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# Development of a New Electrodeposition Process for Plating of Zn-Ni-X (X=Cd, P) Alloys

## I. Corrosion Characteristics of Zn-Ni-Cd Ternary Alloys

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A new Zn-Ni-Cd plating process was developed which offers a unique way of controlling and optimizing the Ni and Cd contents in the final deposit. Zinc-nickel-cadmium alloy was deposited from a 0.5 M NiSO<sub>4</sub> + 0.2 M ZnSO<sub>4</sub> bath in the presence of 0.015 M CdSO<sub>4</sub> and 1 g/L nonyl phenyl polyethylene oxide. Using this process a Zn-Ni-Cd ternary alloy, with a higher nickel content as compared to that obtained from conventional Zn-Ni baths, was synthesized. The Zn-Ni-Cd alloy coatings deposited from an electrolyte containing 0.015 M (0.3%) CdSO<sub>4</sub> has a Zn to Ni ratio of 2.5:1. The increase in nickel content accounts for the observed decrease in the corrosion potential to a value lower than that of Cd but higher than the corrosion potential of iron. The coatings have superior corrosion resistance and barrier properties than the typical Zn-Ni and cadmium coatings. Polarization studies and electrochemical impedance spectroscopy analysis on Zn-Ni-Cd coatings show a barrier resistance that is ten times higher than that of a conventional Zn-Ni coating.

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Cadmium has been used extensively as a corrosion resistant coating in aerospace, electrical, and fastener industries owing to its excellent corrosion resistance and engineering attributes.<sup>1</sup> Cadmium deposition is done from cyanide baths, which are subject to stringent regulations.<sup>2</sup> Alternate baths for cadmium plating are also undesirable due to the toxicity of the metal and its salts.<sup>3</sup> Further during cadmium deposition, large amounts of hydrogen are introduced into the underlying metal.<sup>4</sup> This increases the risk of hydrogen embrittlement failure in the structure. Hence environmental concerns and performance criteria mandate the search for alternatives to cadmium coatings.<sup>5</sup> Various zinc and zinc alloy coatings show promise in this regard. Electrodeposited zinc has been widely used for the protection of steel from corrosion. These electrogalvanized coatings have been shown to be more effective when alloyed with metals such as nickel, iron, and cobalt.

Zinc-nickel alloy coatings have been suggested in the literature as replacement for cadmium coating because this alloy provides good corrosion protection on steel,<sup>6-8</sup> superior formability, and improved weldability.<sup>9-11</sup> Zn-Ni alloys containing 15-20 wt % nickel has been shown to possess four times more corrosion resistance than cadmium-titanium deposit.<sup>12</sup> However, due to the high zinc content in the deposit, these alloys are more negative than cadmium and hence dissolve rapidly in corrosive environments. Although Ni is a more noble metal than Zn, the codeposition 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 the literature.<sup>13,14</sup> Typical nickel composition in the alloy is approximately 5-10%, and any further increase in nickel composition is based on using a higher-than-predicted Ni/Zn ratio in the bath.<sup>15,16</sup> 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.

Several researchers have attempted to decrease the anomaly and increase the nickel content by either introducing inert species in the bath or by developing a ternary alloy.<sup>17-21</sup> Nonyl phenyl polyethylene oxide (NPPO) has been used to reduce this anomaly and to produce uniform deposits.<sup>20,21</sup> NPPO inhibited zinc electrodeposition and acted as a leveling agent as was seen in our earlier studies on deposition of zinc<sup>20</sup> and galvanostatic pulse and pulse reverse plat-

ing of zinc-nickel alloys<sup>21</sup> from sulfate electrolytes. According to our studies,<sup>20,21</sup> adsorption of NPPO on the electrode surface increased the surface overpotential due to the less effective exchange current density of the electroactive species participating in the reduction process. At a specific applied current density, the fractional coverage of the electrode surface with nonyl phenyl polyethylene oxide causes the operating potential to be extended in cathodic direction without creating conditions for concentration depletion of the electroactive species at the interface. The increased polarization under potentiostatic conditions has been explained theoretically.<sup>22</sup> Slower kinetics rather than concentration overpotential compensate for the potential drop, which occurs in the presence of NPPO.

Codeposition of phosphorous along with Zn-Ni improves the corrosion<sup>17</sup> and hydrogen permeation<sup>18</sup> characteristics of the electrodeposit. Zn-Ni-P alloy had superior corrosion properties and inhibited the hydrogen entry in the substrate as compared to Zn-Ni alloy.<sup>18</sup> Zhou *et al.*<sup>19</sup> have studied the effect of tin additions on the anomalous deposition of Zn-Ni alloy. The nickel ratio increased from 6 to 8% with the addition of small amounts of tin. However, the observed small increase of Ni content in the alloy did not improve the Zn-Ni barrier properties.

