CHAPTER-II

EXPERIMENTAL METHODS

2.1 Materials

2.1.1 Specimen

AA 1100 Aluminium specimens (99% pure) cut into uniform size of rectangular area (7 X 1 X 0.1cm) were used as substrate. The composition of the aluminium alloy is presented in Table 2.1 [1].

2.1.2 Chemicals

Chemicals used in the present work with their make are given in Table 2.2

2.2 Pretreatment Methods

2.2.1 Zincating

2.2.1.1 Solvent degreasing

The mechanically polished aluminium specimens were degreased with acetone. The specimens were wiped in a single direction with cotton choked in acetone to remove organic impurities such as oil, grease, dirt etc.

2.2.1.2 Alkaline cleaning

The degreased aluminium specimens were alkaline cleaned in 5% (w/v) NaOH solution at 30°C for 2 min, to remove the naturally formed non-uniform oxide film on its surface.

2.2.1.3 Washing/Rinsing

After alkaline cleaning the specimens were thoroughly washed with running tap water and rinsed with deionised water to remove the excess alkaline cleaning solution.
2.2.1.4 Desmutting

Desmutting was carried out by immersing the specimens in 25% (V/V) HNO₃ at 30°C for 1 min in order to remove the smut (insoluble oxides other than aluminium oxide).

2.2.1.5 Double zincating

Zincating was carried out by a displacement process by immersing the aluminium in the zincating bath at room temperature for 2 min. The first zincating layer was stripped by using 20% (V/V) HNO₃. After stripping, washing and rinsing the specimens were again zincated for 1 min at 30°C. The zincating bath used is given in Table 2.3 and sequence of the zincating process onto aluminium is shown as flow chart [2] in Fig. 2.1. The samples were thoroughly rinsed with water after each stage, in order to avoid contamination carried from the previous stage.

2.2.2 Anodizing

The aluminium specimens were solvent degreased, alkaline cleaned, desmutted, washed and dried as given in the zincating process. Anodization was carried out in a thermostatically controlled electrochemical cell (±1°C). 10% sulphuric acid solution was used as anodizing electrolyte at 20±1°C (with cooling and agitation). Anodization was carried out for 30 min at a current density of 0.8A/dm². The flow chart [3] of the pretreatment of aluminium for anodizing is given in Fig. 2.2.

In the anodization process, aluminium sheet was used as anode, which was connected to positive terminal, and two lead sheets (2.5cm x 10cm) were used as cathodes and connected with negative terminal of the rectifier / DC power supply unit as shown in the Fig. 2.3. The pretreated aluminium specimen was fixed in between the two
lead cathodes of equal size. During anodizing heat develops due to the high potentials supplied. To maintain the original temperature of the anodizing electrolyte at 20°C the anodizing set up was kept in cold water bath. After anodizing, the aluminium panels were removed from the jig, washed in running tape water thoroughly, rinsed well using deionised water, dried, weighed, and subjected to electroless nickel plating.

2.2.3 Pretreatment of anodized aluminium for electroless plating

2.2.3.1 Sensitization

Anodized aluminium was immersed in sensitization solution containing 10g/l SnCl\textsubscript{2} and 40ml/l HCl at 30°C for 2 min. The sensitized anodized aluminium was washed thoroughly in running tape water and rinsed in deionised water. The above said washing/rinsing of the substrate is must to avoid contamination of the subsequent treatment solution by carry over of one into another.

2.2.3.2 Activation

After sensitization treatment, the substrates were activated by immersing in solution containing 1g/l PdCl\textsubscript{2} and 10ml/l HCl at 30°C for 30 s. After activation treatment, the substrate was thoroughly washed in running tape water and rinsed in deionised water so as to avoid contamination of the subsequent electroless plating by carry over of palladium particles or palladium ions into electroless nickel plating solution. One must be careful on such contamination otherwise spontaneous decomposition of the electroless plating solution will occur.
2.3 Electroless Nickel Plating on Zincated/Anodized Aluminium

Throughout the studies, nickel sulphate as the nickel ion provider, three different complexing salts for three different baths such as sodium acetate, tri-sodium citrate and glycine and sodium hypophosphite as a metal reducing agent were used.

Bath solutions were prepared by dissolving known quantities of nickel sulphate, complexing salt and sodium hypophosphite in deionised water separately and mixed together. Dilute sulphuric acid or ammonia solution was added slowly to get the desired working pH value of the plating solution. Electroless nickel bath is very sensitive to impurities and hence prior to use, the solution was filtered on Wattman Paper No. 40 grade. The bath was heated in a hot plate to attain the required temperature of the bath with continuous stirring using a magnetic stirrer. The flow chart [4] for electroless nickel plating on aluminium is given in Fig. 2.4.

