is the faraday, n is the normal charge of the ion, and $a_{M^{n+}}$ is the activity of the metal ion in the solution. When the equilibrium potential of the electrode is reached, the exchange of ions or charges taking place across the interface apparently seems to stop as in the case of a chemical equilibrium, but however from the kinetic point of view the rate of forward reaction (anodic reaction) and the backward reaction (cathodic reaction) are taking place at equal rates. However when there is no equilibrium, the two processes occur at different rates and there is either a net cathodic or anodic reaction at the electrode. Since both the cathodic and anodic processes involve transfer of charged particles across the double layer, the intensity of each of these processes can be expressed in terms of the respective currents which, for the cathodic process, is called the cathodic current, I_c and, for the anodic process, is called the anodic current, I_a . The cathodic current passing through the unit area of the electrode is called the cathodic current density, i_c and similarly, the anodic

current per unit area is called the anodic current density, i_a and both are expressed in A/dm^2 . At equilibrium, the anodic exchange current density, $i_{a,e}$ is equal to the cathodic exchange current density, $i_{c,e}$, but they have opposite signs,

$$|i_{a,e}| = |i_{c,e}| = i_0$$

where i_0 is the equilibrium exchange current density.

In the study of electrode reactions, the relative magnitudes of the exchange current densities are important. High value of the equilibrium exchange current density for a metal deposition process means that the metal can be deposited with little polarization. The exchange current density is decreased by the presence of adsorbed impurities or addition agents since they interfere with the deposition process.

When a metal is made the cathode in the electrolytic solution by connecting to negative terminal of a battery, the excess negative potential at the cathode increases the rate of transfer of metal ions across the double layer to the electrode where they get deposited. At the same time, it diminishes the rate of metal dissolution at the cathode. The extent to which the applied excess potential is effective in accelerating the deposition process at the cathode, as compared to that which slows the dissolution process, is expressed by a fraction called transfer coefficient, α .



The electrode potential changes from the equilibrium potential when a net current is passed through the electrode. In the case of an electrolytic cell, the cathode potential moves towards a more negative value and the anode potential moves towards a more positive value. The deviation of the electrode potential, E from the equilibrium value, E_0 is called the overpotential, η .

$$\eta_a = E_a - E_{0,a}$$

$$\eta_c = E_c - E_{0,c}$$

It is to be noted that η_a is positive and η_c is negative. The dependence of overpotential on current for the specific case of an electrode reaction controlled by the charge transfer step is given by the Butler-Volmer equation

$$i = i_0 \left[e^{(1-\beta)\eta F/RT} - e^{-\beta\eta F/RT} \right]$$

where i_0 is the equilibrium exchange current density, and β is called the symmetry factor and has values greater than zero but less than unity.

The potential corresponding to zero net current when several electrode reactions take place simultaneously on the electrode is called the mixed potential, E_M whose value differs from the equilibrium potentials of each of the participating reactions. In this case also the passage of net current through the electrode changes the potential from the equilibrium value. This change of electrode potential from the equilibrium value is

due to the slowness of one or more steps of the electrode process.

(v) Different types of overpotentials appearing during the metal deposition process :

Electrodeposition is a multistep reaction. These steps are diffusion of the hydrated or complexed metal ion to the double layer, charge transfer step in which the charge carriers (ions or electrons) are transferred across the double layer, chemical reaction step which may precede the charge transfer step, and the crystallization step in which the metal atom gets incorporated into the metal lattice. When the metal ion requires more than one electron to get reduced to the metal atom, there will be more than one charge transfer step, since in the single charge transfer step the transfer of more than one electron is not possible. The overpotential is due to the slowness of the one or more of the steps mentioned above.

The rate of charge transfer reaction depends on the potential difference across the double layer. The metal ions should have energy to cross over the potential barrier due to the electric double layer to reach the electrode surface where they get reduced. The surface diffusion of reduced metal atom and the crystallization step can be inhibited by the presence of adsorbed organic compound or impurities on the electrode surface. Charge transfer overpotential and crystallization overpotential are sometimes called the activation overpotential, $\eta_a = \eta_{CT} + \eta_{Cr}$.

The rate of a chemical reaction preceding the charge transfer step in the metal deposition process depends only on the nature of the reactants and their concentrations. It is independent of the electrode potential. Further as the metal is deposited on a cathode, the solution in its immediate neighbourhood is depleted of metal ions. This process sets up a concentration gradient due to which the metal ions from the bulk of the solution reach the electrode surface by diffusion. The sum of the reaction and diffusion overpotentials are sometimes called the concentration overpotential, $\eta_c = \eta_d + \eta_r$.

