Chapter-4.3

Ni-Cu-P-ZrO$_2$ nanocomposite coatings
Process and properties of electroless Ni-Cu-P-ZrO$_2$ nanocomposite coatings

4.3.1. Introduction

The emergence of electroless Ni-P poly alloy deposits is considered as the most effective method to alter the chemical and physical properties of binary Ni-P alloy deposits [1-6]. Initially the copper ions were added to the electroless Ni-P plating baths as a stabilizer, primarily to replace the other sulfur bearing stabilizers. Copper ions improved the solution stability without significantly retarding the deposition rate [7]. In many electroless plating bath the Pb$^{2+}$ ions are also used as stabilizer. As lead ions in excess are biotoxic and give fatal damage to the brain and nerves, hence lead free processes are in demand. The stabilizer plays a mysterious role in the ENP process. The copper ions are selected as a model stabilizer for replacing lead ions. The introduction of copper ions into electroless Ni-P bath was actually to stabilize the bath by preventing the propagation of colloidal nickel particles that lead to catastrophic precipitation of Ni blacks in the plating bath. The choice of Cu$^{2+}$ ions is mainly based on the facts that, Cu$^{2+}$ ions have been reported with stabilizing functions and they provide a wider concentration window than lead ions for operation [8].

The codeposited copper in Ni-P matrix has immense effect on deposit characteristics and recent studies have indicated that properties like smoothness, brightness, ductility, higher thermal stability and corrosion resistance are superior to those of the electroless Ni-P coatings [9-14]. They show low temperature coefficient of resistance and finds application in thin film resistors and metal film resistors. In addition, the inclusion of Cu in Ni-P matrix increases the wetting property and act as
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an excellent barrier for solder bump [5]. With these profound technological applications the electroless Ni-Cu-P has drawn much interest among the researchers.

Furthermore, composite coatings can be generated for the betterment of deposit properties and they can offer desirable service parameters. Metal carbides, oxides, nitrides, silicides, nonmetals and organic polymers like PTFE powders and fibers are most commonly incorporated particles into Ni-P matrix. The superior mechanical and electrochemical properties of Ni-Cu-P coatings and their composites with PTFE, CNTs advocate the importance of codeposited copper and incorporated nanomaterial [15-17]. Zirconium has been found to be very efficient additive in its oxide form, to electroless Ni-P binary coatings and ternary alloys too. ZrO₂ is a refractory material and it offers chemical and corrosion inertness to temperatures even above the melting point of alumina. Low thermal conductivity, high strength, high fracture toughness, excellent wear resistance, high hardness, good chemical inertness and large oxygen ion conductance are some of important properties exhibited by the ZrO₂. It has been found application in oxygen sensor cells and as the susceptor in high temperature induction furnaces. Its incorporation into metal/alloy matrices showed a great impact on electrochemical properties of the coatings and tribological properties [18-20].

The present work throws light on the fabrication, features and properties of the electroless Ni-P, Ni-P-ZrO₂ the composite with ZrO₂ nanoparticles and its ternary composite with copper as alloying metal. Firstly plain binary Ni-P and Ni-P-ZrO₂ composite coatings were fabricated. Ternary alloy composites Ni-Cu-P-ZrO₂ with various copper amounts were prepared. The alloy composite with suitable concentration of copper which performs better electrochemically was chosen and
nanoparticle amount was varied further. Each coating was analysed using X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) with Electron Dispersive X-ray analysis (EDAX). Electrochemical characterization was studied through measurement of Open circuit potentials, anodic polarization, Tafel plots and Electrochemical Impedance Spectroscopic (EIS) studies and effect of copper and ZrO₂ nanoparticles was evaluated. Microhardness was also measured for the coatings. As previous reports claims the effect and importance of alloying of Ni-P with copper metal and betterment of the properties, our work clearly evidenced role of copper in improving the characters of deposits and as no data is available on electroless Ni-Cu-P-ZrO₂ composite coatings in the literature it makes possible to evaluate the influence of ZrO₂ nanoparticles and copper metal on surface morphology, structure microhardness and electrochemical behavior on electroless Ni-P matrix.

