Chapter-3

METHODS AND MATERIALS
Methods and materials

Electroplating of metals is a complex process involving several factors associated with cathode surface, anode surface, concentrations of bath components, nature of the medium, pH, current density, temperature of the bath solution, anode-cathode distance, anode purity etc. Therefore no single experimental procedure which is found satisfactory to cover all aspects of electroplating of metals. The detailed experimental procedures for various aspects of electroplating are available from the works of several investigators in this field [1] including that of Graham [2, 3], Lowenheim [4], N.V. Parthasaradhy [5] and Brenner [6].

Though absolute reproducibility is rather impossible to achieve due to several factors, reproducibility within a reasonable limit of error is of considerable importance. For satisfactory results, it is necessary to take precautionary measures regarding the size and shape of the cathode, nature of the cathode, design of the experimental setup and plating time. A careful control of the plating conditions is very important because the properties of the deposit are greatly affected by the plating conditions. For developing and optimizing bath solution for plating the following three main steps are generally adopted:

I Pre-plating process,

II Plating process, and

III Post-plating process.

Pre-plating process involves cleaning of cathode surface and activation of anode material. It also includes solution preparation, purification, adjustment of pH, temperature etc. In the plating process the actual electrolysis is carried out under known current or current density, pH, temperature, bath constituents etc. The optimum values for all these
parameters are established to get good deposit. Finally in the post-treatment process the deposit quality is modified to industrial requirements by adopting standard procedures.

The following procedures were adopted during the development and optimization of plating baths:

- Surface preparation prior to electroplating,
- Preparation and purification of electroplating bath,
- Selection and synthesis of brighteners,
- Hull cell studies,
- Measurement of operating voltage, cathode potential, throwing power, current efficiency

The methods adopted for the characterization of the electrodeposits are as follows:

- Porosity test using Ferroxyl method,
- Ductility and adhesion using bend test,
- Measurement of coating thickness by SEM cross section,
- Surface morphology by SEM studies,
- Corrosion resistance test by neutral salt spray method,
- Corrosion studies by cyclic voltammetry,
- Inclusion of addition agent in the deposit by FTIR and EDAX measurements,
- Crystallographic orientation and average particle size by XRD,
- Particles size by TEM studies,
- Determination of brightener consumption and
- Scaling up to 25 liters capacity.
3.1 Pre-treatment of the electrodes

Pretreatment or cleaning of the electrode (steel or iron) surface prior to electroplating is one of the important steps in plating process. The surface to be plated should be clean. The virgin article to be plated may consist of scale of oxide films, heat scale, workshop soils and oils, grease, dirt, etc., on its surface. All these should be removed so that the electrodeposit strongly adheres to the substrate surface. This is achieved in practice in three stages: removal of grease and oil, descaling, and washing.

3.1A Removal of grease and oil

In this step the articles to be plated were treated with trichloroethylene vapours in a closed vessel. This treatment removes grease and oil present on the surface of the articles.

3.1B Descaling and pickling

Preliminary descaling was done by mechanical polishing and was followed by acid pickling in 10% sulphuric acid or 50% hydrochloric acid containing corrosion inhibitor for 10 minutes at a temperature of 323-353 K.

3.1C Bright dipping

In this step the article to be plated was immersed in a solution containing mixture of acids for a time ranging from 1-5 min, to provide a bright surface free of stains. The mild steel plates were given bright dip in a solution containing oxalic acid 25 gL⁻¹, sulphuric acid 0.1 mLL⁻¹, hydrogen peroxide (30%) 13 mLL⁻¹ and at a temperature 298 K.

3.1D Polishing and buffing

In polishing, a few layers of the metal on the surface of the article is removed in stages by passing it through a variety of abrasives: coarse, medium, fine and so on. The purpose of this operation is to smoothen the surface of the article. On the other hand, in buffing operation, very little material is removed and the surface is improved.

