Development of a Plating Process for Deposition of Zn-Ni-X (X=Cu, Cd, P) Alloys as a Replacement for Cadmium Coatings

Swaminatha P. Kumaraguru, Prabhu Ganesan and Branko N. Popov

Center for Electrochemical Engineering
Department of Chemical Engineering,
University of South Carolina, Columbia, SC 29208

A novel plating process for the electrodeposition of Zn-Ni-Cu was developed. The inclusion of the ternary alloying element copper into the deposit decreases the Zn:Ni ratio with simultaneous increase in the nickel content. An effective method to control the Zn:Ni ratio has been optimized. It has been shown that use of 1 g/L of $CuSO_4$ in the Zn-Ni bath leads to copper codeposition along with Zn and Ni. The Zn-Ni alloy deposit is enriched with a high content of nickel and the Zn:Ni ratio is lowered to 1.3:1. Corrosion resistant Zn-Ni-Cu alloy of composition Zn – 45%, Ni - 35% and Cu-20% was obtained. The corrosion characteristics of the Zn-Ni-Cu coating showed a five times increase in the corrosion resistance in comparison with conventional Zn-Ni alloys. The corrosion potential of the Zn-Ni-Cu alloy obtained was –0.69 V vs SCE. This low potential is a result of the decreased Zn content in the deposit. Owing to its high barrier resistance and superior corrosion properties, Zn-Ni-Cu alloy is proposed as an ideal replacement for cadmium coatings.

For further 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 [1,2, 6-8]. Among them cadmium coatings are considered very reliable owing to their superior corrosion and engineering properties [2]. Cadmium coatings are widely used in the aircraft and automobile industries [2], but the cadmium coatings are highly toxic and they are generally prepared from toxic cyanide baths [3]. Also cadmium plating introduces large amounts of hydrogen in the underlying substrate and thus increases the susceptibility 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 coatings exhibit excellent sacrificial behavior. However, the higher dissolution rate owing to its high electronegative potential and poor mechanical properties limits the use of Zn coatings in the automotive industry. Alloying of zinc with noble metals like nickel has proved to improve the corrosion resistance and mechanical properties of zinc coatings. Zn-Ni alloys are considered as a viable alternative for cadmium coatings [6-11]. Zn-Ni alloys containing 15-20 wt% of nickel have been shown to 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. A higher percentage of zinc is observed in the final deposit. Therefore, Brenner classifies Zn-Ni codeposition as anomalous [13]. The mechanism for this preferential deposition of Zn has been discussed extensively in the literature [13,14]. Due to the higher percentage of zinc in the coating, these alloys are more electronegative than cadmium and hence dissolve rapidly in corrosive environments. Indeed the nickel content is as low as 5-10 % in Zn-Ni deposits prepared from commercial baths. Any further increase in nickel composition is based on using a higher than prescribed Ni:Zn ratio in the bath [15,16]. Though Zn-Ni alloys have good corrosion resistance in comparison with Zn coatings, further development for better coating and corrosion characteristics is of commercial interest. An enhancement of the nickel composition would lead to a more anodic open circuit potential, which will in turn reduce the driving force for galvanic corrosion. Also the barrier properties of the coating improve 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 [17-21]. 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.

Codeposition of phosphorous along with Zn-Ni alloy improves the corrosion resistance [17] and hydrogen permeation [18] characteristics of the deposit. Zn-Ni-P coatings have superior corrosion resistance and better prevent hydrogen entry in the substrate compared to Zn-Ni alloy [18]. Zhou et al [19] have studied the effect of tin additions on the anomalous deposition behavior of Zn-Ni alloys. The nickel content increased from 6 to 8 % with the addition of small amounts of tin. However, the observed small increase in the Ni content does not show any significant improvement in the corrosion properties of the coating.

Earlier, we have developed a novel plating process for the electrodeposition of Zn-Ni-Cd coatings [22-24]. It was found that the use of small amounts 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 a ternary element like cadmium prevented hydrogen entry into the substrate as compared to Zn-Ni alloy and cadmium coatings [23]. However, the trace of cadmium present in the bath poses ecological concerns. Hence the objective of the present study is to develop cadmium free coatings that can effectively replace cadmium. The goal of the present study is to develop a unique plating process for the deposition of Zn-Ni-Cu ternary alloys, which will induce barrier properties to the sacrificial Zn-Ni alloy and increase the life of the coating.

Experimental

Sample preparation: Plating and subsequent corrosion studies were done on low-carbon steel foils of thickness 0.5mm and area 25mm x 20mm ($5cm^2$). Initially, the steel sample was mechanically polished with successively finer grades of emery paper. The samples were then degreased with alkali and rinsed with de-ionized water for 2 minutes. Next, the samples were treated in 20% conc. HCl acid for 1 minute to remove any adherent oxide layer that may be present on the surface. Finally, the samples were again washed in de-ionized water. The above sample preparation was repeated several times until a clean surface was obtained.

