STUDY OF Zn-Ni ALLOY COATINGS MODIFIED BY NANO-AL$_2$O$_3$ PARTICLES INCORPORATION

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Abstract

Zn–Ni–Al$_2$O$_3$ nano-composite coatings were electrodeposited on mild steel using a novel sol enhanced electroplating method. The effect of alumina sol on the electrodeposition process, and coating properties was investigated using, X-ray diffraction, scanning electron microscopy (SEM), measurement of microhardness and chronoamperometry and electrochemical impedance spectroscopy were studied in a solution of 3% NaCl. The results indicated that the electro-crystallization processes of Zn–Ni and Zn–Ni–Al$_2$O$_3$ were governed by a three-dimensional nucleation process controlled by diffusion. XRD results showed that the phase structure of both alloy and composite coatings was single Ni$_5$Zn$_{21}$γ phase, and the addition of alumina sol in the Zn-Ni matrix increases the microhardness, and we note the maximum hardness is obtained for 50 g/L Al$_2$O$_3$. Conversely, these coatings showed smaller crystallite size and Surface of coatings was uniform and compact, the values of $R_{ct}$ and $Z_w$ increase, while the values of $C_{dl}$ decrease with increasing alumina nano-particles content values for the Zn–Ni–Al$_2$O$_3$ alloy clearly confirm the better corrosion resistance.

Keywords: Al$_2$O$_3$, Nickel, Zinc, EIS, XRD, SEM, chronopotentiometry

1 Introduction

Electroplated binary Zn–Malloys, where metals are an Fe group such as Ni, Co and Fe, exhibit improved properties compared to pure Zn [1-5]. It is well-known that zinc alloys can provide protection of steel against corrosion, with Zn–Ni, Zn–Co and Zn–Fe being most commonly used [6, 7]. The use of specific bath additives has also been found beneficial with respect to corrosion resistance, even for low contents of Metals [6]. Electrodeposited Zn–Ni alloys exist in the form of three dominant phases: α, γ and η. The α-phase is a solid solution of Zn in Ni with an equilibrium solubility of about 30 % Zn. The η-phase is a solid solution of Ni in Zn, with a Ni solubility of less than 1 %. The composition range of the pure γ-single phase was determined to be between 10 and 30 % Ni. The amount of Ni in the alloy, which finds industrial application in the corrosion protection field, is around 15% and its dominant structure is the γ-phase Zn$_{21}$Ni$_5$ [8]. Electroplated co-deposition is widely used for preparing metal matrix composite coatings because of its low cost and versatility. Electroplated co-deposition is widely used for preparing metal matrix composite coatings because of its low cost and versatility. In general, hard oxide (Al$_2$O$_3$, TiO$_2$, and SiO$_2$) or carbide particles (SiC and WC), or even diamond and carbon nanotubes (CNT) are
used as a second phase [9] and established applications and possess good chemical stability, high microhardness, and good wear resistance and corrosion resistance at elevated temperature [9–14]. Zn–Ni composite coatings for example Zn–Ni–Al2O3 [9, 10, 15, 16], Zn–Ni–TiO2 [11, 17], Zn–Ni–SiO2 [13] and Ni–Zn–P [14], ZnNi–SiC [16, 18], this research work was to codeposit nano-Al2O3 particles into the Zn–Ni alloy coatings deposits on a mild steel substrate. In order to improve the surface properties and the corrosion resistance in aggressive media. Then, the composite coatings had been characterized, morphological (SEM), structural (XRD), and electrochemical properties of the composite coatings had been studied by potentiodynamic polarization and electrochemical impedance spectroscopy in a solution of 3 % NaCl.

2 Experimental
2.1 Coating processes
The deposition of Zn–Ni coatings was carried out onto steel substrates under galvanostatic conditions at operating current density of 30 A cm−2 and a temperature of 30°C, the chemical composition of the basic electrolyte of Zn–Ni alloys deposition was given in Table 1 [8]. Electrodeposits Zn–Ni were obtained by varying the concentration of Al2O3 in the bath (0, 30, 50 g·L−1).

2.2 Coating characterization
XRD characterization of samples was carried out with a D8 Advance-Brucker using a Cu Kα line at λ= 0.1540 nm in the 2θ ranged of 10–95° in steps of 0.02° at a scan speed 2°/min. Bruker GAADS soft-ware was utilized to calculate.