4.3.2. Experimental

Sample preparation

The composition of the plating bath used for the preparation of Ni-P binary deposit, Ni-P-ZrO₂ composite and Ni-Cu-P-ZrO₂ ternary alloy composite is given in table 4.1.1. All the chemicals were used as obtained from HiMedia Laboratories Pvt. Ltd., Mumbai, India, and ZrO₂ nanoparticles from MEL chemicals, UK. Sodium hypophosphite was used as the reducing agent to reduce the nickel and copper metal ions and trisodiumcitrate as complexing agent. ZrO₂ nanoparticles were used for the preparation of composite films. The agglomeration of 30-35nm sized ZrO₂ was minimized by subjecting the electrolyte to magnetic stirring for a period of 12hours prior to plating experiments. Bath solutions were prepared using Millipore water and the pH was 7. Electroless plating experiments were performed under constant stirring of 500 rpm for 1 hr at temperature of 80±5°C. The electroless Ni-P and Ni-P-ZrO₂
were obtained from the bath I and II of table 4.3.1. The ternary alloy composites with various concentrations of CuSO$_4$·5H$_2$O and ZrO$_2$ particles were obtained from bath solutions III to VII.

**Table 4.3.1** Bath compositions used to generate the coatings $C_1 - C_{VI}$. 

<table>
<thead>
<tr>
<th>Bath</th>
<th>CuSO$_4$·5H$_2$O (g/L)</th>
<th>ZrO$_2$ (g/L)</th>
<th>Deposit</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>BB</td>
<td>-</td>
<td>$C_1$</td>
</tr>
<tr>
<td>II</td>
<td>BB</td>
<td>1</td>
<td>$C_{II}$</td>
</tr>
<tr>
<td>III</td>
<td>BB</td>
<td>0.5</td>
<td>$C_{III}$</td>
</tr>
<tr>
<td>IV</td>
<td>BB</td>
<td>1</td>
<td>$C_{IV}$</td>
</tr>
<tr>
<td>V</td>
<td>BB</td>
<td>1.5</td>
<td>$C_V$</td>
</tr>
<tr>
<td>VI</td>
<td>BB</td>
<td>0.5</td>
<td>$C_{VI}$</td>
</tr>
<tr>
<td>VII</td>
<td>BB</td>
<td>2.5</td>
<td>$C_{VII}$</td>
</tr>
</tbody>
</table>

**Basic Bath solution for Ni-P coating (BB):** NiSO$_4$·6H$_2$O- 50g/L, NaH$_2$PO$_2$·H$_2$O- 25g/L, C$_6$H$_5$Na$_3$O$_7$·2H$_2$O- 60g/L, CH$_3$COONH$_4$- 40g/L

### 4.3.3. Results and Discussion

#### 4.3.3.1. Characterization of ZrO$_2$ particles

Fig. 4.3.1 shows the X-ray diffraction patterns, SEM image and size distribution of nanosized ZrO$_2$ particles. The X-ray diffraction pattern of ZrO$_2$ powder confirms the monoclinic crystalline phase with space group $P2_1/c(14)$ and cell parameters $a=5.144$, $b=5.210$ and $c=5.311$ with JCPDS card no.$\#86-1451$ and from the Scherrer equation [22] the mean crystal size calculated was 30–35 nm. The nanosized particles were found to be agglomerated when analyzed by scanning electron microscopy.
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studies. This is due to high surface energy of the particles. Fig. 1c shows the size distribution statistics for the ZrO₂ particles in plating bath composition (Civ) diluted to hundred times and stirred magnetically 12h before use. Here particle produces a polydispersed colloidal system with polydispersity factor 0.34. The diameter of the particle varies from 150 – 300 nm.

Fig.4.3.1. (a) SEM image and (b) XRD pattern of ZrO₂ Particles, (c) Particle size distribution (in the plating bath IV)

4.3.3.2 Surface morphology

Chemical resistance of electroless nickel coatings is strongly dependent on the P content of Ni-P deposits and its inclusion is influenced by the constituents especially the metal salts as well as nanosized inert metal oxides in the bath. The Ni-P (C₁), Ni-P-ZrO₂(C₁I), Ni-P-Cu-ZrO₂(C₁II-C₁VII) coatings were generated and effect
of copper metal and ZrO$_2$ codeposition with Ni-P matrix on the morphology of ternary alloys can be visualized from the SEM pictures depicted in Fig. 4.3.2.

The surface morphologies of Ni-P-ZrO$_2$ and Ni-Cu-P-ZrO$_2$ alloy deposit were investigated by SEM with reference to Ni-P deposit. The results of EDX spectra in Fig. 4.3.3, reveals that the deposit C$_1$ (plain Ni-P) is highly amorphous with high P content 9.12 wt. % and exhibits coarse nodular structure. The SEM image (b) represents the surface nature of C$_{II}$ which contains 5.9 wt. % of ZrO$_2$ in Ni-P. Microstructure of Ni-P-ZrO$_2$ is comparable with C$_1$ even though it possesses smooth

Fig. 4.3.2. SEM images of the deposits C$_1$ – C$_{VII}$. 