Electrolyte preparation and deposition: Preliminary studies were performed from an electrolytic bath of 60g/L $NiSO_4.6H_2O$, 30 g/L $ZnSO_4.7H_2O$ and $CuSO_4$. The amount of $CuSO_4$ is varied to control the Zn:Ni ratio as desired. Complexing agents and additives were used to further improve the properties of the deposit. The samples were electrodeposited potentiostatically using an EG&G PAR model 273 potentiostat interfaced with a computer. A three-electrode setup in a jacketed cell was used to plate the deposits. The steel foils prepared as described above were used as the working electrode. Platinum foil of equal area to that of the working electrode was used as a counter electrode and a standard calomel electrode (SCE) was used as a reference electrode. The distance between the working and counter electrode was maintained at a constant value of 1.5 cm. The deposition time was changed according to the required thickness of the coating. All solutions were prepared with analytical-grade reagents and triply distilled water.

Characterization: Energy dispersive spectroscopy (EDAX) was used to analyze the Zn:Ni ratio of the electrodeposits. Electrochemical techniques and Electrochemical impedance spectroscopy (EIS) were used to evaluate the barrier film resistance of the Zn-Ni-Cu deposits. Since chemical dissolution of zinc deposit occurs under acidic or alkaline conditions, the corrosion studies of Zn-Ni-Cu coatings were carried out in a 0.5 M Na_2SO_4 + 0.5 M H_3BO_3 buffer solution of pH 7.0. A three-electrode setup and an EG&G PAR model 273 potentiostat and a Solatron impedance analyzer were used to carry out the corrosion measurements. A standard calomel electrode was used as the reference and a platinum mesh electrode as the counter electrode.

Results and Discussion

Figure 1 represents the EDAX analysis for a conventional Zn-Ni alloy that exhibits anomalous behavior and that of a Zn-Ni-Cu alloy. The Zn:Ni ratio in the commercial alloy was as high as 7.5 : 1. With the addition of 1g/L of $CuSO_4$ in the bath, the ratio of Zn:Ni decreases to 1.3 : 1. It was observed that the Zn:Ni ratio can be varied with the use of the ternary alloying element copper. Now we proceed step by step to obtain an insight into the deposition process of Zn-Ni-Cu.

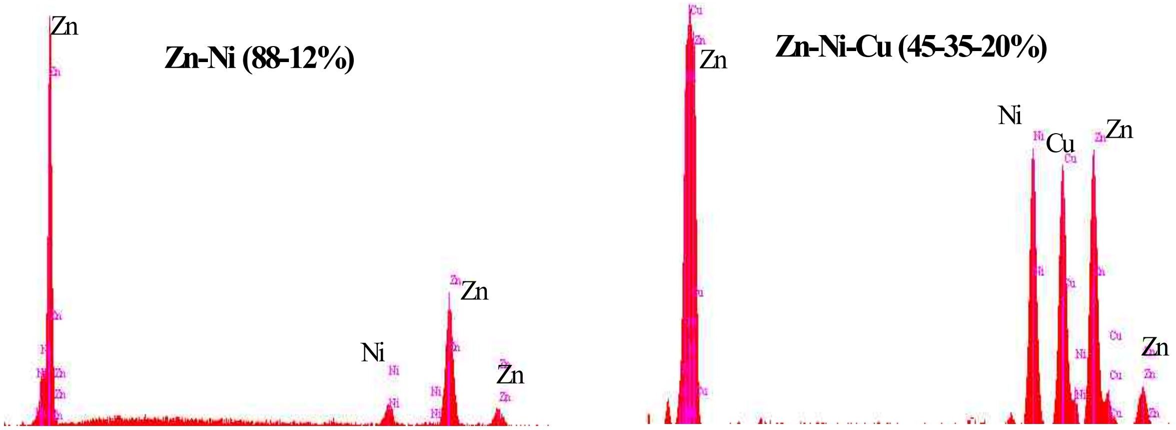


Figure 1: EDAX analysis of Zn-Ni alloy (88-12 %) and Zn-Ni-Cu alloy (45-35-20%).

