Methods and materials

3.1 Introduction

Electroplating of alloys is a complex process. A number of experimental conditions influence the electrodeposition process, such as the nature of metals to be deposited, surface condition of cathode and anode, concentration of the bath constituents, purity of constituents, nature of medium, pH, addition agents, brighteners, current density, temperature, agitation, plating duration, anode purity, anode-cathode distance geometry of cathode and so on. Therefore no single universal experimental procedure is found satisfactory to cover all aspects of electroplating of alloys. The detailed experimental procedures for various aspects of electroplating are available from the work of several investigators in this field [350] including that of Graham [351, 352], Lowenheim [353], N.V. parthasaradhy [354] and Brenner [355].

Though absolute reproducibility is not always possible to achieve due to several factors, but reproducibility with in 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 set up and plating time. A careful control of the plating conditions is very important because the properties and composition of alloy deposits are greatly affected by the plating conditions.

For developing and optimizing bath solution for plating of zinc alloys, 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 experimental steps were adopted during development of acid and alkaline baths for industrial electroplating of Zn-Ni and Zn-Fe alloys.

a) Cathode surface preparation prior to electroplating.
b) Preparation and purification of plating bath solution.
c) Hull cell studies.
d) General experiments for electroplating of alloys.
e) The determination of alloy composition, measurement of electrode potential, throwing power, cathode current efficiency.
f) The testing of coating thickness, adhesion of the alloy deposits to the base metal, porosity, hardness, ductility, internal stress and tensile strength, paintability of the alloy coatings.
g) Salt spray test for examining the corrosion resistance of deposits.
h) Post plating treatment.
i) Determination of brightener consumption.
j) Measurements of brightness of alloy deposit and studies of surface morphology.
k) Basic studies.
l) Pilot plant studies.

3.2 Pre-treatment of electrode

Pretreatment or cleaning of electrode (steel) surface prior to electroplating is one of the important steps in plating process. The surface to be plated may consists of oxide films, grease, oil, rust, dust, workshop soils, heat scale, etc during stamping, drawing or machining. Lyons [356] has summerized the objectives of cleaning of the cathode surface before electroplating. The cleaning can be carried out either by chemical or by mechanical method. The detailed experimental procedure for cleaning the surface prior to electroplating has been reviewed.

Mild steel (AISI 1079 composition, carbon 0.5% Mn 0.5% P and S 0.05% and the rest Fe) panels of 3 mm thick were cut into different sizes according to the type of performing experiment (Hull cell, throwing power, current efficiency etc.) The panels were subjected to mechanical polishing, brushing and buffing. Finally, the panels were polished with different grades of emery paper using alcohol as lubricant. The polished panels were placed in a degreasing tank containing trichloro ethylene for 2 hours at 60-70°C.

The degreased components were placed in pickling bath (10% HCl, thiourea). The immersion period varied from 2-10 minutes depending on the amount of rust, scale and oxide on the panels. After this procedure, the panels were given alkali dip (10% NaOH) and followed by acid dip (10% HCl). Subsequently the dipped components were thoroughly rinsed and washed with water and used for plating experiments. The general process sequence for the pre-treatment of electrode was given below.
Process sequence for pretreatment of cathode

1. Polishing
2. Washing with water
3. Degreasing with organic solvent
4. Water wash
5. Dipping in 10% HCl solution

3.3 Preparation and purification of bath solution

Electroplating bath must be pure otherwise it will result in producing unwanted deposit. Laboratory grade hydrated zinc sulphate, nickel sulphate and ferrous ammonium sulphate were used to prepare plating bath solutions. All other chemicals like conducting salts – sodium chloride, sodium sulphate, ammonium chloride, sodium hydroxide, buffer – boric acid, reducing agent – ascorbic acid, wetting agents – sodium lauryl sulphate, cetyl trimethyl ammonium bromide, brighteners – glutaraldehyde, DL-alanine, gelatin, 3,4,5-trimethoxybenzaldehyde, DL-valine, L-arginine, furfural and condensation products were used. These chemicals were of AR grade and used for the experiments without further purification.

All solutions were prepared by using distilled water. The plating bath 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 333K 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 standard method [357, 358].

To electroplate Zn-Ni and Zn-Fe alloys, various baths (both acidic and alkaline) with different metal ion ratios were used. It is known that at pH > 4.5, the iron (ferric state) in the bath solution precipitates in the form of hydroxide which has a significant
effect on the alloy plating. To overcome these difficulties, ascorbic acid was used in the bath solution to convert ferric iron (if any) to ferrous iron. The pH of the bath solution was adjusted by adding dilute sulphuric acid or sodium hydroxide using a digital pH meter. To avoid the variation of pH during alloy plating, boric acid was used as buffer. Sodium lauryl sulphate was used in acid bath as a wetting agent in order to avoid the formation of pits due to the hydrogen evolution at cathode surface in acidic medium.

