DEVELOPMENT OF NANOSTRUCTURED Ni-Zn-P ALLOYS BY ELECTROLESS DEPOSITION FOR REPLACEMENT OF CADMIUM COATINGS

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ABSTRACT

The most promising alternative to Cd coating for corrosion protection of steel is Zn and its alloys, Zn-Ni in particular. However, deposition of these alloys is anomalous and hence they exhibit high rate of dissolution in corrosive media. A novel nanostructured Ni-Zn-P alloys with increased Ni content was developed by electroless process as a possible replacement for Cd coatings. The operating parameters, such as the concentration of the electroactive species, the pH, temperature and the concentration of the reducing agent were optimized. Corrosion studies revealed a four-times increase in corrosion resistance of the deposit as compared to cadmium, while providing sacrificial protection to steel. Also, the mechanical properties of the developed coating were seen to be comparable to that of Cd, thus making it a suitable alternative to Cd coatings.

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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 H_2 is evolved and introduced into the substrate, thus making the substrate susceptible to hydrogen embrittlement [3]. Hence, alternatives for substituting Cd coating in protecting steel substrates are being actively pursued. Zinc, by the virtue of its low standard electrode potential ($E^\circ = -0.76V$ vs. NHE) is a very active metal, which corrodes easily [4]. This characteristic of zinc makes it suitable to act as a sacrificial coating on many metals and alloys with standard electrode potentials higher than zinc. The difference in electronegativities of the coating and the substrate acts as the driving force for the dissolution of the sacrificial coating under corroding conditions, thus providing corrosion protection to the substrate. Owing to the huge difference in electronegativities of Zn and Fe, rapid dissolution of Zn happens under corroding conditions. The problem of accelerated corrosion of Zn can be overcome by alloying it with another metal which will bring the standard electrode potential of the alloy much closer to the substrate metal while still remaining on the cathodic side to provide sacrificial protection.

Zn-Ni alloys possess better corrosion resistance compared to zinc and have been studied extensively for automotive applications. The co-deposition of Zn-Ni is anomalous and a higher percent of Zn is present in the final deposit. The mechanism for this preferential deposition has been discussed extensively in literature [5-7]. Typical nickel composition in the alloy is approximately 10% and any further increase in nickel composition is based on using a higher-than-predicted Ni/Zn ratio in the bath [8,9]. An enhancement in the nickel composition would lead to more anodic open circuit potential, which in turn will reduce the driving force for the galvanic corrosion. Also the barrier properties associated with nickel rich deposits are superior compared to other coatings [10,11].

We recently developed a novel electroless process to deposit Ni-Zn-P alloys, with varying proportions of zinc (10-18 %) in the coating [12]. It was observed that the deposit contained 70-78% Ni and the effect of the deposition parameters on the composition and the surface morphology of the coating was reported. In the present study, we are analyzing the bath chemistry and the effect of the deposition parameters on the deposition process. Also, the corrosion properties of the coating as compared to different sacrificial coating are 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 deionized water. This procedure was repeated until a clean and smooth surface was obtained.

Electrolyte preparation and deposition:
Ni-Zn-P composites were prepared from sulfate electrolytes. 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 $ZnSO_4.7H_2O$ in the bath. The deposition was carried out at 85 ^{o}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:
Adhesion of the coating was compared to that of Zn-Ni and Cd coating by developing coatings with a thickness of 12.5 µm and then bending the specimen until the two ends become parallel. Subsequent to this, it is bent backward to the original position and the adhesion of the coating is determined by visual analysis of peeling of the coating from the substrate. 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:
The surface morphology and the microstructure of the coating were analyzed using SEM analysis with the help of Hitachi S-2500 Delta Scanning Electron microscope. EDAX analysis was used to analyze the distribution of the elements in the final deposit. To ensure accuracy of the elemental 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%.

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 $ZnSO_4$ concentration

Figure 1 shows the deposition rate and the thickness of the coatings obtained as a function of $ZnSO_4$ concentration in the bath. The results obtained clearly shows that the addition of Zn^{2+} ions in Ni-P bath acts as an inhibitor for the deposition process. As the deposition rate is inversely proportional to the $ZnSO_4$ concentration, it is essential to optimize the $ZnSO_4$ concentration in the bath in order to obtain a coating with the optimal Zn content in order to exhibit sacrificial properties.