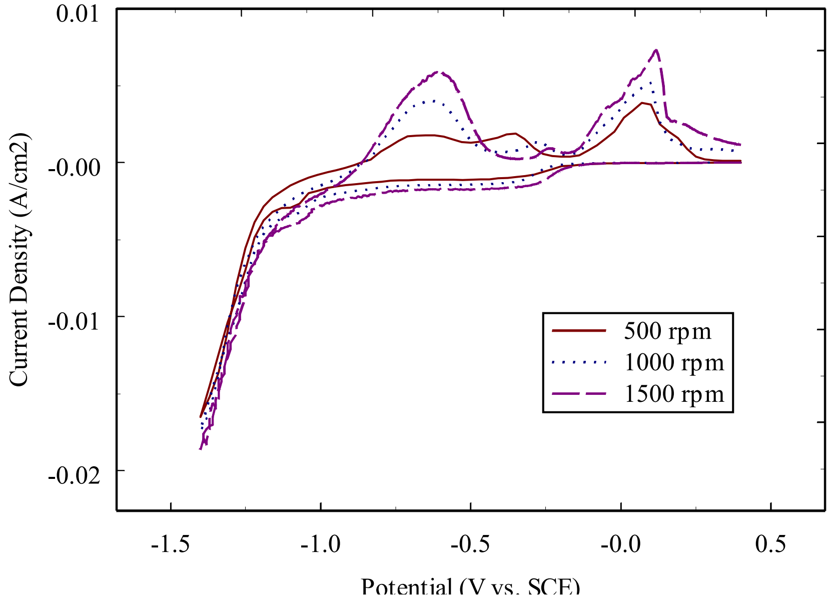


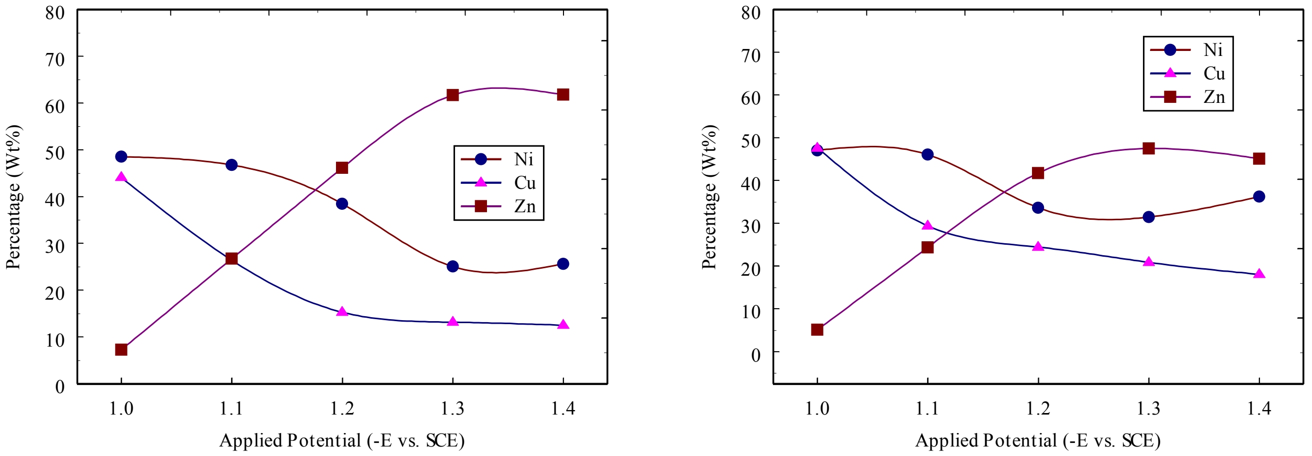
Figure 2: Cyclic voltammogram of Zn-Ni-Cu film electrodeposited from a solution of 40 g/L of NiSO4.6H2O, 20 g/L of ZnSO4 and 1 g/L of CuSO4 at a scan rate of 30 mV/s.

Stripping Cyclic Voltammetry:

Stripping cyclic voltammograms (SCV) were obtained to analyze the behavior of the Zn-Ni-Cu deposition process. Electrodeposition of the Zn-Ni-Cu was performed on a gold rotating disc electrode of 0.458 cm^2 area. The composition of electrolyte used was 40 g/L of $NiSO_4.6H_2O$, 20 g/L of $ZnSO_4.7H_2O$, 71 g/L of Na_2SO_4 and 1 g/L of $CuSO_4$. The potential was varied at a scan rate of 30 mV/s from –0.5 V (vs. SCE) to a cathodic potential of –1.4 V (vs. SCE) and back to the initial potential, –0.5 V (vs. SCE). This potential range is representative of the hydrogen evolution and metal dissolution reactions occurring at the surface of the coating under normal corroding conditions. Figure 2 represents the SCV analysis of Zn-Ni-Cu deposits obtained at different rotation speeds. Deposition of Zn, Ni and Cu takes place during the forward cathodic scan. Beyond a potential of –1.1 V (vs. SCE), the steep increase in the current can be attributed to the hydrogen evolution reaction. During the reverse scan distinct current peaks were observed. These peak currents are attributed to the dissolution of the metal alloy components. The first dissolution peak occurring at –0.77 V (vs. SCE) corresponds to the zinc dissolution [21]. The second anodic peak occurring at –0.43 V (vs. SCE) can be attributed to the dissolution of the nickel rich phase. The final dissolution peak in the anodic scan corresponds to the dissolution of the copper rich phase. The SCVs were performed at three different rotation speeds to determine the mass transfer effect limitations on the deposition process. The peak currents corresponding to the Zn and Cu dissolution potentials increase with increase in the rotation speed, indicating the mass transfer controlled nature of the deposition processes. These are in agreement with the previous studies [21]. Nickel deposition is kinetically controlled [25]. The dissolution peak decreases with increase in rotation speed. The observed decrease in the nickel peak current is due to the effect of side reactions that are under mass transfer control. With this preliminary knowledge of the deposition process, we next proceed to study the effect of electroactive species on the composition of the deposit.