The resistance polarization, η_Ω is another factor introduced in the measurement of overpotential which is due to the ohmic potential drop within the electrolyte or surface films on the electrode surface. η_Ω does not have any influence on the electrochemical process. The total overpotential,

$$\eta_t = E - E_o = \eta_{CT} + \eta_r + \eta_d + \eta_{cr} + \eta_\Omega$$

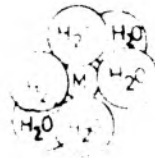
When only one of these steps is slow and others are faster, the total overpotential, η_t is approximately equal to the overpotential corresponding to the slow step and the overall reaction rate is controlled by the slow process. If more than one steps are slow, then the overall rate is controlled by all these slow steps.

(vi) Electrocrystallization process :

It is believed that the hydrated metal ion after crossing the double layer, in course of which it transfers a part of its

charge, reaches the electrode surface at some point to form an adsorbed intermediate called the adion. In all likelihood the adion retains a part of the charge of the previous state as well as some water molecules. The adion, thus formed, first diffuses to one of the growth steps, and then to a kink and finally gets incorporated into the lattice (Fig. 2)²⁴. As more and more adions get incorporated into a microstep which might be present originally at the emergence points of a screw dislocation or due to other defects or might be formed by two-dimensional nucleation in the presence of impurities and additives, the step grows and advances. In the course of its growth if it encounters adsorbed impurities, then further progress is stopped and a new microstep is formed over the older one. This may be repeated several times leading to the bunching of microsteps into a macrostep which is visible in the microscope. The lateral growth of the deposit proceeds from various centres until the neighbouring lattices meet. The crystals which touch each other in a continuous fashion to make up a metallic body are called grains. In a polycrystalline deposit the orientation of each grain can be specified by giving the angles formed by the crystallographic directions of the crystal and the axes of a reference system fixed with respect to the macroscopic substrate. If one axis in all the crystallites is fixed relative to the substrate and the other two axes are randomly oriented with respect to the substrate then the polycrystal is said to have a preferred orientation. If all the three axes are randomly oriented then the polycrystal is said to exhibit random orientation. Certain crystal faces may grow much more rapidly than others leading to the preferred orientation. If the lattices of the basis metal and the

M-hydrated metal ion



Charge transfer

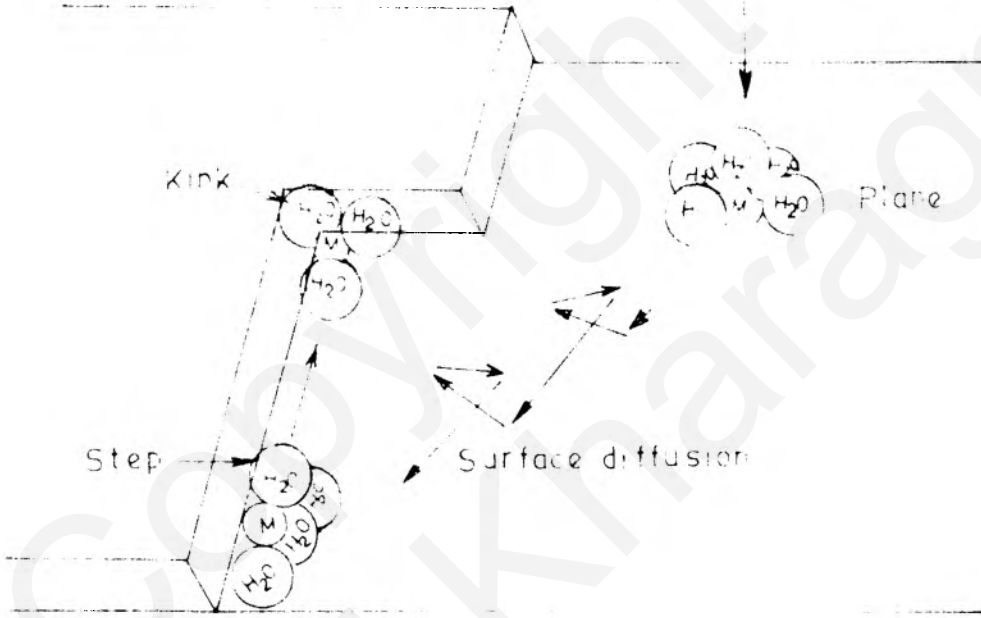


FIG 2. CONSECUTIVE STEPS INVOLVED IN THE INCORPORATION OF AN ION AT A KINK SITE

coating are similar in geometry and dimensions, then the basis structure may be extended into the deposits and such growths are called epitaxial growths. The different structural forms of electrodeposits fall into one of the two basic structures, namely, (i) pyramids²⁵⁻²⁷ and (ii) layers^{25,27,28} or to some other form related to one of these structures, i.e., blocks (truncated pyramid),^{or} ridges (special type of layer growth). Apart from the above, other less frequently observed growth structures are : (i) spiral, (ii) whiskers and (iii) dendrites.