The surface morphologies of Ni-P-ZrO$_2$ and Ni-Cu-P-ZrO$_2$ alloy deposit were investigated by SEM with reference to Ni-P deposit. The results of EDX spectra in Fig. 4.3.3, reveals that the deposit C$_1$ (plain Ni-P) is highly amorphous with high P content 9.12 wt. % and exhibits coarse nodular structure. The SEM image (b) represents the surface nature of C$_{II}$ which contains 5.9 wt. % of ZrO$_2$ in Ni-P. Microstructure of Ni-P-ZrO$_2$ is comparable with C$_1$ even though it possesses smooth
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surface nature because of the inclusion of ZrO₂ nano particles. Images of deposits C_{III} – C_{V} which were derived from different amounts of copper metal within Ni-P-ZrO₂, can be characterized by uniform morphology with refined nodules. Also these alloys possess smooth, uniform crystallinity with smaller grain boundary. This refinement is brought about by the introduction of copper into Ni-P-ZrO₂ matrix. Further the coatings C_{VI} and C_{VII} with varied amounts of ZrO₂ could not lead to significant change in the morphologies but their incorporation in the matrix generates small (dot) white patches as can be seen in SEM image figure 2f and 2g. As the concentration of Cu and ZrO₂ increases in the bath solution their amount of codeposition also increased in the Ni-P matrix.

These SEM images depict the microstructure of nodularity and smoothness. The formation of nodular structure depends on nucleation rate and growth of the deposit. Zhong et al., [23] explained in their patent that, controlled introduction of copper activates natural nucleation sites and produce more nuclei and affects the nucleation rate. Also the deposition of copper to the Ni-P-ZrO₂ matrix suppresses the growth of nodules and inhibits the growth of nuclei. Thus copper plays a major role in reducing or inhibiting the activation of additional nodule sites resulting in the attainment of smooth, uniform and bright Ni-Cu-P-ZrO₂ deposit.

4.3.3.3. Effect of Cu on deposit composition

The EDX spectra revealed that, as the concentration of CuSO₄ increased from 0-1.5 g/L in the plating bath, there is simultaneous decrease in the amount of Ni and P in the deposit i.e., Ni decreases form 90 to 81 wt.% whereas P is from 9 to 1.4 wt.%.

This is because of displacement of the deposited Ni by Cu²⁺ ions through the
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following electrochemical redox reactions since Cu possess higher reduction potential than Ni and P.

\[
\begin{align*}
\text{Cu}^{2+} + \text{Ni} & \rightarrow \text{Cu} + \text{Ni}^{2+} \quad [E^\circ = 0.597 \text{ V}] \\
\text{Ni}^{2+} + 2e & \rightarrow \text{Ni} \quad [E^\circ (\text{NHE}) = -0.25 \text{V}] \\
\text{Cu}^{2+} + 2e & \rightarrow \text{Cu} \quad [E^\circ (\text{NHE}) = 0.34 \text{V}] \\
\text{H}_2\text{PO}_4^- + e & \rightarrow \text{P} + 2\text{OH}^- \quad [E^\circ (\text{NHE}) = -1.82 \text{V}]
\end{align*}
\]

Consequently, the deposited nickel gets dissolved into the plating bath, with simultaneous deposition of copper resulting in the increasing its content in the deposit. The Cu is preferentially deposited because of its higher reduction nature than that of Ni and P.

![Graph showing percentage composition of Ni, Cu, P, and ZrO₂ in deposits CI - CVII.]

**Fig.4.3.3.** Percentage composition of Ni, Cu, P and ZrO₂ in the deposits CI - CVII.

The data from EDX analysis represented in Fig. 4.3.3 clearly displays the variation composition of coatings by the influence of its components. As concentration of CuSO₄ increased in the plating bath, incorporation of ZrO₂ nanoparticles also found to be enhanced in the composites Cᵢᵢᵢ, Cᵣᵣ and Cᵥ. Also it
can be easily noted that the increased addition of ZrO₂ content led to lower amount of copper in CᵥⅠ and CᵥⅦ composites. Thus the variation in the amount of CuSO₄ and ZrO₂ in the bath, affects the composition of corresponding deposit.

