NANOSTRUCTURED ZN-NI ALLOYS AS A REPLACEMENT FOR CADMIUM COATINGS

Swaminatha P Kumaraguru, Basker Veeraraghavan, Bala S. Haran and Branko N. Popov* Department of Chemical Engineering University of South Carolina Columbia, SC 29208

In the current work, a new Zn-Ni plating process was developed which offers a unique way of controlling the Zn-Ni ratio. Nanostructured Zn-Ni alloys are electrodeposited by direct and pulse current from alkaline sulfate electrolytes in the presence of additives and complexing agents. The ratio of the zinc and nickel was effectively controlled by varying the concentration of the electroactive species and operating parameters. The new electrodeposited Zn-Ni alloy has an increased content of nickel as compared to the conventional Zn-Ni alloy. The increase in the nickel content accounts for the decreased corrosion potential of the Zn-Ni coatings. The corrosion potential of the Zn-Ni alloy is -0.69 V (vs. SCE), which is still electronegative when compared to steel and offers sacrificial protection to steel. The coatings have superior corrosion resistance and barrier properties when compared to conventional Zn-Ni coatings show a barrier resistance that is higher than the conventional Zn-Ni coatings by an order of magnitude. The compositions of the coatings were analyzed by EDX. The surface morphology of the coatings was studied using SEM (Scanning Electron Microscope). Improved corrosion and hydrogen inhibition properties make it a potential alternative for the cadmium coatings.

For more information, contact:

Dr. Branko N. Popov, Professor, Chemical Engineering Department, University of South Carolina, Columbia, SC 29208 Ph: (803) 777-7314 FAX: (803) 777-8265 Email: popov@engr.sc.edu

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 allovs are considered as a viable alternative to cadmium coatings [6-11]. Zn-Ni allovs containing 15 - 20 wt% of nickel possess four times more corrosion resistance than cadmiumtitanium 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. Electrodeposited coatings of nanaostructured grains have better corrosion and mechanical properties. In this study, we tried to develop similar Ni-Zn composites with high Ni content and nanostructured grain size using pulse deposition technique. In a broad sense, the present study is 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 nanostructured coatings have been compared to that of cadmium.

EXPERIMENTAL

Sample Preparation:- Plating and subsequent corrosion studies were done on low carbon coldrolled 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) H₂SO₄ 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]. Complexing agents were used 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 pulse parameters and also by varying the amount of ZnSO₄.7H₂O in the bath. 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 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

Effect of Zn²⁺ 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 ZnSO₄ 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 ZnSO₄ to 30-wt% in the case of 20 g/L ZnSO₄. The amount of Ni decreases from 77-wt% to 70-wt% with increase of ZnSO₄ concentration in the bath. It can also be seen from the graph that the composition does not undergo any significant change after a ZnSO₄ concentration of 15 g/L. However, the surface morphology of the coatings was seen to improve with ZnSO₄ concentration in the bath. The coating obtained at a ZnSO₄ concentration of 5 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 ZnSO₄ concentration than 15 g/L, the ZnSO₄ concentration was optimized at 15 g/L.



Figure 1. Variation in the composition of Ni-Zn composites as a function of ZnSO₄.7H₂O in the bath.

Effect of Applied Current density:

The applied average pulse current density is an important parameter determining the composition of the deposit. The average pulse current was varied from 2 mA/cm² to 20 mA/cm² to obtain deposits with varying amount of Nickel and zinc. The Zinc content increased from 28 % to 52 % with increase in the applied pulse current. The t_{on} and t_{off} were optimized to yield deposits with higher nickel content and nanostructured grain size. With increase in the average current density, the zinc content and the particle size increases. Hence it is essential to optimize the average pulse current based on the corrosion characteristics of the coatings.

To check the suitability of the coating as a sacrificial layer, the corrosion characteristics of the coatings were tested in a 0.5 M Na₂SO₄ + 0.5 M H₃BO₃ 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 2. 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. For the coatings, even though the corrosion current density increases from 2.5 μ A/cm² (for Ni) to 8.6 μ A/cm² (for 28% Zn-72%Ni), the corrosion potential becomes more electronegative (-0.67 V vs. SCE) to steel. Deposits obtained at average current densities

greater than 5 mA 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%.



Figure 2. 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

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 μ m 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 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 3. 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 cadmium coatings.



Figure 3. 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 4 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.



Film Dissolution Studies:

Film dissolution studies were performed in pH 7.0 solution of 0.5 M $Na_2SO_4 + 0.5$ M H₃BO₃. 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 5 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 (n) 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 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.



Figure 5. E_{corr} vs. time plot for the various alloy coatings (thickness=2 mm) immersed in 71 g/L Na₂SO₄+30.5 g/L H₃BO₃ (pH=7.0).

CONCLUSION

Composite Ni-Zn alloys with different amounts of Zn were prepared by controlling the deposition parameters such as average pulse current density, pH and amount of $ZnSO_4$ in the bath. Material characterization studies on the resultant coatings showed the co-deposition of Zn and Ni and the coatings were nanostructured. The decreased grain size was achieved by optimizing the pulse plating parameters. The Zn content in the alloy can be controlled by varying the applied pulse current density, 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 ZnSO₄ concentration of 15 g/L, at pH 10.5. The high Ni content (72-wt%) ensures the superior corrosion resistance of the composite alloy as compared to conventional Zn-based coatings obtained by electrodeposition. 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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