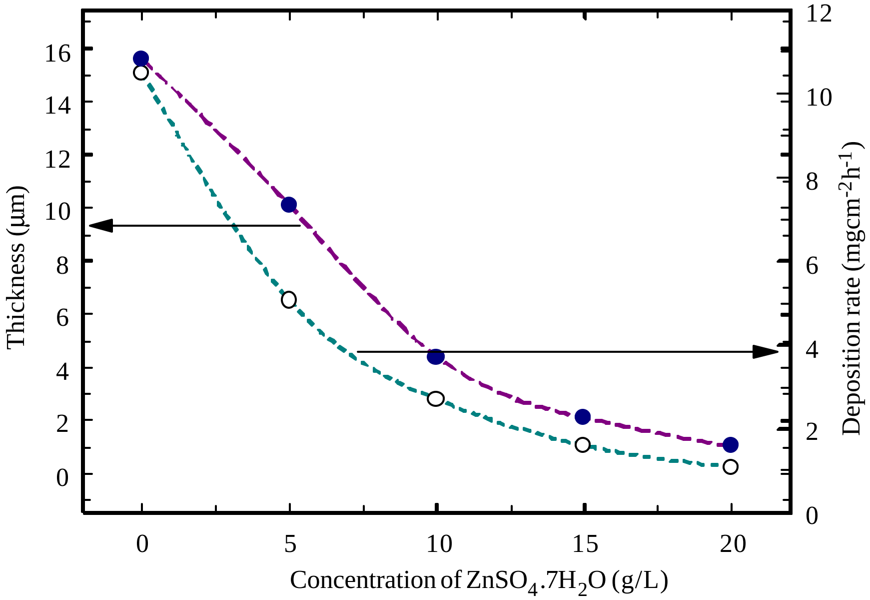


Figure 1. Variation in the deposition rate and the thickness of the coating as a function of concentration of $ZnSO_4.7H_2O$ in the bath.

To check the sacrificial properties of the coating, their Tafel behavior were analyzed in a 0.5 M Na_2SO_4 + 0.5 M H_3BO_3 solution at pH 7.0. 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 $\mu A/cm^2$ (for Ni-P) to 8.6 $\mu A/cm^2$ (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 $ZnSO_4$ concentration of 15 g/L in the bath. Hence, the $ZnSO_4$ content in the bath was optimized at 15 g/L and gave rise to Ni-Zn-P coating with 16.2-wt% Zn.

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	2.5×10^{-6}
10.8	-0.500	3.2×10^{-6}
13.8	-0.558	4.0×10^{-6}
16.2	-0.652	8.6×10^{-6}
17.9	-0.663	1.2×10^{-5}

Bath Analysis

Another critical parameter that can affect the composition of the coating is the pH of the deposition bath. A complete analysis of the equilibrium reactions between the various species in the bath is necessary to identify the optimal pH of deposition. In order to accomplish this, material balances coupled with various equilibrium reactions and electroneutrality conditions was carried out to elucidate the change in the equilibrium concentration of the various electroactive species in the bath. The solution chemistry of the bath was studied by determining the equilibrium concentrations of the various species at different pH levels. The concentrations of all the electroactive species were determined by using various element balances, equilibrium conditions, and the electroneutrality condition at a specified pH. Suitable concentrations of NaOH were used in the computation to obtain the concentration dependence as a function of pH. The governing equations for the various regions are as follows:

The variables to be determined are: $[Zn^{2+}]$, $[Ni^{2+}]$, $[Zn(OH)^+]$, $[Ni(OH)^+]$, $[Zn(OH)_2]$, $[Ni(OH)_2]$, $[Zn(NH_3)_4^{2+}]$, $[Ni(NH_3)_6^{2+}]$, $[Zn_2(OH)^{3+}]$, $[OH^-]$, $[SO_4^{2-}]$, and $[HSO_4^-]$. The concentration of $[H^+]$ depends on the specified pH. The equations used for the determination of the equilibrium concentrations are

