CHAPTER 2

EXPERIMENTAL METHODOLOGY AND CHARACTERIZATION

2.1 Bath formulation

Table 2.1 presents the detailed bath composition, concentrations and deposition conditions employed for the fabrication of alloy deposits. The bath solution was prepared using Analar grade chemicals with twice distilled water. Every bath constituent has crucial role during plating process. The plating bath uses NiSO$_4$.6H$_2$O and Na$_2$WO$_4$.2H$_2$O as a source of Ni$^{+2}$ and W ions, trisodium citrate as complexing agent, ammonium chloride as buffering agent and sodium chloride as conducting salt. The bath solution was prepared at ambient temperatures with incessant stirring. Many different trial and error experiments were done, in order to optimize the deposition conditions. Prior to the electrodeposition, pH of the electrolyte was adjusted to 8 using Elico-LI 120 pH meter, by the respective additions of sulphuric acid or sodium hydroxide. To the freshly prepared bath, additives were added in a concentration of 0, 50, 100, 250 and 500 ppm. All the deposition experiments were done in a thermostat glass cell, containing 40cm$^3$ electrolytes.
2.2 Coating processes

The mild steel samples were prepared in a rectangular form with dimensions of 25mm x 25mm x 0.3mm as substrate material. Prior to applying the coating, steel substrates were wiped with cotton gently to remove the loosely adhered particles, ultrasonically degreased with acetone for about fifteen minutes and then mechanically polished (Ra ≤ 1μm); to attain mirror finish, with diamond paste using twin disc polisher, edges and corners of samples were also rounded in order to eliminate the edge effect, followed by electro cleaning in the conventional alkaline cleaner solution (contain 3.5g/l NaOH and 2.5 g/l Na₂CO₃) for about two minutes. Another sequence of washing with distilled water to remove any residual contamination and samples were pickled and activated in 5% H₂SO₄ solution for 10 seconds and after rinsing well using twice distilled water, substrates were immediately transferred to the beaker containing 40 cm³ of electrolytes. After deposition the plates were well rinsed, to remove the loosely adsorbed oxide particles and left for air drying. A two electrode system, containing platinized titanium (25mm x 25mm x 1.5mm) as an anode and mild steel (Fe-96.14 wt%, O-3.86 wt%) plates were used as cathodic substrates. Experiments were done in triplicate for each concentration in order to optimize the additive concentration in the bath solution. In order to achieve a

### Table 2.1 Basic bath composition and operating parameters

<table>
<thead>
<tr>
<th>Bath constituents</th>
<th>Concentration (M)</th>
<th>Operating conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄·6H₂O</td>
<td>0.1</td>
<td>Temperature 333±3 K</td>
</tr>
<tr>
<td>Na₂WO₄·2H₂O</td>
<td>0.2</td>
<td>Current density 5 Adm²</td>
</tr>
<tr>
<td>C₆H₅Na₃O₇·2H₂O</td>
<td>0.5</td>
<td>pH 8</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.1</td>
<td>Deposition time 15 min</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>0.5</td>
<td>Anode- platinized titanium</td>
</tr>
<tr>
<td>Additives</td>
<td>0-500 ppm</td>
<td>Cathode- mild steel</td>
</tr>
</tbody>
</table>
better distribution of cathodic current, the average current density of 5A·dm$^{-2}$ was set for electrodeposition of Ni-W alloy coatings. The direct current was employed for the fabrication of alloy deposits by the use of a sigma instrument, connected to the digital multimeter (Mastech-M 92-A) for accurate and consistent passage of current. The nickel-tungsten coatings were uninterruptedly fabricated at a constant plating temperature of 60±3°C for fifteen minutes.

2.3 Corrosion analysis

Characterization of corrosion behavior of the Ni-W alloy deposits obtained in the absence and in the presence of additive in the bath; were done by two electrochemical techniques namely

a) Potentiodynamic polarization method (Tafel) - It is one of the D.C technique used to know the material behavior during an exposure to a corrosive solution. The following parameters were extracted from the obtained Tafel plots: corrosion potential ($E_{corr}$), corrosion current ($i_{corr}$), polarization resistance ($R_p$), corrosion rate (CR) and protection efficiency (PE).

b) Electrochemical impedance spectroscopy (EIS) - Electrochemical impedance spectroscopy (EIS) is one of the powerful and non-destructive techniques that help in studying the corrosion behavior of specimen at the electrode/electrolyte interface in the simulated physical environment. The coated sheets were then mechanically sheared into 10 mm × 10 mm for corrosion testing and analysis. An alloy coated substrate with an exposed area of 0.2 cm$^2$ was used for corrosion analysis in 0.2 M H$_2$SO$_4$ solution throughout the study.

The electrochemical measurements of the coatings were measured using a computer controlled potentiostat/galvanostat CHI-660C (USA)., using
a three electrode electrochemical cell system, where the coating of interest acts as a working electrode, a platinum wire as a counter electrode and reference electrode as a standard saturated calomel electrode. After attaining the steady state open circuit potential (OCP), tafel polarization curves were recorded, at a potential sweep rate of 10mV/s in a scanning potential range of −200 to +200 mV with respect to the OCP. The $E_{corr}$ and $I_{corr}$ were determined from the intercepts by Tafel’s extrapolation method. EIS measurements were carried out at open circuit potential of the working electrode by applying a 5mV AC sine wave perturbation in the frequency ranging from 1 Hz to 100 kHz. All the electrochemical characterizations were carried out at room temperature of 35±2°C. Impedance spectra were represented in the form of Nyquist plots, where the imaginary component of the impedance is plotted as a function of the real component. Charge transfer resistance (Rct) was determined from the diameter of the semicircles. In order, to estimate the values of solution resistance (Rs) and capacitance of electrode processes (CPE$_{dl}$) a simple randles equivalent circuit was employed, which was well used for the alloy coated systems. The circuit fitment and the data analysis was done by using Z-view software (V.3.0). Each type of electrochemical measurement was repeated at least three to four times until good reproducibility of the data was obtained. For comparison purposes Ni–W deposit which is having high corrosion resistance, i.e. obtained from optimized bath and deposit obtained in the absence of additive are subjected to the further characterization analysis.

2.4 Coating physical property evaluation

The structural characterization of the coatings was investigated using X-ray diffractometer, Shimadzu XRD 6000 (Japan) instrument equipped with Cu-Kα radiation source. XRD spectra were recorded at room temperature in standard 0–20 mode operated at 40kV and 30 mA. The diffraction patterns were
collected over a 2θ (deg) range from 10° to 90°, using continuous scan mode with a scan speed of 10.0 deg/min.

The crystallite size of the deposits from the obtained XRD results was calculated using the Scherrer equation,

\[ d = \frac{(0.9\lambda)}{(\beta \cdot \cos \theta)} \]  

(1)

where \( d \) is the average grain size, \( \lambda \) is the wavelength of X-rays, \( \beta \) is the full-width at half-maximum (FWHM), and \( \theta \) is the scattering angle.

The coating surface morphology and elemental composition of alloy deposits were observed and analyzed using scanning electron microscopy couple energy dispersive spectroscopy (SEM-EDS) analyzer (JSM-360; JEOL) at 20 kV accelerating voltage. The topography of Ni-W alloy deposits was analyzed using a high-resolution atomic force microscopy (AFM) (Bruker-Dimension icon AFM equipped with a Scan Asyst) to know the surface roughness of the alloy deposits at atomic resolution. The corresponding 2D and 3D images which affirms the above subject were depicted respectively. Determination of additive incorporation in the alloy deposits during electrodeposition was substantiated with the aid of Fourier transform infrared spectroscopy (FTIR) (IR Prestige-21 Shimadzu, Japan). The scrapped deposits were pelletized using KBR pellet method and spectra were recorded in a range of 500-4000 cm\(^{-1}\). The Ni-W alloy deposits of as such and with that of aldehyde coated were further scrutinized for the evaluation of adsorption of additive on the alloy surface by Photoluminescence instrument JASCO model FP-8200 system with a xenon flash lamp for the wavelength (\( \lambda_{ex} \)) 246.0nm.