3.4 Hull cell experiments

Any factor that affect the appearance of the electrodeposit 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 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 addition agent concentration or assessing the outcome of purification treatment. 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. Hull cell experiments are very useful in optimizing plating conditions for industrial alloy plating. The standard Hull cell of 267mL capacity made of perspex material was used for optimizing the bath constituents and operating variables. The experimental set up for the Hull cell study is as shown in Figure 3.1a.

Mild steel cathode of dimension 10 cm x 7.5 cm (covering full cross section of the cell) was used along with zinc anode (99.99% pure and area of 6cm x 6.5cm). The electrodes were kept at a distance of 5 cm and at an angle of 45° (at one end) with increasing distance from one end to the other. The cathode was placed along the slant side of the cell (as shown in Figure 3.1a). By keeping the cell current at 1, 2 and 3 amperes, it is possible to get deposits in a range of current densities from 0-4, 0-8 and 0-12 Adm⁻² respectively. The nature of the deposit at different parts of the cathode was
recorded. The current density (cd) at any point on Hull cell cathode is calculated by the equation.

\[ I = C (5.10 - 5.24 \log L) \]

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 to 8.35 cm on the cathode panel. The variation of current density on cathode surface with cell currents is shown in Figure 3.1b.

A direct current (DC) power supply of 15 A and 20 V capacity was used as constant current source (UNI – INSTA, Universal Instruments, MFG, Co. Pvt., Ltd. Bangalore, India). The bath solution was prepared having suitable conducting salts and other ingredients. During the experiments the solution was stirred continuously with air bubbler. The temperature of the solution was 298K. Fresh solution was used for each experiment. The cleaned anode was given acid dip in 10% hydrochloric acid for 30 seconds and washed with water. Experiments were conducted from fresh solution for 5 minutes at each cell current at room temperature. After the experiment, the cathode was rinsed thoroughly with water, immersed in bright dip bath (1% HNO\(_3\)) for 2-5 seconds, rinsed with water, then with alcohol and finally dried. The results were interpreted in the form of standard Hull cell codes (as shown in Figure 3.1c). The plating process sequence was given below.

**Plating process sequence**

1. Pre-treatment of cathode surface
2. Plating bath preparation and purification
3. Stirring of the bath solution
4. Plating experiments
5. Cathode water wash
6. Bright dip and water wash
7. Passivation and water wash
8. Drying and preserved for observation
Figure - 3.1a: Experimental set up for Hull cell studies
Figure 3.1b: The variation of current density on cathode surface with cell current

Distance from high current density end of cathode (cm)

Figure 3.1c: Hull cell codes

a) Bright   b) Semibright   c) Dull
   d) Burnt   e) Streaks    f) Uncoated
3.5 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 content in Zn-Ni alloy deposit was determined using gravimetric method. The iron content in Zn-Fe alloy deposit was determined by potentiometric method. The percentages of nickel and iron in the deposits were determined by using the relation.

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

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

3.6 Throwing power measurement

The ability of the bath solution to produce alloy deposits of more or less uniform thickness on the cathode with macroscopic irregularities (less than 0.25 mm in dimensions) is called throwing power. Haring – Blum cell was used to measure throwing power. Provisions were made to agitate the bath solution and also keep an anode and two cathodes as shown in Figure 3.2.

The optimised bath solution was taken in the cell. Two pretreated mild steel cathodes (each 7.5 cm x 4.8 cm) were kept at a distance of 1:5 ratio on either side of zinc anode (7.5 cm x 4.8 cm). The DC current was passed through the cell for 10 minutes. After the experiment, the cathodes were removed and rinsed with water, alcohol and finally dried. The weights of the deposit on the nearer cathode (\(W_1\)) and on farther cathode (\(W_2\)) were determined. Throwing power (TP) of the bath solution was calculated using the equation.

\[
\text{% TP} = \left( \frac{5 - R}{R} \right) \times 100 \quad \text{where} \quad R = \frac{W_1}{W_2}
\]
Figure 3.2: Experimental set up for throwing power measurement
3.7 Cathodic current efficiency measurement

In a plating process, it is expected that the entire current passed be utilized for electroplating. If a fraction of the current is used for any other reaction (including heating of bath) then it is a wasteful process. Unfortunately, very often this is the case. Brass deposition from cyanide solutions is accompanied by hydrogen evolution, where most of the current is spent for hydrogen evolution. The cathode current efficiency in electroplating is the percentage of the total current used for the deposition of metal.