Material balance on zinc

$$[ZnSO_4]_{ad} = [Zn^{2+}] + [Zn(OH)^+] + 2[Zn_2(OH)^{3+}] + [Zn(OH)_2] + [Zn(NH_3)_4^{2+}]$$

Material balance on nickel

$$[NiSO_4]_{ad} = [Ni^{2+}] + [Ni(OH)^+] + [Ni(OH)_2] + [Ni(NH_3)_6^{2+}]$$

Electroneutrality conditions

$$[H^+]+2[Zn^{2+}]+2[Ni^{2+}]+[Zn(OH)^+]+[Ni(OH)^+]+3[Zn_2(OH)^{3+}]$$
$$+2[Zn(NH_3)_4^{2+}]+2[Ni(NH_3)_6^{2+}]=[HSO_4^-]+2[SO_4^{2-}]+[OH^-]$$

The equilibrium conditions

$$[H^+][SO_4^{2-}]-k_1[HSO_4^-]=0$$
$$[Zn^{2+}][OH^-]-k_2[Zn(OH)^+]=0$$
$$[Ni^{2+}][OH^-]-k_3[Ni(OH)^+]=0$$
$$[H^+][OH^-]-k_4=0$$
$$[Zn^{2+}]^2[OH^-]-k_5[Zn_2(OH)^{3+}]=0$$
$$[Zn(OH)^+][OH^-]-k_6=0$$
$$[Ni(OH)^+][OH^-]-k_7=0$$
$$[Zn(OH)_2][NH_3]_{ad}^4-k_8[Zn(NH_3)_4^{2+}][OH^-]^2=0$$
$$[Ni(OH)_2][NH_3]_{ad}^6-k_9[Zn(NH_3)_6^{2+}][OH^-]^2=0$$

The above equations were solved simultaneously by using Maple®. As the pH increases, the concentration of the bivalent ions decreases with increase in pH. According to Pourbaix [13], both Zn^{2+} and Ni^{2+} ions will precipitate as $Zn(OH)_2$ and $Ni(OH)_2$ respectively at pH values greater than 7.0. For the deposition to be carried out in alkaline conditions, use of complexing agents is necessary to prevent the metal ions from spontaneous precipitation. For this purpose, sodium citrate and ammonium chloride have been used in the bath. In the presence of ammonia, the following complex ions are formed:

$$Zn^{2+}+2OH^-\rightarrow Zn(OH)_2$$
$$Zn(OH)_2+4NH_3\rightarrow Zn(NH_3)_4^{2+}+2OH^-$$
$$Ni^{2+}+2OH^-\rightarrow Ni(OH)_2$$
$$Ni(OH)_2+6NH_3\rightarrow Ni(NH_3)_6^{2+}+2OH^-$$

Ammonia is released through the following redox reactions:

$$Zn(NH_3)_4^{2+}+2e^-\rightarrow Zn+4NH_3$$
$$Ni(NH_3)_6^{2+}+2e^-\rightarrow Ni+6NH_3$$

The equilibrium concentrations of the various species as a function of bath pH are shown in Figure 2. As seen from the plot, the ratio of the concentrations of the complexed Zn and Ni ions remains constant from pH 7.5 to 9.5. However, above pH 9.5, the concentration of the complexed ions changes rapidly and beyond pH 11.5, the complexed ions precipitate as their respective hydroxides. The decrease in complex Ni ion concentration is much larger than the decrease in complexed Zn ion concentration. This leads to an increase in the Zn/Ni ion ratio in the pH range 9.5 to 11.5. Hence the change in pH of the bath can be expected to increase the amount of Zn in the deposit. Since higher Zn ion concentration in the bath lowers the deposition rates, the drop in the complexed Zn ion concentration (in the pH range 9.5-11.5) will play a crucial role in determining the deposition rate.