The mild steel (AISI 1079, composition C 0.5%, Mn 0.5%, P and S 0.05% and rest Fe) panels of 2 mm thick were cut into different sizes depending on the type of
measurement (Hull cell, throwing power, current efficiency etc). The steel panels were subjected to mechanical polishing using the emery paper of varying grit size from 100 to 2000. By using different grades of muslin wheels, the steel plates were subjected to buffing.

3.1E Electropolishing

Electropolishing is usually done either to achieve a very smooth surface or to obtain a smooth and bright surface. This also removes any damage formed during the earlier processes, such as grinding, polishing, and so on. Electropolishing has the following advantages:

i) Smoother deposits with higher corrosion resistance,

ii) Better adhesion of deposits to the substrate.

Degreased and polished mild steel plates were subjected to electropolishing in a solution containing phosphoric acid 520 mL, sulphuric acid 420 mL, water 300 mL and Teepol 0.25 mL, at an anodic current density 4-6 Adm⁻², and at a temperature 298-303 K for 4-5 minutes with air agitation. The panels were given alkali dip (10% NaOH) followed by acid dip (10% HCl). Subsequently the articles were swirled and washed with water and used for plating experiments. The general sequence of steps for pre-treatment of electrode is given in Flow-chart 3.1.

Flow-chart 3.1: The general sequence of steps for pre-treatment of electrode

3.2 Bath preparation and purification

Electroplating bath must be pure otherwise it will result in producing unwanted deposit. Laboratory grade zinc sulphate and zinc chloride were used to prepare plating baths. All other chemicals used: conducting salts-sodium chloride, sodium sulphate and
ammonium chloride, buffer-boric acid, surfactants-cetyltrimethyl ammonium bromide, gelatin and other organic compounds were of AR grade. Therefore, these chemicals were used without further purification.

Zinc sulphate and zinc chloride solutions were treated with zinc dust at 323 K for 24 hours with air agitation in order to remove metallic impurities. The treated solutions were subjected to pre-electrolysis (10V DC) for a period of 6 hours. To remove organic impurities, the solutions were treated with activated charcoal at 333 K for 6 hours with constant air agitation. The solutions were filtered and used for plating experiments. The zinc content of the bath solutions was estimated by EDTA [7, 8].

3.3 Hull cell experiments

Any factor that affects the appearance of the electrodeposits over a spectrum of current densities can be assessed by Hull cell test. The test is simple and quick in execution. In practice, a certain amount of personal skill in the interpretation of data is required. The Hull cell test is frequently complementary to analytical control method and is very often the only method of controlling the addition agent concentration. It is used to control the concentrations of addition agents (brighteners, grain-refining agents, etc), to study the influence of impurities, to assess the efficacy of the purification treatment carried out on the bath, and to determine the influence of any parameter on the appearance of the deposit.

The standard Hull cell of 267 mL capacity made of Perspex material was used for optimizing the bath constituents and operating variables. The experimental set up for Hull cell study is as shown in Figure 3.1.
Mild steel cathode of dimension 10 cm $\times$ 7.5 cm (covering full cross section of the cell) was used along with zinc anode (99.99% pure and area of 6 cm $\times$ 6.5 cm). The cathode was placed along the slant side of the cell (as shown in Figure 3.1). At the end of the test, the cathode was removed, washed, dried and inspected visually. The nature of the deposit at different parts of the cathode was recorded. The current density at a given point on cathode was obtained from the graph (Figure 3.2) or calculated using the formula:

$$I = C(5.10 - 5.24)\log L$$

where $I$ is the current density in Adm$^{-2}$ at any point on the cathode, $C$ is the cell current in amperes and $L$ is the distance in centimeters of the point from high current density end of the cathode to the point at which the current density is desired. This formula is applicable over a distance of 0.64-8.35 cm on the cathode panel. The variation of current density on cathode surface with cell currents is shown in Figure 3.2.
A direct current (DC) power supply of 15A and 12 V capacity was used as constant current source (UNI-INSTA, Universal-Instruments, MFG. CO. PVT. LTD., Bangalore, India). The bath solution was prepared using suitable conducting salts and other ingredients. During the experiment the solution was stirred continuously with air bubbler. The temperature of the solution was 298 K. Fresh solution was used for each experiment. Prior to the experiment the anode was given acid dip in 10% hydrochloric acid for 30 seconds and washed with water. Experiment was conducted for 5 minutes at a given cell current. After the experiment, the cathode was rinsed thoroughly with water, immersed in bright dip bath (1% HNO₃) for 2-5 seconds and finally rinsed with water and dried. The plating process sequence followed is shown in the Flow-chart 3.2.