4.3.3.4. Crystal structure

Fig. 4.3.4. XRD patterns of the coatings C₁ - CᵥⅦ.

The diffraction patterns of electroless Ni-P and its composite alloy coatings with different Cu and ZrO₂ are shown in Fig. 4.3.4 and corresponding peak position and crystalline sizes are given in table 4.3.2. The XRD patterns obtained from the deposits show that their structure is amorphous. Diffraction patterns exhibit strong reflection corresponding to (111) plane of a face-centered cubic (fcc) phase of nickel at 2θ = 44. It is evident from Fig. 4.3.4 and table 4.3.2 that Ni-P coating had only a broad diffraction peak with the absence of copper in the deposits indicating amorphous structure of Ni-P coating. With increasing Cu content of deposits, the
broadening decreased with simultaneous sharpening of the peaks. As we can see, rise in P content and fall in Ni content with increase in the amount of Cu and this can possibly be the reason for increasing crystallinity in coatings. Previous studies report, electroless Ni-P coatings with P content greater than 7 wt. % will be amorphous and with the introduction of Cu into Ni-P deposits, there will be marginal change in peak broadness and grain size [24]. This can be explained by the formation of a fcc Ni–Cu solid solution. The incorporated copper showed increase in the crystallinity however nanoparticles did not show any marked changes in this regard. For all the as deposited coatings, grain sizes have been calculated by Scherrer formula and are given in table 4.3.2. From the table it is evident that crystalline size for plain Ni-P deposit is 1.44nm. The crystalline size of ternary deposits varies between 1.59 – 1.98nm. Increase in grain size is due to the low P content with increased incorporation of ternary metal copper.

4.3.3.5. Electrochemical Studies

To examine the effect of ZrO2 nanoparticles and Cu content on corrosion resistance, Ni-P coatings were fabricated by composing varying amount of nanoparticles and copper ions. Corrosion behavior of different coatings was studied by utilizing electrochemical parameters generated by anodic polarization, Tafel plots and electrochemical impedance spectroscopic studies.

When an electrode surface comes in contact with an electrolyte, an interface is formed between them. The potential of the interface between electrode and electrolyte which could be measured using a reference electrode, changes when the nature of interface changes to attain equilibrium or deviate from it due to some surface reactions occurring on the electrode surface or due to some changes in the electrolyte.
Table 4.3.2 Position of the main diffraction peak and grain size as derived from the Debye-Scherrer formula for different coatings.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak position (2θ)</th>
<th>Crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>44.81</td>
<td>1.44</td>
</tr>
<tr>
<td>C₁Ⅰ</td>
<td>42.53</td>
<td>1.58</td>
</tr>
<tr>
<td>C₁Ⅱ</td>
<td>42.77</td>
<td>1.59</td>
</tr>
<tr>
<td>C₁Ⅲ</td>
<td>42.78</td>
<td>1.60</td>
</tr>
<tr>
<td>C₁Ⅳ</td>
<td>43.12</td>
<td>1.98</td>
</tr>
<tr>
<td>C₁Ⅴ</td>
<td>44.74</td>
<td>1.79</td>
</tr>
</tbody>
</table>

Fig. 4.3.5. Open circuit potentials of different coatings for 12 hours in 3.5 wt.% NaCl solution.
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The equilibrium potential in the open circuit i.e., without any electrical disturbance or without application of any external load, is normally termed as open circuit potential (OCP) or steady state potential. Normally OCP is considered as a measure of nobleness of the electrode surface. In the present work, the OCPs of the specimens, immersed in 3.5 wt.% NaCl solution were measured and potentials are referred with respect to the saturated calomel electrode. The variation of potential with respect to the time is shown in the Fig. 4.3.5. After 45 mints, the corrosion potentials tend to reach the steady state and it continues to be constant over the 12h of immersion. At the initial stages up to around 1hr, the potential tends to shift towards more negative values. It is because of obvious reason that, the selective dissolution of nickel metal in the presence of P which promotes anodic and cathodic reactions. The OCP value of the Ni-P coating was found to be more positive by the incorporation of 1g/L of ZrO$_2$ nanoparticles. OCPs are measured for alloy composites (C$_{III}$ - C$_V$) fabricated by different concentrations of copper. Among these, Ni-Cu-P-ZrO$_2$ deposit obtained from the bath solution containing 1g/L of copper salt attained more positive OCP. Further deposits C$_{VI}$ and C$_{VII}$ were made to attain their OCPs but the coating C$_V$ generated from 1g/L of ZrO$_2$ display most positive steady state value. So it can be noted that, both copper and ZrO$_2$ nanoparticles make the coating noble at some optimized concentrations.