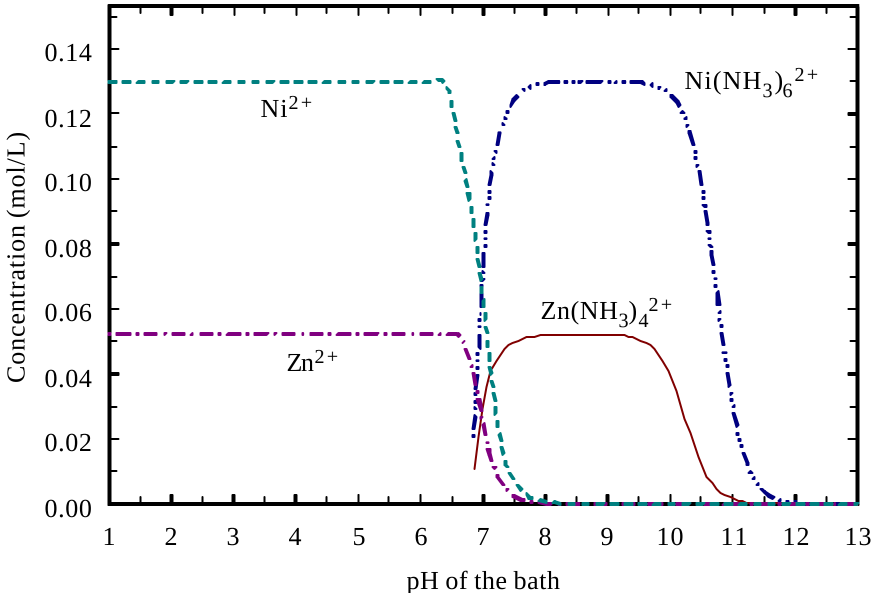
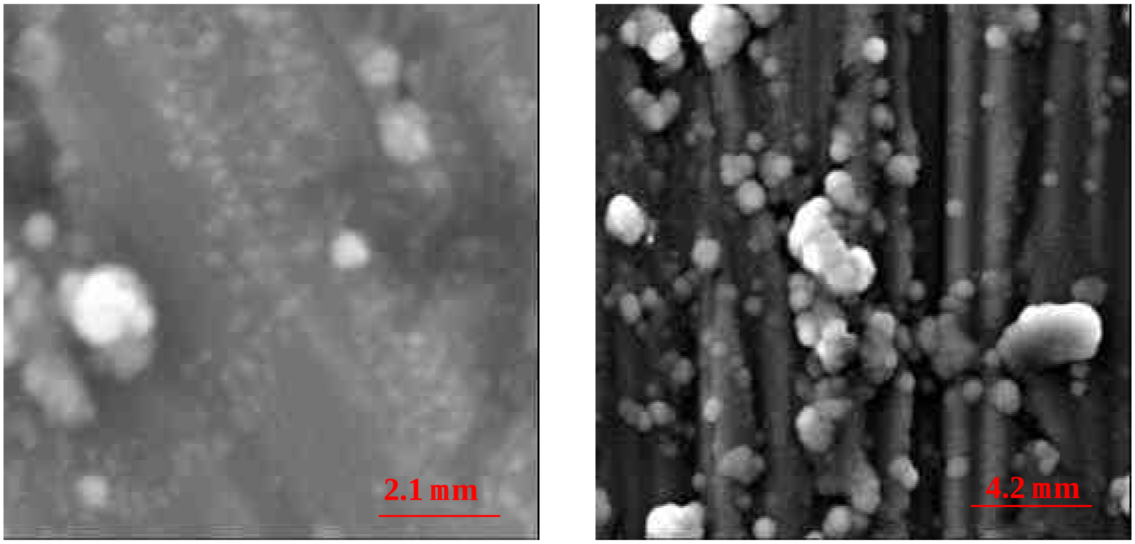


Figure 2. Effect of pH on the equilibrium concentrations of the electroactive species