Flow-chart 3.2: The plating process sequence.
3.4 Experimental set up for the composite coatings

After the optimization of bath constituents and bath variables through Hull cell experiments, the deposition was carried out using single compartment cell of 250 mL capacity. An equal area of (4 x 4 cm²) cathode and anode were used for the electrodeposition process. Electrodeposition was carried out for 10 min in each case under stirred conditions. The Experimental setup is as shown in the Figure 3.3.

3.5 Throwing power measurement

Haring and Blum cell was used to measure throwing power. Provisions were made to agitate the bath solution and also to place the anode and two cathodes (Figure 3.3).

The bath solution was taken in the cell. Two mild steel cathodes (each 7.5 x 4.8 cm²) were kept at a distance of 1:5 ratio on either side of perforated zinc anode (7.5 x 4.8 cm²). The DC current was passed through the cell for 10 minutes. After the experiment, the cathodes were rinsed with water, alcohol and finally dried. The weights of the deposit on the nearer cathode (W₁) and on farther cathode (W₂) were determined.
Throwing power (TP) of the bath solution was calculated using the equation

\[
\%TP = \left( \frac{K - M}{K + M - 2} \right) \times 100
\]

where \( K \) is the ratio of the distance from the anode of the farther and nearer cathodes, respectively, and \( M \) is the ratio of the metal obtained on the nearer and farther cathodes.

![Diagram of experimental setup](image)

Figure 3.4: Experimental set up for the throwing power measurement.

The throwing power and polarization of the bath solution was also calculated from the polarization diagram using the Gardam's equation

\[
\% TP = \frac{100}{1 + 2L/N}
\]

where \( L \) is the linear electrode distance, \( m \) is the slope of the polarization line and \( \rho \) is the resistivity of the bath solution.

\[
N = m/\rho
\]
3.6 **Cathode current efficiency (CCE)**

To determine the cathode current efficiency of a given electrolytic process, it is necessary to measure accurately the quantity of electricity that flows through the solution. This may be done by measuring the current with an ammeter in series and the time with a calibrated stopwatch. Alternatively, an ampere-hour meter may be used in series with the plating vat. This is particularly useful where fluctuations in the current occur and are somewhat precise.

A rectangular cell was used to measure the current efficiency. A mild steel cathode (10 cm × 5 cm) was used along with zinc anode having the same dimension. A known amount of DC current was passed through the cell for 10 minutes. After the experiment, the cathode was washed with water, rinsed with alcohol and finally dried. The weight of the deposit (W₁) was determined. The theoretical weight (W₂) was calculated using Faraday's law:
where $I$ is the current (Amps), $t$ is the time (seconds), $A$ is atomic weight of the metal, $z$ is the valency and $F$ is Faraday (96,500 coulombs). The cathode current efficiency (CCE) was calculated using the equation

$$W_2 = \frac{ItA}{zF}$$

The weight of the alloy deposit was calculated from the cathode weight before and after plating. From this the composition and weight of the individual metal were calculated. The percentage cathode current efficiency (%CE) of alloy deposition is given by the equation.

$$\% \text{CCE} = \frac{W_1}{W_2} \times 100$$

The cathode current efficiency of alloy deposition is the sum of the separate cathode current efficiencies of the individual metals. Where $W_1$ and $W_2$ are the weight in grams of metals 1 and 2 in the alloy deposit. $Q_1$ and $Q_2$ are the electrochemical equivalents of the metals 1 and 2 in grams per coulomb. $I$ is the current passed in amperes and $t$ is the time of passage of current during electrodeposition in seconds.