Fig. 4.3.6 shows the anodic polarization behavior of the coatings. The polarization curves obtained for different coatings provide information about the dissolution potential, extent of passivation and thus resistance towards the corrosion process in 3.5% NaCl solution. As the anodic potential increases towards positive direction corrosion current started to increase slowly. The current plateau is clearly
associated with the metallic oxidation. The deposit $C_{II}$ with the incorporation of $ZrO_2$ to Ni-P coating, showed a shift in its potential to slightly positive values compared to the deposit $C_I$ which is plain Ni-P deposit. The Ni-P-ZrO$_2$ deposits with introduction of copper to obtain the Ni-Cu-P-ZrO$_2$ ($C_{III}$–$C_{VII}$) alloy coatings were subjected to the evaluation. From the Fig.6 it can be noticed that the coating $C_{IV}$ obtained from 1g/L of CuSO$_4$ in the bath, possess higher corrosion resistance. The potential of this coating was more positive in the entire current region covering broader passivation plateau. This coating was found to have high corrosion resistance than those coatings $C_{III}$ and $C_{V}$ obtained from the bath solutions of 0.5g/L and 1.5g/L of CuSO$_4$ respectively. Further to investigate the effect of ZrO$_2$ concentration, the coatings $C_{VI}$ and $C_{VII}$ obtained from bath with varying concentrations (0.5 and 2.5g/L) of ZrO$_2$ having 1g/L of CuSO$_4$ in common are examined and compared for their chemical stability with the deposit $C_{IV}$ which was fabricated from the bath solution containing 1g/L ZrO$_2$. The deposit $C_{IV}$ found to have more positive dissolution potential and possess highest corrosion resistance. The ZrO$_2$ nanoparticles involve in the betterment of corrosion resistance and play a major role. In the electroless coating process, ZrO$_2$ nanoparticles may turn out to be nucleation sites thereby decreasing the nodule dimension by blocking nodule boundaries which are main corrosion paths and decrease the corrosion rate [25-27].

Fig. 4.3.7 shows the Tafel polts registered for the coatings in 3.5% NaCl solution. Corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$), Polarization resistance ($R_p$) and the Tafel lines’ inclinations ($b_c$ and $b_a$) are shown in table 4.3.3. The Tafel plot Ni-P-ZrO$_2$ composite coating show positive shift of the potential with respect to Ni-P coating.
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Fig. 4.3.6. Potentiodynamic anodic polarization curves for different coatings in 3.5% NaCl solution.

This can be attributed to inclusion of ZrO₂ nanoparticles in metal matrix. The Ni-Cu-P-ZrO₂ coatings showed positive shift in their corrosion potential value and show lower corrosion rates than Ni-P-ZrO₂ coating. Among Ni-Cu-P-ZrO₂ coatings C₃III, C₄IV & C₅V produced from the bath solutions with CuSO₄ content 0.5, 1 and 1.5g/L, the deposit C₄IV with 1g/L of CuSO₄ possess highest corrosion resistance of corrosion potential value -0.3935, highest linear polarization resistance value of 31448Ω with lowest corrosion rate.