The zincated/anodized aluminium specimen was immersed into electroless bath. Optimization of electroless nickel plating bath was carried out by changing the concentration of metal ion, complexing agent and reducing agent, temperature, pH, time and coating area/volume ratio. On studying the effect of one parameter, the others were kept at constant values.

2.4 Measurements

2.4.1 Thickness

After electroless plating the panel was washed, rinsed, dried and weighed \( w_1 \). The electroless nickel coating was dissolved in 10-20% HNO₃ solution. Then the panel was washed, rinsed, dried and weighed \( w_2 \). The actual weight of the deposit was...
calculated from the difference in weight before and after plating \((w_1-w_2)\). From the weight of the deposit, total plated area and density of the nickel, thickness was calculated [5] as follows

\[
\text{Thickness (µm)} = \frac{W \times 10^4 \times 60}{A \times D}
\]

where,

\(W = (w_1-w_2)\) = Weight of deposit in gram
\(w_1\) = Weight after plating
\(w_2\) = Weight after stripping
\(A\) = Total plated area of the substrate \((\text{cm}^2)\)
\(D\) = Density of the Nickel \((\text{gm/cc})\)

2.4.2 Rate of deposition

Rate of the electroless nickel deposit [6] was calculated using the following equation

\[
\text{Rate of deposition (µm/h)} = \frac{\text{Thickness}}{\text{Deposition time}}
\]

2.4.3 Atomic % of phosphorus and nickel

At.% P, Ni and other elements, which are present in the electroless Ni-P coated on zincated and anodized aluminium, were calculated from the EDAX spectra.

2.4.4 Adhesion testing

As electroless nickel plating is carried out on zincated and anodized aluminium (non-conducting substrate), there may be a question whether the as plated nickel on aluminium is adherent or not. For that, a qualitative adhesion test was carried out. Qualitative adhesion of the coating could be found out by tape test, bend test, grinding
and quenching tests. Quantitative tests include pull and shear tests. Among which the simple qualitative tests like tape, bend and heat treatment tests were used.

2.4.4.1 Tape test [7]

An adhesive tape was pressed evenly on the deposit and pulled off with swift rapid motion. If there is a coating on the adhesive part of the tape, then the deposit is non-adherent. If no coating comes off with the adhesive tape, then the deposit is considered to be adherent.

2.4.4.2 Bend test [8]

The panel along with the coating was subjected to bending away from the coating to 180° and made visual observation on the bend portion of the coated panel. If the coating comes off then the coating is non-adherent. If not comes off at the bend portion of the panel, then it is considered to be adherent.

2.4.4.3 Heat treatment test [9]

The electroless nickel-phosphorous coated on zincated and anodized aluminium panels were kept in electric oven / furnace. The temperature is slowly raised to 400°C, kept at that temperature for one hour, and slowly cooled down to ambient temperature. If the deposit is not peeling off or without any cracks, the coating is considered as highly adherent.

2.5 Surface Analysis

2.5.1 Surface morphology (SEM)

The surface morphology of the deposits was examined by scanning electron microscopy (SEM, JEOL-Japan-JSM-840A). The SEM photograph is shown in Fig. 2.5. The surface topography of the zincated, anodized, sensitized and activated electroless
nickel coated aluminium before and after heat treatment was found out by scanning the sample using the Scanning Electron Microscope (SEM) under different magnifications of X 3,000, X 20,000, and X 40,000. The surface morphology of the deposits in various coatings was compared.

2.5.2 Elemental Composition (EDAX)

The elemental compositions of the deposits were determined by energy dispersive X-ray microanalysis. (EDAX, Oxford link ISIS 300). The EDAX photograph is shown in Fig. 2.6. The zincated, anodized, sensitized, activated and electroless nickel-phosphorous coated aluminium panels in the as-deposited state were subjected to elemental analysis using EDAX instrument.

2.5.3 Nanostructure (AFM)

The topographic morphology of the Ni–P deposits was analyzed by atomic force microscopy (AFM) (Digital Instruments CP-II Veeco Company, USA) which is shown in Fig. 2.7. The surface topography of the bare, zincated, anodized and electroless nickel coated aluminium in the as-deposited condition and heat-treated conditions was found out by AFM and compared. The surface topographical 2D view, depth profile analysis and 3D view were recorded using WSxM software. The surface roughness and route mean square average (RMS) values were also measured.