The goal of the present study is to develop Zn-Ni alloy based coatings for the protection of steel substrates. Our objective was to develop an electrodeposition process for plating of Zn-Ni-X (X=Cd, P) ternary or quaternary alloys, which will induce barrier properties to the sacrificial Zn-Ni alloy thereby extending the life of the coating. By introducing a new element in the Zn-Ni alloy we expected to decrease the Zn-Ni ratio in the alloy and consequently to decrease the Zn-Ni alloy corrosion potential from -1.14 V vs. SCE to even lower values than the corrosion potential of Cd (-0.79 V) but more negative than the Fe corrosion potential. Also, by introducing a third element in the alloy we expected to modify the rate of hydrogen evolution reaction, the hydrogen proton recombination and adsorption kinetics at the surface and to impede completely the proton penetration in the alloy thus eliminating the hydrogen embrittlement. The hydrogen permeation study is presented in the second part of this paper.

A variety of electrochemical techniques were used to evaluate the barrier film resistance of Zn-Ni-Cd deposits. Energy dispersive spectroscopy (EDAX) has been used to analyze the Zn-Ni ratio of the electrodeposits.

### Experimental

*Sample preparation.*—Plating and subsequent corrosion studies were done on low-carbon steel foils of thickness 0.5 mm and area 50 × 50 mm. Initially, the steel sample was mechanically polished

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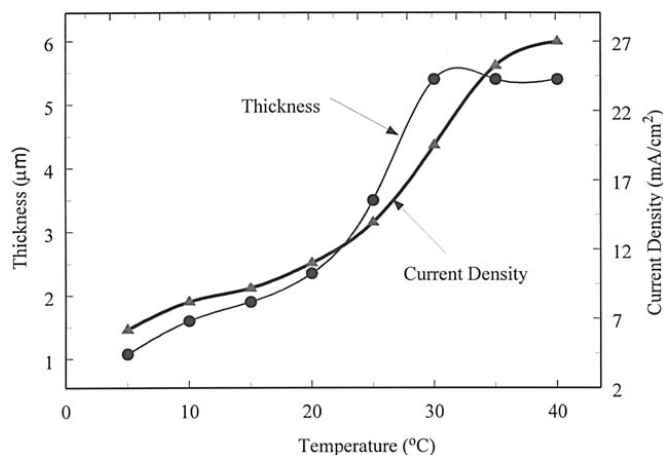
with successively finer grades of emery paper. The samples were then degreased with alkali and rinsed with deionized water for 2 min. Next, the samples were treated in 20% conc. HCl acid for 1 min to remove any adherent oxide layer that may be present on the surface. Finally, the samples were again washed in deionized water. The above sample preparation was repeated several times until a clean surface was obtained.

**Electrolyte preparation and electrodeposition.**—Zinc-nickel-cadmium alloy composites were deposited from a 0.5 M NiSO<sub>4</sub> + 0.2 M ZnSO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub> bath in the presence of 0.015 M CdSO<sub>4</sub> and 1 g/L nonyl phenyl polyethylene oxide. Zn-Ni-Cd alloys of different Cd contents were obtained by varying the amount of cadmium sulfate in the bath. Deposition and subsequent electrochemical characterization was done 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 as that of the working electrode was used as a counter electrode and standard calomel electrode (SCE) was used as a reference electrode. All depositions were carried out potentiostatically at  $-1.2$  V vs. SCE. The distance between the working and counter electrode was maintained at a constant value of 2.5 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.**—EDAX was used to analyze the Zn-Ni ratio of the electrodeposits. A variety of electrochemical techniques including electrochemical impedance spectroscopy (EIS), were used to evaluate the barrier film resistance of Zn-Ni-Cd deposits. Since chemical dissolution of zinc deposit occurs under acidic or alkaline conditions, the corrosion studies of Zn-Ni-Cd coatings were carried out in a 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub> 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 perform the corrosion measurements. A standard calomel electrode (SCE) was used as the reference and a platinum mesh electrode as the counter electrode.

