CHAPTER 5
DEVELOPMENT AND OPTIMIZATION OF Ni-P-ZnO COMPOSITE COATING BY ELECTROLESS TECHNIQUE

5.1 INTRODUCTION

A detailed discussion about the electroless plating, their types (including Ni, Ni-alloy, Ni-based composite coatings, etc.), properties and applications are discussed in Chapter 2. Further, it is summarized here again ‘it is a chemical reduction process, which depends on the catalytic reduction of a metallic ion from aqueous solution containing a reducing agent, and the subsequent deposition of the metal without the use of electrical energy’. Composite coatings can be obtained by co-deposition of inert particles into a metal matrix from an electrolytic or electroless bath. ZnO belongs to a group of metal oxides that are characterized by the following properties: photo catalytic ability, electrical conductivity, UV absorption, photo oxidizing capacity versus chemical and biological species, antimicrobial and self-sterilization [117-121].

In the present study, electroless coatings of Ni-P and composite Ni-P-ZnO were developed by co-deposition process on mild steel and non conductive glass substrates. The ‘as synthesized’ and heat treated Ni-P and Ni-P-ZnO composite coatings were characterized by XRD, FESEM and AFM, and optimization of ZnO concentration in Ni-P-ZnO composite coatings were carried out by varying the concentration of ZnO particles (5, 10 and 15 g/l of average particle size 20 μm) in electroless bath.

5.2 EXPERIMENTAL METHODS

5.2.1 Ni-P and Ni-P-ZnO Composite Coatings

Ni-P and Ni-P-ZnO composite coatings were developed by electroless coating technique on the flat surface of mild steel substrate (having dimensions 20×20×0.5 mm³) by conventional method. Since for comparison analysis of as-coated samples were also carried out but in as-coated form coating get oxidized in atmospheric condition and the mild steel substrate sometimes get corroded under experimental conditions. Therefore, these coatings on the glass substrate have also been carried out. Composition of universal basic (pH= 9.0) electroless bath is given below in detail:
(a) Composition of universal basic (pH = 9.0) electroless bath

The electroless plating bath setup used for the present study is given in Fig. 5.1. Pretreatment and coating solutions (pH = 9.0) used are shown in Fig. 5.2. The electroless bath contains source of metal ions, reducing agent, complexing agent and stabilizers. The composition of reagents used in the bath is given in Table 5.1.

![Fig. 5.1: Setup for electroless plating bath.](image)

<table>
<thead>
<tr>
<th>Reagents Used</th>
<th>Quantity</th>
</tr>
</thead>
</table>

Table 5.1: Electroless plating bath composition and operating conditions.
<table>
<thead>
<tr>
<th>Volume of distilled water</th>
<th>250 ml</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel sulphate</td>
<td>6.25 g</td>
</tr>
<tr>
<td>Sodium hypophosphite</td>
<td>5 g</td>
</tr>
<tr>
<td>Tri sodium citrate</td>
<td>22.5 g</td>
</tr>
<tr>
<td>Ammonium sulphate</td>
<td>12 g</td>
</tr>
<tr>
<td>ZnO</td>
<td>2.5 g</td>
</tr>
<tr>
<td>Coating time</td>
<td>45-60 min</td>
</tr>
<tr>
<td>pH controlling reagent</td>
<td>Ammonia</td>
</tr>
<tr>
<td>Operating conditions of electroless bath ( pH: value 9.0 ±0.2 , Temperature: 90±2 °C )</td>
<td></td>
</tr>
</tbody>
</table>

(b) Preparation and activation of substrate surface

The composite electroless Ni-P-ZnO coatings were deposited on the flat surface of mild steel and glass substrate. Sample surface was mechanically cleaned from foreign matter and corrosion products in order to ensure a good adhesion between the substrate and coating. Steel samples were polished following the standard method using emery papers up to 4/0 grade.

(c) Substrate surface preparation

The steps followed for the surface preparation, based on the literature are given below:

1. Substrate first degreasing with acetone (organic solvent),
2. After acetone substrate degreasing with NaOH,
3. Washing with water,
4. Etching in dilute HNO₃ or HCl for steel and HF used for a glass substrate,
5. Washing with distilled water and at last dry the substrate.

(d) Pretreatment of a substrate surface
Surface preparation is followed by pretreatment of the surface of the substrate in which the surface is first sensitized and then activated by immersing the substrate in the freshly prepared solutions of 0.1% SnCl$_2$ and 0.01% PdCl$_2$, respectively, shown in Fig. 3.2 (a), for a specific time period (~10 sec) at room temperature. During the pretreatment process, Sn ions deposit onto the surface, over that only the Pd ions can be deposited as it acts as a nucleus /catalyst for the electroless deposition to start with.