### 3.7 Estimation of zinc alloy composition

After each experiment, the plated alloy deposit was dissolved in small volume of 1:3 HCl, made up to 100 ml in a standard flask. The nickel and iron content in Zn-Ni and Zn-Fe alloy deposits respectively were determined using gravimetric and potentiometric methods. The cobalt content in Zn-Co alloy was determined by gravimetric method and the manganese content in Zn-Mn alloy deposit was determined by potentiometric method. The percentages of nickel, iron, cobalt and manganese in the deposits were calculated by using the relation;
% \text{Ni} = \left( \frac{\text{weight of Ni}}{\text{weight of Ni} + \text{weight of Zn}} \right) \times 100

% \text{Fe} = \left( \frac{\text{weight of Fe}}{\text{weight of Fe} + \text{weight of Zn}} \right) \times 100

% \text{Mn} = \left( \frac{\text{weight of Mn}}{\text{weight of Mn} + \text{weight of Zn}} \right) \times 100

% \text{Co} = \left( \frac{\text{weight of Co}}{\text{weight of Co} + \text{weight of Zn}} \right) \times 100

3.8 Operating voltage

Hull cell experiments were conducted using bath solution containing different amounts of conducting salts (sodium chloride, sodium sulphate, ammonium chloride, etc). The operating voltage of the cell at different cell currents (1-3 Amps) was determined for each case. The operating voltage was plotted against the concentration of conducting salt. On the basis of the comparison of results (type and concentration of the conducting salt), a suitable conducting salt was chosen having a definite concentration to prepare the plating bath solution.

3.9 Electrochemical corrosion measurements by cyclic voltammetry

The electrochemical experiments were carried out using an Chemilink Electro Analyser (Model EA-201), coupled to a personal computer equipped with corrosion software for data acquisition. All galvanostatic and voltammetric experiments were performed using single compartment three-electrode cell of 100 ml capacity.

Potentiodynamic polarization measurements were carried out in aqueous 3.5 wt.% NaCl solution using mild steel (7 mm²), platinum foil, saturated calomel as working, counter and reference electrodes respectively. The potentiodynamic polarization measurements were performed by sweeping the potential between -600 to -1800 mV from open circuit potential at the scan rate of 10 mVs⁻¹. The corrosion potential (E_{corr}) and corrosion current (i_{corr}) were measured using Tafel extrapolation method. The cathode potential was recorded galvanostatically with respect to saturated calomel electrode at different current densities.
Cyclic voltammetric studies were carried out using glassy carbon (7 mm²), platinum and saturated calomel as working, counter and reference electrodes respectively. Prior to each experiment, the working electrode was polished to a mirror finish using alumina 0.05 μm (Buehler). After polishing, the electrodes were electrochemically pretreated in a solution containing 0.1M K₄Fe(CN)₆ and 1M KNO₃. This pretreatment gives a better electrochemical response and assures reproducibility. The temperature of the cell was kept at 303 K.

3.10 Testing of electrodeposits

Electroplating process has two specifications: process specification and product specification. In process specification, the sequence of operations through which a job has to be taken to get a specific finish on a part is described. Customers are not interested in the process specification or the materials specifications used by the electroplater. They are concerned only with the specifications as applicable to the plated products. So the electroplating industries are mainly concerned with methods of testing electrodeposits. Routine methods are established for making tests and there are many industrial specifications [9].

3.10A Coating thickness

The performance of an electroplated job is roughly proportional to the deposit thickness. This statement applies to almost all properties of the deposit, particularly corrosion resistance and wear resistance. Since the nature of the deposit and substrate vary in practice and hence different methods are reported to measure the thickness of deposits. The average thickness of the deposit was calculated using SEM cross sectional photomicrographs and as well as using the equation [10]

\[ T = \frac{m}{Ad} \times 100 \]

where \( T \) is the thickness of the deposit in μm, \( m \) is the mass of the deposit, \( A \) is the area in cm² and \( d \) is the density of the coated metal in gcm⁻³.
3.10B Corrosion resistance

Corrosion resistance test was carried out to assess the protection of substrate by the deposit against corrosion. Performance of the plated article in service can be examined by field trials but is time consuming. Therefore, there are a few methods, which are accelerated tests carried out over short periods (hours or few days) simulating the expected environment to which the plated part is to be exposed.

