CORROSION RESISTANCE CHARACTERISTICS OF Zn-Ni/SiO₂ COMPOSITE COATINGS

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ABSTRACT

Composite electrodeposits of Zn-Ni/SiO₂ were produced electrolytically using direct current. Their corrosion resistance characteristics were investigated through the use of neutral salt spray, linear polarisation resistance and potentiodynamic anodic polarisation methods. Neutral salt spray data shows that times to 5% red rust were longer for the coatings embedded with SiO₂ particles than those without particles. Effect of current density shows that deposits produced at higher current densities consistently exhibited a tendency to decrease in corrosion resistance. In addition, the linear polarisation resistance of coatings containing SiO₂ tends to increase with increasing particle content up to 5.5wt% SiO₂ and then decreases. However, there was no significant difference observed for the anodic dissolution current densities for coatings containing SiO₂ particles and their SiO₂-free counterparts. The mode of protection appears to be a combination of sacrificial and barrier protection to the underlying steel substrate.

KEYWORDS

Composite electrodeposition, corrosion resistance, SiO₂, nanoparticles

1 INTRODUCTION

Zn-Ni electrodeposition produces alloy coatings with optimum corrosion resistance when the alloy contains 12-15 wt% Ni [1]. Although known for their exceptional sacrificial protection, these alloys lose their protective abilities quickly when subjected to certain aggressive media, especially those which promote a high degree of wear [2]. Despite attempts to replace zinc-nickel alloys as sacrificial coatings on steel, concerted efforts have not led to significant alternatives and the former continues to maintain a predominant position as one of the most widely researched and utilized sacrificial coatings. The versatility of composite electrodeposition as a way of fabricating coatings with a combination of properties has aroused the curiosity of many researchers [3-6] in recent years. It has become an attractive way of improving the mechanical, chemical and physical properties of engineering components. In this manner, surfaces can be modified to obtain enhanced properties such as, magnetism [7], photocatalysis [8], corrosion resistance [9-17], hardness, electrocatalytic activity [12], wear resistance [18-21] and self lubrication [22] etc as a function of the type of second phase inclusion. Composite electrodeposition of Zn-Ni/SiO₂ coatings have also been reported [23,24]. In a recent study [16], it was reported that the anticorrosion properties and hardness of Zn-Ni-Al₂O₃ were improved compared to Zn-Ni alloy alone. However, this improvement does not depend only on the content of the particles but also on how well dispersed the particles are on the metal matrix as well as the matrix-particle bond strength. Other composite coatings containing SiO₂ particles for enhanced corrosion resistance have also been reported [25].

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Although the corrosion resistance of Zn-Ni has been widely reported [26-33], there appears to be limited investigations on the corrosion resistance characteristics of their composite electrodeposits. The object of this paper is therefore, to present findings of a study on the corrosion resistance behaviour of Zn-Ni/SiO$_2$ composite electrodeposits.

2 MATERIALS AND METHODS

2.1 Production of coatings.

The composite coatings were produced from acid sulphate Zn-Ni/SiO$_2$ baths made from standard laboratory reagents. Bath composition is as shown in Table 1.

<table>
<thead>
<tr>
<th>Bath formulation</th>
<th>Concentration (g/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSO$_4$.7H$_2$O</td>
<td>57.5</td>
</tr>
<tr>
<td>NiSO$_4$.6H$_2$O</td>
<td>131</td>
</tr>
<tr>
<td>Na$_2$SO$_4$.10H$_2$O</td>
<td>162</td>
</tr>
<tr>
<td>SiO$_2$ (20 nm)</td>
<td>13-52</td>
</tr>
</tbody>
</table>

Silica (SiO$_2$) particles of approximately 20 nm in aqueous suspension were used (from Alfa Aesar). Agitation was effected using vibro-agitation with a vibromixer [34]. The diameter of the perforated plate attached to the vibromixer, which effected the agitation was 4.5 cm. A Zenith Variac supplied power to the vibromixer.