![SnCl$_2$ and PdCl$_2$ solutions](image)

**Fig. 5.2:** (a) Pretreatment solution and (b) electroless bath solution before and after coating.

The following steps are carried out for pretreatment:

a. Substrate dipped in 0.1% stannous chloride (SnCl$_2$) solution, 1 min for steel and 2 min for glass followed by rinsing with distilled water and then dried.

b. Dipped in freshly prepared 0.01% palladium chloride (PdCl$_2$) solution for 30 sec. followed by rinsing with distilled water and then dried.

After pretreatment of develop Ni-P-ZnO composite coating on activated substrate, ZnO particles (2.5 g/l, as-received of average size 20-30 μm) were added to the electroless bath with continuously stirring, and activated substrate was immersed in the bath. Temperature of the bath was kept at 90 ±2 °C with pH value of 9.0 ±0.2, pH is controlled by pH controlling reagent (ammonia). After plating, the samples were taken out, rinsed with distilled water and air dried. Same procedure was followed for Ni-P and Ni-P-ZnO coating on the glass substrate.

(c) **Heat treatment**

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To improve the properties of the produced Ni-P and Ni-P-ZnO coatings, the samples were thermally treated at 400°C in the argon atmosphere. The samples were heat treated for 1h at 400 °C in a vacuum furnace. Then the samples were allowed to cool down, for at least 15 min prior to their exposure to the atmosphere. Ni-P and Ni-P-ZnO as coated and heat treated samples were characterized by XRD, FESEM/EDAX and AFM.

5.3 ANALYSIS OF DEVELOPED COATING BY VARIOUS TECHNIQUES

5.3.1 XRD Study

Representative XRD spectra of the coating on mild steel have been presented in Fig. 5.3. The XRD pattern of the mild steel substrate, Ni-P coated substrate, Ni-P-ZnO coated substrate and further heat treated Ni-P-ZnO coated substrate are shown in Fig. 5.3 (a-d). In the XRD spectra the peaks observed for Ni-P and Ni-P-ZnO prepared under the similar experimental conditions, in 2θ angle range (25-80°) corresponds to the amorphous (as-coated) and crystalline (heat treated) Ni-P matrix and crystalline ZnO (wurtzite).

* Ni-P
# Ni-P-ZnO

HT Ni-P-ZnO

Fig. 5.3: XRD patterns of (a) Mild Steel (MS) substrate, (b) Ni-P coating on MS, (c) Ni-P-ZnO coating on MS and (d) Heat treated Ni-P-ZnO coating.

5.3.2 FESEM STUDY
FESEM Analysis of Ni-P and Ni-P-ZnO coating on mild steel and the glass substrate

Fig. 5.4 and Fig. 5.5 show the surface morphology with chemical composition by FESEM/EDAX technique, for blank substrate (without coating), as-coated Ni-P and Ni-P-ZnO coating, respectively, for both the substrate (mild steel and the glass substrate). The electroless Ni-P and Ni-P-ZnO coatings exhibit good adherence on the mild steel and the glass substrate. ZnO particles are used for the present study having irregular shape that is clearly seen by the FESEM micrograph (Fig. 5.5 a). For Ni-P-ZnO coating, EDAX results suggest that the particles of ZnO are embedded in Ni-P coating matrix. Zn in the localized region is found to be ~ 10 wt % for both the substrate Fig. 5.5 (b and c). On the glass substrate the Ni-P coating is developed with nodular globules which are observed by FESEM. The presence of ZnO particles in Ni-P-ZnO matrix is uniformly distributed as seen by the micrograph Fig. 5.5 (c) and the incorporation of the ZnO particles into the matrix is also confirmed by the presence of ZnO peak in EDAX spectrum Fig. 5.5 (b and c). The embedded ZnO grains into the amorphous matrix distinctly reduce the surface development of the composite Ni-P–ZnO layer, compared to plain electroless Ni-P coating.

In the EDAX spectra one peak is clearly observed corresponding to the base material, i.e., iron peak (for mild steel substrate) and silica peak (for glass substrate). Spectra gave in Fig. 5.4 (d) confirm the presence of nickel and phosphorous with the base material peak (silica). Fig. 5.5 (b and c) indicate a peak of ZnO particles in the Ni-P-ZnO composite coating EDAX spectra since zinc and oxygen peaks appear with nickel, phosphorous and silica peaks, which indicate the incorporation of zinc oxide particles in the Ni-P matrix.

