Chapter-4.2

Ni-Zn-P/nano TiO₂ composite coatings

Maximizing Hiding Power
Enhancing Dispersion Performance
Assuring Batch to Batch Uniformity
Increased Durability
Improving Tint Strength
Achieving White Bright Color
Development of electroless Ni-Zn-P/nano TiO$_2$ composite coatings

4.2.1. Introduction

The electroless Ni poly alloy deposition is considered as the most successful method to alter the physical and chemical properties of binary Ni-P alloy deposits [1-4]. The incorporation of Zn into Ni-P matrix has great impact on its microstructure, mechanical and electrochemical properties [5]. The electrochemical properties of Ni-Zn-P alloy have revealed that these coatings possess more noble character compared to other ternary alloys [6]. Also Ni-Zn-P coatings have been found applications in electrocatalysis and under-bump metallization of solder joints [7, 8] and turned out to be of great importance. Previous efforts in literature have shown that Ni-Zn-P plating follows normal deposition with high Ni content of about 80-90%. However, in these cases, the amount of Zn remains low at around 10 wt% and hence the potential will be more positive to steel [9]. Thus these deposits, although offering excellent corrosion resistance, could not be used as a sacrificial coating to steel. Basker Veeraraghavan et. al. increased the Zn content in the coating from 10.8 to 17.9 wt% and resulted coatings performed the sacrificial behavior [10]. Incorporation of Zn causes transformation of the amorphous structure of Ni-P into a crystalline, which is due to reduced P content [11, 12]. It was also mentioned that, addition of Zn into electroless Ni-P matrix improves the corrosion resistance of the coating [13].

Also the incorporation of nanosized particles with in Ni-P autocatalytic coatings greatly improved their properties and imparts new functional features to the coating performance, which finally enhanced their application in different fields [14].
Chapter 4.2  

Electroless Ni-Zn-P/nano TiO$_2$ composite coating

The productions of particle reinforced composite films can be achieved by deposition of the matrix material from a plating solution containing particles such as TiO$_2$, SiC, Al$_2$O$_3$, ZrO$_2$, WC, MoS$_2$, SiO$_2$, PTFE, and PE. Of these particles, TiO$_2$ has attracted much interest in research community due to its wide applications in engineering materials. It improves wear resistance, hardness and corrosion resistance and other properties such as electrocatalysis and photocatalysis [1, 15-23].

The present work aims to prepare Ni-Zn-P and Ni-Zn-P-TiO$_2$ electroless coatings on mild steel and to evaluate its microstructure, hardness and corrosion resistance.

4.2.2. Experimental

Nanosized TiO$_2$ was synthesized by a sol-gel method according to a procedure reported elsewhere [25]. Titanium isopropoxide Ti(OiPr)$_4$ (8mL 27mmol) dissolved in absolute ethanol (82mL) under nitrogen blanket was added drop wise to 250mL of a solution of ethanol/water 1:1 under rapid stirring for 10 min, then filtered to obtain a white precipitate, which was dried at 100 °C for 15 h. The prepared TiO$_2$ are 100-200 nm and it was confirmed by SEM and XRD studies (Fig. 4.2.1).

![SEM and XRD results of prepared TiO$_2$ particles.](image)

Fig. 4.2.1. SEM and XRD results of prepared TiO$_2$ particles.
Chapter 4.2  Electroless Ni-Zn-P/nano TiO₂ composite coating

The Ni-Zn-P ternary alloy deposits are derived from the following bath: NiSO₄·6H₂O 27g/L, ZnSO₄·7H₂O 4g/L, NaH₂PO₂·H₂O 32g/L, C₆H₅Na₃O₇·2H₂O 59g/L, (NH₄)₂SO₄ 27g/L and lactic acid 10g/L. The pH of the bath was 9 and it was adjusted by sodium hydroxide. TiO₂ nanoparticles of 1.5g/L were added to the bath to deposit the composite coating. The agglomeration of TiO₂ was minimized by subjecting the electrolyte to magnetic stirring for a period of 12h prior to plating experiments. Electroless plating experiments were performed under constant stirring of 500 rpm for 3.5 hrs at the temperature of 80 ± 5°C. These Ni–Zn–P and composite deposits were annealed in air for 1 h at 400°C, followed by air cooling to room temperature.