Coatings were electroplated onto mild steel after the mild steel panels were cathodically cleaned in an alkaline bath containing 25.0 g/l of NaOH, 25.0 g/l of Na$_2$CO$_3$ and 50.0 g/l of Na$_3$PO$_4$ and etched in 50 vol.% (S.G 1.18) hydrochloric acid for approximately 20 seconds, washed in running tap water and then in deionised water. They were then transferred immediately into the bath for electroplating to avoid re-oxidation of the surface. All the electrodeposition experiments were carried out galvanostatically using DC currents and 99% zinc foil as anode.

Coating compositions and morphologies were analysed using Scanning Electron Microscope (SEM) and a Field Emission Gun Scanning Electron microscope (FEGSEM) both fitted with an energy dispersive analysis (EDX) facilities. Weight percent of silicon in the deposits was analysed with the EDX analyser and converted to the weight percentage of silica.

2.2 Neutral salt spray test

Neutral salt-spray corrosion investigations were conducted according to ASTM B117. An C and W Equipment Ltd, salt-spray cabinet, model number SF 450-CASS under constant humidity conditions, at 35 °C and in a 5wt% sodium chloride solution was utilised. All coatings tested had a nominal thickness of 8 µm. The edges of each sample were securely masked with inert tape. Effective surface area of samples exposed to the salt fog was approximately 50 cm$^2$. Time to 5% red rust was used to describe the level of corrosion resistance of each sample.
2.3 Linear polarisation resistance studies

Linear polarisation resistance (LPR) studies were conducted for Zn-Ni alloys, with different amounts of silica particles. Polarisation was achieved using an ACM Instruments computer controlled potentiostat, model Auto Tafel HP, linked to a personal computer. Each test was carried out on a panel blanked off with chemically inert tape to expose an area of 10 cm$^2$ (2.5 cm x 4 cm). These panels were then immersed in 350 ml of fresh 5wt% NaCl solution and left for approximately 25 minutes to allow an equilibrium state to be obtained within the test cell, before polarisation. Each sample was polarised from -25 mV to +25 mV either side of its open circuit potential at a scan rate of 6 mV/min. The reference electrode was a Russell SRR5 saturated calomel supplied with a salt bridge. A sheet of platinum foil 25 cm$^2$ (5cm x 5cm) was used as the counter electrode.

2.4 Anodic polarisation

Apparatus used for the anodic polarisation experiments was the same as that utilised for the linear polarisation resistance studies. The counter electrode material was platinum and the volume of electrolyte was 350 ml in each case. These investigations were conducted on Zn, Zn-Ni, and Zn-Ni/SiO$_2$ composite electrodeposits. The electrolyte was 5wt% NaCl solution. The sample surface area was 0.8 cm$^2$. Prior to polarisation, samples were allowed to equilibrate for approximately 25 mins. On attaining an equilibrium rest potential, samples were polarised from -50 mV cathodic to the rest potential to a potential of 1500 mV anodic with a sweep rate of 120 mV/min.

3 RESULTS AND DISCUSSION

3.1 Neutral Salt spray performance

Figs 1 and 2 are salt spray data for Zn-Ni/SiO$_2$ coatings produced from similar baths and electrodeposition conditions with and without bath agitation. In both figures, the results indicate that time to 5% red rust was longer for coatings produced from baths with 26g/l of SiO$_2$ particles with or without bath agitation.
Figure 1. Influence of current density on the corrosion resistance of Zn-Ni and Zn-Ni/SiO$_2$ electrodeposits produced from baths without agitation but containing (A) 0 g/l SiO$_2$ and (B) 26 g/l SiO$_2$.

Figure 2. Influence of current density on the corrosion resistance of Zn-Ni and Zn-Ni/SiO$_2$ electrodeposits produced from baths with agitation and containing (A) 0 g/l SiO$_2$ and (B) 26 g/l SiO$_2$. Vibratory agitation amplitude 0.64mm.

Furthermore, the influence of a higher bath concentration of particles was investigated using 52 g/l of SiO$_2$ with similar conditions as those in Figs 1 and 2. The results as presented in Figs 3 and 4 shows that samples produced from baths containing silica particles exhibited better corrosion resistance behaviour than those without particles. This tends to corroborate previous work [35] suggesting that the rate of corrosion of electrodeposited zinc in near-neutral chloride solutions can be lowered by as much as 75% by adding fine inert particles to a well stirred solution which tends
to stop the spread of local areas of etching. It might be reasonable to suggest that this effect could even be greater if such particles are embedded in the zinc coating itself. The overall trend above shows that samples produced from baths containing silica particles exhibited better corrosion resistance than those from baths without particles.