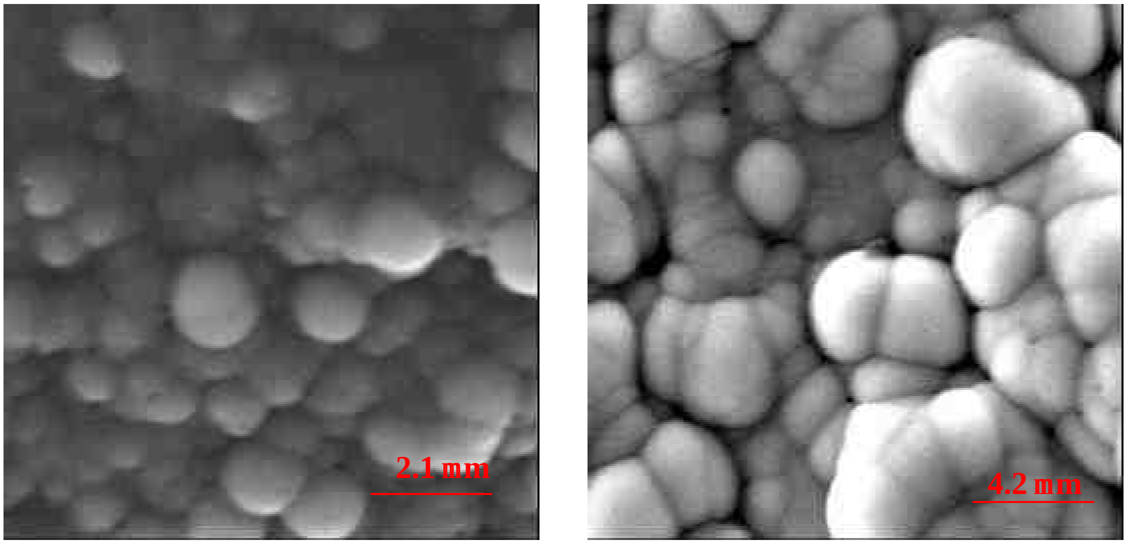
To understand the effect of pH, experiments were done at four different pH values in the range 8.5-11.5. Increasing the pH beyond 11.5, results in the spontaneous precipitation of the bath. This result is consistent with the findings in the pH-concentration diagram as shown in Figure 2. Figure 3 shows the morphology of the coatings prepared at different pH values. The SEM pictures show that the depositions carried out at pH values lower than 10.5 gives rise to coatings that do not cover the substrate surface completely. The SEM pictures show that the deposition at pH 10.5 results in the coating of uniform layers of spherical particles across the entire surface. With the increase in pH to 11.5, the deposits tend to agglomerate. The surface also shows the existence of cracks on the surface that will undermine the performance of the coating in corroding media.

Figure 3. SEM pictures of Ni-Zn-P coatings prepared as a function of bath pH-a) pH 8.5, b) pH 9.5, c)pH 10.5 and d)pH 11.5