Different tests are available [11], which are related to the actual service conditions. The main objectives of all these tests are:

1. To assess the available systems for their corrosion resistance,
2. To develop coatings having higher corrosion resistant than the existing one, and
3. To ensure that a given electrodeposit-substrate combination meets the specifications.

The salt spray test [12, 13] has probably received more attention in the literature than any other laboratory corrosion tests for electroplated coatings since it is an accelerated corrosion test. In principle, it consists of exposing the test specimen to a controlled fog (mist) of a reagent solution (depending on the type of coating) and observing the condition of the specimen after a specified number of hours.

In zinc electroplating industries, the zinc coatings are given bright dip and passivation treatments before it is subjected to accelerated corrosion tests. Therefore zinc coatings were subjected to bright dip in 1% nitric acid solution for 2-5 seconds. These coatings after bright dip were passivated in a solution containing sodium chromate, 200 gL⁻¹, and pH 1.9 for 10-15 seconds (pH was adjusted with sulphuric acid). Passivated panels after drying in a clean oven at 373 K for 24 hours were subjected to salt spray test according to ASTM specification (B117-73, 5% NaCl solution, pH 6.5-7.3, temperature 308 K). The test was carried out for 120 hours. There was no appearance of white rust on the electroplated coatings indicating the service life of zinc coatings more than 24 years (out door exposure-natural environment).
3.10C Adhesion

Adhesion is an important property of any electrodeposit since without adequate bonding between the coating and substrate, the plated component cannot be put into the application for which it is meant. There are various test methods are available: bend test, burnishing test, file test, grinding test, heat test, peel test, etc. But standard bend test method was adopted to measure the adhesion of zinc deposits. Mild steel panels (3 cm × 10 cm × 1 mm) were electroplated with zinc to different thicknesses (5-25 μm). Each plated sample was subjected to bending through 180°. The deposit was closely observed at the point of bending to detect the crack or peel off.

3.11 Porosity

Electrodeposits contain pores and cracks to a varying degree, and hence they constitute the openings in the deposit. The corrosive medium together with moisture enters the substrate surface through these pores and cracks. Therefore the electroplater is interested in checking the porosity of the deposits. The corrosion tests or exposure to the atmosphere will indicate the porosity, but there are some less time-consuming tests like ferroxyl test, electrographic test and hot water test are also available.

Ferroxyl test was widely adopted to test the porosity in the deposit. Mild steel panels (8 × 8 cm²) were used for porosity test. Zinc was deposited on these panels upto 10-20 μm thickness. Good quality filter paper was dipped into the solution of 50 gL⁻¹ of sodium chloride and 50 gL⁻¹ gelatin and dried, and then cut into pieces (4 × 4 cm²). Then the test paper was placed on the deposited sample and wetted with 50 gL⁻¹ sodium chloride solution. After 10 minutes the Paper was taken out and dipped in 10 gL⁻¹ potassium ferricyanide solution. Appearance of blue spots on the filter paper with time was taken (number of blue spots/unit area) as the measure of porosity.

3.12 Immersion test

The corrosion resistance of the zinc deposits with and without additive was studied by immersing coated sample in 3.5 wt% NaCl solution in a specified number of
hours, the extent of corrosion was studied by using SEM cross sectional photomicrographs.

3.13 Weight-loss measurements

The corrosion behavior of zinc coated samples with and without additive were studied by weight-loss measurements at 298 K. The exposed area of the specimen was $3 \times 4 \text{ cm}^2$. The coating thickness was in the range of 15-20 $\mu\text{m}$. The coated samples were immersed in 3.5 wt% NaCl solution and the plates were weighed periodically for every 24 h in 15 days. From weight-loss the corrosion velocity was determined.