<table>
<thead>
<tr>
<th>Electrolyte I ingredients</th>
<th>Concentration (g·L−1)</th>
<th>Plating parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO4·7H2O</td>
<td>57.5</td>
<td>30 °C and pH=3-4.5</td>
</tr>
<tr>
<td>H3BO3</td>
<td>9.3</td>
<td>constant current densities at 10 mA cm−2 for 60 s</td>
</tr>
<tr>
<td>Na2SO4</td>
<td>56.8</td>
<td></td>
</tr>
<tr>
<td>Na3C6H5O7</td>
<td>56.8</td>
<td></td>
</tr>
</tbody>
</table>

The biaxial stress along the lateral and longitudinal directions with 2D area detector using a standard 2Θ sin2Ψ method [19]. The average grain size of the coatings was determined from X-ray peak broadening by applying the Scherrer formula [20, 21]:

\[ D = \frac{0.9\lambda}{\beta \cos\theta} \] (1)

where \( D \) is the grain size, is the X-ray wavelength (\( \lambda = 1.5406 \) A), \( \beta \) is the full width at half-maximum (FWHM), and \( \theta \) is Bragg angle position of peak. For (330) reflections and peak broadening was measured by the integral width method [22]. Surface morphology of the deposits was followed with a JEOL (model JSM6390LV). Microhardness of coatings was measured using a load of 100 g with a holding time of 15 s by using a Vickers hardness tester (HV) of deposits were performed in the surface by using a Wolpert Wilson Instruments (model 402UD) [23]. Corrosion behavior and protection performance of Zn–Ni and Zn–Ni–Al2O3 alloy coatings was studied by using electrochemical impedance spectroscopy (EIS) and electrochemical Tafel...
extrapolation in 3% NaCl solution. The tests were performed using a potentiostat/galvanostat (using a Volta Lab 40), the working electrode was a coated sample, the counter electrode was platinum with an area of 1 cm² and the reference electrode was Hg/HgO/1 M KOH. All potentials in the text have been referred to this reference electrode. Electrochemical impedance spectroscopy (EIS) measurements were obtained at the open circuit potential (OCP) in a frequency range of 10 kHz–0.001 Hz, with an applied AC signal amplitude perturbation of 10 mV. During the measuring process of Tafel polarizing curves, the polarization curve scanning rate was 5 mV/s, with a scanning range from −0.25 V of open circuit potential to +0.25 V of open circuit potential. The $E_{\text{Corr}}$ and $I_{\text{Corr}}$ were determined from the intercepts by Tafel extrapolation method. The chronoamperometric studies were conducted to identify the nucleation mode of Zn–Ni–Al₂O₃ composite and Zn–Ni alloy coatings at potentials $E=500\text{mv}$, vs. Hg/HgO applied for 1 hours of 3% NaCl. This potentiostatic technique has proved to be a powerful tool for evaluation of the nucleation mode by electrocrystallization.

3 Results and discussions
3.1 X-ray diffraction
Fig.1 shows the XRD results for Zn–Ni composite coatings, the phase structure is single $\gamma$-Ni₅Zn₂₁ phase [2, 10]. The grain sizes, being the (330) plane always the most intense, crystallite sizes of the coatings were calculated from the X-ray peak broadening of the (330) diffraction peak using Scherrer's formula, which is well suited to detect grain diameters less than 100 nm, and has been used widely for Zn–Ni deposits [10, 24]. The grain sizes of all of the coatings were on a nanometer scale, confirming the nanocrystalline structure of coatings. Zn–Ni–Al₂O₃ coatings showed a smaller grain size compared to the Zn–Ni alloy coating. Zn–Ni alloy deposited in electrolyte I, exhibited a crystallite size of 45 nm, whereas the crystallite size of Zn–Ni alloy coating deposited in electrolyte I+50 g·L⁻¹ Al₂O₃ decreased to 24 nm. This finer structure presence of smaller grains explained probably the increase microhardness.

![XRD patterns of Zn–Ni alloy coatings](image)

Fig. 1 XRD patterns of Zn–Ni alloy coatings electrodeposited onto steel substrate at different concentrations of Al₂O₃). Composite coatings were deposited at 30 mA/cm², $T = 30$ °C, and pH 3-4, 5 for 60 s.

3.2 Surface morphology
The morphology of these coatings plated in different compositions is presented in Fig. 2, further that the Zn–Ni alloy exhibits a uniform [8], Zn-Ni-Al₂O₃ composite coating was uniform and
compact, with a fine grained morphology. Therefore, the presence of Al₂O₃ in the electroplating bath and incorporation of Al₂O₃ in the Zn–Ni coating, increased refinement of crystal size [10].

3.3 Effect of Al₂O₃ content in the bath on microhardness of the coatings

The microhardness of Zn–Ni alloy and the Zn–Ni–Al₂O₃ nanocomposite coatings results are presented in Fig. 3, the microhardness of the nanocomposite coatings increases with increasing weight percentage of the nano- Al₂O₃. The hardness increased from 246 Hv for Zn–Ni [8], alloy to 350 and 383 Hv for 30 and 50 g /l Al₂O₃ nanocomposite coating respectively. Microhardness of composite coatings containing Al₂O₃ has been attributed to the hindrance of dislocation movement by Al₂O₃ particles [9, 15, 25], the microhardness of nanocomposite coating depends directly on the alumina content of nanocomposite coating.

Table 2 Values of micro-hardness Vickers hardness (HV) registered different electro deposition

<table>
<thead>
<tr>
<th>Coating</th>
<th>hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>167.7</td>
</tr>
<tr>
<td>Zn Ni</td>
<td>246</td>
</tr>
<tr>
<td>Zn-Ni-Al₂O₃ (30 g /l)</td>
<td>350</td>
</tr>
<tr>
<td>Zn-Ni-Al₂O₃ (50 g /l)</td>
<td>383</td>
</tr>
</tbody>
</table>

Fig. 2 Surface morphology of (a) Zn–Ni alloy coatings and (b) Zn–Ni–Al₂O₃ (30 g /l Al₂O₃), (c) Zn–Ni–Al₂O₃ (50 g /l Al₂O₃) Composite coatings deposited at 30 mA/cm², T = 30 °C, and pH 3-4.5 for 60 s.
3.4 Corrosion studies

3.4.1. Potentiodynamic polarization studies

Fig. 4 shows the Tafel curves measured for the Zn–Ni alloy coating and Zn–Ni–Al₂O₃ nanocomposite coating in 3 % NaCl solution. The corrosion potentials and corrosion currents calculated from Tafel plots were determined from this figure and cited in Table 3. The corrosion potential $E_{corr}$, the polarization resistance $R_p$, and corrosion current ($i_{corr}$) values were determined from this figure and cited in Table 3. The corrosion potential and corrosion current for the Zn-Ni-Al₂O₃ (50 g/l) nanocomposite coating, obtained from the polarization curves were $-1.0376$ V and $0.255$ mA/cm² respectively and those for the Zn–Ni alloy coating were determined to be $-1.0614$ V and $0.1025$ mA/cm² respectively. It is seen that the nanocomposite coatings have higher positive corrosion potentials and smaller corrosion current densities than that of Zn–Ni alloy coating. The Zn–Ni–Al₂O₃ nanocomposite coatings have better corrosion resistance than that of Zn–Ni alloy, the corrosion potential increased with the increase of nano-alumina content.

Fig. 4 Polarizing curves obtained for the alloy coatings in a 3 % NaCl solution at different concentrations of Al₂O₃
Table 3 The electrochemical parameters \((E_{corr}, I_{corr}, \beta_a, \beta_c)\) of the coatings samples in a 3 \% NaCl solution

<table>
<thead>
<tr>
<th>Coating</th>
<th>(E_{corr}) (mV)</th>
<th>(I_{corr}) (mA/cm(^2))</th>
<th>(\beta_a) (mV/dec)</th>
<th>(\beta_c) (mV/dec)</th>
<th>(R_p) ((\Omega) cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn Ni</td>
<td>-1061</td>
<td>0.255</td>
<td>246,2</td>
<td>-259,4</td>
<td>169.13</td>
</tr>
<tr>
<td>Zn-Ni-Al(_2)O(_3) (30 g/l)</td>
<td>-1047</td>
<td>0.159</td>
<td>180,9</td>
<td>-256,8</td>
<td>103.19</td>
</tr>
<tr>
<td>Zn-Ni-Al(_2)O(_3) (50 g/l)</td>
<td>-1037</td>
<td>0.102</td>
<td>157,5</td>
<td>-215,0</td>
<td>109.43</td>
</tr>
</tbody>
</table>

3.4.2. Electrochemical impedance spectroscopy (EIS) studies

Fig. 5 presents a comparison of Nyquist responses obtained for Zn-Ni alloy coatings and Zn-Ni alloy composites elaborated under the same quantities of electricity in 3\% NaCl solution. L'impédance, Dans le Plan de Nyquist, is represented by a boucle capacitive.