4.2.3. Results and discussion

4.2.3.1. SEM and EDX analysis

The surface morphology of Ni-Zn-P and Ni-Zn-P-TiO₂ coatings was studied using SEM and is given in Fig. 4.2.2. The surface morphology of Ni-Zn-P coating shows the spherical nodular structure (Fig. 4.2.2a) where as composite exhibits coarse nodular compact structure (Fig. 4.2.2b). Also the images show that the coatings are uniform and non porous in appearance. After heat treatment to 400°C for 1h, the surface morphology of the coatings were visualized and shown in Fig. 4.2.3. The higher and lower magnified images of the heat treated coatings show the different morphology compared to the as-plated coatings. After heating the coating became more uniform and crystalline and they possess a needle shaped structure (Fig. 4.2.3). In heat treated composite coatings we can observe finer grained needle like structure with uniformly dispersed TiO₂ nanoparticles in the Ni-Zn-P matrix (Fig. 4.2.3 (c) and (d)).
Fig. 4.2.2. Surface morphology of electroless a) Ni-Zn-P and b) Ni-Zn-P-TiO$_2$ composite coatings.

Fig. 4.2.3. Surface morphologies of a) and b) Ni-Zn-P and c) and d) Ni-Zn-P-TiO$_2$ composite coatings after 1hr heat treatment at 400°C.

EDS technique was used to obtain the quantitative and qualitative analysis of the Ni-Zn-P-TiO$_2$ composite coating. The results confirm the presence of Ni, Zn, P and Ti elements in the coating. The results show that the major component in the coating is Ni, with 6.18 wt% Zn, 10.56 wt% P and 2.30 wt% TiO$_2$. 
4.2.3.2. XRD studies

X-ray diffraction patterns of Ni-Zn-P and Ni-Zn-P-TiO₂ coatings are compared in Fig. 4.2.4. A peak displayed at 2θ=45° in curve (a) and (b) represents the Ni (111) phase of the polycrystalline Ni-Zn-P. The presence of Zn into Ni-P matrix resulted in transformation of the amorphous structure of Ni-P into crystalline and this is in accordance with the earlier studies [11]. After heating at 400°C for one hour, the crystallinity of the coatings increase as evidenced by the higher intensity and smaller width of peaks. After heat treatment peaks corresponding to metastable Ni₁₂P₅ and stable Ni₃P phases appear in the diffraction patterns for both Ni-Zn-P and Ni-Zn-P-TiO₂ coatings (Fig. 4.2.5a & 4.2.5b). The Ni-Zn-P and Ni-Zn-P-TiO₂ coatings become crystalline with formation of f.c.c Ni and b.c.t Ni₃P phases. The extent of Ni₃P phase formation is higher for both the Ni-Zn-P and Ni-Zn-P-TiO₂ coatings.

![XRD patterns of as plated electroless Ni-Zn-P and Ni-Zn-P-TiO₂ coatings.](image)

**Fig. 4.2.4.** XRD patterns of as plated electroless Ni-Zn-P and Ni-Zn-P-TiO₂ coatings.

4.2.3.3. Microhardness studies

The microhardness evaluated for Ni-Zn-P and Ni-Zn-P-TiO₂ coating samples of thickness around 16μm were compared with those of heat treated samples and are charted in Fig. 4.2.6. The hardness values of the coatings were in the order Ni-Zn-P (as plated) < Ni-Zn-P-TiO₂ (as plated) < Ni-Zn-P (heat treated) < Ni-Zn-P-TiO₂ (heat
Chapter 4.2 Electroless Ni-Zn-P/nano TiO₂ composite coating

treated). The incorporation of the TiO₂ particles into the metal matrix increased the hardness of the coating.

Fig. 4.2.5. XRD patterns of electroless (a) Ni-Zn-P and (b) Ni-Zn-P-TiO₂ coatings after heat treatment at 400°C for 1h.

This may be due to the grain filling and dispersive strengthening effects offered by the hard ceramic TiO₂ particles which form barrier to plastic deformation of metal matrix under the load and obstruct dislocation of alloy matrix. Higher hardness values were observed for heat treated samples of both pure alloy and composite alloy coatings compared to their respective as plated deposits. This increased hardness of the coatings after heat treatment can be related to the precipitated metastable Ni₁₂P₅ and stable Ni₃P phases. The heat treated composite coating shows a highest value among all the deposits. This can be attributed to both effects of transformation of Ni-P to Ni₃P phase and incorporated TiO₂ particles in the matrix.
4.2.3.4. Anodic polarization