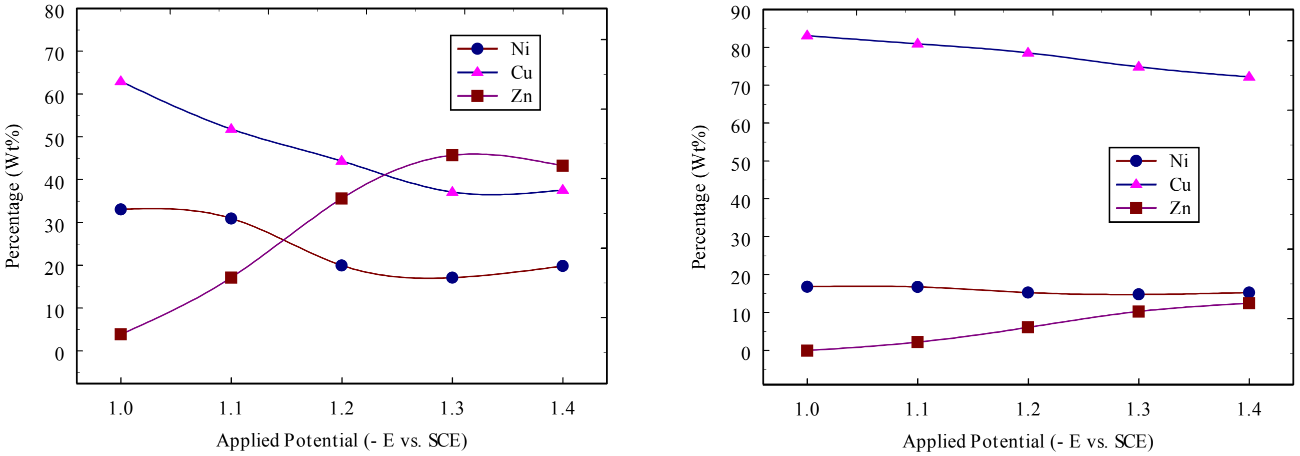
Effect of $CuSO_4$ concentration:

To analyze the effect of CuSO4 concentration on the ratio of Zn: Ni, depositions were carried out from an alkaline bath of 60 g/L $NiSO_4.6H_2O$, 30 g/L $ZnSO_4.7H_2O$, with the amount of copper sulfate varied between 0.5 g/L and 4 g/L. The bath pH was maintained at 9.0 and depositions were carried out potentiostatically at different potentials without stirring. Figure 3 represents the effect of $CuSO_4$ concentration and deposition potential on the composition of the deposit. It is observed that at low potentials, copper and nickel deposition dominate the process resulting in increased content of copper and nickel in the deposit. The Zn content is as low as 30% in the presence of 0.5 g/L of $CuSO_4$. This is due to the low applied potential of the deposit. With increase in the deposition potential, Zn content in the deposit increases with decrease in the nickel and copper composition. The addition of $CuSO_4$ in the deposit, alters the Zn-Ni ratio. When deposited at -1.3 V (vs. SCE), the nickel content increases from 12.4% (not shown in Fig 3) to 25 % with the addition of 0.5 g/L of $CuSO_4$ in the Zn-Ni bath. When the concentration of CuSO4 is about 1g/L, the nickel content is as high as 31 %. It can be observed that the nickel content in the deposit increases with the addition of $CuSO_4$ in the bath. The increase in the concentration of $CuSO_4$ in the bath leads to an increase in the copper content in the deposit. Anomalous deposition of Zn-Ni is due to the preferential adsorption of Zn ion on the depositing