The classification stated above is based on the visible surface topography and consequently somewhat arbitrary because the submicroscopic elementary features are often not clear. For instance, pyramids may originate from elementary spirals whereas observed spirals might be due to complex aggregates of elementary screw dislocations; often surface of dendrites shows some kind of layer structure.

It is to be recognised that the activity of the surface depends strongly upon the growth forms which develop during the deposition process. It has been found in some experiments at constant current density, that the overpotential changes markedly as the crystal grows. This can be related to the formation, on the growing surface, of crystal faces having different activity, although a part of the change may also be ascribed to the alterations in the real surface area. The difference in activity between the newly formed crystal faces and the original ones left behind may cause a nonuniform distribution of current density that ultimately affects the growth process as well as the current distribution at a later stage.

1.2.b Electrodeposition of bright metals :

Two distinct techniques have come into use for obtaining bright metal deposits. The first one is the periodic current reversal technique (or PR technique) and the other one involves the use of brightening additives which are mostly organic compounds.

In the case of PR technique the polarity of the substrate is reversed for brief intervals of time so that it acts as the anode during some of these intervals of time and consequently gets partly polished. This polishing takes place because there is more metal dissolution from the peaks on account of high current density prevailing there than from the recesses. Since the cathodic phase is longer than the anodic phase, there is however a net deposition of metal which assumes bright appearance.

Compared to PR technique, the use of organic additives to obtain bright deposits is more widely employed as an industrial practice. The development of brightening additives however has been carried out mostly on an empirical basis without the proper understanding of much of the basic principles involved. It is only during the recent years that some serious efforts have been made to systematise the knowledge and understand the mechanism in this area. One complicating situation that baffles the investigators in this field is that the action of the additives is often specific in nature and their presence may produce different effects on the deposition of different metals. For example, a particular organic compound may act as a brightening agent for the deposition of one metal, but may fail to do so in case of

another metal. Structurally these additives may be quite different and their number is not only large but also include diverse types of compounds containing different functional groups. Because of this, a systematic and exact classification of brightening agents cannot yet be given except for nickel brighteners, for which some progress has been made. However it is found that the general susceptibility of different metals to the brightening agents increases in the order :

lead < tin < silver < cadmium < zinc < copper < iron < nickel

It is presumed that the additives which are used in small amounts get adsorbed on the electrode surface and inhibit the deposition process particularly on more active growth points like peaks, profoundly influencing thereby the appearance and structure of electrodeposits. The adsorption of such addition agents on the electrode may result from any one or more of the following causes :

(a) due to the attraction of the electrode towards the component ion of an ionizable compound or towards a molecule which possesses permanent or induced dipole moment,

(b) by the interaction of the surface atoms of the electrode with π electrons of the organic molecule, and

(c) by the partial displacement of water molecules.

Inhibition of metal deposition on more active growth points may be brought out by the adsorption by the following ways :

(1) they may reduce the area available for the electron transfer and thereby affect the rate of electron transfer

(2) they may block the growth steps and consequently affect the surface diffusion of adions, and

(3) they may suppress the growth of existing crystallites and require the formation of more energetic new crystal nuclei for the deposition to continue.

Bright electrodeposits have mostly banded or laminated structure. The formation of laminated structure appears to be due to the periodic fluctuation of the concentration of additives on the electrode surface¹¹. Most of the bright electrodeposits do not have preferred orientation because the adsorption of brighteners on fast growing crystal faces inhibits their growth and brings about an equalization of growth rates of different crystal faces²⁹. Generally bright electrodeposits are more brittle than that obtained from the bath containing no additive. The brittleness of the bright electrodeposits results mainly due to the incorporation of the additives themselves or their degradation products. Brightening agents also affect the internal stress of electrodeposits. Some of the brighteners increase the stress while some others reduce it. For example, Class I nickel brighteners like naphthalene trisulphonic acid reduce the tensile stress whereas Class II nickel brighteners like 2-butyne-1,4-diol containing triple bonds increase the tensile stress.

Bright plating baths usually require careful control of brightener concentration, pH, current density, bath composition etc

and they are much sensitive to impurities. The degradation or reduction products of some brighteners and some metallic ions sometimes act as harmful impurities. These impurities affect the brightness of the metal deposit and should be removed from the bright bath for obtaining better results.