## Results and Discussion

**Temperature studies.**—Initially, various Zn-Ni-Cd deposits were obtained potentiostatically in the presence of 1 g/L of nonyl phenyl polyethylene oxide at temperatures ranging from 5 to 50°C. Constant temperature was maintained by circulating water in the jacketed cell in which the deposition was carried out. Deposition time and other parameters were kept the same for all the depositions. As shown in Fig. 1 both the current density and the deposit thickness increase with deposition temperature up to 30°C. The current density and consequently the thickness of the deposit increase with temperature



**Figure 1.** Effect of deposition temperature on thickness and current density of the deposit.

due to the increased transport of the electroactive species from the bulk of the electrolyte. The increase in deposition rate with temperature could also be due to overcoming activation overpotential. At temperatures higher than 30°C, the thickness and the current density level off. Deposits obtained at 30°C and at higher temperatures show good appearances compared to those obtained at lower temperatures, which were black in color indicating lower zinc content.<sup>20</sup> Hence the temperature was maintained at 30°C for all subsequent depositions.

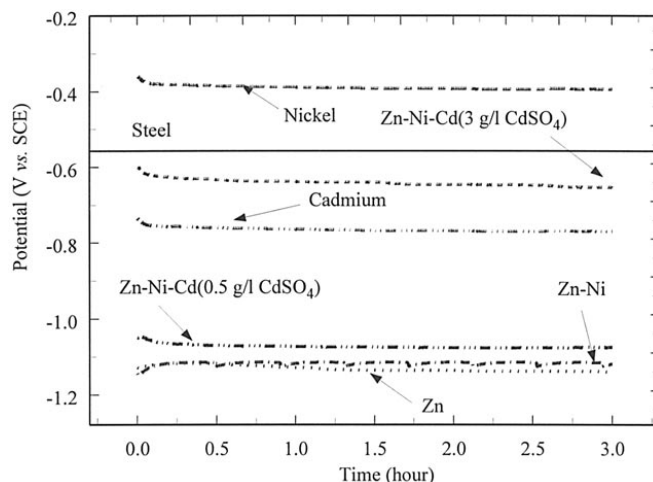
**Thick film studies.—Stability tests.**—Zn-Ni alloy coating acts as a sacrificial alloy. It dissolves in the corroding media to protect the underlying steel from corrosion. The changes in surface potential associated with the dissolution of the sacrificial metal often discourage the use of steady-state techniques like impedance spectroscopy. Also the anodic polarization studies on these coatings enhance dissolution and can render inaccurate data if proper care is not taken.

Since it was necessary to prepare coatings with electrochemical properties, which do not change during the test period, thick films of Zn-Ni-Cd were deposited by increasing the deposition time to 90 min. The deposit thickness was estimated by dividing the weight of a unit area of the coating with the average density of the alloy. Thus, the estimated value of the thickness of 15 µm is an average value.

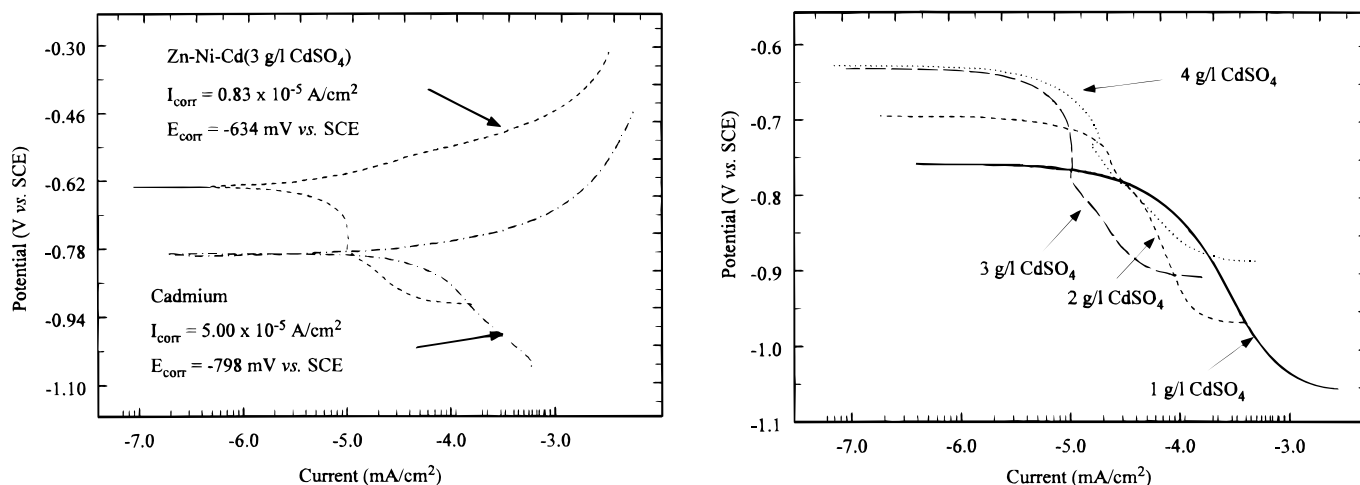
In Fig. 2 the corrosion potentials and the stability of deposited alloys as a function of time are compared with the corrosion potential and stability of nickel, cadmium, and steel substrates in the corroding media (0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub> buffer solution of pH 7.0). The observed shift in the corrosion potential from  $-1.14$  V (Zn-Ni alloy) to a corrosion potential of  $-0.635$  V corresponding to Zn-Ni-Cd (3 g/L CdSO<sub>4</sub> + 1 g/L nonyl phenyl polyethylene oxide) ternary alloy coatings indicates a change in the Zn-Ni alloy content ratio in the alloy. From the corrosion potentials presented in Fig. 2 one may conclude that a presence of 3g/L of CdSO<sub>4</sub> in the Zn-Ni sulfate bath results in a deposition of an Zn-Ni-Cd ternary alloy with lower zinc content and higher corrosion resistance when compared with the Zn-Ni alloy. This has been confirmed in the following set of studies.