2.5.4 Phase Composition (XRD)

XRD data of bare, zincated, AC anodized and electroless nickel coated aluminium obtained from sodium acetate, tri-sodium citrate and glycine baths in the as-deposited and heat treated conditions were determined from a Philips X’pert X-ray diffractometer with Cu Kα radiation (λ=0.15418 nm) as shown in Fig. 2.8. Crystalline size was calculated
from the Scherrer’s formula [10] using XRD data. The observed d-spacing values were matched with JCPDS standard data and plane orientations, type of coatings, lattice parameters and crystalline structures were determined.

2.5.5 Reflectance (UV-Visible spectroscopy)

The UV-Visible reflectance spectra of the as-deposited Ni-P films formed in the sodium acetate, tri-sodium citrate and glycine baths on anodized aluminium were recorded using Hitachi U-3400 spectrophotometer.

The as plated electroless nickel-phosphorous coated on anodized aluminium panels show different colours ranging from brown to black depending upon the plating time compared to bare and anodized aluminium. Hence, the absorbance/reflectance data were noted in the visible region (400-800 nm) using the spectrophotometer.

2.6 Corrosion studies

2.6.1 Potentiodynamic polarization

The corrosion resistance behaviour of the coatings was conducted by means of potentiodynamic polarization test. The potentiodynamic polarization has been carried out in 3wt.% NaCl solution at 30°C. The measurements were made using an Electrochemical Workstation (CHI Instruments, Model 760) as given in Fig. 2.9, which was connected to a three-electrode electrochemical cell. In the present study bare and electroless nickel-phosphorus coated on aluminium were used as working electrodes. A platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The exposed surface area of the electroless Ni-P coating was 1cm². Block diagram of the experimental set up is given in Fig. 2.10. Before each experiment,
the steady state open circuit potential was noted first and then potentiodynamic polarization curves were recorded at a scan rate of 1 mV/s. Corrosion potential (\(E_{corr}\)) and corrosion current density (\(i_{corr}\)) were determined by extrapolating the straight line section of the anodic and cathodic Tafel lines. Polarization resistance (\(R_p\)) and corrosion rate were obtained from the following equation [11].

\[
R_p = \frac{b_a x b_c}{2.303 (b_a + b_c) I_{corr}}
\]

where, \(R_p\) is polarization resistance, \(b_a\) and \(b_c\) are the magnitude of the slopes of the anodic and cathodic Tafel lines respectively.

\[
CR (mpy) = \frac{0.129 X i_{corr} (\mu A/cm^2)}{Density (gm cm^{-3})}
\]

### 2.6.2 Electrochemical impedance spectroscopy

Electrochemical Workstation CHI, Model 760 was used for AC impedance measurements. The impedance measurements were made in unstirred, 3wt.% NaCl solutions at 30°C, over the frequency range from 100 kHz to 0.01kHz under controlled potential conditions, with an AC potential signal of 10 mV varied about the open-circuit potential. The real and imaginary parts of impedance were plotted in Nyquist plots. From the Nyquist plots, the charge transfer resistance (\(R_{ct}\)) and double layer capacitance (\(C_{dl}\)) values were calculated.

The charge transfer resistance values were obtained from the plots of \(Z'\) Vs \(Z''\). The value of \(R_s\) and \(R_{ct}+R_s\) which corresponds to the point where the plot cuts \(Z'\) axis at low and high frequency respectively. The difference between the two values gives the charge transfer resistance (\(R_{ct}\)) values.
The $C_{dl}$ values were calculated from the following equation [12]

$$C_{dl} = \frac{1}{2 \times 3.14 \times R_{ct} \times f_{\text{max}}}$$

where,

$C_{dl} =$ double layer capacitance

$R_{ct} =$ charge transfer resistance

$f_{\text{max}} =$ frequency at $Z''$ value maximum.

### 2.7 Cyclic Voltammetry Analysis

The cyclic voltammograms were recorded using the above electrochemical cell setup consists of a three electrode system. The electrodes were same as those used for corrosion studies. The cyclic voltammograms were performed in alkaline (1 M KOH) solutions for electroless nickel phosphorus coatings formed in sodium acetate, tri-sodium citrate and glycine baths, at various concentration of metal ions, reducing agents, complexing agents and pH at different scan rates. The scan rate was varied between 0.05 V/s to 0.5 V/s. The anodic peak potential ($E_{pa}$), cathodic peak potential ($E_{pc}$) and anodic peak current ($i_{pa}$) cathodic peak ($i_{pc}$) currents were measured from the cyclic voltammograms.