1.2.c Commercial Watts bath for electrodeposition of nickel :

It was W. Bottger who began nickel plating in 1843 from a double salt bath containing nickel ammonium sulphate. Following him, Adams^{30,31} introduced nickel plating on commercial basis in 1869. He deposited nickel from similar double salt baths using nickel ammonium sulphate and nickel ammonium chloride and noted the importance of impurities in the bath. Later on Weston introduced boric acid into the bath and Bancroft and others introduced chloride ion to improve the dissolution of anodes. In 1915 O.P. Watts³², the pioneer of rapid plating at higher temperature, introduced a nickel plating solution which provides the best case for the modern bright nickel plating. Following the accurate pH control introduced by Thompson³³ and low pH baths suggested by Phillips³⁴, Schlotter² introduced commercial modern bright nickel plating solutions. The modern Watts bath is more concentrated than the original one and has the following composition.

Nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$)	-	240-340 g/l
Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	-	30-60 g/l
Boric acid (H_3BO_3)	-	30-40 g/l

Nickel sulphate contributes most of the nickel ion content of the bath. Nickel sulphate is preferred due to the following reasons : (i) it is less expensive, (ii) it has stable anion which is not reduced at the cathode or oxidized at the anode and (iii) it is highly soluble. The main purpose of chloride ion in the bath is to improve anode dissolution. It also increases the conductivity of the bath. Boric acid which acts as a buffering agent controls the pH of the cathodic film and produces whiter deposits. Apart from these three important constituents, about 0.1 to 0.5 g/l of antipitting agents are also used in these baths.

Electrolytic nickel and sulphur depolarized electrolytic nickel are widely used as anode for nickel plating. The anodes are kept in a titanium basket and the basket is kept in a cotton bag to avoid the mixing of the anodic sludge formed at the anode with the bath solution.

Copper, zinc, lead, tin, chromium and iron (Fe^{3+}) ions contaminate Watts bath. These harmful impurities are removed by raising the pH of the bath to 5.2 with nickel carbonate or freshly precipitated nickel hydroxide and filtering the bath solution and then by electrolysing the bath solution at a low current density (0.2 A/dm^2) for several hours. Organic contaminants are removed by adsorption on activated carbon.

The effects on plating characteristics produced by various factors during nickel plating may be summarized as follows :

Cathodic current efficiency increases with the increase of current density, temperature and total metal ion concentration, but decreases rapidly with the fall in pH of the bath. Throwing power of the bath improves with the increase in pH, temperature, and nickel and chloride contents of the bath. The electrodeposits obtained at 55°C and pH 2 have a columnar structure which grows coarser with increasing thickness. As the pH and chloride content of the bath are increased or the temperature is decreased, grain refinement occurs^{35,36}. At pH 4.5, soft and ductile electrodeposits are obtained. The tensile stress of the electrodeposits increases with the increase of chloride content of the bath. Under comparable plating conditions, superimposition of an alternating current on the direct current reduces the stress.

1.2.d Immersion Deposition :

Immersion deposition process is based on the principle of electron transfer from a less noble metal to a more noble metal ion present in the aqueous solution as shown in equations 1.1 and 1.2 below :



where M_1 is a less noble metal and M_2 is a more noble metal. The net reaction as given in equation 1.3 represents the mere displacement of a more noble metal from solution by a less noble

metal. Hence immersion coatings are also called displacement coatings. Due to the presence of pores and discontinuities in the monoatomic layer of the more noble metal on the less noble one, the immersion deposition continues with the formation of a local galvanic cell between the substrate and coating metal. Hence it is possible to get thick immersion coatings.

In the beginning of the immersion deposition process, the electrode potential of the two metals are far apart from each other. With time, the potential of the two metals approach each other. When both of them become equal, i.e., when they reach the mixed potential of the two reactions, the net action ceases.

Although it is possible to get immersion deposits from aqueous baths containing the simple salts of the metal to be deposited, yet such deposits at times have burnt appearance because in some areas of the deposit the momentary current density exceeds the limiting current density for defect-free coating. In order to avoid this, either complexing agents or additives are added to the bath. Deposits obtained from such baths are not only smooth but also have better appearance. Immersion baths for depositing other metals on aluminium have the additional requirement that these should contain substances, e.g., alkalis and alkali halides which can remove the oxide layer from the surface of aluminium to facilitate its dissolution. At times, it is also necessary to condition the aluminium surface properly, i.e., by repeated immersion plating and stripping of zinc to get adherent immersion deposits subsequentl

1.3. Physico-chemical studies related to metal deposition

(a) Kinetics and mechanism of the deposition process :

Physico-chemical investigations of the electrodeposition process is rather difficult and complicated. It is certainly more difficult than those of redox reactions on insoluble electrodes because of the following reasons :

(i) In the deposition process the electrode surface advances and changes with time.

