Deposition of Non-anomalous Ni-Zn-P Alloys for Replacement of Cadmium Coatings

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Non-anomalous Ni-Zn-P coatings with high Ni content have been developed using Electroless deposition technique. These coatings show promise as a possible replacement for Cd as a protective coating for steel substrates. Ni-Zn-P coatings were deposited from a solution containing NiSO₄, Sodium citrate and Ammonium chloride. The deposition parameters were optimized based on Zn content of the coating and the surface morphology. Coatings with 16.2-wt% Zn were found to display a potential of – 0.652 V vs. SCE that is more electronegative to steel and hence can be used as a sacrificial coating for protection of steel. Finally, studies in corroding media show that Ni-Zn-P coatings show a higher barrier resistance and better stability as compared to Cadmium coatings.

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304

INTRODUCTION

Cadmium has been the coating of choice for protection of steel substrates [1]. However cadmium and its salts are toxic and cadmium deposits are obtained from cyanide baths, which are subject to stringent environmental regulations [2]. Further, during cadmium deposition, large amount of H₂ is evolved and introduced into the substrate, thus making the substrate susceptible to hydrogen embrittlement [3]. Hence, alternate coatings to cadmium are being actively explored. Zinc has a low standard electrode potential ($E_0 = -0.76V$ vs. NHE), which makes it an attractive alternate sacrificial coating [4]. However, due to the large difference in the standard potentials of Zn and Fe, rapid dissolution of Zn happens under corroding conditions. The high dissolution rates of zinc under corroding conditions has been alleviated to some extent by alloying it with metals like Ni, Co and Sn [5]. Zn-Ni alloys show better corrosion resistance, formability and weldability and are projected as the most promising candidate as a replacement for Cd coatings [6-7].

The innate problem with the deposition of such alloys is that it is anomalous in nature. Although Ni is more noble than Zn, the co-deposition of these metals results in a higher amount of Zn in the final deposit and as a result, the rate of dissolution of these alloys still remains high under corroding conditions. The mechanism for this preferential deposition has been analyzed in detail in literature [8-9]. Several attempts have been made to decrease the anomaly of the deposit. Such attempts have focused on the use of inert species in the bath or development of a ternary alloy [10-12]. Previously, we have reported the effect of Nonyl phenyl polyethylene oxide (NPPO) on the inhibition of zinc electrodeposition [10]. Zhou et. al. have found that the amount of Ni in the deposit was found to increase marginally from 6 to 8 wt% when small amounts of tin is included in the bath [11]. However, such a small increase in Ni content has negligible effect on the barrier properties of the coating. We have found that the development of ternary alloys decreases the Zn content in the deposit to an appreciable extent. For example, addition of small amounts of Cd to the Zn-Ni plating bath increases the barrier properties and hydrogen permeation resistance properties of the ternary alloy coating in comparison to Zn-Ni alloys [12]. However, Cd addition in the bath is undesirable owing to the stringent regulations involved in the disposal of the metal and its salts. However, in all these cases, the amount of Zinc in the final deposit still varies between 70-90% and hence their rate of dissolution remains high.

Autocatalytic reduction of metals and alloys offers an attractive and alternate method of increasing the amount of Ni in the final deposit. Previous efforts have shown that Ni-Zn-P plating follows normal deposition with high Ni content (80-90%) [13-15]. However, in these cases, the amount of Zn remains low (~10 wt%) and hence the potential (-476 mV vs. SCE) is more positive to steel (-590 mV vs. SCE). Thus these deposits, although offering excellent corrosion resistance, could not be used as a sacrificial coating to steel. We have reported the development of Ni-Zn-P alloy with sufficient amount of Zn in the deposit, so that it can be used as a sacrificial coating. The effect of the deposition parameters on the composition and the surface morphology of the coating has been analyzed in detail and reported [16]. In the present study, we are reporting the corrosion and the mechanical properties of the coating. The performance of the coating as compared to different sacrificial coating is also reported.

EXPERIMENTAL

Sample preparation:

Plating and subsequent corrosion studies were done on low carbon cold-rolled steel foils of thickness 0.5 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-P composites were prepared from a bath containing NiSO₄, Sodium citrate and NH₄Cl. Sodium hypophosphite was used as a reducing agent for the autocatalytic process. Ni-Zn-P coatings with different amounts of Zn were obtained by varying the amount of ZnSO₄.7H₂O in the bath. The deposition was carried out at 85 $^{\circ}$ C for 1 hour. The pH was maintained at 10.5 by the addition of NaOH. All solutions were prepared with analytical grade reagents (obtained from Sigma-Aldrich) and triply distilled water.

Physical Characterization:

Cross-sectional SEM analysis was used to check the thickness of the deposit in accordance with ASTM standards [17]. Adhesion of the coating was compared to that of Zn-Ni and Cd coating by developing coatings with a thickness of 12.5 μ m and then bending the surface to 180°, so that the two ends become parallel to each other. Subsequent to this, it is bent backward to the original position and the adhesion of the coating is determined by visual appearance. The coating is said to have good adhesion in the absence of flaking or detachment from the substrate. Wear resistance of the coating is checked by measuring the weight difference of the coating subjected to abrasion for 200 cycles. The micro-hardness of the coating is measured using a Buehler micro-hardness measurement instrument by applying a 25 gpf load for 10 s.

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 Na₂SO₄ and 0.5 M H₃BO₃ 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

Optimization of the concentration of ZnSO₄.7H₂O: -

Cross-sectional SEM analysis was used to analyze the thickness of the coatings obtained. Figure 1 shows the cross-sectional SEM pictures for Ni-P and Ni-Zn-P (10.8-wt% Zn) coating (obtained at a ZnSO₄ concentration of 5 g/L). The plot clearly shows the decrease in thickness for Ni-Zn-P coating as compared to Ni-P coating. Figure 2 shows the deposition rate and the thickness of the coatings obtained as a function of ZnSO₄ concentration in the bath. The results obtained clearly shows that the addition of Zn²⁺ ions in Ni-P bath acts as an inhibitor for the deposition process. As the deposition rate is inversely proportional to the ZnSO₄ concentration, it is essential to optimize the ZnSO₄ concentration in the bath in order to obtain a coating with the optimal Zn content in order to exhibit sacrificial properties.



a) Ni-P coating Magnification – 3000 X Figure 1. Cross-sectional SEM analysis on Ni-P and Ni-Zn-P (prepared with 5 g/L ZnSO₄.7H₂O).

In order to obtain a sacrificial coating, it is essential to estimate the amount of Zn in the final deposit and to check the corrosion properties of the coating using electrochemical techniques. EDAX analysis was used to analyze the composition of the coating. Figure 3 shows the distribution of Zn, Ni and P in the coating as a function of ZnSO₄ added in the bath. It can be seen from the plot that the Zn content in the deposit increases from 10.8-wt% in the case of 5 g/L ZnSO₄ to 17.9-wt% in the case of 20 g/L ZnSO₄. The amount of Ni decreases from 78.9-wt% to 72.1-wt% with increase of ZnSO₄ concentration in the bath. However, the P content in the deposit remains unaffected with the increase in Zn concentration. As seen from Figs. 1 and 2, with increase in ZnSO₄ concentration, the deposition rate of the process decreases while the Zn content in the coating increases. As the objective of this effort is to obtain a sacrificial coating for steel, it is essential to characterize the corrosion properties of the coating.



Figure 2. Variation in the deposition rate and the thickness of the coating as a function of concentration of $ZnSO_4.7H_2O$ in the bath.



Figure 3. Change in the Ni, Zn and P content in the deposit as a function of ZnSO₄.7H₂O concentration added in the bath.

To check the suitability of the coating as a sacrificial layer, the rest potentials of the coatings were tested 0.5 M Na₂SO₄ + 0.5 M H₃BO₃ solution at pH 7.0. Figure 4 shows the rest potential of the coatings with various amounts of Zn. The steel substrate exhibits a potential of -0.590 V vs. SCE. It can be seen from the graph that increase in Zn content leads to a shift in the potential to a more negative value. Coatings with no Zn show a rest potential of -0.4 V vs. SCE. Coatings with 10.8-wt% Zn and 13.8-wt% Zn have potentials more positive to steel and hence cannot act as a sacrificial coating. The graph also shows that the potential of the coating with 16.2-wt% Zn displays a potential (-0.652 V vs. SCE) that is sufficiently negative to the steel substrate. Further increase in the Zn content to 17.9-wt% results in the

potential being shifted to -0.663 V vs. SCE. As the Zn and Ni content in the deposits vary, it can be expected that the coatings containing higher amount of Ni to possess higher corrosion resistance. Hence, Tafel studies were done to evaluate the corrosion resistance of the coatings.



Figure 4. Rest potentials of the Ni-Zn-P deposits as a function of Zn content in the coatings.

Tafel studies were carried out by scanning the potential from -200 mV to 200 mV with respect to the corrosion potential. Table I summarizes the corrosion potential and the corrosion rate of the coating as a function of Zn content in the deposit. Even though the corrosion current density increases from 2.5 μ A/cm² (for Ni-P) to 8.6 μ A/cm² (for 16% Zn-74%Ni-10%P), the corrosion potential becomes more electronegative to steel. From the rest potential and Tafel polarization studies, the optimized Zn content in the deposit is seen to be 16.2-wt% obtained at a ZnSO₄ concentration of 15 g/L in the bath. Hence, the rest of the depositions were carried out at the optimized ZnSO₄ content of 15 g/L.

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	
10.8	-0.500	3.2 x 10 ⁻⁶	
13.8	-0.558	4.0 x 10 ⁻⁶	
16.2	-0.652	8.6 x 10 ⁻⁶	
17.9	-0.663	1.2 x 10 ⁻⁵	

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

309

Performance comparison with various sacrificial coatings:

As the whole endeavor of this work is to develop a sacrificial coating that can replace Cd coatings, it is critical to compare the performance of the developed coating to Cd and other sacrificial coatings. The coatings that have been chosen for comparison in this study are electrodeposited Zn, Zn-Ni and Cd coatings, as these are the most commonly used sacrificial coatings for protection of steel. Ni-Zn-P with 16.2-wt% Zn was chosen as the optimal Zn content alloy based on rest potential and tafel studies. The chief reason for the use of Cd in engineering applications is the good wear resistance and hardness of the coating. Hence, in order to develop a viable alternative to Cd, it is important to compare the mechanical properties of the alternative coating with that of Cd. Adhesion, Wear resistance and the Micro-hardness of the coatings were measured for the four coatings chosen for comparison in accordance with the ASTM standards. Table II compares the results obtained from these test measurements. It can be clearly seen from the table that the Ni-Zn-P coatings developed has good adhesion, wear resistance and micro-hardness as compared to Cd. Hence it can be surmised that the developed alternative coating has good engineering attributes as Cd.

Coating	Adhesion	Wear resistance measured by weight loss after 200 cycles (mg)	Micro-hardness (HK ₂₅)
Zn	Good	29.7	82
94.6% Zn-5.4% Ni	Good	18.5	105
Cd 74% Ni-16.2% Zn- 9.8% P	Good Good	6.0 8.0	240 198

Table II. Comparison of Physical properties for different sacrificial coatings.

In order to compare the corrosion performance of the coatings, Linear polarization studies were carried out to find the polarization resistances of the various coatings. The thicknesses of the various coatings were approximately 2 μ m for these comparison studies. The deposit thickness was estimated by dividing the weight of a unit area with the average density of the alloy. The potential was swept from -10 mV to +10 mV vs. E_{eorr} at a scan rate of 0.5 mV/s. The resulting graphs of overpotential *vs.* current density for the different coatings are shown in Figure 5a. The slope of these lines yields the value of the polarization resistance. The low polarization resistance for the Zn and Zn-Ni alloy coatings show that the corrosion rates for these coatings are much higher than Ni-Zn-P coatings. The corrosion rates have been calculated using the polarization resistance found from the linear polarization technique. Figure 5b 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 electroless Ni-Zn-P (16%Zn) coatings is five times lower than Cd coatings.

These studies show that the electroless Ni-Zn-P coating possesses superior mechanical and corrosion characteristics as compared to the other sacrificial coatings.



Figure 5a. Linear polarization plots for the various sacrificial coatings as compared with optimized Ni-Zn-P (16.2-wt% Zn) coating.



Figure 5b. Comparison of corrosion rates for various alloy coatings.

CONCLUSIONS

Composite Ni-Zn-P alloys with different amounts of Zn were prepared by controlling the amount of Zn^{2+} ions added in the bath. Material and electrochemical characterization studies reveal that composites with 16.2-wt% Zn show a potential that is 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 ZnSO₄ concentration of 15 g/L, at pH 10.5 and 85 °C. The high Ni

311

content (74.0-wt%) ensures the superior corrosion resistance of the composite alloy as compared to conventional Zn-based coatings obtained by electrolysis. The engineering properties of the coating was found to be comparable to that of Cd. Polarization resistance studies reveal a four-time increase in the resistance value for the Ni-Zn-P coating over that of Cd. Finally, 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.

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