Magnification 12000X
a) pH 8.5

Magnification 6000X
b) pH 9.5



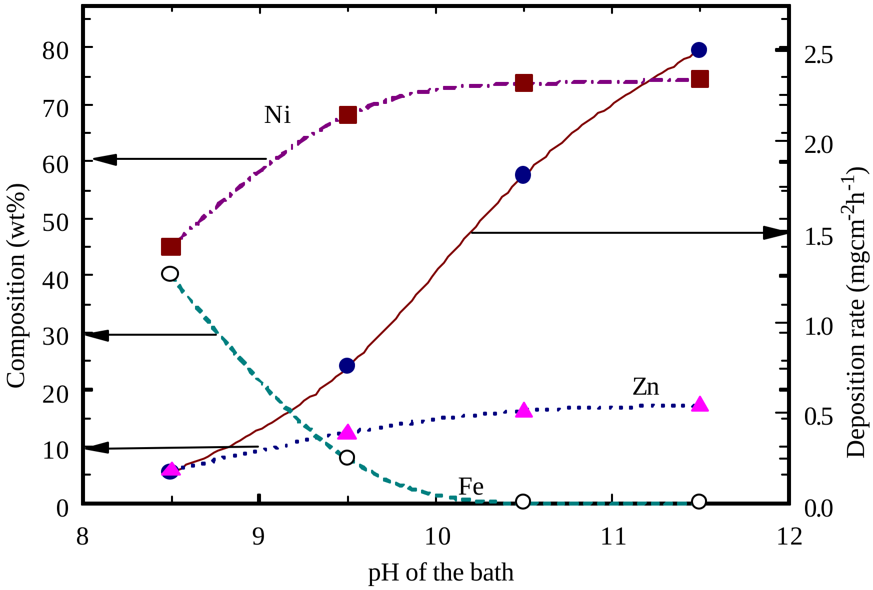
Magnification 12000X
c) pH 10.5

Magnification 6000X
d) pH 11.5

EDAX analysis was done to determine the deposit constituents. Figure 4 shows the effect of pH on the rate of deposition and the composition of the coating deposited at 85 ^{o}C and in the presence of 15 g/L $ZnSO_4$ in the bath. Below pH 8.5, no deposition occurs on the surface. The rate of deposition increases linearly with increase in pH. It is also seen that a high percentage of

Fe is detected in the case of pH 8.5 and 9.5. The thickness of the coating was measured by both cross-sectional SEM analysis and using the weight gain method. It is seen that deposits obtained at pH 8.5 and 9.5 have thickness less than 1 µm. 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. As seen in Fig. 2a and 2b, the surface is not completely covered with the coating for deposits obtained at pH 8.5 and 9.5, and this could be the reason for detecting Fe. However, with an increase in pH, the Fe content decreases and reaches a value of <0.1-wt% at pH 10.5. The change in the composition of the coating is negligible after a pH of 10.5, as seen from Zn and Ni content at pH 10.5 and 11.5.

Figure 4. Variation in the rate of deposition and Ni, Zn and Fe content as a function of bath pH.



Since the composition of the coating remains the same after a pH of 10.5, use of pH 11.5 might look attractive superficially for the benefit of increased rate (as seen in Fig. 4). However, the presence of cracks on the coating surface discourages the use of pH higher than 10.5. According to literature [14], cracks are developed in Ni-Zn-P coatings due to internal strain developed in the coatings due to incorporation of zinc in the alloy formation. Hence, the extent of crack formation is directly dependant on the rate of deposition. At pH 11.5, the rate of deposition as well as the amount of zinc in the deposit increases. As a result of larger zinc deposition at a higher rate, cracks are developed for coatings deposited at pH 11.5. Hence the bath pH was optimized at a value of 10.5.

Performance comparison with various sacrificial coatings

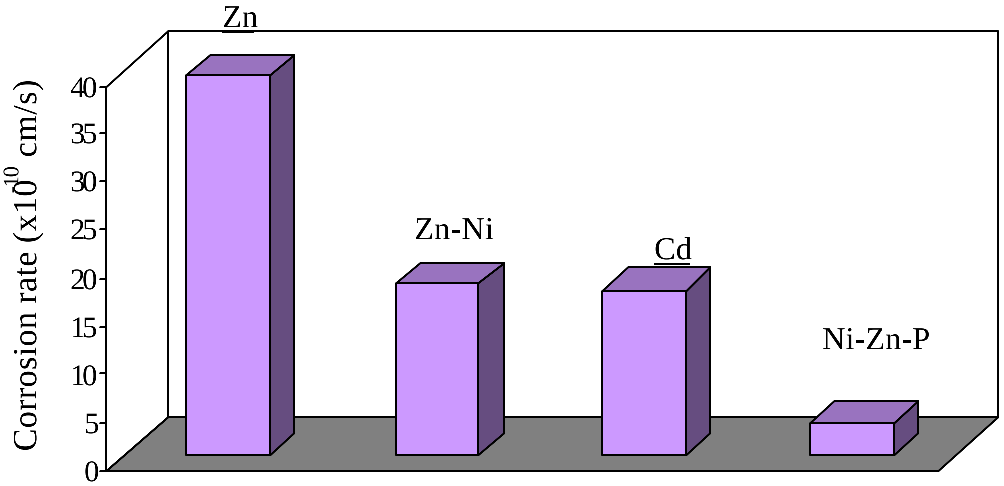
As the whole endeavor of this work is to develop a sacrificial coating that can replace Cd coatings, it is critical to compare the performance of the developed coating to Cd and other sacrificial coatings. The coatings that have been chosen for comparison in this study are electrodeposited Zn, Zn-Ni 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 alloy to be compared 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.