(ii) As the deposition proceeds the topographical features of the surface changes, making it difficult to measure the actual current density.

(iii) Due to the change of rate constants of various partial steps of the deposition process and the concentration of some intermediate species with time, the rate determining step may change with time.

(iv) The crystallization stage is a cooperative one and its description in terms of chemical reaction is difficult.

(v) The side reactions occurring at the electrode sometimes complicate the investigation of the deposition process.

In spite of these difficulties, some of the electrochemical methods, which have been used for redox reactions successfully may be employed with suitable modifications to gain some knowledge about the kinetics and mechanism of the electrodeposition process.

The study of electrode potential - current density curves are of special interest for understanding the nature of the electrodeposition process, since polarization is the principal factor which controls the rate of any irreversible electrochemical reaction. The determination of some parameters like equilibrium exchange current density and transfer coefficient which are useful in finding out the mechanism of the electrode processes, can be done by polarization measurements, when charge transfer step is the rate determining step.

The electrode potential measurements are carried out by applying a constant current to the electrode under study, the so called 'test electrode', and measuring the steady state potential difference between the test electrode and a suitable reference electrode which are connected by a Luggin capillary containing saturated potassium chloride solution or potassium chloride-agar-agar. This method which is called the direct compensation method nevertheless introduces errors in the measurement due to the ohmic voltage drops at the contact between the electric conductor and the electrode as well as in the electrolyte layer between the electrode and the Luggin capillary tip.

However the ohmic voltage drop in the metallic conductors is usually small and can be minimized by proper design of the connections. Although it is not possible to eliminate the voltage drop in the electrolyte between the electrode and the Luggin capillary, it can nevertheless be reduced by using a properly designed Luggin capillary (to avoid the shielding effect) and keeping it close to the electrode. The error introduced in the

polarization measurements can be assessed easily by the commutator method in which the measurement of the electrode potential is done in a short time after the interruption of the polarization current.

The problems due to the changing of the surface with time during deposition are overcome by galvanostatic and potentiostatic techniques since the measurement is done so quickly that the surface has not changed during the measurements.

In the galvanostatic transient technique a constant current step is applied by using a variable high resistance in the circuit to the system at a time, $t = 0$ and the change of electrode potential with time is followed in an oscilloscope. Using this technique, it is possible to find out the concentration of intermediates, heat of activation for diffusion across the surface, charge on the adion and exchange current density³⁷⁻³⁹. The variables that can be used in galvanostatic studies are the concentration of reactants, current density, temperature and the structure of the substrate.

In potentiostatic studies, a constant potential step is applied to the system and the change of current with time is followed. Although the variables used, and quantities that can be obtained from both potentiostatic and galvanostatic techniques are the same, the more accurate solution can be obtained easily by potentiostatic measurements^{39,40}. One can get better information about the deposition process by using both galvanostatic and potentiostatic transient techniques. For example, it is possible with the help of such techniques to say whether the charge

transfer process or the surface diffusion is the rate determining step⁴¹.

From impedance measurements the double layer capacity can be deduced, and if the capacity in the presence and absence of organic compound is known, then the change of double layer capacity can be related to the surface concentration of organic compounds. The anion concentration, very near to the equilibrium potential also can be derived from the resistive component of low amplitude measurements⁴².

The difficulties encountered in this method are the frequency dispersion (dependence of double layer impedance on frequency due to non-faradaic processes) associated with solid electrodes due to the microcrevices and the dipole admittance due to the adsorbed water dipole on the electrode⁴³. Hence it is difficult to get the desired kinetic parameters by impedance measurements unless the capacitance of the double layer is assumed to be frequency independent and its parallel resistance infinite.

1.3.b Efficiency of the process :

Current efficiency :

In electrodeposition, the current efficiency is an important parameter since it represents the efficiency of the deposition process in relation to the electricity used for deposition. It is defined as the percentage of the total current usefully employed for the deposition of metal. Current efficiency can also be

defined as the percentage of the amount of metal deposited to that of the theoretical amount in accordance with Faraday's laws. If any electrodic process other than the metal deposition (e.g., reduction of hydrogen ions or processes like $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$) takes place then the current efficiency will be less than 100%.