Figure 3. Influence of current density on the corrosion resistance of Zn-Ni and Zn-Ni/SiO$_2$ electrodeposits produced from baths without agitation but containing (A) 0 g/l SiO$_2$ and (B) 52 g/l SiO$_2$.

Figure 4. Influence of current density on the corrosion resistance of Zn-Ni and Zn-Ni/SiO$_2$ electrodeposits produced from baths with agitation and containing (A) 0 g/l SiO$_2$ and (B) 52 g/l SiO$_2$. Vibratory agitation amplitude 0.64 mm.
In addition, Figs 1-4 shows the effect of cathode current density on the time to 5% red rust for coatings from baths with either 26g/l or 52g/l SiO\textsubscript{2}. The overall trend indicates a decrease in the time to 5% red rust beyond 5A/dm\textsuperscript{2}. Apart from the influence of Ni and SiO\textsubscript{2} contents in the coating, this consistent decrease in corrosion resistance beyond 5A/dm\textsuperscript{2} appear to be associated with coating porosity due to high current densities. The reason that coatings deposited at highest current densities exhibited lower corrosion resistance is that they had higher levels of coating porosity [33]. Higher current densities tend to form not very compact layers often containing voids and agglomeration of grains of different sizes and shapes [1]. This behaviour was attributed to the nucleation of Zn crystal [1]. Table 2 shows the corrosion resistance data for Zn and Zn-12%Ni and Zn-12%Ni/SiO\textsubscript{2} coatings with different contents of silica particles. Zn-Ni alloy coating with 12 wt% Ni was chosen as it falls within the range of 10 to 15% Ni for best sacrificial protection [1, 29]. The results show that corrosion resistance of Zn-Ni coatings with 12% Ni appears to increase with increase in the particle content up to 5.5wt% SiO\textsubscript{2} and then decreases. The enhanced corrosion resistance behaviour of these coatings is probably due to support of corrosion products in the presence of particles [11]. As evident from Figs 1-4 coatings produced from the bath without agitation showed better corrosion resistance than those with agitation. This appears to be an issue of the amount of particle incorporation. For the bath with agitation, it appears agitation was detrimental to particle incorporation probably due the nanometric size of the particles and may have been due to their residence time at the interface of the cathode for incorporation. Residence time of particles on the surface of the cathode for incorporation is crucial as reported in a previous work [13]. Also, the incorporation of particles into the Zn-Ni matrix may have modified its microstructure to a nanocrystalline form. The main morphological changes usually observed for Zn-Ni alloys depends on the additive used and stirring conditions [1].

Table 2 Relationship between Ni and SiO\textsubscript{2} contents in the deposit with time to 5% red rust

<table>
<thead>
<tr>
<th>Type of coating</th>
<th>Time to 5% red rust (hours)</th>
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<tbody>
<tr>
<td>Zn</td>
<td>40</td>
</tr>
<tr>
<td>Zn-12% Ni</td>
<td>502</td>
</tr>
<tr>
<td>Zn-12% Ni-3.3% SiO\textsubscript{2}</td>
<td>685</td>
</tr>
<tr>
<td>Zn-12% Ni-4.2% SiO\textsubscript{2}</td>
<td>716</td>
</tr>
<tr>
<td>Zn-12% Ni-5.0% SiO\textsubscript{2}</td>
<td>740</td>
</tr>
</tbody>
</table>

3.2 Linear polarisation resistance studies

A limited amount of information can be obtained using neutral salt spray test data hence electrochemical techniques are useful in providing supplementary data [36].