Fig. 4.2.7 shows anodic polarization curves recorded for as plated and heat treated Ni-Zn-P alloy and Ni-Zn-P-TiO$_2$ composite coatings in 3.5wt % NaCl solution. The experiments were initiated at -0.8V v/s SCE in a positive direction up to 0.2V v/s SCE. As the anodic potential increases towards positive direction, the corrosion current started to increase slowly. The current plateau is clearly associated with the metallic oxidation. The dissolution of metal matrix begins at -0.539V and -0.394V v/s SCE for as plated Ni-Zn-P and Ni-Zn-P-TiO$_2$ coating respectively. After this the anodic current increased significantly and also, the potentials of composite coated sample were more positive in the entire current region compared to pure alloy coating. This behavior indicated higher noble character of composite coating. It is evident from literature reports on Ni-P coatings that preferential dissolution of nickel occurs at open circuit potential, leading to the enrichment of phosphorus on the surface layer. The enriched phosphorus surface reacts with water to form a layer of adsorbed hypophosphite anions. This layer in turn will block the supply of water to
Chapter 4.2  Electroless Ni-Zn-P/nano TiO₂ composite coating

the electrode surface, thereby preventing the hydration of nickel, which is considered to be the first step to form either soluble Ni²⁺ species or a passive nickel film [22, 26]. In the case of Ni-Zn-P-TiO₂ composite coating, the TiO₂ particles form a barrier by filling up the very small pores present in the metal matrix which makes the film more compact and minimize the solution (corrosive media)-metal interaction, this may lead to remarkable improvement in the corrosion resistance of composite coating compared to pure alloy coating. The potentials of annealed samples were more positive in the entire current region compared to as plated coatings. From all the above results and discussion, the anticorrosion property of the deposits against the Cl⁻ attack promoted by the annealing treatment in air as well as by the increase in the phosphorous content within the deposits at its open circuit potentials.

![Fig. 4.2.7. Potentiodynamic anodic polarization curves for as plated and heat treated Ni-Zn-P and Ni-Zn-P-TiO₂ coatings in 3.5 wt % NaCl solution.](image)

4.2.3.5. Tafel studies

Fig. 4.2.8 shows Tafel curves recorded in 3.5wt % NaCl solution for Ni-Zn-P alloy and Ni-Zn-P-TiO₂ coatings before and after heat treatment. The corrosion
potential ($E_{corr}$), corrosion rates (CR) and anodic/cathodic tafel slopes ($\beta_a$ and $\beta_c$) were obtained from the Tafel plots and are listed in table 4.2.1.

The results indicate that Ni-Zn-P-TiO$_2$ composite coating shows a positive shift in the potential and decreased corrosion current. In other words, the composite coatings have lower chemical activity than pure alloy coating and hence possess better chemical stability in external environment also helps to prevent the corrosive pits from growing up and contributes to accelerate the passivation process of the metal matrix as well. In the presence of TiO$_2$ there will be formation of many micro cells in which TiO$_2$ acts as cathode and nickel as anode because of the standard potential of TiO$_2$ is more positive than nickel. Such corrosion micro cells facilitate anodic polarization and therefore localized corrosion is inhibited, and mainly homogeneous corrosion occurs [23].

Log (i)-E curves for the Ni-Zn-P and Ni-Zn-P-TiO$_2$ deposits with an annealing treatment in air at 400 °C for 1 h are shown in Fig. 8 as curves c and d respectively. The corrosion potential of the heat treated Ni-Zn-P and Ni-Zn-P-TiO$_2$ deposits is positively shifted in addition; $i_{corr}$ also decreased compared as plated deposits. The above results are attributable to the following reasons. First, the phase transformation of a Ni-P deposit from the amorphous solid solution to the crystalline structure occurs at 400°C since the crystallization of a Ni-P deposit with a supersaturated P content has been found to occur. Second, the corrosion potential of the annealed deposits positively moved due to the formation of Ni oxide on the surface of deposits since the surface P has been found to be replaced by oxygen species from the air after the annealing treatment. In fact, the main purpose of the annealing treatment in air is to form a uniform film consisting of Ni-P and NiO on the deposit surface, increasing the
Chapter 4.2  

Electroless Ni-Zn-P/nano TiO$_2$ composite coating

anticorrosive ability of Ni-P deposits. Third, the annealing treatment also favors the movement of surface Ni and/or P atoms, resulting in the formation of compact, smooth and homogenous deposits, which was found from the SEM observation [24].

![Fig. 4.2.8. Potentiodynamic polarization curves for as plated and heat treated Ni-Zn-P and Ni-Zn-P-TiO$_2$ coatings in 3.5% NaCl solution.](image)