The current efficiency (CE) of individual metal was calculated using the equation

\[
\% \text{ of CE} = \frac{W_1}{W_2} \times 100
\]

Where, \( W_1 \) is weight of the metal actually deposited

\( W_2 \) is the theoretical weight of the metal to be deposited

To determine the cathode current efficiency of a given electrolytic process, it is necessary to measure accurately, the quantity of electricity flows through the solution. A rectangular cell similar to Haring-Blum cell was used to measure the current efficiency of alloy deposition. A mild steel cathode (7.5cm x 5cm) was used along with zinc anode having the same dimension. The optimised bath solution was taken in the cell and a copper coulometer was connected in series. A suitable DC current was passed through the cell for 10 minutes. After the experiment, the cathode was rinsed with water, alcohol and finally dried. The weight of the alloy deposit was calculated from the cathode weight before and after plating. From this the composition and the weight of the individual metal were calculated. The percentage cathode current efficiency (%CE) of alloy deposition is given by the equation.
% CE of alloy deposition = \[ \left( \frac{W_1}{Q_1 I t} \right) + \left( \frac{W_2}{Q_2 I t} \right) \]

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.

3.8 Conductance of plating bath

Hull cell experiments were conducted using bath solution containing different amounts of conducting salts (NaCl, Na₂SO₄, 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 cell current. On the basis of the comparison of results (type and concentration of the conducting salt), a suitable conducting salt was chosen with a definite concentration to prepare the plating bath solution.

3.9 Polarization measurements

Mild steel panels in the form of sheets (2cm x 2cm) were used for polarization measurements. Experiments were conducted, galvanostatically, in a thermostated three compartment cell (Figure 3.3). The external current was passed between the working electrode (steel plate) and auxiliary (zinc) electrode. A saturated calomel electrode was used as a reference electrode. Over potentials were recorded using a digital potentiometer (Equip-Tronics, Model, EQ-600, India) with an accuracy of ± 2 mV. Steady state over potentials values were used to construct polarization diagram. The throwing power of the bath solution was also calculated from the polarization diagram using the Gardam’s equation.

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

\( N = m/\rho \)
Figure 3.3: Experimental set up for polarization measurement
Where $L$ is the linear electrode distance, $m$ is the slope of the polarisation line and $\rho$ is the resistivity of the bath solution.

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 the methods of testing electrodeposits. Routine methods are established for making tests and there are many industrial specifications [359].

3.10a Coating thickness

For many applications thickness is primary importance to the quality of electroplated coating. Usually the minimum thickness of coating is specified. A wide variety of test methods have been developed. Most of these methods [360] are based on the estimation of weight per unit area. The thickness ($T$) in microns was calculated using the equation.

$$T = \frac{m}{Ad} \times 100$$

Where $m$ is the mass of the coated alloy deposit, $A$ is the area of the specimen ($cm^2$) and $d$ is the density of the coated deposit $g$ per $cc$. In the present study drop test and BNF jet methods [354] were used to measure the thickness. The values of the thickness of zinc alloy coatings obtained by these methods were in good agreement with other methods with in the limit of experimental error.
Drop test method

A dropping funnel was taken and tube was attached to the end of small bore tip. The reagent was placed in the funnel and the tip was arranged to be 9 ± 1 cm away from the surface of the test sample. The test sample itself was kept inclined at 45° to the horizontal. The stripping reagent (a solution containing 200gL⁻¹ chromic acid and 50gL⁻¹ sulphuric acid was employed, temperature range was of 293 to 303K) was allowed to drop on to the clean plated surface at a rate of 100 ± 5 drops per minute. The time required to strip the deposit was recorded and thickness of the deposit was calculated.

3.10b 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 like bend test, burnishing test, file test, grinding test, heat test, peel test, etc. are available. But standard bending test was used to measure the adhesion of the zinc alloy deposits. Mild steel panels (3cm x 10 cm x 1 mm) were electroplated with zinc alloy to different thickness (5-25μm). 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.

3.10c 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. 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 available.