Table 3 Linear polarisation resistance data for Zn-Ni/SiO\textsubscript{2} composite coatings with 12%Ni in 5% NaCl solution

<table>
<thead>
<tr>
<th>20 nm Silica in deposit (wt%),</th>
<th>Average polarisation resistance (Ω/cm\textsuperscript{2})</th>
<th>Average open-circuit potential (mV vs. SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.2</td>
<td>810</td>
<td>-996</td>
</tr>
<tr>
<td>3.5</td>
<td>873</td>
<td>-983</td>
</tr>
<tr>
<td>5.5</td>
<td>1100</td>
<td>-949</td>
</tr>
<tr>
<td>6.0</td>
<td>962</td>
<td>-984</td>
</tr>
</tbody>
</table>
The results presented in Table 3 shows values of the open circuit potential and linear polarisation resistance data for Zn-Ni/SiO$_2$ composite coatings containing 12 wt%Ni. Although not a strict linear relationship, it is evident from this table that there is a tendency for the linear polarisation resistance to increase to a maximum value of 1100 $\Omega$/cm$^2$ at a particle content of 5.5% and then decreases with further increase in the particle content of the coating. Also, at the maximum LPR of 1100 $\Omega$/cm$^2$, the open circuit potential was -949 mV vs SCE being more anodic than the open circuit potentials of both the coatings with lower and higher particle contents. The OCP being more cathodic on both sides of -949mV is an indication of the possible presence of biphasic structures in the coating that may contain hexagonal phase of Zn and $\gamma$-Ni$_5$Zn$_2$. The greater the hexagonal phase in the coating the lower its OCP value [1]. The overall trend indications that the coating with an LPR of 1100 $\Omega$/cm$^2$ and OCP of -949 mV vs SCE was better corrosion resistant than the others. The tendency for the LPR to decrease at higher particle content could also be due to porosity. During linear polarisation the corrosion current is inversely proportional to the linear polarisation resistance [37]. Generally it is expected that the higher the amount of inert components in the composite system, the less reactive such a system could become which could lead to lower dissolution rates and consequently better corrosion resistance. However, this may not always be the case as evident from Table 3, especially if there are porosities and the interfacial bonds between the particles and the metal matrix are weak and incapable of holding the particles in place. Coating porosity is a possibility at relatively high particle contents in composite coatings (see Fig. 7)

### 3.3 Anodic polarisation studies

Fig. 5 shows the anodic polarisation behaviour of Zn, Zn-Ni and Zn-Ni/SiO$_2$ coatings labelled A, B and C respectively. The corrosion potentials of Zn-Ni and Zn-Ni/SiO$_2$ coatings were slightly more anodic than that of zinc up to the maximum dissolution current densities. The dissolution behaviour of Zn-Ni and Zn-Ni/SiO$_2$ shows that the open circuit potentials of these coatings are quite close initially but as the applied potential is increased, that of Zn-Ni/SiO$_2$ tends to shift slightly towards more anodic potentials than the Zn-Ni coatings. Similar observations were reported elsewhere in the literature [16]. The overall trend appears to indicate that the corrosion resistance of Zn-Ni and Zn-Ni/SiO$_2$ are likely to be better than that of pure Zn. However, at a potential of approximately -500 mV (SCE), it appears the corrosion rate of Zn seems to be lower than Zn-Ni and Zn-Ni/SiO$_2$ due to the evident passivation behaviour. The trend between Zn-Ni and Zn-Ni/SiO$_2$ curves indicates that the presence of SiO$_2$ particles may have promoted shifting of the dissolution potential of the Zn-Ni/SiO$_2$ coatings towards more anodic values than for the Zn-Ni coatings without particles probably due to the inertness of the SiO$_2$ particles. Similar influence of SiO$_2$ on other composite systems has been reported elsewhere in the literature [25]. A number of reasons could be responsible for such behaviour; (i) apart from being incorporated in the deposit; presence of SiO$_2$ in the bath probably changed the deposition mechanism of Zn-Ni which could lead to changes in deposit texture, morphology and microstructure. Presence of particles in the electrodeposition bath is known to affect the microstructure of the coatings and their corrosion resistance [35], (ii) as inert particles they are able to provide barrier protection to the zinc matrix by filling crevices, gaps and microholes [38] and (iii) support corrosion products [15].
Fig 5. Anodic polarisation curves for coatings produced from (A) Zn (B) Zn-Ni and (C) Zn-Ni/SiO₂ baths