3.14 Open circuit potential (OCP) measurements

When a metal specimen is immersed in the corrosive medium, both oxidation and reduction process occur on its surface. Typically the specimen oxidizes (corrodes) and the medium (solvent) is reduced. If the system is not in connection with any instrumentation, the specimen assumes a potential relative to reference electrode, after attaining the equilibrium condition. This potential is termed as open circuit potential (OCP). At OCP, specimen has both anodic and cathodic current present on its surface. However, these currents are exactly equal in magnitude so there is no current to be measured. If the system is disturbed from the equilibrium condition by polarization, the net current can be measured.

The variation of OCP of steel deposited samples with and without additive were measured in a solution of 3.5 wt% NaCl as a function of time at 298 K. The exposed area of the specimen was $3 \times 4 \text{ cm}^2$. The corrosion potentials were measured for every 30 min interval for a period of 15 h.

3.15 FTIR study

Infrared spectrum gives information about the type of functional groups present in the compound. From the literature it is reported that some organic compounds (brighteners) are included in the deposit during electrodeposition. To know the inclusion of the brightener in the deposit, IR spectra of the scraped zinc deposits obtained from different baths were taken.
3.16 SEM studies

In order to understand the nature of the deposits obtained, the deposits obtained from different electrolytes studied by using scanning electron microscope model JEOL-JSM-35 LF at 25kV. SEM images of the coated specimens before and after corrosion tests were used to assess their corrosion performance in 3.5 wt% NaCl solution.

3.17 XRD analysis

The XRD patterns of the deposits were recorded Philips (TW 3710) X-ray diffractometer Cu-Kα as the radiation source and Ni as the filter to identify the phases formed. The average crystallite size was obtained by the line broadening method used in XRD. The average crystallite size values were estimated using the following equation of Scherrer and Warren,

\[ D = \frac{0.9\lambda}{(B^2 - b^2)^\frac{1}{2} \cos \theta} \]

where D is the crystallite size, \( \lambda \) is the wavelength of the radiation, \( \theta \) is the Bragg’s angle \( B \) and \( b \) are the FWHMs observed for the sample and standard respectively. Silicon powder with a mean particle diameter of 25 \( \mu m \) was used to measure the instrumental peak broadening.

3.18 TEM studies

The particles size of the zinc deposit obtained from optimum bath was examined by TEM (Philips TW-3710). An accelerating voltage of 200 keV was used. TEM samples were prepared by sonicating a small portion of each sample in acetone for ~30 sec and then placing a small drop of the resulting suspension on 3-mm holey carbon-copper grid.

3.19 Consumption of brightener

In electroplating, the addition agents play an important role in producing lustrous deposits. The addition agents are consumed during plating and thus their concentration decreases. When this concentration goes below the critical value the deposit becomes dull in appearance. In this study, to know the amount of addition agents consumed during plating 2.5 L of bath solution was taken and plating was carried out at different current
densities. The total number of coulombs of current passed to the bath solution was recorded at the time when the bath just started to give semibright deposit. The bath solution after use was subjected to Hull cell test by adding different amount of addition agents. The concentration of addition agents required to get the bright deposit once again is determined. The consumption of brightener is expressed in grams per liter for 1000 amps-hour.

3.20 Vat plating-scaling up to 25 liter capacity

Bath solution with optimum concentration of bath constituents was prepared. The plating experiments were carried out in a rectangular methacrylate cell of 25L capacity. Steel components of different size and shape were degreased, electrocleaned and given water wash. These pretreated steel components were rigged by means of copper wire and connected to the negative terminal of DC source. Two sufficiently large zinc plates were placed inside the plating Vat and were connected to the positive terminal of DC source. The plating experiments were carried out at different current densities. Provisions were made to agitate the bath solution during plating. The deposit properties were assessed by adopting standard procedures.
References:


