CHAPTER IV

MATERIALS AND METHODS

This chapter explains the method of electrochemical polymerization of indole-co-pyrrole, indole-co-thiophene and ceria coating on indole-co-pyrrole (bilayer). The as-synthesized coatings were characterized by using various sophisticated analytical techniques. Further this chapter deals with the methods of electrochemical characterizations towards anti corrosive performance of the as-synthesized polymers on LN SS in sulphuric acid medium.

4.1 MATERIALS

All the chemicals indole, pyrrole, thiophene, LiClO₄, acetonitrile and cerous nitrate were of analar grade and are used without any further purification. All the aqueous solutions were prepared using double distilled water.

4.2 PREPARATION OF ELECTRODES

In the present work, 201 grade austenitic low nickel stainless steel samples were used as specimens for the corrosion studies. The chemical composition of low nickel stainless steel was determined by analytical techniques and its composition is given in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>N</th>
<th>Cu</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (Wt. %)</td>
<td>0.063</td>
<td>0.35</td>
<td>7.05</td>
<td>0.054</td>
<td>0.01</td>
<td>16.03</td>
<td>4.16</td>
<td>0.1</td>
<td>1.24</td>
<td>Balle ee</td>
</tr>
</tbody>
</table>
All the test specimens of low nickel stainless steel were cut into an overall apparent size of $1 \times 1 \times 0.3$ cm and embedded using epoxy resin with an electrical connection and having an exposed area of $1 \text{ cm}^2$. These specimens were polished with different grits of SiC emery papers from 120 to 1200 grit and final polishing was done with 6 μm and 1 μm diamond paste and degreased with acetone. Further the specimens were cleaned by ultrasonication, washed with double distilled water then finally dried and kept in dessicator for further studies.

4.3 DEVELOPMENT OF COATINGS

4.3.1 Cathodic Electrodeposition of CeO$_2$

Ceria was cathodically electrodeposited on LN SS from the electrolyte 0.25 M Ce(NO$_3$)$_3$.6H$_2$O by cyclic voltammetry (CV) between -0.6 to -2.6 V at a scan rate of 20 mV s$^{-1}$ [203, 226, 227]. All the potential in the text are related to saturated calomel electrode (SCE).

4.3.2 Electropolymerization of poly(indole-co-pyrrole)

The coating of poly(In-co-Py) on LN SS substrate was obtained by cyclic voltammetry from ACN-LiClO$_4$ containing monomers of 0.1 M of indole and 0.1 M of pyrrole at different mole ratios (3:2, 3:1, 2:1, 1:1, 1:2, 1:3 and 2:3). The cyclic voltammogram was scanned between 0.2 and 2.0 V for the different monomer feed ratios. The 1:1 monomer feed ratio has been optimized to have a better coating on LN SS and the coating obtained using 1:1 monomer feed ratio is further studied at varied scan rates of 10, 30 and 50 mV s$^{-1}$ [183]. The polymer coated specimens were rinsed with acetonitrile to remove the oligomers and then dried for subsequent tests.
4.3.3 Electropolymerization of poly(indole-co-thiophene)

The poly(In-co-Th) coatings were electrochemically synthesized on LN SS substrate using cyclic voltammetry from ACN-LiClO$_4$ solution containing each indole and thiophene monomers at different monomer feed ratios say 3:2, 1:1, 1:2, 1:3, and 2:3. The coatings obtained from the optimized concentration 1:1 were further examined at varied scan rates say 10, 30 and 50 mV s$^{-1}$. The cyclic voltammetry was scanned between 0 to 3.0 V for all the coatings [42,228].

Finally all the polymer coated specimens were rinsed with acetonitrile to remove oligomers, dried and used for subsequent tests.
4.3.4 Preparation of bilayer (poly(In-co-Py) on CeO$_2$) coated LN SS

The electropolymerization of poly(In-co-Py) on CeO$_2$ coated low nickel stainless steels was carried out using 0.1 M of indole and 0.1 M of pyrrole using cyclic voltammetry in the potential range of 0.2 to 2.6 V at a scan rate of 50 mV s$^{-1}$. The optimized monomer feed ratio of poly(In-co-Py) i.e. 0.1 M of indole and 0.1 M of pyrrole was used to obtain the copolymer coating on the CeO$_2$ coated LN SS and the as formed bilayer coating is keenly preserved for further studies.

4.4. SPECTRAL CHARACTERIZATIONS OF COATINGS

4.4.1 Fourier Transform Infrared Spectroscopic Studies

The formation of the copolymer coatings by electrochemical deposition was characterized by Fourier transform infrared spectroscopy. The FT-IR spectrum of the coating was recorded in the transmittance mode on a NICOLET 380 FT-IR spectrometer with KBr pellets in the wave number range of 4000 - 400 cm$^{-1}$ to investigate the chemical bonding of the coating.

4.4.2 $^1$H-NMR Spectral Studies

The structural elucidation of the as-synthesized copolymers poly (indole-co-pyrrole) and poly(indole-co-thiophene) were confirmed by $^1$H-NMR spectral technique. The Jeol GSX make NMR spectroscope is used for the analysis with the frequency of 400 MHz. The samples were dissolved in deuterated dimethyl sulphoxide (DMSO) by using as a solvent.