Fig 6 shows the corrosion trend of coatings produced at different current densities from a bath with 26g/l and 52g/l of SiO₂ respectively. A unique trend in this fig shows that the corrosion resistance of coatings produced at 3A/dm² from the bath with a higher concentration of particles were lower than that with a lower concentration of particles with or without agitation. However, above 3A/dm², coatings produced from a higher bath concentration of particles exhibited better corrosion resistance. A number of reasons may be responsible for this behaviour. The lower corrosion resistance behaviour at 3A/dm² for coatings from the bath with 52 g/l SiO₂ may not be unconnected with high levels of particle incorporation at this current density as reported in our previous work [2]. At a current density of 3A/dm², SiO₂ contents of approximately 8wt% and 12wt% were reported [2] for coatings produced from baths with 26g/l and 52g/l of SiO₂ without bath agitation and approximately 2wt% and 5.5wt% with bath agitation. Values of 8wt% and 12wt% incorporation are quite high for nanosize particles. Comparing the aforementioned to Table 3, 5.5wt% SiO₂ appears to be the optimum value for maximum corrosion resistance in the present investigations. It is worthy of note that excessively high levels of particle in the coating could cause stress and cracks; leaving porous sites for the ingress of corrosive species especially if these cracks are quite substantial as seen in fig 7c. However, this may not always be the case as initial corrosion products of Zn and Zn-Ni such as ZnO and Zn(OH)₂ are known for their low capacitance [33] and could get deposited in these cracks and provide further stifling effect to the coatings thereby enhancing further corrosion resistance.
3.4 Influence of morphological changes on the corrosion resistance

Morphological changes which are closely related to deposit microstructure plays a crucial role in the corrosion resistance behaviour of Zn-Ni/SiO\textsubscript{2}. Fig 7A, B and C shows morphologies of Zn-Ni, Zn-11%Ni1%SiO\textsubscript{2} and Zn-11%Ni11%SiO\textsubscript{2} respectively. With the incorporation of SiO\textsubscript{2} particles into the Zn-Ni matrix, there is evident transformation of the morphology to that which contains small irregular shaped crystallites (see Fig. 7B) with a particle content of about 1% SiO\textsubscript{2}. The incorporation of SiO\textsubscript{2} particles appears to have reduced the crystal size [39] of the Zn-Ni matrix consequently producing fine grains. Finer grain sizes synergistically provides better corrosion resistance [33]. However, as evident from Fig. 7C, further increase in particle content of the coatings up to 11% SiO\textsubscript{2}, becomes detrimental to the integrity of the coatings as cracks are initiated which could become potential sites for the ingress of corrosive species. These changes may not only be due to particle incorporation but also as a result of changes in the electrocrystallisation mechanism. Difference in morphological changes under agitation and quiescent modes has been attributed to nucleation and growth processes, likely controlled by either charge transfer or mass transfer reactions depending on the prevalent conditions during the deposition [40] process.
Figure 7. SEM micrographs showing morphologies of (A) Zn-11\%Ni (B) Zn-11\%Ni 1\%SiO₂ (C) Zn-11\%Ni-11\%SiO₂. SiO₂ (20 nm)
4.0 Conclusions

- The electrolytic incorporation of SiO$_2$ particles in a Zn-Ni matrix was found to improve the corrosion resistance of these coatings. The corrosion resistance tends to increase with increasing particle content of the deposit.
- For all the deposition conditions investigated, the overall trend shows that the corrosion resistance of samples produced from the baths containing SiO$_2$ particles were higher than those without particles in the bath.
- The linear polarisation resistance of the coatings tends to increase with increase in SiO$_2$ particle content to a maximum and then decreases.
- The anodic dissolution potential of Zn-Ni/SiO$_2$ appears to shift towards more positive values than Zn-Ni coatings indicating a tendency for better corrosion resistance than Zn-Ni.
- Bath agitation appears detrimental to the corrosion resistance of the coatings in the prevalent experimental conditions.
- Unlike Zn and Zn-Ni whose mode of protection is mainly sacrificial, the mode of protection offered by Zn-Ni/SiO$_2$ appears to be a combination of sacrificial and barrier protection.

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REFERENCES