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

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	Good	6.0	240
74% Ni-16.2% Zn-9.8% P	Good	8.0	198

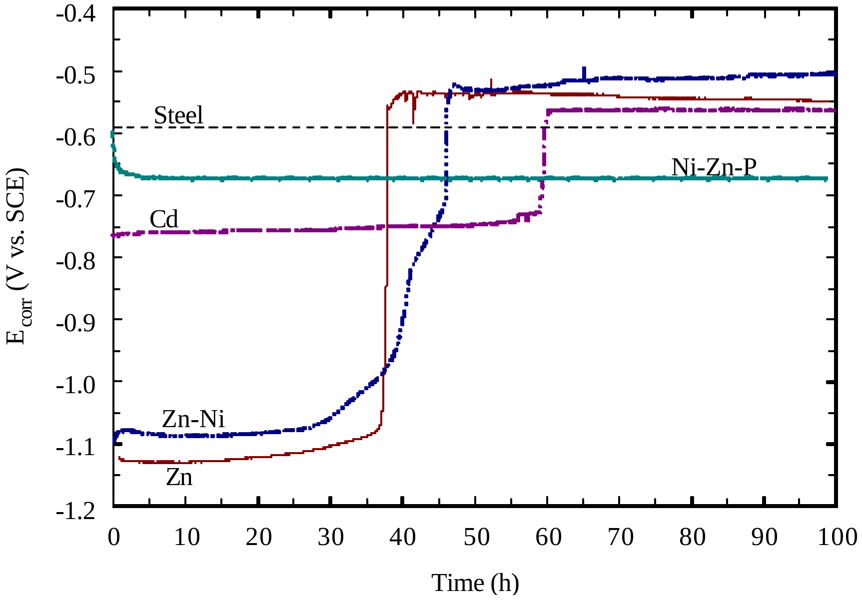
Linear Polarization studies: - In order to compare the corrosion performance of the coatings, linear polarization studies were carried out to find the polarization resistances of the various coatings. The thicknesses of the various coatings were approximately 2 μm for these comparison studies. The deposit 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_{corr} at a scan rate of 0.5 mV/s. The slope of these lines yields the value of the polarization resistance. The corrosion rates have been calculated using the polarization resistance found from the linear polarization technique. Figure 5 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.

Figure 5. Comparison of corrosion rates for various sacrificial coatings.



Film dissolution studies:- In order to check the stability of the different coatings in corroding media, a known surface area of the coated samples were immersed in the corroding media and the open circuit potential was continuously monitored as a function of time. Figure 6 shows the plot of the E_{corr} values of the various coatings as a function of time. As time passes, all the coatings dissolve in the corrosion media due to their sacrificial nature. The rate of dissolution will depend on the potential difference between the substrate and the coating. Greater the potential difference, lesser is the time taken for the coating to dissolve. The change in the potential to the substrate potential will give indication of the complete dissolution of the coating. The time for dissolution for the Zn-Ni alloy is longer than the sample coated with Zn, which is due to the higher corrosion resistance of the Zn-Ni alloy. Ni-Zn-P coatings last longer than Cd, Zn and Zn-Ni coatings. The potential of the coating does not change for the time period in which these tests were carried out. The primary reason for this prolonged corrosion resistance is the low potential difference between the coating (-0.652 V vs. SCE) and the substrate (-0.590 V vs. SCE). These studies show that the electroless Ni-Zn-P coating possesses superior corrosion characteristics as compared to the other commonly used sacrificial coatings.

Figure 6. Dissolution studies of the various sacrificial 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. Electrochemical 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. The bath chemistry was analyzed using various material balances in conjunction with equilibrium relations and was used to identify the role played by the different electroactive species that control the deposition process. Using these studies, the deposition pH was optimized as pH 10.5. 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. The high Ni content (74.0-wt%) ensures the superior corrosion resistance of the composite alloy as compared to conventional Zn-based coatings obtained by electrolysis.

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