Metal distribution :

Metal distribution depends on the following factors :

(i) the shape and dimensions of the object, (ii) geometry of the plating cell arrangement, (iii) conductivity of the bath, and (iv) agitation. The ability of a bath to produce deposits over the entire cathode surface including recesses is called the covering power. It can be determined by measuring the distance from the high current density edge of a Hull cell cathode to the point where there is no deposit⁴⁴. The ability of the bath to produce deposits of more or less uniform thickness on cathodes having macroscopic irregularities is called the macrothrowing power, and if the depth of the profile under consideration is small, i.e., less than 0.01 cm, then it is called the microthrowing power. Macrothrowing power can be determined by using Haring-Blum cell⁴⁵ or by measuring the ratio of the thickness of the deposit on two selected points in a Hull cell cathode⁴⁶.

Coating thickness :

The thickness of the coating is of primary importance to assess the quality of a coating. It can be measured by a variety of methods. Their number is so large that they may be broadly classified as follows :

- (i) methods using thickness gages^{47,48}
- (ii) X-ray method^{4),50}
- (iii) chemical method⁵¹, and
- (iv) methods based on length measurement⁵².

The principle of measuring the thickness by thickness gages is based on the electrical and magnetic properties of the metallic coating which vary with thickness of the coating. By this method, it is possible to get the thickness with an accuracy better than $\pm 5\%$.

In the X-ray method, the specimen is subjected to a beam of X-ray. The primary X-ray beam gets diffracted by the basis metal. The intensity of the diffracted X-ray is measured after the attenuation by the coating. The primary X-ray beam also excites fluorescent X-radiations of the basis metal or the coating. The intensity of the fluorescent X-rays can also be measured for determining the coating thickness.

The chemical methods are somewhat imprecise. In the chemical methods the time required for a solution to dissolve the coating over a small area is determined.

The different methods based on the length measurements are :
(i) microscopic method, (ii) chord method, (iii) tracer method, and (iv) dial gage method. Among these methods, microscopic method is universally applicable. However this method requires skill to avoid errors in the measurements. In the microscopic method the coating thickness is measured in a magnified image of a cross section of the coating.

While the foregoing methods give the thickness only at certain points of the coating, they do not however give the average thickness which is a more sought after property unless of course a large number of measurements are made and the results are statistically analysed to give the average value. The average thickness of a coating can be calculated by the formula,

$$\text{average thickness} = \frac{\text{weight}}{\text{density} \times \text{area}}$$

if the weight of the coating and area are known. The average thickness can be determined by any one of the following methods :

- (i) chemical analysis method
- (ii) quantitative stripping⁵³
- (iii) weight gain method
- (iv) density method⁵⁴, and
- (v) calorimetric method⁵⁵.

1.3.c Physical properties of electrodeposits :

Adhesion :

Adhesion of a coating is the extent to which the coating sticks to the basis metal. In all adhesion tests which are destructive, a force is applied to the test specimen which tends to pull away the coating from the basis metal. The component of this force which is perpendicular to the interface of the coating and the basis metal is used as a measure of adhesion. If the separation occurs within one of the two metals instead of at the interface, then the adhesion is greater than the strength of the

metal which parted. Adhesion can be tested qualitatively by the following methods : (i) by repeated bending, (ii) filing, (iii) grinding, (iv) heating, (v) heating and rapid cooling, (vi) subjecting to cathodic discharge of hydrogen at a high current density, and (vii) by applying an adhesive tape and pulling the tape off. The following tests are used for testing adhesion quantitatively :

- (i) peel test⁵⁶
- (ii) Ollard test⁵⁷
- (iii) direct pull test^{58,59}, and
- (iv) high speed rotor test.

Among these tests Ollard test has better reproducibility (5%). For testing adhesion by this method, one end of a metal cylinder is first plated to substantial thickness after which it is machined to have a shoulder for supporting in a die. A load is then applied to the cylinder to separate the coating from the basis metal.

Hardness :

Hardness is related to tensile strength and ductility. The methods used for measuring hardness are based on the measurement of the following properties : (i) scratch width, (ii) abrasion resistance, and (iii) resistance to penetration. The hardness of the electrodeposit is measured usually by the Vickers method or Knoop method. In both the methods, the depth of penetration due to a load applied through an indenter is measured.

Strength and ductility :

Tensile strength and ductility of electrodeposits have much importance in the fabrication of electroplated articles. Ductility is the ability of a material to deform plastically without fracturing. Hydraulic bulge test⁶⁰ is widely used for testing ductility. In this method, the test foil is clamped on a flat base plate; oil is pumped through a hole in the base plate under the foil and the deformation of the foil is measured together with the oil pressure producing the same.

Stress :

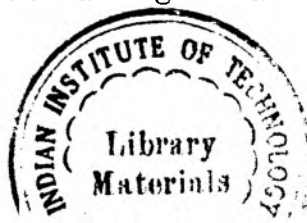
The stress in electrodeposits may arise from the mismatch of lattice parameters or from the incorporation of foreign material such as oxides, hydroxides etc. Depending on whether the deposit is in a compressed state or an elongated state, the stress is called either the tensile stress or the compressive stress. Macrostress can be determined by the spiral contractometer and stressometer. To measure the stress by spiral contractometer the change in the radius of curvature of a helix is measured as the helix is plated. Compressive stress winds the helix more tightly while tensile stress unwinds the helix. The stressometer contains a thin metal disk attached to a chamber containing a liquid. The chamber is connected to a vertical capillary tube. For measuring the stress, the stressometer is placed in the plating solution and the metal is deposited on the disk. As the deposition proceeds, the deformation of the metal disk due to the stress brings a change in the liquid level of the capillary. This change in the liquid

level of the capillary is measured. Tensile stress raises the liquid level in the capillary whereas the compressive stress lowers the liquid level. While the foregoing methods may be used for determining macrostresses, they are unsuitable for determining microstresses. Microstress is usually determined from the analysis of X-ray line broadening⁶¹.

Smoothness and brightness :

Smoothness and brightness are interrelated in the sense that they depend on the size, shape and spacing of surface irregularities. Both the properties can be estimated visually by comparing the sample with a standard one. However instrumental methods are available for evaluating these two properties accurately. Smoothness can be determined by microscope, electron microscope or by electromechanical means. Electromechanical instruments have fine tracer tip, the vertical movements of which over the surface are translated into electrical impulses. These impulses are magnified and recorded or measured by an averaging meter. This method cannot be used for measuring the smoothness of soft coatings since the tracer tip itself changes the nature of the surface.

Brightness is an important property of metallic coatings electrodeposited for decorative purposes. The brightness of a surface can be determined by measuring the amount of specularly reflected and diffused or scattered light. The amount of specularly reflected light and scattered light can be determined by Guild reflectometer.



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Porosity :

Since pores are the potential sites for corrosion, it is very much essential to test the metallic deposits for their porosity. Many porosity tests are chemical in nature. However porosity can also be determined by several physical methods. These are : (i) electrolytic methods⁶², (ii) X-ray methods⁶³, (iii) electronmicroscopy⁶⁴ and (iv) visual and photographic examination of the detached coatings. In chemical methods⁶⁵, a reagent is applied over the coating which will react only with the substrate to produce a colour reaction. In electrolytic methods, the specimen is made anodic in an electrolyte with auxiliary and reference electrodes. The anodic current and corrosion potential which depend on the area of the substrate exposed through pores are determined.

Corrosion :

The major function of electroplated coatings is the protection of the basis metal against corrosion. The corrosion protection offered by a coating depends on the following factors : (i) thickness of the coating, (ii) service environment, (iii) the nature of the coating metal, and (iv) composition and structure of the coating. The corrosion performance of the coating can be evaluated by atmospheric exposure tests and laboratory tests. Laboratory tests include the following : (i) salt spray test⁶⁶, (ii) acetic acid-salt spray test⁶⁷, (iii) copper chloride test, (iv) modified acetic acid-salt spray test (CASS test)⁶⁸, (v) Corrodokote test⁶⁹, (vi) sulphur dioxide

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test⁷⁰, and (vii) electrolytic accelerated corrosion test (EC test)⁷¹. In the salt spray test, acetic acid-salt spray test and CASS test, the specimen is exposed to the controlled fog of the corroding solution. The condition of the specimen after a stated number of hours is examined. To test the specimen by corrosion test a corrosive paste containing copper nitrate, ferric chloride, ammonium chloride and kaolin is applied over the specimen and exposed to humid atmosphere. In sulphur dioxide tests the specimen is exposed to humid atmosphere containing sulphur dioxide. In the EC test^{the} specimen is made anodic at 0.3 V (vs saturated calomel electrode) in a specified electrolyte. After electrolysis for 1 minute, the electrolysis is stopped for 2 minutes. This cycle is repeated a number of times and the penetration to the basis metal is detected either by using an indicator which can produce a colour reaction with the corrosion products or by microscope.

1.3.d Structure of electrodeposits :

Several methods are available for studying the structure of the electrodeposits. Some of these offer information only about the surface structure while the others throw light on the crystal structure, grain size and preferred orientation. In the first category come the optical and electron microscopic methods including the scanning electron microscopy, while in the latter category come methods like X-ray and electron diffraction.

Optical microscopic methods such as Nomarski interferometry, are useful in studying the surface structure⁷². Ellipsometry can be used to get information about the surface films

formed during electrodeposition⁷³. Optical microscopic techniques have the advantage of observing the crystal growth during the electrodeposition.

The better resolution and depth of focus of the electron microscope makes it an ideal tool for studying the structure of electrodeposits in recent years^{74,75}. For studying the surface structure of thick electrodeposits by this method, it is necessary to make some replica of the surface and then examine the same. Thin electrodeposits on the other hand can be analysed directly by transmission electron microscopy to get information regarding the dislocations and sites of codeposited foreign materials⁷⁵.

The scanning electron microscope (SEM) which has been developed more recently is a valuable tool for surface topographical studies due to its large depth of focus available. It is also capable of giving a three dimensional image of a metal surface. In SEM, electrons from a filament are accelerated to a voltage in the range 5 to 30 KV and focussed down into a fine beam on the surface of the specimen by three magnetic lenses. The scanning coil placed in between second and third lenses causes the electron spot to scan across the specimen surface in the form of a square raster similar to that of a television screen. The currents passing through the scanning coils are also made to pass through the corresponding deflection coils of a cathode ray tube (CRT) so as to produce a similar but larger raster on the viewing screen. The secondary electrons emitted from the surface of the specimen are collected and the resulting current is amplified to

modulate the brightness of the cathode ray tube. The magnification of the image depends on the ratio of the sizes of the raster on the cathode ray tube and the specimen surface. The foregoing technique which is known as emissive mode of operation is the most common way of operating the SEM. In addition to this, there are also other modes of operation such as reflective, absorptive, and transmissive modes each of which corresponds to the collection of different types of electrons arising from the impact of primary electron beam incident on the sample.

Whenever quantitative measurements of signal intensities are required, a single line consisting of photoelectric viewer is made to trace across the image formed on a CRT and the resulting signal is applied to the Y-plates of a separate CRT which is synchronously scanned. In this way a plot of signal intensity versus distance is obtained. This technique which is commonly known as the Y-modulation technique can also be used to display intensity variations over the complete image covering the full scanned raster and thereby providing a more useful alternative to the conventional intensity modulated image⁷⁶. The main advantages of the technique are that it can provide considerable quantitative informations on a single micrograph and can produce strikingly a three dimensional image of the intensity variation.

X-ray diffraction techniques are useful in studying the crystal structure, grain size, and preferred orientation of electrodeposits. The study of preferred orientation of electrodeposits provides useful information about the physical properties

of the electrodeposits. The preferred orientation of grains of electrodeposits can be determined reliably by Laue X-ray diffraction method or electron diffraction method. In the Laue method, the stationary specimen is bathed in a beam of white X-radiation. Each set of crystal planes chooses the appropriate radiation from the white spectrum to give Bragg reflection. Using a flat film camera, either a transmission or a back reflection photograph may be taken. The pattern of spots produced lies on ellipses in the transmission case and hyperbolae in the back reflection case. All the spots on any ellipse or hyperbola are reflections from planes of a single zone, i.e., where all the lattice planes are parallel to a common direction, the zone axis. By plotting the zones taken from the film on to a stereogram and comparing the angles between them with a standard projection of that crystal structure, the preferred orientation of the electrodeposit is determined.

1.3.e Chemical composition of the electrodeposit :

Electron microprobe analysis :

The impurities present in the electrodeposits may affect its physical and chemical properties. Hence, the analysis of impurities in the electrodeposits has much importance. This analysis can be done by various physical and chemical methods.

The composition of the electrodeposits can be conveniently analysed either qualitatively or quantitatively by electron microprobe. The electron microprobe works on the principle that each chemical element emits its characteristic X-ray when excited by electrons of sufficient energy. The intensity of the

characteristic X-ray depends on the amount of the element present in the irradiated volume. To carry out quantitative analysis, the intensity, I_A of a characteristic line of an element, A in the sample and intensity of the same line I_S for pure element, generated under identical electron bombardment conditions are measured. The weight fraction, C_A of the element is given by, $C_A = \frac{I_A}{I_S}$. The calculated C_A values should be corrected for the following errors : (i) error due to absorption of the generated X-ray, (ii) error due to fluorescence effect, (iii) error due to difference in atomic number of the elements present in the matrix, and (iv) error introduced by instrumental factors. The correction procedures for these errors are given by Briks⁷⁷.