Addition of 3 g/L of CdSO<sub>4</sub> in the Zn-Ni sulfate bath resulted in a deposit with a rest potential of  $-0.635$  V vs. SCE, which is higher than the corrosion potential of Cd ( $-0.798$  V) but lower than the corrosion potential of steel. Thus, the new Zn-Ni-Cd coating has a galvanic compatibility with many metals that need protection including steel and aluminum. The overvoltage (galvanic driving overpotential) when steel is protected with Zn-Ni-Cd alloy is approximately 100 mV or less compared to 670 mV overpotential when Zn-Ni alloy protects a steel substrate.

As shown in Fig. 2, the corrosion potential of deposited alloys does not change significantly over a period of 3 h. Thus, characteri-



**Figure 2.** Comparison of  $E_{\text{corr}}$  vs. time plots for zinc, nickel, cadmium, and various Zn-Ni-Cd alloy composites (thickness = 15 µm) immersed in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub> at pH 7.0.



**Figure 3.** (a, left) Tafel polarization plot of Zn-Ni-Cd alloy deposit obtained from a bath containing 3 g/L CdSO<sub>4</sub> as additive. Tafel plot of Cd is shown for comparison. Corrosion rate of the coating is obtained by extrapolating the anodic and cathodic polarization curves. (b, right) Cathodic polarization curves of Zn-Ni-Cd alloys with different amounts of CdSO<sub>4</sub> additives in the bath.

zation techniques such as Tafel, cyclic voltammetry, and EIS can be completed within the 3 h at the conditions prescribed in this work and hence the accuracy of the analysis will be still preserved.

**Tafel studies.**—Tafel polarization studies were carried out to measure the corrosion rates of the plates. Figure 3a shows Tafel plot of Zn-Ni-Cd and cadmium coatings. As shown in Fig. 3a, the corrosion current is one order of magnitude smaller for Zn-Ni-Cd (obtained by addition of 3 g/L CdSO<sub>4</sub> to the bath) than that of cadmium. Figure 3b shows cathodic polarization curves of Zn-Ni-Cd alloy coatings deposited from baths containing different concentrations of the CdSO<sub>4</sub>. As shown in Fig. 3b by increasing the concentration of CdSO<sub>4</sub> in the Zn-Ni sulfate bath from 1 to 3 g/L, the polarization curves (due to a change in the kinetics of the hydrogen evolution reaction on deposited Zn-Ni-Cd alloy coatings) shifted to lower currents. Further increase of the concentration of CdSO<sub>4</sub> in the plating bath does not change the corrosion rate significantly. It appears that 3 g/L of CdSO<sub>4</sub> in Zn-Ni sulfate bath is the lowest concentration to be used for improving the barrier properties of Zn-Ni coatings.

The open-circuit potentials and corrosion rates obtained from the polarization plots for Zn-Ni-Cd alloy coatings are compared in Table I with the those of pure zinc, nickel, and cadmium in the cor-