4.4.3 X-ray Diffraction Analysis

To identify the phase purity of the CeO$_2$ coatings formed on low nickel stainless steels the X-ray diffraction patterns of the ceria coated polymers have been
carried out in Bruker D8 Advance diffractometer with the monochromatic Cu Kα (λ = 1.5418 Å) radiation. The relative intensities were recorded within the range of 20-80º (2θ) at a scanning rate of 0.5° min⁻¹.

4.4.3 Thermogravimetric Analysis

The thermal analysis of the as-synthesized polymers were performed in Dupont 2000 instrument. The TGA/DSC analysis was carried out under N₂ atmosphere with the temperature ranging from 30 °C to 1000 °C for ceria coated polymers. The thermogram for the as-synthesized polymers have been observed in the temperature ranging from 30 °C to 500 °C. The heating and cooling speed of the experiment was 10 °C per minute. The samples used for the thermal analysis were prepared using the ceria coating formed on LN SS that were rinsed with water and dried for at least 24 h in a dessicator before analysis. The scrapping off the deposit is realized at least after 1 h of the deposition to avoid expansion of the lattice parameter due to non-stoichiometric cerium oxide phase transformation.

4.5 SURFACE CHARACTERIZATION

4.5.1 Scanning Electron Microscopic Studies

The surface morphology and elemental composition of the as-deposited poly(In-co-Py), poly(In-co-Th), and CeO₂/poly(In-co-Py) (Bilayer) coatings on LN SS were investigated using scanning electron microscope (JEOL Model JSM-6390LV) coupled with energy dispersive X-ray analysis (JEOL Model JED-2300). The samples have been fitted in Al substrate by carbon paste. The intensity of the electron beam used for operating the SEM was 30 keV.
4.5.2 Atomic Force Microscopic Studies

The AFM images were obtained with a Multimode Scanning probe microscope (NTMDT, NTEGRA prima, Russia) operating in the semi contact mode. The silicon tips having a resonance frequency in the range 47-150 KHz and a force constant in the range of 0.35-6.06 N/m, were standard silicon nitride cantilevers with a length, width and thickness of 135, 30 and 1.0-2.0 µm. The AFM images were processed presented and the height profile was measured with the aid of the Nova software.

4.6 MECHANICAL CHARACTERIZATIONS

4.6.1 Adhesion Test

Tape test (ASTM D3359), also called peel test, was carried out to evaluate the adhesion of the coatings on the LN SS substrate. The degree of adhesion between the coatings and the substrate was counted as the percentage of the residual layer on the substrate after peeling off by tapes (3M-610).

4.6.2 Microhardness Tests

The microhardness of the coatings was measured by a microhardness tester with a loading force of 50 g. Each microhardness value was an average of five test results. In the wear resistance test, the counter-body was made from LN SS. The experimental parameters are as follows: applied load - 10 N, frequency - 2.5 Hz, time - 10 minutes.
4.7 PREPARATION OF ELECTROLYTE

0.5 M H$_2$SO$_4$ prepared from double distilled water was used as an electrolyte for all the corrosion studies such as potentiodynamic polarization and electrochemical impedance spectroscopy. 50 ml of the electrolyte was taken in a 100 ml glass beaker.

4.8 ELECTROCHEMICAL CORROSION STUDIES

4.8.1 Potentiodynamic Polarization Studies

All the electrochemical corrosion measurements were performed using the Electrochemical Workstation (Model No: CHI 760, CH Instruments, USA) and a constant temperature of 28 ± 1 °C is maintained and 0.5 M H$_2$SO$_4$ was used as an electrolyte. A platinum electrode along with the saturated calomel electrode (SCE) were used as auxiliary and reference electrodes respectively while the working electrode composed of LN SS specimen of 1 cm$^2$ exposed area.

Fig. 16. Electrochemical workstation - model CHI 760C (USA)
Materials and Methods

The tip of the reference electrode was positioned very close to the surface of the working electrode by the use of a fine Luggin capillary in order to minimize the ohmic potential drop. The remaining uncompensated resistance was also reduced by the electrochemical workstation. Potentiodynamic polarization studies of uncoated, copolymer coated and bilayer coated LN SS were carried out in the 0.5 M H₂SO₄, recorded with the potential sweep ranging between -1000 mV to 1200 mV at a scan rate of 0.1 mV s⁻¹.

4.8.2 Electrochemical Impedance Spectroscopic Studies

Electrochemical Impedance Spectroscopy is of great importance in the analysis of electrochemical systems such as corrosion, which helps to identify the electrochemical process occurring in a system. The studies were carried out using the same setup as that of potentiodynamic polarization studies and the applied AC perturbation signal was 10 mV within the frequency range 100 kHz to 1 Hz. All the electrochemical impedance measurements were carried out at an open circuit potential. Each experiment was repeated at least three times to check the reproducibility.

4.9 ICP-AES Analysis

The protective performance of the coatings in 0.5 M H₂SO₄ medium was further analyzed using the Inductively Coupled Plasma Atomic-Emission Spectroscopy (ICP-AES) (Model: Thermo Electron IRI+-S INTREPID II XSP DUO) in the range of 165 to 1000 nm. For this analysis, the uncoated and coated LN SS specimens were removed from the electrolyte (0.5 M H₂SO₄) and the solutions were collected and analyzed so as to estimate even the trace level leach out of metal ions during the polarization measurements.