a) 0.5 g/L

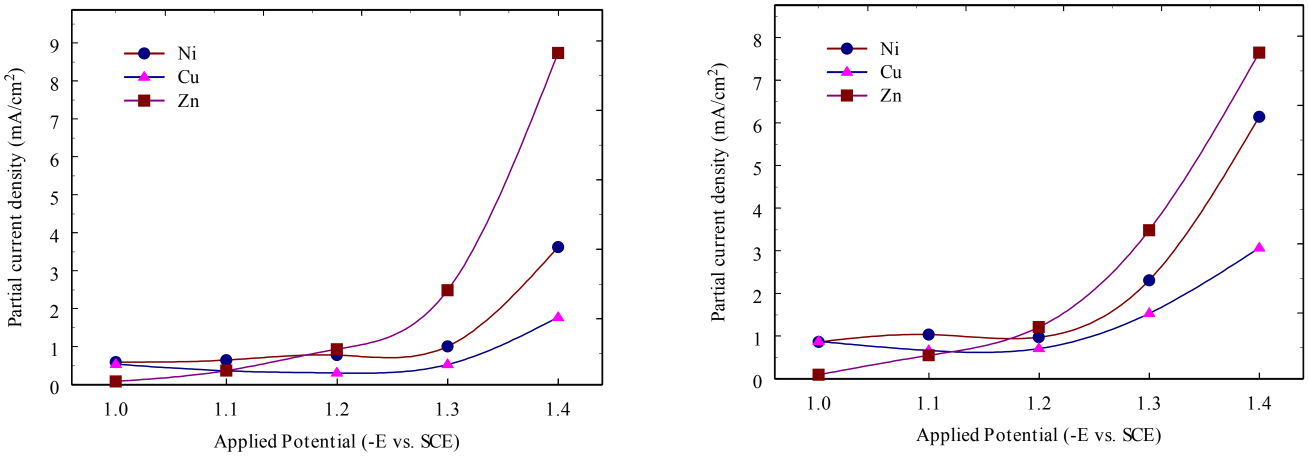
b) 1 g/L



c) 2 g/L

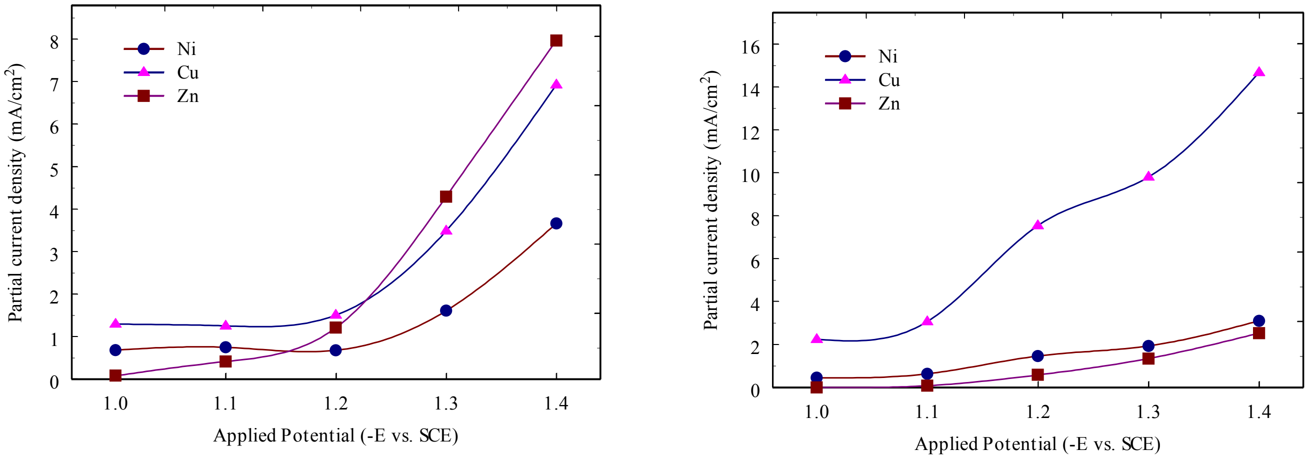
c) 4 g/L

Figure 3: Effect of $CuSO_4$ *concentration on the alloy composition of electrodeposited Zn-Ni-Cu as a function of applied (negative) potential.*



a) 0.5 g/L

b) 1 g/L



c) 2 g/L

c) 4 g/L

Figure 4: Effect of $CuSO_4$ concentration on the partial current density of electrodeposited Zn-Ni-Cu as a function of applied (negative) potential.

surface. The adsorption is not necessarily, electrochemical in nature. Presence of Cu ions in the solution decreases the preferential adsorption of zinc ions to the surface there by favoring the nickel deposition. But with the concentration of $CuSO_4$ in the bath 2 g/L and beyond, copper deposition dominates the whole process leading to a decrease in both Ni and Zn content. The decrease in Ni content is less pronounced compared to that of Zn. To have a better insight in to the deposition process, the partial current densities were calculated using faraday's law. Figure 4 shows the plot of partial current density as a function of applied potential and concentration of $CuSO_4$. When the concentration of $CuSO_4$ in the bath is less than or equal to 1 g/L, the limiting current of Cu is lower than the partial current density of Ni. As seen from our preliminary studies with SCV, Zn and Cu are mass transfer controlled. Since Cu is mass transfer controlled, the concentration of the Cu in the deposit does not increase once the limiting current density for the deposition is reached. However, further increase in the concentration of the $CuSO_4$ in the bath lead to an increase in the limiting current density of copper. When the limiting current density of Cu exceeds the partial current densities of Ni and Zn, Cu deposition dominates the whole process. As high as 80 % of Cu was observed in the deposit when the concentration of $CuSO_4$ was 4g/L and further increase in the potential showed minimal change in the composition of the deposit. Hence the prominent factor in determining the composition of the deposit is the concentration of $CuSO_4$ in the bath.