X-ray mapping results provide the information regarding the distribution of the particles present in the coating. Fig. 5.6 (a-e) shows the scanning of separately distribution of particles Ni, P, Zn, O and Ni-P-ZnO in a typical Ni-P-ZnO coating matrix. These figures reveal that the particles are distributed uniformly on the surface of the substrate. Uniform and grayish bright coatings were observed on both the substrate surfaces.
Fig. 5.4: FESEM and EDAX (a) for blank Mild steel (b) for blank glass substrate (c) Ni-P coating on mild steel and (d) Ni-P coating on glass substrate.
Fig. 5.5: FESEM/EDAX micrographs of (a) ZnO particles used for coating (as received) (b) Ni-P-ZnO coating on mild steel and (c) Ni-P-ZnO coating on a glass substrate.
5.4 OPTIMIZATION OF ZNO CONCENTRATION IN Ni-P-ZnO COMPOSITE COATINGS

Since the second phase particles were added in the electroless bath for their co-deposition into the Ni-P matrix. But it has been reported that the properties of coatings are improved
upto certain concentration of second phase particles into the metal matrix, concentration higher than the limiting value can have an effect on the coating properties. For higher concentrations, more number of particles presents in the bath and gets agglomerate into metal matrix and form colonies onto the substrate surface for which diffusion of the particles present in the upper layer is weak. Therefore, the optimization of ZnO particles into the Ni-P matrix is considered as a necessary step and was carried out for the present study.

5.4.1 FESEM Analysis

FESEM micrographs of Ni-P-ZnO coated samples with increasing concentration of ZnO before and after heat treatment are shown in Fig. 5.7(a, b & c) and Fig. 5.8, respectively, which shows the effect of ZnO particles on the surface morphology of the coatings. The surface of the composite coatings exhibits ZnO particles of spherical shape, occasionally assembled in small aggregates, and the results of chemical composition obtained by FESEM-EDAX are presented in Fig. 5.7 (a, b and c). Morphology of coatings by FESEM analysis suggests that the ZnO particles are embedded in Ni-P coating matrix covered a broad surface as the concentration of ZnO particles increase in the bath, Fig. 5.7 (a) lesser number of ZnO particles are seen in comparison to particles seems on the surface of the other two substrate having concentration, i.e., 10 g/l and 15 g/l, respectively. As the concentration of ZnO particles increases in the electroless bath up to a certain concentration the deposition of ZnO in the sample surfaces also increase which is also confirm by the EDAX analysis, by elemental % of Zn and O.

When concentration of ZnO particles increases in the bath agglomeration of small size globules occur. The surface morphology of a particle free Ni-P coating deposited at 90 °C reveals a white smooth surface Fig. 5.4 (a). EDAX analysis confirms the chemical composition of the particles and of the matrix. The presence of the ZnO in the Ni-P layer affects the heterogeneity of the surface and increases the number of boundaries between
Before heat treatment

Fig. 5.7: The surface morphology by FESEM/EDAX analysis of the as-plated Ni-P–ZnO composite coating deposits with different concentrations of ZnO in electroless bath (a) 5 g/l, (b) 10 g/l and (c) 15 g/l coating on mild steel substrate.
Fig. 5.8: The surface morphology of the as-plated Ni-P and Ni-P–ZnO composite deposits with different ZnO concentrations in electroless bath (a) 0 g/l, (b) 5 g/l, (c) 10 g/l and (d) 15 g/l coating on mild steel substrate.

Ni and other particles in the matrix. The embedded ZnO grains into the amorphous matrix distinctly enlarge the surface development of the composite. Fig. 5.8 shows the morphology change after vacuum heat treatment under the argon atmosphere for one hour at 400 °C of the coated samples. Particles fused, and coating becomes crystalline in nature that is also confirmed by XRD analysis and their AFM results show the surface roughness of the coated samples.

5.4.2 Atomic Force Micrographs (AFM)
Atomic force microscope (AFM) is used to determine surface roughness of the Ni-P and Ni-P-ZnO coatings, and is shown in Fig. 5.9-5.11. AFM characterization of the Ni-P and Ni-P-ZnO coatings revealed a granular, morphology of the surface. The presence of ZnO particles in Ni-P layer affects the homogeneity of the surface and increases the number of boundaries between Ni and other globules in the matrix [134]. The surface roughness values obtained by AFM study are, for as coated Ni-P (8.20 nm), Ni-P-ZnO (39.45 nm) and heat treated Ni-P-ZnO (16.625 nm), respectively. The higher surface roughness value of Ni-P-ZnO coating as compared to plain Ni-P coating can be explained by considering when the ZnO particles embedded into the Ni-P matrix agglomeration of small size globules occur. This creates larger size of the island of composite Ni-P-ZnO, therefore, surface roughness value confirms that the formation of Ni-P-ZnO layer on the substrate.