Table 4.2.1  

Electrochemical parameters of the coatings derived from Tafel Plots.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ V</th>
<th>$I_{corr}$ A/cm$^2$</th>
<th>$\beta_c$ V$^{-1}$</th>
<th>$\beta_a$ V$^{-1}$</th>
<th>Linear Polarization</th>
<th>Corrosion rate in gm/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Zn-P</td>
<td>-0.495</td>
<td>6.324X10$^{-5}$</td>
<td>5.795</td>
<td>6.29</td>
<td>5686</td>
<td>6.925X10$^{-6}$</td>
</tr>
<tr>
<td>Ni-Zn-P-TiO$_2$</td>
<td>-0.449</td>
<td>2.224X10$^{-5}$</td>
<td>6.273</td>
<td>6.62</td>
<td>15152</td>
<td>2.435X10$^{-6}$</td>
</tr>
<tr>
<td>Ni-Zn-P heat treated</td>
<td>-0.448</td>
<td>1.161X10$^{-5}$</td>
<td>4.655</td>
<td>5.77</td>
<td>16364</td>
<td>5.650X10$^{-6}$</td>
</tr>
<tr>
<td>Ni-Zn-P-TiO$_2$ heat treated</td>
<td>-0.404</td>
<td>3.46 X 10$^{-7}$</td>
<td>5.984</td>
<td>4.63</td>
<td>18190</td>
<td>3.793 X10$^{-7}$</td>
</tr>
</tbody>
</table>

148
4.2.3.6. Electrochemical impedance spectroscopy studies.

The anticorrosive ability of Ni-Zn-P deposits can be investigated by the EIS. The Nyquist and Bode plots obtained for as plated and heat treated Ni-Zn-P and Ni-Zn-P-TiO$_2$ coatings in 3.5wt% NaCl solution at their respective OCPs are shown in Fig. 4.2.9 & 4.2.10. An equivalent circuit model given in Fig. 4.2.9 has been utilized to simulate the metal-solution interface and to analyze the acquired data. It consists of the double layer capacitance ($C_{dl}$) which is parallel to the charge transfer resistance ($R_{ct}$) both of which are in series with the solution resistance ($R_s$). This is the commonly proposed equivalent circuit model for the simple corrosion process. The values were derived by fitting the data using ZSimpWin 3.21 software and are compiled in table 4.2.2.

![Nyquist plots and equivalent circuit](image)

Fig. 4.2.9. Nyquist plots for as plated and heat treated Ni-Zn-P and Ni-Zn-P-TiO$_2$ coatings in 3.5 wt% NaCl solution and equivalent circuit of the coatings.

In general, these Nyquist diagrams show a semi-elliptic arc in the investigated frequency range and in addition, the increased axial radius of this semi-elliptic arc is indicative of the better anticorrosive property of the deposits. The Nyquist plots of both as plated and heat treated coatings exhibit distinct sized single semicircles. This
Chapter 4.2  Electroless Ni-Zn-P/nano TiO₂ composite coating

indicates that both the coatings follow the same electrochemical process which exhibit charge transfer behavior between deposit-solution (corrosive media, 3.5wt% NaCl) interfaces. This result is in accordance with the reports of the other authors [22, 26].

The results of the EIS studies also indicate a similar trend in the corrosion resistance that is observed by potentiodynamic polarization studies. The higher values of $R_\text{ct}$ obtained for the heat treated Ni-Zn-P-TiO₂ implied that composite coating has more protection ability against corrosion. The double-layer capacitance ($C_{dl}$) is small indicating the smooth nature of these deposits. These results reveal the fact that the annealing treatment further improves the anticorrosion ability of the Ni-Zn-P-TiO₂ deposit.

Table 4.2.2  Electrochemical impedance analysis data.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_s$ (Ω)</th>
<th>$R_p$ (Ω)</th>
<th>$C_{dl}$ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Zn-P</td>
<td>64.03</td>
<td>9942</td>
<td>1.574e⁻⁵</td>
</tr>
<tr>
<td>Ni-Zn-P-TiO₂</td>
<td>37.56</td>
<td>16400</td>
<td>1.826e⁻⁵</td>
</tr>
<tr>
<td>Ni-Zn-P heat treated</td>
<td>46.02</td>
<td>19239</td>
<td>0.769e⁻⁵</td>
</tr>
<tr>
<td>Ni-Zn-P-TiO₂ heat treated</td>
<td>46.12</td>
<td>21368</td>
<td>0.824e⁻⁵</td>
</tr>
</tbody>
</table>

4.2.4. Conclusions

✓ The inclusion of TiO₂ nanoparticles in Ni-Zn-P ternary alloy matrix was achieved successfully from an electroless plating bath.

✓ Surface morphology of both pure and composite coated specimens changed significantly after heat treatment.
Chapter 4.2 Electroless Ni-Zn-P/nano TiO₂ composite coating

- Codeposited particles did not influence structure and phase transformation behavior. The presence of metastable and stable phases was identified in both the deposits heated at 400°C temperature.
- The composite coatings exhibited higher microhardness than pure alloy.
- Electrochemical measurements showed that the annealed Ni-Zn-P-TiO₂ coatings have good corrosion resistance in 3.5 wt% NaCl solution compared to Ni-Zn-P coatings.

References


Chapter 4.2: Electroless Ni-Zn-P/nano TiO₂ composite coating


Chapter 4.2  Electroless Ni-Zn-P/nano TiO$_2$ composite coating


