NON-ANOMALOUS NI-ZN COATINGS FOR THE CORROSION PROTECTION OF STEEL - AS A REPLACEMENT FOR CADMIUM COATINGS

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A novel technique for obtaining non-anomalous Ni-Zn coatings with high Ni content (72-wt% as compared to 15-20 wt% in conventional Zn-Ni deposition) has been developed. Ni-Zn coatings were cathodically deposited from alkaline sulfate electrolytes in the presence of complexing agents and additives. The Zn content in the coating was optimized based on the corrosion resistance and corrosion potential of the final deposit. The higher amount of nickel content in the deposit induces barrier properties and the presence of zinc helps to maintain the sacrificial nature of the coating. Corrosion potential of the optimized Ni-Zn alloy was –0.678 V vs. SCE. This low potential is a result of the decreased Zn content in the deposit. Deposition parameters such as applied potential and pH have been optimized based on composition of the coating and the surface morphology. Corrosion studies show that Ni-Zn coatings obtained using this method show a higher barrier resistance and better stability as compared to Cadmium coatings.

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INTRODUCTION

Steel substrates are electrodeposited with sacrificial coatings for corrosion protection. Zn, Zn-Ni, Zn-Co and Cadmium alloys are some of the widely used sacrificial coatings [1-8]. Among them cadmium coatings are considered very reliable owing to their superior corrosion and engineering properties [2]. But the cadmium coatings are highly toxic and they are generally prepared from toxic cyanide baths [3]. Also cadmium plating introduces large amount of hydrogen in the underlying substrate and thus increases the susceptibility of the substrate to hydrogen embrittlement [4]. Growing ecological concerns in recent years have led to the search for an alternative coating that can effectively replace cadmium coatings. Zinc deposits exhibit excellent sacrificial behavior. However, a high dissolution rate and poor mechanical properties limit the use of Zn coatings in the automotive industry. Alloying of zinc with noble metals like nickel has proved to increase the corrosion resistance and mechanical properties of zinc coatings. Zn-Ni alloys are considered as a viable alternative to cadmium coatings [6-11]. Zn-Ni alloys containing 15 - 20 wt% of nickel possess four times more corrosion resistance than cadmium-titanium coatings [12]. Although zinc is less noble than nickel, the electrodeposition of Zn-Ni results in the preferential deposition of the zinc and a higher amount of zinc is observed in the final deposit. Therefore, Brenner classifies Zn-Ni codeposition as anomalous [13]. The mechanism for the preferential deposition of Zn has been discussed extensively in literature [13,14]. Due to the higher percent of zinc in the coating, these alloys are more electronegative than cadmium and hence dissolve rapidly in corrosive environments. Any further increase in nickel composition is based on using a higher than predicted Ni/Zn ratio in the bath [15,16]. Though Zn-Ni alloys have good corrosion resistance in comparison with Zn coating, further development for better coating and corrosion characteristics is of commercial interest. An enhancement in the nickel composition of these alloys would lead to more anodic open circuit potential, which will in turn reduce the driving force for galvanic corrosion. Also the barrier properties of the coating increases with increased nickel content in the deposit. Several attempts have been made earlier to decrease the anomaly and increase the nickel content by either introducing an inert species in the bath or by developing a ternary alloy [17-24]. Nonyl phenyl polyethylene oxide (NPPO) has been used to reduce the Zn-Ni ratio and produce more corrosion resistant deposits. NPPO inhibited zinc electrodeposition and acted as a leveling agent as seen in our earlier studies on the deposition of zinc and galvanostatic pulse and pulse reversal plating of Zn-Ni alloys from sulfate electrolytes[20,21].

Codeposition of phosphorous along with Zn-Ni alloy improves the corrosion resistance [17] and hydrogen permeation [18] characteristics of the deposit. Zhou et al [19] have studied the effect of tin additions on the anomalous deposition behavior of Zn-Ni alloys. The nickel ratio increased from 6 to 8 % with the addition of small amounts of tin. Earlier, we have developed a novel plating process for the electrodeposition of Zn-Ni-Cd coatings [22-24]. It was found that use of small of ternary alloying elements like cadmium can effectively control the Zn-Ni ratio. Cadmium codeposition was observed with a significant decrease in the Zn-Ni ratio. The Zn-Ni ratio [24] was as low as 1.7:1. Also the corrosion resistance of the coating was improved by an order of magnitude when compared to that of commercial Zn-Ni and cadmium coatings. The inclusion of ternary element like cadmium prevented the hydrogen entry in to the substrate as compared to the Zn-Ni alloy and cadmium coatings [23]. However, the use of the cadmium salts in the bath poses ecological concerns.

Autocatalytic reduction of metals and alloys offers an attractive and alternate method of increasing the amount of Ni in the final deposit. In our earlier study [25], we developed Ni-Zn-P composites using electroless method with enhanced Zinc content in the alloy. Such an approach ensured that the coating exhibit sacrificial properties by virtue of its zinc content while the presence of high Ni content provided extended life in corroding media. It has also been previously observed [26] that Zn is co-deposited during potentiostatic deposition from a Zn-Ni bath in the potential range –0.7 to–0.9 V vs. Ag/AgCl. This produces a non-anomalous coating with 70-wt% Ni. [16]. However, the deposits have high stresses and poor adhesion in such cases and hence cannot be used as a protective coating. Further, as the applied potential is increased, the deposition becomes anomalous and the deposits contain 85-wt% Zn. In this study, we tried to develop similar Ni-Zn composites with high Ni content using an electrodeposition technique. Hence, the present study focused on developing non-anomalous Ni-Zn coatings that will provide sacrificial protection to steel and have low dissolution rates. The corrosion characteristics of these newly developed composite coatings have been compared to that of cadmium.

EXPERIMENTAL

Sample Preparation: Plating and subsequent corrosion studies were done on low carbon cold-rolled steel foils of thickness 0.5 mm and area 25 x 25 mm. Initially, the steel sample was mechanically polished with successive finer grades of emery paper. The samples were then degreased with alcohol and rinsed with de-ionized water. Next, the samples were treated in 10 % (v/v) H_2SO_4 solution for 1 minute to remove any adherent oxide layer present on the surface. Finally, the samples were again washed in de-ionized water. This procedure was repeated until a clean and smooth surface was obtained.

Electrolyte preparation and deposition: Ni-Zn composites were prepared from a bath of alkaline sulfate electrolytes similar to the bath used in our electroless process [15]. Sodium citrate and ammonium chloride were used as complexing agents to prevent Ni and Zn from precipitating at an alkaline pH. Steel foil prepared as mentioned above was used as the substrate. Ni-Zn coatings with different amounts of Zn were obtained by varying the applied potential and also by varying the amount of $ZnSO_4.7H_2O$ in the bath. The deposition was carried out at 80 ^oC unless otherwise mentioned. The pH was maintained at 10.5 during the deposition by the addition of NaOH. All solutions were prepared with analytical grade reagents (obtained from Sigma-Aldrich) and triply distilled water. The deposition time was changed according to the required thickness of the coating.

Material Characterization: Energy Dispersive Analysis using X-rays (EDAX) was used to analyze the distribution of the elements in the final deposit. To ensure accuracy of the element distributions, EDAX analysis was done at several points on the surface of the substrate. The accuracy of the measurements for the equipment used was rated as ±0.1-wt%. The surface morphology and the microstructure of the coating were analyzed using Scanning Electron Microscopy with the help of Hitachi S-2500 Delta Scanning Electron microscope.

Electrochemical Characterization: A variety of electrochemical techniques including Linear and Tafel polarization were used to evaluate the barrier resistance properties of the coating. Since chemical dissolution of Zn occurs in both acidic and alkaline media, corrosion testing was performed in 0.5 M Na_2SO_4 and 0.5 M H_3BO_3 solution at pH 7.0. The electrochemical characterization was done using an EG&G PAR model 273A potentiostat/galvanostat interfaced with a computer and a three-electrode setup. The steel substrate with the coating was used as the working electrode and a platinum mesh was used as the counter electrode. A standard calomel electrode (SCE) was used as the reference electrode. All potentials in this study are referenced to the SCE.

RESULTS AND DISCUSSION

Effect of Zn^{2+} ions on the coating composition:

The primary objective of this work was to obtain a sacrificial coating for the protection of steel. Hence it is essential to estimate the amount of Zn in the final deposit. EDAX analysis was used for this purpose. Depositions were carried with different concentrations of $ZnSO_4.7H_2O$ in the bath for 1 hr. Figure 1 shows the distribution of Zn and Ni in the coating as a function of $ZnSO_4$ added in the bath. It can be seen from the plot that the Zn content in the deposit increases from 23-wt% in the case of 5 g/L $ZnSO_4$ to 30-wt% in the case of 20 g/L $ZnSO_4$. The amount of Ni decreases from 77-wt% to 70-wt% with increase of $ZnSO_4$ concentration in the bath. It can also be seen from the graph that the composition does not undergo any significant change after a $ZnSO_4$ concentration of 15 g/L. However, the surface morphology of the coatings was seen to improve with $ZnSO_4$ concentration in the bath. The coating obtained at a $ZnSO_4$ concentration of 5 g/L shows cracks on the surface while the deposit obtained at a concentration of 15 g/L shows a uniform deposit. Since the variation in Zn content, deposition rate and the morphological changes are negligible for the deposits obtained at a higher $ZnSO_4$ concentration than 15 g/L, the $ZnSO_4$ concentration was optimized at 15 g/L.

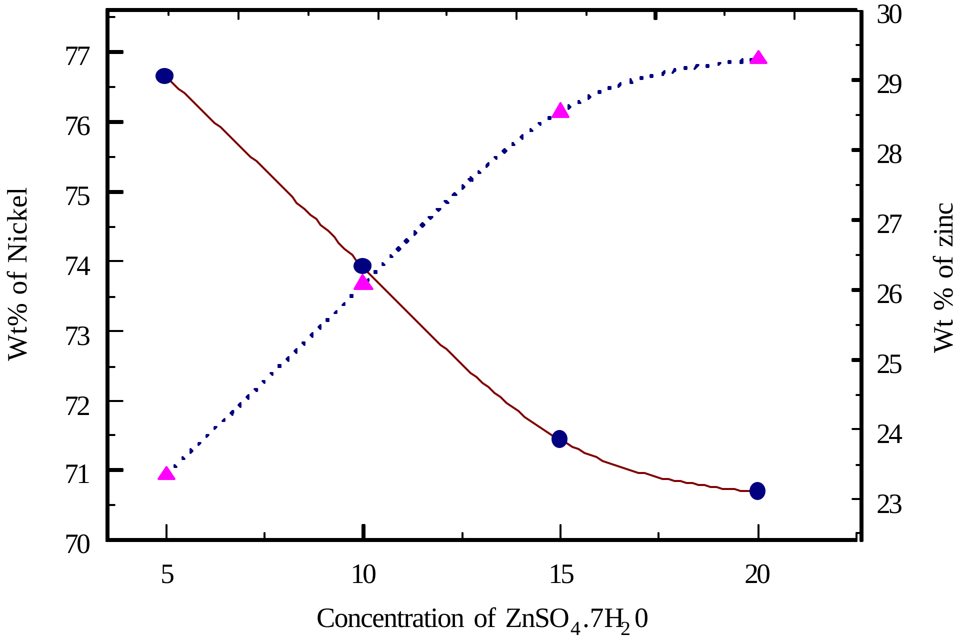

Figure 1. Variation in the composition of Ni-Zn composites as a function of $ZnSO_4.7H_2O$ in the bath.

Effect of Applied Potential:

Figure 2 shows the variation in the thickness of the coating as a function of the applied potential. The thickness of the coatings was estimated by dividing the weight of a unit area with the average density of the alloy. The density used in these calculations is found out by the weighted average of the density of the constituents in the coating, as found from EDAX analysis. From Figure 2, for an applied potential of –1.0 V *vs*. SCE, the thickness of the deposit obtained is very low (0.5 µm). It can be observed that an increase in the applied potential leads to an increase in the thickness of the deposit. EDAX analysis results in detecting elemental distribution to a depth of 1 µm. If the coating thickness is less than 1 µm, the underlying substrate constituents are also detected. At an applied potential of –1.0 V *vs*. SCE, the coating thickness is less than 1 *m*m and hence Fe is detected (as seen in Fig.3). However, with an increase in applied potential, the Fe content decreases and reaches a value of <0.1-wt% for potentials greater than –1.0 V vs. SCE. This trend shows that operating at a potential of –1.1 V gives rise to uniform coatings with thickness greater than 1 *m*m.

Figure 3 shows the variation in the composition of the coating as a function of applied potential. We can clearly see from the graph that with an increase in the applied potential, the amount of Zn in the deposit starts to increase.

The reduction of Nickel ion occurs according to the reaction [27],

$$Ni^{2+} + 2e^{-} \rightarrow Ni \qquad E_0=-0.53 \text{ V } vs. \text{ SCE} \qquad (1)$$

The reduction of Ni ions is accompanied by the hydrogen evolution reaction [27],

$$2H^{+} + 2e^{-} \rightarrow H_{2} \qquad E_0 = -0.28 \text{ V } vs. \text{ SCE} \qquad (2)$$

The reduction of Zn proceeds according to the following reaction [27]

$$Zn^{2+} + 2e^{-} \rightarrow Zn \qquad E_0 = -1.043 \text{ V } vs. \text{ SCE} \qquad (3)$$

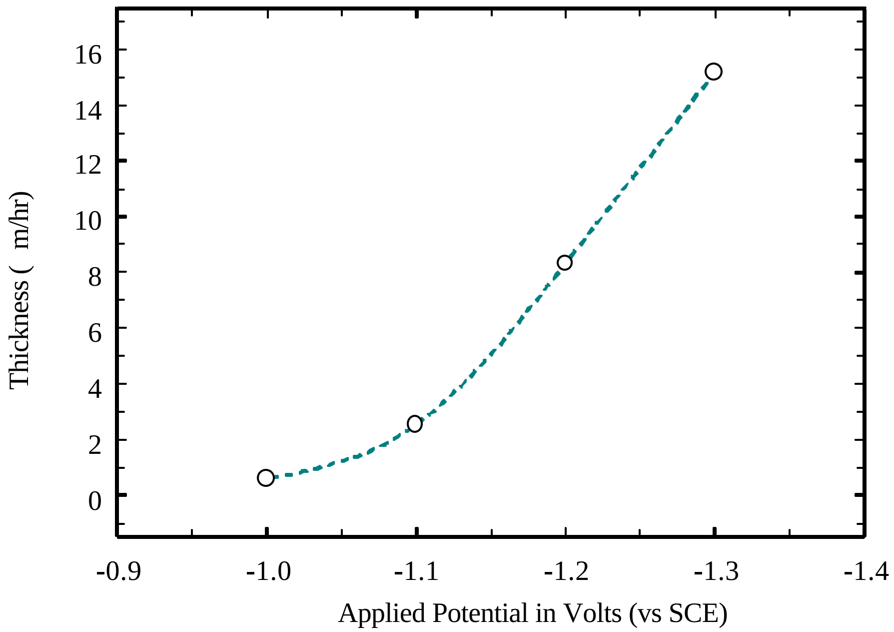

Figure 2. Variation in the thickness of the coatings obtained as a function of applied potential for deposition.

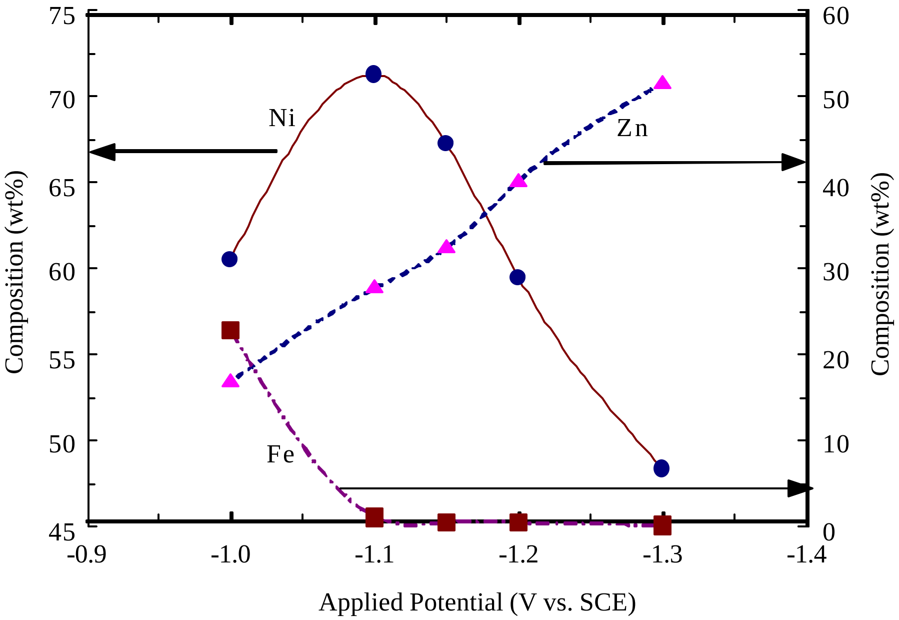

Figure 3. Change in the composition of the coating as a function of applied potential.

Figure 3 shows that at an applied potential of -1.0 V vs. SCE, the deposits obtained contains a Zn content of 17-wt%. Due to thermodynamic considerations Zn deposition through Zn^{2+} ion reduction is not possible at these potentials. However, Miranda *et. al.* [28] have observed that the formation of Ni rich phase in Zn-Ni alloy occurs at low potentials through the formation and subsequent reduction of $ZnNi^{+}_{ad}$ species. This observation tends to suggest that a similar phenomenon occurs in our Ni-Zn deposition. Our present studies are focused on understanding the mechanism of Zn inclusion in the deposit. In the present paper, studies on optimizing the deposition parameters for the non-anomalous Ni-Zn deposits are presented. Increasing the deposition potential leads to an increased amount of Zn in the deposit, suggesting that the deposition becomes more anomalous in nature. A similar trend was observed by Roventi *et. al.* [26], wherein they obtained non-anomalous Ni-Zn deposits at low potentials (-0.7 to -0.9 V vs. Ag/AgCl). However, they have also observed that the deposits obtained at such low potentials have high stress and result in powdery deposits with poor adhesion. Hence, such deposits cannot be used as a sacrificial coating. However, in our case, at low potentials, no cracks were observed on the coating. It was also observed that the increase in potential leads to higher amount of stress in the deposit and cracks appear on the surface. This result is shown in Figure 4, where the coating obtained at an applied potential of -1.1 V vs. SCE has an uniform surface morphology while the coating obtained at a potential of -1.3 V shows excessive cracking. Figure 3 shows that with increasing applied potential, the Zn content in the deposit increases while Figure 4 shows that with increase in the applied potential, the coating becomes cracked. Hence it is essential to optimize the applied potential based on the corrosion characteristics of the coatings.

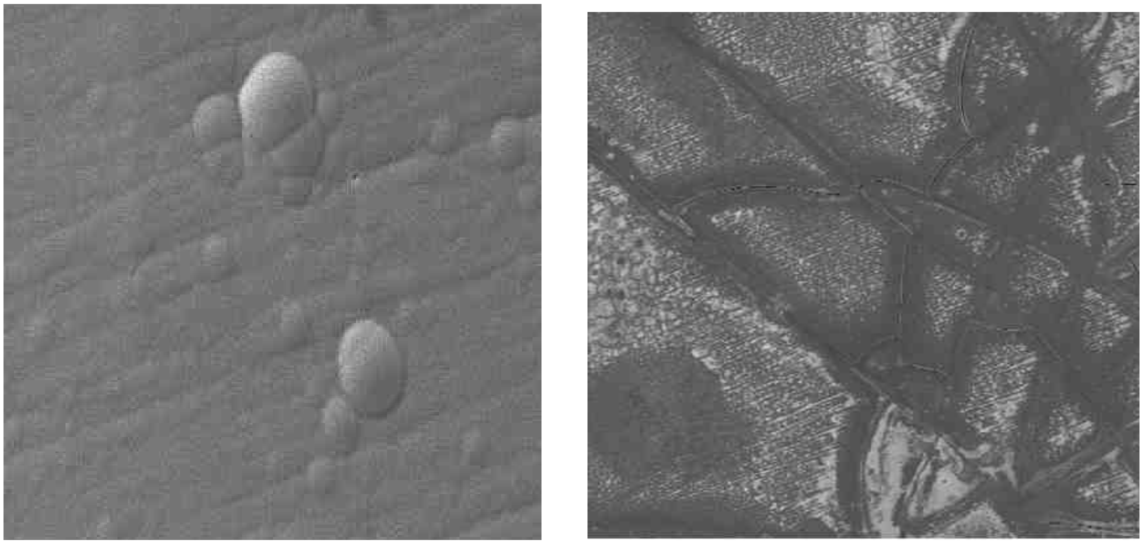

Figure 4. Change in the morphology of the coatings prepared at (a) 1.1 V and (b) 1.3 V

To check the suitability of the coating as a sacrificial layer, the corrosion characteristics of the coatings were tested in a 0.5 M Na_2SO_4 + 0.5 M H_3BO_3 solution at pH 7.0. Tafel polarization was performed to evaluate the corrosion rates of the coatings with different Zn contents. Tafel studies were carried out by scanning the potential from –200 mV to +200 mV with respect to the corrosion potential at a scan rate of 10 mV/s. The resultant Tafel plots are shown in Figure 5. As shown in the plot, the corrosion current of the deposits increases with increase in the amount of Zn content in the deposit. This is due to the fact that with higher amounts of Zn in the deposit, the dissolution rate of the alloy is increased. However, it has to be noted that the corrosion potential shifts to a more negative value with increase in Zn content. Table I summarizes the corrosion potential and the corrosion rate of the coating as a function of Zn content in the deposit. The corrosion characteristics of the coatings obtained at a potential of -1.0 V has not been shown as these coatings did not uniformly cover the surface (as shown by the high Fe content detected for such deposits in Figure 4). For the other coatings, even though the corrosion current density increases from 2.5 $\mu A/cm^2$ (for Ni) to 8.6 $\mu A/cm^2$ (for 28% Zn-72%Ni), the corrosion potential becomes more electronegative (-0.67 V vs. SCE) to steel. Deposits obtained at potentials greater than –1.1

V show a further increase in the corrosion potential as compared to steel. However, their corrosion current density also increases as shown in Table I. Hence, from the Tafel polarization studies, the optimized Zn content in the deposit is seen to be 28-wt%. Hence, the rest of the depositions were carried out at the optimized deposition potential of –1.1 V *vs.* SCE

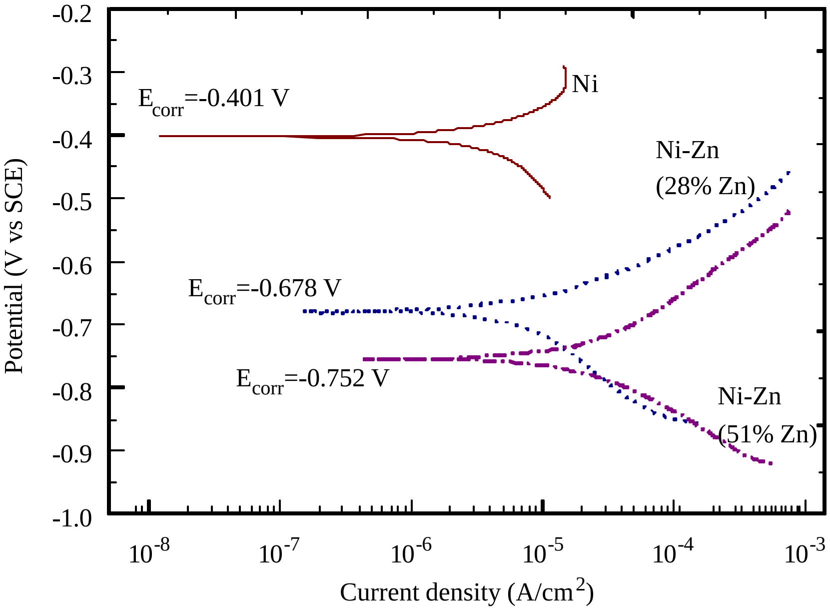

Figure 5. Tafel analysis of the Ni-Zn composites as a function of Zn content in the final deposit. The corrosion potential becomes more electronegative as more Zn is included in the deposit

Table I.Variation in Corrosion potential and Corrosion current density As a function of Zn content in the coatings

Zn content in the deposit (wt %)	Corrosion potential E_{corr} (V vs. SCE)	Corrosion current density I_{corr} (A/cm^2)
0	-0.401	2.5 x 10^{-6}
28	-0.678	4.8 x 10^{-6}
31	-0.695	6.1 x 10^{-6}
40	-0.722	8.6 x 10^{-6}
52	-0.752	1.5 x 10^{-5}

Effect of pH on the coating composition:

Another critical parameter that can affect the composition of the coating is the pH of the deposition bath. To understand the effect of pH, experiments were performed at different pH values in the range of 8.5-11.5. Increasing the pH beyond 11.5, results in the spontaneous precipitation of the bath.

Figure 6 shows the morphology of the coatings prepared at pH values of 8.5 and 10.5. The SEM pictures show that the depositions carried out at a pH value of 8.5 gives rise to coatings that has high internal stress and thus resulting in the cracking of the coating.

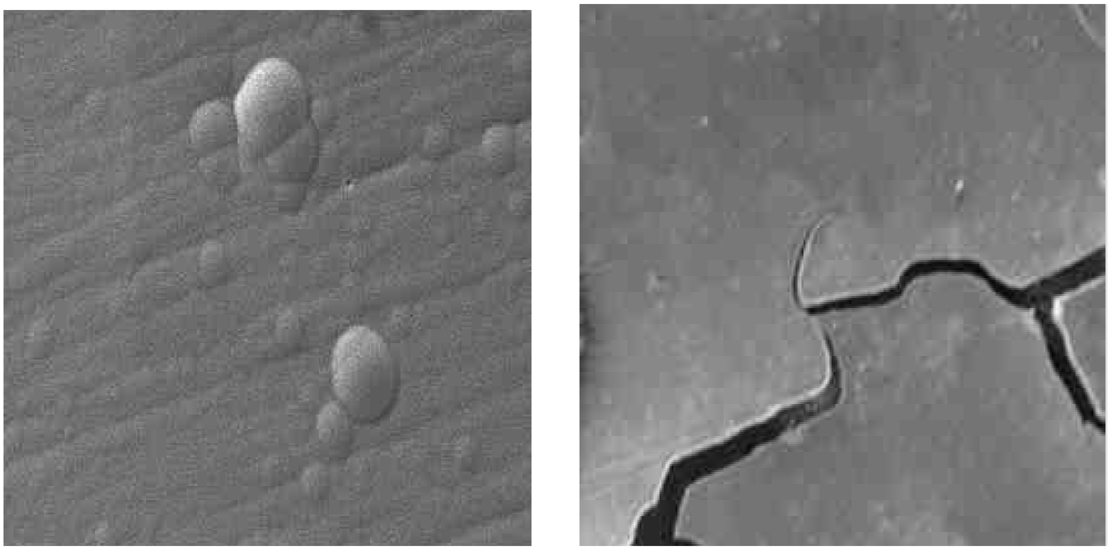

Figure 6. Morphology of the coatings prepared at (1) pH 8.5 @ 500 X and (b) pH 10.5 @ 1000 X

The SEM pictures show that the deposition at pH 10.5 results in the deposition of uniform coating across the entire surface. Increasing the pH values also results in deposits similar in morphology (picture not shown here). The pH of the operating bath plays a significant role in the composition of the deposit. Increase in the pH leads to an increase in the Zn content in the deposit. At a pH of 8.5, the Zn content in the deposit was as low as 12 %. An optimal amount of Zn in the deposit is essential to maintain the sacrificial properties of the coating. The amount of Zn in the deposit is at a maximum at pH of 10.5 for an applied potential of 1.1 V vs. SCE. Since coatings obtained at pH 10.5 have an optimum amount of Ni and Zn, they result in coatings with high corrosion resistance and optimum electronegative potential sufficient enough to offer sacrificial protection to steel. Hence the bath pH was optimized at a value of 10.5.

Corrosion Characteristics of the Coating:

As the whole endeavor of this work is to develop a sacrificial coating that can replace Cadmium coatings, it is critical to compare the performance of the non-anomalous Ni-Zn coating to Cadmium and other sacrificial coatings. The coatings that have been chosen for comparison in this study are Zinc, Zinc-Nickel and Cadmium, as these are the most commonly used sacrificial coatings for protection of steel. Ni-Zn with 28-wt% Zn was chosen as the optimal Zn content alloy based on linear polarization and tafel studies. The thickness of the various coatings was kept constant at 2 μm for these comparison studies.

Linear Polarization Studies:

Linear polarization studies were carried out to determine the polarization resistances of the various coatings. Linear polarization studies were carried out on Cd, Zn, conventional Zn-Ni and non-anomalous Ni-Zn alloy coatings. The non-anomalous Ni-Zn alloy presented for comparison was electrodeposited from alkaline sulfate electrolytes at an applied potential of –1.1 V vs. SCE. The potential was swept linearly from + 10 mV to –10 mV vs. E_{corr} at a scan rate of 0.5 mV/s. The resulting graphs of overpotential vs. current density for Ni-Zn and various Zn-Ni alloy coating are shown in Figure 7a. The slope of these lines yields the value of the polarization resistance. The slopes of overpotential vs. current density plots are very high for the

Ni-Zn alloys suggesting that they have excellent barrier properties. The low polarization resistance of the Zn and Zn-Ni alloy suggests a high corrosion rates for these coatings in comparison with electrodeposited non-anomalous Ni-Zn alloy. The resistance values in the case of electrodeposited Ni-Zn alloy were five times higher than those of the Zn-Ni alloy.

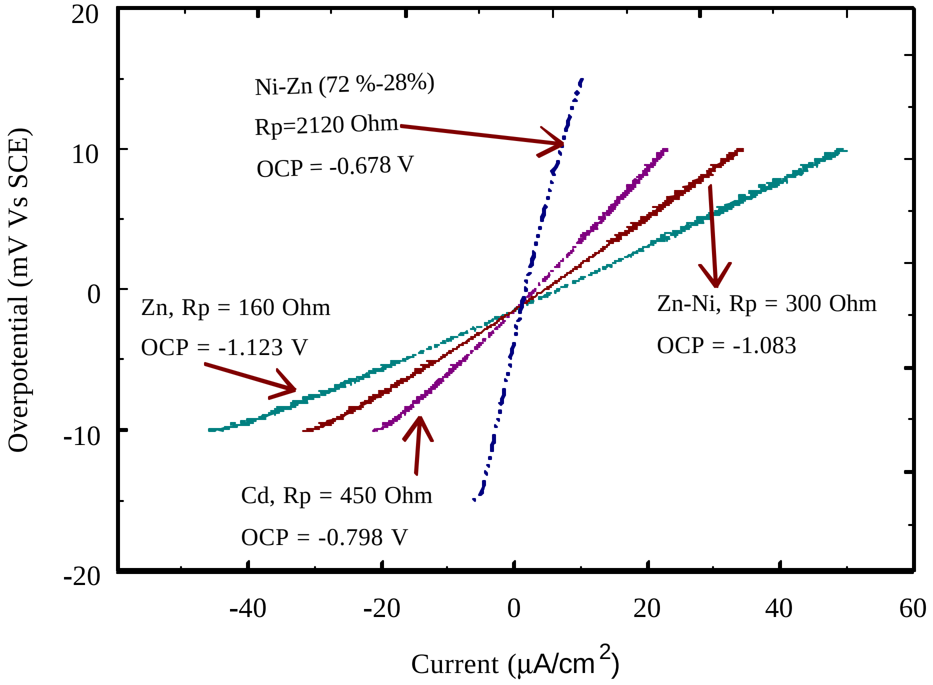

Figure 7a. Linear polarization plots for the various sacrificial coatings as compared with optimized Ni-Zn (28-wt% Zn) coating. The graph shows a five-times increase in the polarization resistance for Ni-Zn coating as compared to Cd coating.

Figure 7b shows the corrosion rates of the various coatings in the form of a bar plot. It can be readily seen from the plot that the corrosion rate for the electrodeposited non-anomalous Ni-Zn (28-wt% Zn) coatings is five times lower than Cd coatings. These studies show that the non-anomalous Ni-Zn coating possesses superior corrosion characteristics as compared to the other sacrificial coatings.

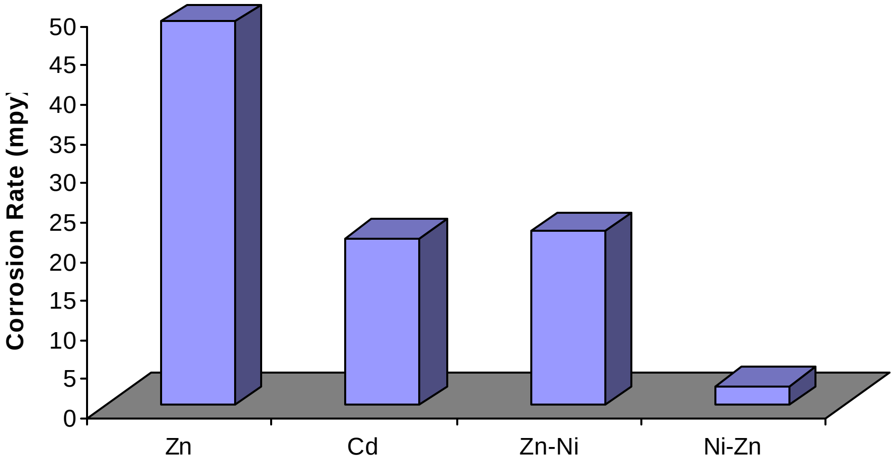

Figure 7b. Comparison of corrosion rates for various alloy coatings

Film Dissolution Studies:

Film dissolution studies were performed in pH 7.0 solution of 0.5 M Na_2SO_4 + 0.5 M H_3BO_3. A sample of known surface area was exposed to the corroding media and the rest potential was monitored. The dissolution studies on the coatings were performed till the rest potential of the coatings progressed to positive values and reached the rest potential of steel. The duration gives an estimate of the life of the coating. The rate of dissolution is proportional to the potential difference between the coating and the underlying substrate steel. Figure 8 shows the plot of E_{corr} vs time for different coatings. The zinc coating dissolves at a very fast rate. The potential decreased from –1.123 to –0.56 V vs. SCE in less than 38 hours. Zn exists in elemental form and its electronegative sacrificial potential leads to the faster dissolution. In the case of Zn-Ni alloy, the dissolution went through several phases. Zn-Ni alloys deposit in three different phases: a) Zn-rich phase termed eta (η) phase, (E_{corr} = -1.050 V vs. SCE), b) an intermediate gamma phase (γ), (E_{corr} = -0.780 V vs. SCE) and a nickel rich alpha phase (α), (E_{corr} = 0.450 V vs. SCE). The eta (η) phase has a rest potential comparable to that of pure zinc as it is mostly composed of zinc. Eta (η) phase dissolves rapidly as a galvanic couple is formed and the surface becomes enriched in gamma phase. The intermediate phase or the gamma (γ) phase has a Zn-Ni ratio of 4:1, it exhibits good barrier resistance against dissolution. Dissolution of the γ phase would expose the nickel rich phase to the corroding environment. A small defect in the coating in such a case would lead to the preferential dissolution of the less noble metal, namely steel. Thus, an increase in the life of the protective coating would simply depend on the life of the more electronegative phase namely the η phase and γ phase. In the plot it is shown that the Zn-Ni alloy dissolution rate was very fast. This again is due to the large potential difference between the Zn rich phase (η) (E_{corr} = -1.050 V vs. SCE) and the underlying substrate, steel (E_{corr} = -0.550 V vs. SCE). However, the rest potential of Ni-Zn remained electronegative to steel for long durations of time when compared to conventional Zn, Zn-Ni and Cd coatings. Due to the significant increase in the Zn-Ni ratio, the corrosion potential of the alloy decreases. The corrosion rest

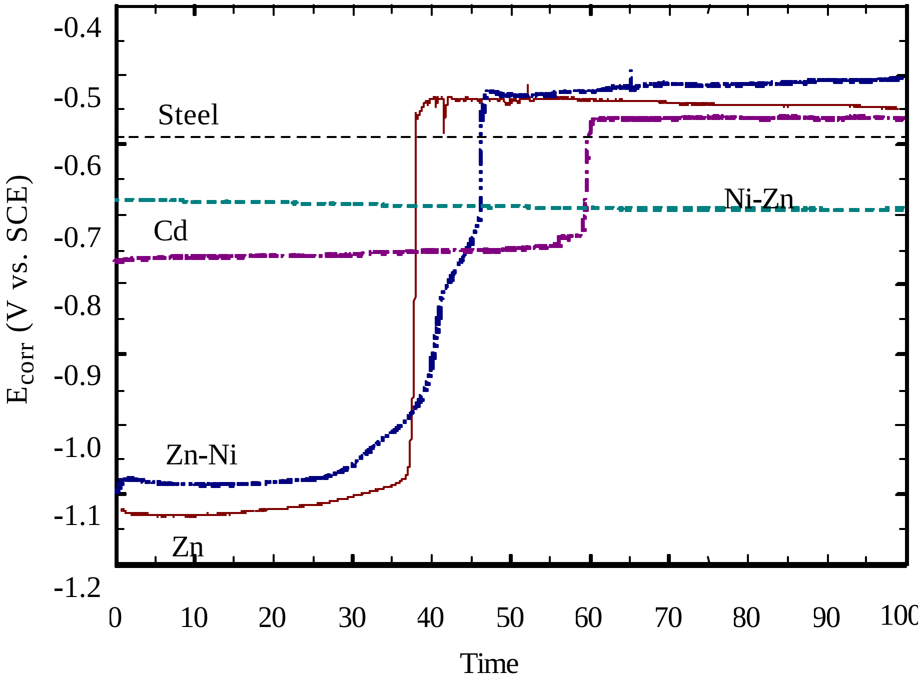

Figure 8. E_{corr} vs. time plot for the various alloy coatings (thickness=2 mm) immersed in 71 g/L Na_2SO_4+30.5 g/L H_3BO_3 (pH=7.0).

potential of the non-anomalous Ni-Zn alloy was –0.67 V vs. SCE. This value is low compared to that of conventional Zn-Ni alloy (-1.05 V vs. SCE). However it is electronegative to steel and offers sacrificial protection to steel. The low potential difference between the Ni-Zn alloy coating and the underlying steel ensures the slow dissolution rate and longer life of the coating. Also the increased nickel content in the deposit increases the barrier properties of the coating. Thus the non-anomalous Ni-Zn alloy obtained from alkaline sulfate electrolytes can be an ideal sacrificial coating for the corrosion protection of steel.

CONCLUSION

Composite Ni-Zn alloys with different amounts of Zn were prepared by controlling the deposition parameters such as applied potential, pH and amount of $ZnSO_4$ in the bath. Material characterization studies on the resultant coatings showed the co-deposition of Zn and Ni. The Zn content in the alloy can be controlled by varying the applied potential, Zn^{2+} concentration in the bath or by adjusting the bath pH. Electrochemical characterization studies reveal that composites with 28-wt% Zn have rest potential more electronegative to steel and hence are applicable as a sacrificial coating for the protection of steel. This optimal Zn content in the alloy is obtained when deposition with a $ZnSO_4$ concentration of 15 g/L, at pH 10.5 and 80 ^{o}C. The high Ni content (72-wt%) ensures the superior corrosion resistance of the composite alloy as compared to conventional Zn-based coatings obtained by electrolysis. Polarization resistance studies reveal a five-time increase in the resistance value for the Ni-Zn coating over that of Cd. The low potential difference that exists between the coating and the substrate results in a lower dissolution rate for the deposited alloy as compared to Zn, Zn-Ni and Cd coatings. Owing to its excellent corrosion properties, this new non-anomalous Ni-Zn alloy can be considered as an ideal replacement for cadmium coatings.

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