Fig. 5.9: The surface topography of Ni-P coating on mild steel substrate by AFM (a) before heat treatment and (b) after heat treatment.
Fig. 5.10: The surface topography by AFM of Ni-P-ZnO composite deposits with different ZnO bath concentrations (a) 5 g/l, (b) 10 g/l and (c) 15 g/l on mild steel substrate.
Further, on increasing the concentration of ZnO in electroless bath surface roughness value decreases due to the formation of small size globules. The coatings were heat treated at 400 °C for one hour in an argon atmosphere to attain crystalline nature of coating. The electroless Ni-P and Ni-P-ZnO coatings exhibit good adherence on the mild steel and glass substrate.

5.4.3 Study of Hardness of Ni-P/Ni-P-ZnO coating

The microhardness (VHN) measurements were performed using a make Future-Tech Corporation, calibrated with a load of 10 gf, allowing to obtain a reproducible imprint area in order to improve the measuring accuracy and Ni–P and Ni–P–ZnO coated samples hardness was determined with a load of 10 gf, and dwelling time of 15 sec and the results are given in Table 5.2. The hardness of electroless Ni-P composite coatings increases with the incorporation of ceramic hard particles, whereas with soft particles, the hardness tends to
decreases as the concentration of particles increase into the bath. The level of incorporation of particles, the phosphorous content of the matrix and heat treatment determines the hardness of coating [135]. The results of the micro-hardness determined by Vicker hardness apparatus suggest that the addition of ZnO nanoparticles in the coating does not contribute significantly to the microhardness of the sample as ZnO nano particles are soft metal oxide as well as on further increasing the concentration of the ZnO particles, the hardness value decreases.

Table 5.2: Typical Vickers microhardness measurements for the as-plated and heat treated Ni-P and Ni-P-ZnO composite coatings.

<table>
<thead>
<tr>
<th>ZnO bath load (g/l)</th>
<th>Hardness (HV)* (As-Plated)</th>
<th>Hardness (HV)* (After Heat Treatment)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mild steel substrate</td>
<td>250</td>
<td>-</td>
</tr>
<tr>
<td>Ni-P</td>
<td>450</td>
<td>490</td>
</tr>
<tr>
<td>Ni-P-ZnO (2.5 g/l)</td>
<td>465</td>
<td>510</td>
</tr>
<tr>
<td>Ni-P-ZnO (5 g/l)</td>
<td>470</td>
<td>540</td>
</tr>
<tr>
<td>Ni-P-ZnO (10 g/l) as-coated</td>
<td>510</td>
<td>540</td>
</tr>
<tr>
<td>Ni-P-ZnO (15 g/l) as coated</td>
<td>470</td>
<td>510</td>
</tr>
</tbody>
</table>

* All of the tests were carried out in triplicates, and an average value has been reported.

It could be presumed that low bath ZnO load (5 g/l) results in very fine particle dispersion through the Ni-P–ZnO composite deposit, therefore, after rapid vacuum heat treatment these particles are coherent to the precipitated Ni₃P and Ni grains, giving rise to aim proved hardness of the coatings (Table 5.2). However, with an increase in the bathing load, larger particles or their agglomerates can be embedded into the coatings, and it will eventually be easier for a dislocation to loop between particles rather than to shear them. This probably results in reducing to some extent the hardness of these coatings (Table 5.2).

### 5.5 CONCLUSION

As the concentration of ZnO increases the agglomeration takes place and coating become crystalline but after a certain level of ZnO concentration in electroless bath, i.e., 15g/l there was no more effect seen on surface morphology of the coated substrate surface. As the
concentration of the second phase particles into the bath increases the distribution of particles into the coating is also increases, which is shown by the FESEM and particle imaging technique. The stoichiometric presence of ZnO particles into the Ni-P matrix is also given by the EDAX analysis. For higher concentration of ZnO particles into the bath higher roughness value is observed in their AFM study. Higher roughness values suggest the agglomeration of reinforced particles into the Ni-P matrix. The Vicker microhardness value determined for these samples, suggests that there was no significant effect observed on hardness of the coating after addition of higher concentration of ZnO particles in coating. The substrate having 5 g/l and 10 g/l concentration of ZnO and in electroless bath shows a nearly same hardness. However, a decrease in hardness is observed for 15 g/l concentration of ZnO particles in the bath. It shows that the higher concentration does not show much affection the hardness properties. From the study, it has been concluded that 5 g/l is the optimum concentration for co-deposition of ZnO particles into Ni-P matrix by conventional method.