Fig. 4.3.7. Tafel plots for different coatings in 3.5% NaCl solution.
## Table 4.3.3 Electrochemical parameters for the coatings C\textsubscript{1} – C\textsubscript{VII} derived from Tafel plots in 3.5% NaCl solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>b\textsubscript{c} (V/dec)</th>
<th>b\textsubscript{a} (V/dec)</th>
<th>LP (Ω)</th>
<th>i\textsubscript{corr} (A/cm\textsuperscript{2})</th>
<th>Rate (g/hr)</th>
<th>E\textsubscript{corr} (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{1}</td>
<td>0.0237</td>
<td>0.0142</td>
<td>4516</td>
<td>8.543 × 10\textsuperscript{-5}</td>
<td>9.354 × 10\textsuperscript{-6}</td>
<td>-0.507</td>
</tr>
<tr>
<td>C\textsubscript{II}</td>
<td>0.0176</td>
<td>0.0128</td>
<td>10732</td>
<td>3.003 × 10\textsuperscript{-6}</td>
<td>3.288 × 10\textsuperscript{-6}</td>
<td>-0.491</td>
</tr>
<tr>
<td>C\textsubscript{III}</td>
<td>0.0153</td>
<td>0.0155</td>
<td>27086</td>
<td>1.158 × 10\textsuperscript{-6}</td>
<td>1.268 × 10\textsuperscript{-6}</td>
<td>-0.4095</td>
</tr>
<tr>
<td>C\textsubscript{IV}</td>
<td>0.0149</td>
<td>0.0136</td>
<td>31448</td>
<td>1.045 × 10\textsuperscript{-6}</td>
<td>1.145 × 10\textsuperscript{-6}</td>
<td>-0.3935</td>
</tr>
<tr>
<td>C\textsubscript{V}</td>
<td>0.0131</td>
<td>0.0156</td>
<td>7659</td>
<td>4.053 × 10\textsuperscript{-6}</td>
<td>4.437 × 10\textsuperscript{-6}</td>
<td>-0.4504</td>
</tr>
<tr>
<td>C\textsubscript{VI}</td>
<td>0.0213</td>
<td>0.0132</td>
<td>2714</td>
<td>1.306 × 10\textsuperscript{-6}</td>
<td>1.430 × 10\textsuperscript{-6}</td>
<td>-0.5633</td>
</tr>
<tr>
<td>C\textsubscript{VII}</td>
<td>0.0170</td>
<td>0.0154</td>
<td>5582</td>
<td>6.295 × 10\textsuperscript{-5}</td>
<td>6.892 × 10\textsuperscript{-5}</td>
<td>-0.5137</td>
</tr>
</tbody>
</table>

To verify the effect of ZrO\textsubscript{2}, the tafel plots are registered for Ni-Cu-P-ZrO\textsubscript{2} coatings C\textsubscript{VI} & C\textsubscript{VII} produced from the bath solutions with 0.5 and 2.5g/L of particles where in CuSO\textsubscript{4} concentration was kept same i.e., 1g/L. When compared with the coating C\textsubscript{IV} with 1g/L of ZrO\textsubscript{2} the increasing concentration of particles from 0.5g/L to 1g/L, nobleness of the deposit enhanced by shifting the potentials to positive with corresponding increase in the polarization resistance value. But the deposit with 2.5g/L of particles shifted corrosion potential in negative direction and turned the coating to less corrosion resistant. It has been evidenced from electrochemical experimental techniques that Ni-Cu-P-ZrO\textsubscript{2} specimen was the most noble among all and majorly to Ni-P with a decreased corrosion rate by 7 folds and correspondingly twice the Ni-P-ZrO\textsubscript{2} in 3.5 wt.% NaCl solution.

Fig. 4.3.8 show typical Nyquist impedance plots for the Ni-P alloy coatings of different composition, in 3.5 wt.% NaCl solution. The equivalent circuit shown in Fig. 4.3.9 was used to simulate and describe the EIS data. For quantitative analysis,
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the spectra are usually fitted to an "equivalent circuit", which corresponds to a physically plausible model of the system [28]. The equivalent circuit so chosen represents the main electrical characteristics of the model and yield a high quality of fit. In the present case, equivalent circuit is composed of two sets of resistance and CPEs with a solution resistance however the CPEs instead of capacitors indicate the non-ideality of the capacitors. One set of resistance and CPE which describe the double layer behavior at the metal/electrolyte interface. Another set describes the coating resistance and coating capacitance.

Fig. 4.3.8. Nyquist plots for the deposits in 3.5% NaCl solution.

Fig. 4.3.9. Equivalent circuit model for the coatings.
The presence of CPE element is believed to be because of existence of microscopic roughness on solid electrodes, causing an inhomogeneous distribution of solution resistance as well as the double layer capacitance [29].

The Nyquist plot shows the two semi circles each one at high and low frequencies which corresponds to the two time constants or the relaxation processes in the entire range of frequency applied. For each deposit, Ni-P and Ni-P-ZrO2 and Ni-Cu-P-ZrO2 with different Cu and ZrO2 content correspondingly, the impedance data were recorded. The Nyquist diagrams show two semi-elliptical arcs in the investigated frequency range and in addition, increased axial radius of this semi-elliptical arc is indicative of the better anticorrosive property of the deposit. The Ni-P-ZrO2 coating exhibits a loop which covers larger area compared to plain Ni-P coating. With the introduction of copper to the coating, the coatings deliver the arcs with increased area and thus behave superior in 3.5wt.% NaCl. Among different Ni-Cu-P-ZrO2 alloy composite coatings deposited from varying amounts of CuSO4, the deposit with 1g/L of CuSO4 was very noble with highest polarization resistance (Rp) value.