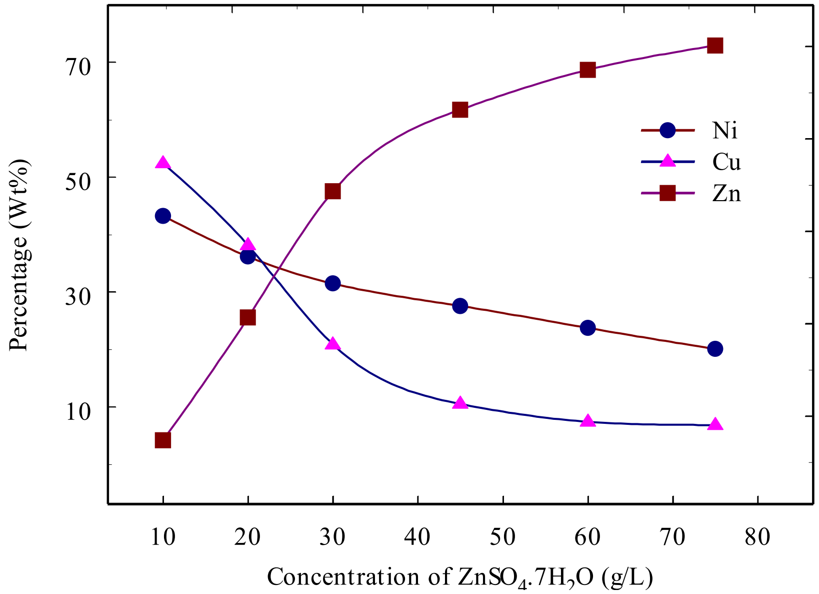


Figure 5: Effect of $ZnSO_4.7H_2O$ concentration on the composition of the Zn-Ni-Cu alloy electrodeposited from 60 g/L of $NiSO_4.6H_2O$, $ZnSO_4$.7H2O in the presence of a) 1 g/L of $CuSO_4$,

Effect of $ZnSO_4.7H_2O$ concentration:

The concentrations of the electroactive species in the bath play a significant role in determining the composition of the alloy. This is due to the kinetics of the deposition processes. Figure 5 shows the variation in composition of the alloy as a function of the $ZnSO_4.7H_2O$

concentration in the bath. Depositions were made from 60 g/L of $NiSO_4.6H_2O$ and 1 g/L of $CuSO_4$, pH 9.0 at –1.3 V (vs. SCE). It is observed that the zinc content in the deposit increases with increasing $ZnSO_4.7H_2O$ in the bath. The Cu and the Ni contents decrease. Increase in the Zn content shifts the corrosion potential to more negative value, leading to a decrease in the corrosion resistance of the coating. From the studies, the concentration of $ZnSO_4.7H_2O$ should be 30 g/L for an optimum Zn:Ni ratio in the deposit. In the case of 1 g/L of $CuSO_4$ in the bath, the increase in zinc content in the deposit is well pronounced with increase in $ZnSO_4$ concentration in the bath. But when the concentration of $CuSO_4$ in the deposit is 4 g/L (not shown in Fig 5), an increase in the concentration of $ZnSO_4$ in the solution doesn't have significant change in the composition of the deposit. Copper was found to dominate the alloy composition. Thus it becomes imperative to fix the concentration of $CuSO_4$ less than 1g/L.

Corrosion Characteristics of the Coating:

As the primary objective of the work is to find a replacement for cadmium coatings, the corrosion characteristics of the Zn-Ni-Cu alloy were determined and compared with other conventional coatings available in the industry. The Zn, Zn-Ni and cadmium coatings chosen for the comparison were deposited from commercial industrial baths. All the coatings were deposited to a thickness of 2 μm. The thickness of the coatings was estimated by dividing the weight of a unit area by the average density of the alloy. The following studies were performed to evaluate the performance of the coating.