The data of the charge transfer resistance, \(R_{ct}\) and the capacity of the double layer (\(C_{dl}\)) were calculated using both the Nequist and Bode plots of the impedance spectrum (Table 3). However, the Warburg impedance (\(Z_w\)) is determined from the following equations:

\[
Z' = \sigma \frac{1}{\omega^{1/2}} - j \frac{\sigma}{\omega^{1/2}} \\
|Z| = \frac{\sigma}{\omega^{1/2}}
\]

The Warburg coefficient \(\sigma\), can be determined from the slope of the Warburg plot (the slope of real parts of \(Z\) vs. \(1/\omega^{1/2}\); \(\omega=2\pi F\)), or by fitting to an equivalent circuit model which includes a Warburg impedance. However, most equivalent circuit modeling programs return “\(Z_w\)” rather than \(\sigma\), \(Z_w\) is the Warburg impedance (\(Z_w=W\)) which are calculating from the following equation (Table 4):

\[
\sigma = \frac{1}{Z_w,\sigma}
\]

The data of the charge transfer resistance, \(R_{ct}\), and the capacity of the double layer (\(C_{dl}\)) were calculated using both the Niequist and Bode plots of the impedance spectrum (Table 4) is determined from the following equations:

The \(R_{ct}\) can be related to \(i_{corr}\) [26]

\[
R_{ct}= \frac{b_a b_c}{2.3(b_a b_c)_{corr}}
\]

\(R_{sol}\): solution resistance
\(R_{ct}\): charge transfer resistance
\(b_a\) and \(b_c\) anodic and cathodic tafel slopes

The double layer capacitance \(C_{dl}\) can be related to \(Z_{ima\ max}\) [26]

\[
\omega(Z_{ima\ max}) = \frac{1}{R_{dl}C_{dl}}
\]

From the data obtained in Table 3, one can conclude that the values of \(R_{ct}\) and \(Z_w\) increase, while the values of \(C_{dl}\) decrease with increasing alumina nano-particles content, and this behavior is in good agreement with that obtained of the Tafel plot measurements, the spectra presented show at least two time constants. The first time constant, recorded at higher frequency,
is displayed as a depressed incomplete semicircle. The electrical-equivalent-circuit (EEC) parameters, describing the process included in this time constant are $R_{ct}$ and $C_{dl}$ [27, 28]. The second time constant, depicted at lower frequencies, corresponds to a straight line Figs 6. This linear dependence between the imaginary and real part of the capacitance is related to the diffusion process of the soluble species, while is called Warburg impedance ($Z_{w}$). Therefore, EEC parameters describing the process included in the second time constant clearly indicates the diffusion control of the soluble species. From the electrode surface to the bulk of solution [27, 28]. Zn–Ni–Al$_2$O$_3$ provides better protection against corrosion on the steel substrate [13].

Table 4 Extracted fitted data from the equivalent circuit of Zn–Ni alloy coatings in a 3 % NaCl

<table>
<thead>
<tr>
<th>Coating</th>
<th>$R_p$ (Ω cm$^2$)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_{ct}$ (Ω cm$^3$)</th>
<th>$C_{dl}$ (µF/cm$^2$)</th>
<th>($Z_w$) (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn Ni</td>
<td>1.259</td>
<td>0.405</td>
<td>78.5</td>
<td>1.310</td>
<td>0.669</td>
</tr>
<tr>
<td>Zn-Ni-Al$_2$O$_3$ (30g/l)</td>
<td>1.762</td>
<td>0.677</td>
<td>135</td>
<td>0.936</td>
<td>0.827</td>
</tr>
<tr>
<td>Zn-Ni-Al$_2$O$_3$ (50 g/l)</td>
<td>1.797</td>
<td>0.697</td>
<td>183</td>
<td>0.918</td>
<td>1.157</td>
</tr>
</tbody>
</table>

Fig. 5 The Nyquist plots obtained Zn–Ni–Al$_2$O$_3$ composite and Zn–Ni alloy coatings electrodeposited at different concentrations of Al$_2$O$_3$