Ferroxyol test was widely adopted to test the porosity in the zinc alloy deposit. Mild steel panels (7.5cm x 7.5cm) were used for porosity test. Zinc alloy was deposited
on these panels up to 5-20 μm thickness. Good quality filter paper was dipped into the
solution containing 50 gL⁻¹ of sodium chloride and 50 gL⁻¹ gelatin and the paper was
taken out and dried then cut in to pieces (4cm x 4cm). Then the test paper was placed on
the zinc alloy 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 of potassium ferricyanide
solution. Appearance of blue spots on the filter paper with time was noticed. The
number of blue spots appearing on the filter paper (number of blue spots/unit area) is the
measure of the porosity of the deposit.

3.10d Hardness

To distinguish the hardness of an alloy deposits from those of massive metals, the
terminology 'micro hardness' is used. Since an alloy deposits are thin in cross-section
compared to the substrates/massive materials, the load employed for micro hardness
measurement are in the range of a few grams to 200 g and most frequently in the range
25-100g; the higher the load chosen, the higher the micro hardness is expected to be.

Methods of determining the hardness and their applications to the electrodeposits
have been discussed by Read [361]. The more useful method involves making an
indentation with an indent of specified geometry under a specified load. The length of
the indentation is measured and hardness (Vickers) is calculated (Vickers hardness
tester-British make) by using the equation.

\[ H_v = \frac{1.854 L}{d^2} \text{ Kg/mm}^2 \]

Where \( H_v \) is the Vickers number, \( L \) is the load in kilograms and \( d \) is the diagonal
in millimeters.

Zinc alloy was electroplated on mild steel panels upto thickness of 20-25μm and a
load of 50-200 g was employed. The hardness is expressed in Vickers hardness number
(VHN).
3.10e Stress, ductility, brightness and surface morphology

To determine the internal stress of an alloy deposits, the alloy is plated on one side of a thin sheet of metal so that stress with in the alloy deposit will cause the plated cathode to bend. The extent of bending is a measure of the internal stress of the alloy deposit and can be converted into conventional stress units. Various methods are in use to measures the internal stress of alloy deposits [362]. Stressometer (Blue star, India) was used to measure the internal stress of alloy deposits.

The ductility of the alloy deposits was measured by a bending test method. Zinc alloy was deposited on mild steel panels (2.5cm x 10cm) up to a thickness of 1 mill (25 μm). The panels were subjected to bending test up to 180°. No cracks or peel off at the point of bending shows that alloy deposits have good ductility.

For surface smoothness and brightness measurements, instruments are in vogue [363] which record a magnified profile of the surface. Glass reflectance meter (Elico, India) was used to measure the brightness of alloy deposits. After each experiment, surface morphology of zinc alloy deposits was studied by using scanning electron microscope. Surface microphotographs were taken and surface morphology of zinc alloy deposits was examined.

3.11 Corrosion resistance test

Corrosion resistance test was carried out to assess the protection of substrate by the alloy deposit against corrosion. Performance of the alloy plated article in service can be examined by field trials but is time consuming. Therefore, there are 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 [364] 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 corrosion resistant than the existing one
3. To ensure that a given alloydeposit-substrate combination meets the specifications.

The salt spray test [365] has probably received more attention in the literature than any other laboratory corrosion tests for electroplated alloy 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 alloy electroplating industries, the zinc alloy coating are given bright dip and passivation treatment before it is subjected to accelerated corrosion tests. Therefore, zinc alloy coating of known thickness were subjected to bright dip in 1% nitric acid solution for 2-5 seconds. These coatings were passivated in a solution containing sodium chromate, 200 g L\textsuperscript{-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 308K). The test was carried out for 120 hours. There was no appearance of white rust spots on the electroplated panels indicating the corrosion resistant property of alloy coatings and its service life more than 24 years (out door exposure natural environment).

3.12 Cyclic voltammetric study

Cyclic voltametry is another technique, which is used to study the red-ox behaviour of a given compound. By analysing the CV curve of a given compound, it is possible to explain the facts like, feasibility of the reaction, type of mechanism involved, complex formation and its stability, solvation effect etc. Here cyclic voltammetric studies were under taken to know the complex formation between the zinc, nickel, iron ions and organic addition agents and also the solvation effect.
3.13 Infrared spectral study

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

3.14 Surface morphology

During electroposition of alloys, formation of fresh nuclei and its subsequent growth in its size will take place. The addition agent influences the electrodeposition process and thereby produces good quality deposit. To know the nature of the crystal growth, SEM (SEM-JOEL, Model: JSM 540A) photomicrographs of the alloy deposits obtained in presence of different addition agent were taken and investigated.

3.15 Consumption of brightener

In electroplating of alloys, 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 agent consumed during plating 2.5L 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 semi bright 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 litre for 1000 amps-hour.
3.16 Pilot plant studies

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.