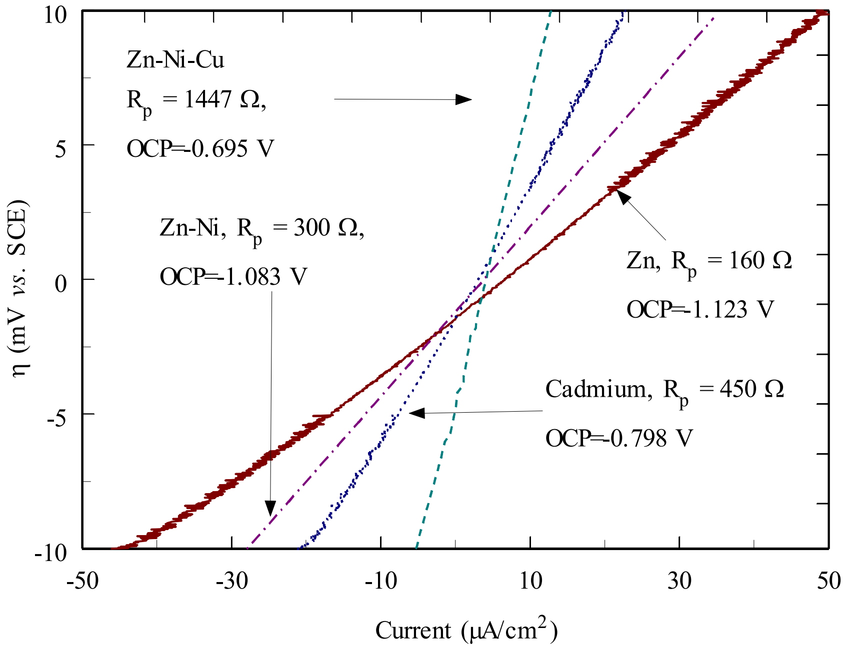


Figure 6: Linear polarization plots for Zn, Zn-Ni, Cd and Zn-Ni-Cu coatings in 0.5 M Na_2SO_4 + 0.5 M H_3BO_3, pH 7.0 solution.

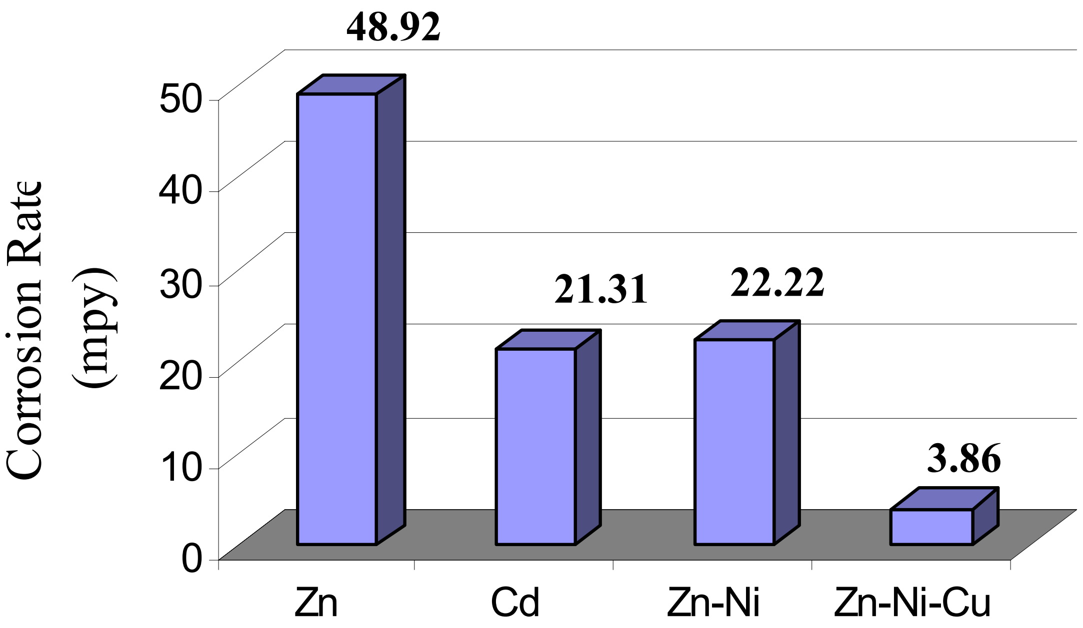


Figure 7: Comparison of corrosion rates for various coatings

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, Zn-Ni and Zn-Ni-Cu alloy coatings. Zn-Ni-Cu alloy was electrodeposited from alkaline sulfate electrolytes in the presence of 1 g/L of $CuSO_4$ in the plating bath. 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 Zn-Ni-Cu and various alternative coatings are shown in Figure 6. The slopes of these lines yield the values of the polarization resistance. The slope of the overpotential vs. current density plot is very high for the Zn-Ni-Cu alloys suggesting that they have excellent barrier properties. The low polarization resistance of the Zn and Zn-Ni alloy suggests high corrosion rates for these coatings in comparison with the Zn-Ni-Cu alloy coating. The resistance in the case of the Zn-Ni-Cu alloy was five times higher than for the Zn-Ni alloy. Figure 7 shows the corrosion rates for different coatings. The low corrosion rate for the Zn-Ni-Cu electrodeposit is evidently from the high barrier resistance of the deposit. Thus the Zn-Ni-Cu alloy obtained with the addition of 1 g/L of $CuSO_4$ to the Zn-Ni bath can be an ideal sacrificial coating for the corrosion protection of steel.

Conclusion

A novel electroplating process has been devised to obtain corrosion resistant Zn-Ni-Cu coatings. It has been shown that use of a ternary alloying element like $CuSO_4$ in small amounts can alter the Zn:Ni ratio in the deposit. Material characterization studies performed on the resulting deposits showed the codeposition of Cu along with Zn and Ni. Increasing the stirring speed increases the Cu and Zn content in the deposit with a decrease in the Nickel content. This is attributed to the kinetics of the deposition process; Cu and Zn deposition are diffusion limited while Nickel deposition is a kinetically limited process. The observed decrease in the nickel content arises out of the increase in the mass transfer limited Cu and Zn reduction processes. Beyond a concentration of 1 g/L of $CuSO_4$, Cu deposition dominates the whole process. With the use of 1 g/L of $CuSO_4$, a corrosion resistant Zn-Ni-Cu deposit with a Zn:Ni ratio of 1.3:1 and corrosion potential of –0.69 V was obtained. Electrochemical Impedance Spectroscopy and polarization studies show the corrosion resistance of this sacrificial coating is nearly five times that of the conventional Zn-Ni alloy. This increased corrosion resistance is attributed to the barrier properties arising from the higher nickel content in the deposit.