3.4.3. Chronoamperometry studies

The chronoamperometric studies were conducted to identify the nucleation mode of Zn–Ni–Al$_2$O$_3$ composite and Zn–Ni alloy coatings at potentials $E=500$mV. The chronoamperometric studies were performed at 30 °C vs. Hg/HgO applied for 1 hour of 3 % NaCl. Fig. 7, the transients can be divided into two regions. The first region corresponds to the increase in current density up to a maximum, which is typical of crystal nucleation and growth processes. During this stage, the nuclei develop diffusion zones around themselves. The second region corresponds to the decrease in the current density, which is typical of a diffusion-controlled process [10, 29-31]. Scharifker and coworkers derived analytical expressions for multiple nucleation phenomena followed by diffusion-controlled growth of three-dimensional islands. The resulting expressions for the normalized current densities allow to distinguish between instantaneous nucleation and progressive nucleation, according to Eq. (5) for instantaneous nucleation and Eq. (6) for progressive nucleation:
\[
\left(\frac{t}{t_m}\right)^2 = 1.9542 \frac{t_m}{t} \left[ 1 - \exp\left(-1.2564 \frac{t}{t_m}\right) \right]^2
\]  
(7.)

\[
\left(\frac{t}{t_m}\right)^2 = 1.2254 \frac{t_m}{t} \left[ 1 - \exp\left(-2.3367 \frac{t}{t_m}\right) \right]^2
\]  
(8.)

The experimental and theoretical data for Zn–Ni alloy and Zn–Ni–Al$_2$O$_3$ deposition a potentials $E=500$mv are shown in Fig. 8a and 8b. In these figures, the instantaneous nucleation rate is higher than the progressive nucleation rate [10, 25, 26]. As seen in Fig. 5, the experimental data more closely approximated theoretical progressive curve for the Zn–Ni alloy coating (Fig. 8a). Thus, the progressive nucleation mode would be predominant for the Zn–Ni alloy. However, for the Zn–Ni composite coating, the nucleation mode was closer to instantaneous nucleation (Fig. 8b). This difference may be explained by the adsorption of alumina nano-particles on the cathode surface which created additional active nucleation sites during electrodeposition on the mild steel substrate [10].

![Fig. 6 Chronoamperograms of Zn–Ni–Al$_2$O$_3$ composite and Zn–Ni alloy coatings at potentials $E=500$mv, vs. Hg/HgO applied for 1 hour of 3 % NaCl](image)

4 Conclusion

This work represented the electrodeposition and the corrosion behavior of Zn-Ni alloy deposits elaborated in absence or in presence of 30 and 50 g/l of nano-Al$_2$O$_3$ in the acid sulfate bath. This study was made to evaluate the influence of nanoparticles addition on some properties such as hardness, morphologic structure characteristics, and corrosion resistance the results revealed that of Zn–Ni alloy and the Zn–Ni–Al$_2$O$_3$ nanocomposite coatings:

- XRD and SEM results indicate all the Zn-Ni alloy coatings have similar phase composition ($\gamma$-phase structure), with smaller crystallite size
- The deposited coating with 50g/l Al2O3 showed the maximum value of hardness 383HV, because the increase of nano-Al$_2$O$_3$ concentration in the plating bath increases of micro-hardness.
- The corrosion potential increased with the increase of nano-alumina content, while the corrosion current decreased from 0.255 mA/cm$^2$ for Zn–Ni matrix to 0.1020 mA/cm$^2$ for Zn–Ni–Al$_2$O$_3$ composite coating containing 50 g /l nano-alumina.
- The data obtained from electrochemical impedance spectroscopy (EIS) assumes that, the charge transfer resistance ($R_{ct}$) is higher and the capacity of the double layer ($C_{dl}$) value
is lower for Zn–Ni–Al2O3 composite coating containing 50 g/l nano-alumina alloy compared with those of Zn–Ni matrix. This behavior is in good agreement with that obtained from Tafel plot measurements.

- The study of nucleation has determined the growth electrochemical processes in the first moments following an instantaneous nucleation mode in three dimensions (3D) controlled diffusional

![Fig. 7 Surface morphology of (a) Zn–Ni alloy coatings and (b) Zn–Ni–Al2O3 (30 g/l Al2O3) Composite coatings deposited at 30 mA/cm², T = 30 °C, and pH 3-4.5 for 60 s.](image-url)

References


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