The coatings deposited with different ZrO2 content also generated the two semicircles indicates the similar mechanism involved in corrosion phenomenon. The deposit with 1g/L of particles performed well against the corrosion than those coatings obtained from 0.5and 2.5g/L. Corrosion trend of the coatings was in good agreement with the results obtained from those of anodic polarization and Tafel experiments and it is well pronounced in electrochemical impedance studies.

In order to explain the observed results, one has to consider that there will be two different ionic-conducting paths available. These paths may not be physical
pores filled up with the electrolyte. It can be assumed that an area of the coating is
behaving differently and the electrolyte solution can be different at these paths/places
compared with the bulk solutions outside the coating. The interface between this
pocket of solution and the substrate metal is modeled as a double layer capacitor in
parallel with a kinetically controlled charge transfer resistor \( R_{ct} \). The resistance and
capacitance values of this low frequency time constant varied as a function of
working electrode material and time of exposure which describe the surface specific
behavior and protective quality of the metallic passivation. So, higher the value of
\( R_{ct} \) more protective will be the coating.

To assume the second ion-conducting path, the pores in the film or coating can
be considered, that might have access into any delaminated areas and they can be
represented as solution/electrolyte filled cylinders. The time constant which describes
the above phenomenon lies at the high frequency end. The order of resistance and
capacitance associated with this time constant is generally independent of electrode
material and the behavior is only influenced to any significant extent by the
composition/conductivity of the electrolyte. The values of coating resistances \( R_{coat} \) is
almost in the same range as the electrolyte composition is constant throughout the
experiment. However, this high frequency time constant is considered to contain a
contribution towards the total resistance provided by the electrolyte i.e., this time
constant is partial component of \( R_s \). The resistance of the electrolyte was never
measured solely as a simple \( R_s \) value associated with a non-capacitive contribution at
the highest contribution at the highest applied frequency.

From table 4.3.4 it can be noticed that, the value of \( n \) is almost 1 in the case of
coating capacitance. But there is deviation in its value with respect to the double
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layer capacitor which indicates the non-uniform distribution of current as a result of roughness and surface defect. Also from the results it can be noted that, relatively significant change in \( R_{ct} \) compared to \( R_{cor} \) indicating charge transfer reactions at the electrical double layer were affected more with all the modifications to the coating. Corrosion morphologies of the Ni-P, Ni-P-ZrO₂ and Ni-Cu-P-ZrO₂ deposited with optimum concentration of Cu²⁺ ions (i.e., 1g/L, deposit C₁₁) were observed using SEM images (Fig. 4.3.11) of the deposits which were immersed in 3.5wt.% NaCl solution for 100 hrs. We can easily make out that, Ni-P deposit has been deteriorated greatly compared to Ni-P-ZrO₂ composite and Ni-Cu-P-ZrO₂ ternary alloy composite. Also, we can observe the accumulation of corrosion products. The corrosion products are mainly concentrated on the nodule boundaries, revealing corrosion initiating from the boundaries. The nodule boundaries in Ni-P deposit are discernable from those of Ni-P-ZrO₂ and Ni-Cu-P-ZrO₂. With the incorporation of ZrO₂ nanoparticles, grain boundaries which are active corrosion paths were blocked. In the closer view to the role of ZrO₂ nanoparticles, they serve as nucleation centers and get deposited with nickel phosphorous forming new nodules. Some nanoparticles exposed on the deposit surface which were uncovered by Ni-P coating. These composite surfaces when come into contact with NaCl solution, aggressive chloride ions were prone to adsorb preferentially at the interface of nanoparticles and nickel phosphorous alloy and corrosion will be initiated from there. When more nickel dissolved, some particles may fall off the coating leading to the formation of the corrosion pits [25-27]. Further, in the case of ternary alloy Ni-Cu-P-ZrO₂ composite, copper fine grains the nickel matrix and there were limited preferential corrosion paths. Simultaneously the
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presence of ZrO₂ further enhanced the protection ability to the Ni-Cu-P-ZrO₂ coating and stands superior over Ni-P and Ni-P-ZrO₂ deposits in anticorrosion behavior.