Thus a novel way of depositing corrosion resistant Zn-Ni-Cu alloy has been proposed. The new Zn-Ni-Cu alloy deposited shows increased corrosion resistance and barrier properties in comparison with conventional Zn-Ni and Cd coatings. Owing to its excellent corrosion properties, this new Zn-Ni-Cu alloy can be considered as an ideal replacement for cadmium coatings.

ACKNOWLEDGEMENTS

Financial Support by Dr. Vinod Agarvala, The Office of Naval Research under Grant No: NOOOO14-03-1-0028 and AESF Research Contract, Project 107 is gratefully acknowledged.

REFERENCES

[1] C.R.Tomachuk, C.M.de A.Freire, M.Ballester, R.Fratesi, G.Roventi, *Surface and Coatings Technology,* **122,** 6 (1999).
[2] K. R. Baldwin, C. J. E. Smith, *Transactions of the Inst. of Met. Finish.,* **74,** 202 (1996)
[3] W. H. Safranek, *Plat. Surf. Finish.,* **84,** 45 (1997).
[4] A. Ashur, J. Sharon, I. E. Klein, *Plat. Surf. Finish.,* **83,** 58 (1996).
[5] A. J. Boehm, *Plat. Surf. Finish.*, **80**, 52 (1993).
[6] Y. P. Lin, J. R. Selman, *J. Electrochem. Soc.,* **140,** 1299 (1993).
[7] Y. Miyoshi, *J. ISIJ Int.,* **31,** 1 (1991).
[8] Y. H. Yau, S. G. Fountolakis, in *Proceedings of Zinc based Steel Coating Systems: Metallurgy and Performance,* p.143 Minerals, Metals and Materials Society, (1990).
[9] A. Shibuya, T. Kurimoto, K. Korekewa, K.Noti, *Tetsu-To-Hagane,* **66,** 71 (1980).
[10] N. Muira, T. Saito, T. Kanamaru, Y. Shindo, Y. Kitazawa, *Trans. Iron Steel Inst. Japan,* **23**, 913 (1983).
[11] M. R. Lambert, R. G. Hart, Paper # 860266, presented at the SAE meeting in Detroit, MI, Feb 24 (1986).
[12] *The Properties of Electrodeposited Metal and Alloy*, W. H. Safranek, Editor, p.466, AESF, Orlando, FL (1986).
[13] A. Brenner, *Electrodeposition of Alloys, Principles and Practice,* Chap. 1, Academic Press, New York (1963).
[14] N. S. Grigoryan, V. N. Kudryavtsev, P. A. Zhdan, I. Y. Kolotyrkin, E. A. Volynskaya and T. A. Vagramyan, *Zasch. Met.,* **25,** 288 (1989).

[15] D. E. Hall, *Plat. Surf. Finish.,* **70** , 59 (1983).

[16] K. Higaashi, H. Fukushima, T. Urakawa, T. Adaniya, K. Matsudo, *J.Electrochem. Soc.,* **128,** 2081 (1981).

[17] A. Krishniyer, M. Ramasubramanian, B. N. Popov, R. E. White, *Plat. Surf. Finish.,* **1,** 99 (1999).

[18] A. Durairajan, A. Krishniyer, B. N. Popov, B. Haran, R. E. White, *Corrosion,* **56**,283 (2000).

[19] Z. Zhou, T. J. O. Keefe, *Surface and Coatings Technology*, **96**, 191 (1997).

[20] B.N.Popov, D.Slavkov, T.Grcev, Lj.Arsov and S.Kariavanov, Kem. Ind., **1**,1(1986).

[21] B.N.Popov, M. Ramasubramanian, S.N.Popova, R.E.White and K.M.Yin, *J.Chem. Soc ., Faraday Trans.,* **92**, 4021 (1996).

[22] Anand Durairajan, Bala S.Haran, Ralph E.White, Branko N. Popov, *J.Electrochem. Soc.,* **147**, 1781 (2000).

[23] Anand Durairajan, Bala S.Haran, Ralph E.White, Branko N. Popov, *J.Electrochem. Soc.,* **147**, 4507 (2000).

[24] Hansung Kim, Anand Durairajan, Branko N.Popov, *J.Electrochem. Soc.,* (in press).

[25] B.N.Popov, S.N.Popova, K.M. Yin, R.E.White, *Plat. Surf. Finish.,* **81**,65 (1994)