Table 4.3.4 Electrochemical impedance data for the coatings C₁ – CᵥⅡ derived from EIS in 3.5% NaCl solution.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rs (Ω)</th>
<th>CPE 1 (F)</th>
<th>CPE 2 (F)</th>
<th>R_{coat}(Ω)</th>
<th>R_{ct} (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₁</td>
<td>0.13</td>
<td>8.18×10⁻⁷</td>
<td>1</td>
<td>8.92×10⁻⁵</td>
<td>29.06</td>
</tr>
<tr>
<td>CᵥⅡ</td>
<td>0.15</td>
<td>7.42×10⁻⁷</td>
<td>1</td>
<td>4.27×10⁻⁵</td>
<td>32.44</td>
</tr>
<tr>
<td>CᵥⅢ</td>
<td>0.079</td>
<td>9.69×10⁻⁷</td>
<td>1</td>
<td>2.31×10⁻⁵</td>
<td>36.35</td>
</tr>
<tr>
<td>CᵥⅣ</td>
<td>0.08</td>
<td>9.44×10⁻⁷</td>
<td>1</td>
<td>2.26×10⁻⁵</td>
<td>36.65</td>
</tr>
<tr>
<td>CᵥⅤ</td>
<td>0.09</td>
<td>8.39×10⁻⁵</td>
<td>0.918</td>
<td>4.93×10⁻⁵</td>
<td>35.68</td>
</tr>
<tr>
<td>CᵥⅥ</td>
<td>0.095</td>
<td>1.16×10⁻⁶</td>
<td>1</td>
<td>3.864×10⁻⁵</td>
<td>20.85</td>
</tr>
<tr>
<td>CᵥⅦ</td>
<td>0.084</td>
<td>9.844×10⁻⁷</td>
<td>1</td>
<td>5.33×10⁻⁵</td>
<td>32.86</td>
</tr>
</tbody>
</table>

4.3.3.6. Microhardness

Fig. 4.3.12 displays the variation in the microhardness of Ni-P deposits of 14 μm with different concentration of copper and ZrO₂ nanoparticles. Plain Ni-P coating with some lower hardness value gets enhanced by the addition of zirconium oxide nanoparticles. The increased microhardness of Ni-P-ZrO₂ composite coating compared with Ni-P coating might be due to strengthening effect with the incorporation of inert particles and hard nature of ZrO₂. In fact, the hardness of composite coatings is influenced by two aspects: one is the amount of incorporated hard particles, which increase the hardness of composite coatings; other one is the hardening of metal matrix.
Fig. 4.3.10. SEM images showing corrosion morphologies for the coatings (a) Ni-P (C\textsubscript{i}), (b) Ni-P-ZrO\textsubscript{2} (C\textsubscript{ii}) and (c) Ni-Cu-P-ZrO\textsubscript{2} (C\textsubscript{iv}) for 100 h immersion in 3.5% NaCl solution.

Fig. 4.3.11. Bar diagram showing the Vickers microhardness values of the coatings.
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It is observed that, as concentration of ternary metal copper increases, the hardness of the deposit increases. This can be accounted for hardening of metal matrix by the addition of copper into Ni-P-ZrO\textsubscript{2} forming Ni-Cu-P-ZrO\textsubscript{2} alloy deposit. Further, the variation of ZrO\textsubscript{2} nanoparticles did not show any significant enhancement in the hardness of the composite coatings. The effect of copper metal in increasing the microhardness of the coatings is found to be in good agreement with the previous studies [30].

4.3.4. Conclusions

The structural characteristics, composition and corrosion behavior of Ni-P, Ni-P-ZrO\textsubscript{2} and Ni-Cu-P-ZrO\textsubscript{2} ternary alloy with varying amounts of copper and zirconia were studied. With the introduction of copper metal into Ni-P-ZrO\textsubscript{2} matrix the Ni and P content decrease and it has been found that Cu diminishes amorphous nature of the Ni-P matrix. Apart from crystal structure, copper changes the surface morphology of the deposits significantly. From the experimental results for electroless coatings, the Ni-Cu-P-ZrO\textsubscript{2} and Ni-P-ZrO\textsubscript{2} coatings stand more resistant towards corrosion than plain Ni-P deposit. It has been evidenced from electrochemical experimental techniques that Ni-Cu-P-ZrO\textsubscript{2} specimen was the most noble among all and majorly to Ni-P with a decreased corrosion rate by 7 times and twice the Ni-P-ZrO\textsubscript{2} in 3.5 wt.% NaCl solution. Deposits with the introduction of copper aids to the enhancement of microhardness by forming Ni-Cu solid solution and ZrO\textsubscript{2} inclusion contribute to some extent as it is hard ceramic.

References

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[23] LL.Zhong, CC Liu, Electroless Nickel-Phosphorous coatings with high thermal stability, U.S.Pat. 6,410,104.


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