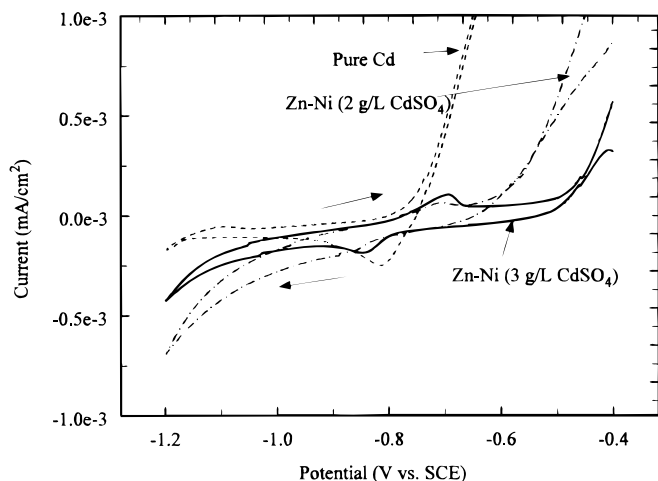
roding solution. The addition of small amounts of CdSO<sub>4</sub> significantly alters the Zn/Ni content ratio in the alloy. Addition of CdSO<sub>4</sub> beyond 3 g/L does not have a significant effect on the deposit properties. As seen from the corrosion potential data, the overpotential (a difference between the Fe and the alloy coating corrosion potentials) for dissolution is smaller for Zn-Ni-Cd deposits compared with Zn-Ni alloy. By increasing the CdSO<sub>4</sub> concentration in the electrolyte from 0.1 to 3 g/L, the open-circuit potential decreases from  $-1.14$  to  $-0.635$  V while the barrier properties of the coating increase, which are reflected in the low corrosion currents. Corrosion current of Zn-Ni-Cd alloy was the lowest in the case of nickel, which is to be expected owing to the high corrosion resistance of the nickel coatings. Zn-Ni coatings with CdSO<sub>4</sub> addition of more than 3 g/L has ten times smaller corrosion current compared to conventional Zn-Ni alloys. Also the corrosion resistance is seen to be better than pure cadmium coatings.

As shown in Fig. 3a and b, the slope of the cathodic polarization curves of Zn-Ni-Cd alloys changes between  $-0.8$  and  $-0.9$  V. This was absent in case of other Zn-Ni alloy coatings and for Zn-Ni-Cd alloy coatings deposited from Zn-Ni plating bath containing low concentrations of CdSO<sub>4</sub> (Fig. 3b). This behavior was highly reproducible and suggests the presence of a reduction reaction in addition

**Table I.** Composition and corrosion rates of Zn-Ni and Zn-Ni-Cd alloys. Values for Zn and Ni coatings are shown for comparison.

Deposit (steel substrate)	Composition analyses (wt %)			Open-circuit potential (mV vs. SCE)	Corrosion rate ( $\times 10^{-10}$ cm/s)
	Zn	Ni	Cd		
Zinc	100	0	0	-1140	39.4
Cadmium	0	0	100	-798	17.2
Nickel	0	100	0	-358	0.7
Zinc-nickel	93.4	6.6	0	-1127	17.7
Zinc-nickel (0.5 g/L CdSO <sub>4</sub> added)	81.6	14.9	3.6	-1060	11.8
Zinc-nickel (2 g/L CdSO <sub>4</sub> added)	76.0	18.0	6.0	-700	6.6
Zinc-nickel (3 g/L CdSO <sub>4</sub> added)	49.6	20.8	29.6	-635	2.6
Zinc-nickel (4 g/L CdSO <sub>4</sub> )	50.4	20.1	29.5	-634	2.6
Zinc-nickel (5 g/L CdSO <sub>4</sub> )	49.4	19.8	30.8	-632	3.0
Zinc-nickel (10 g/L CdSO <sub>4</sub> )	49.4	20.5	30.1	-635	2.7



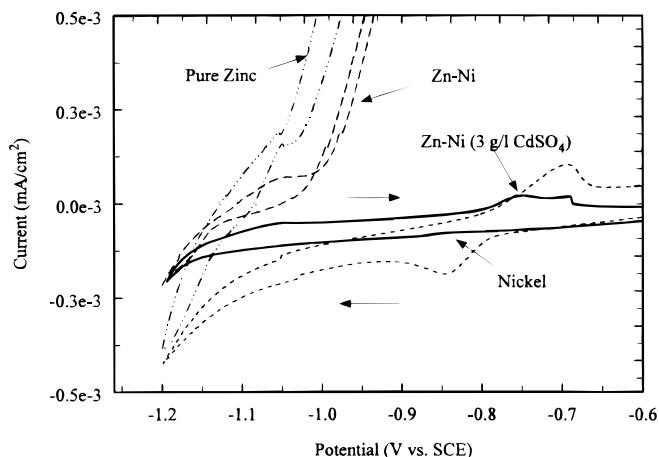


**Figure 4.** CV of Zn-Ni-Cd alloy coatings obtained from bath containing CdSO<sub>4</sub> additive. CV of pure cadmium is shown for comparison.

to hydrogen evolution reaction. In order to explore the origin of the plateau observed at  $-0.8$  V, detailed cyclic voltammetry studies were carried out.

**Cyclic voltammetry studies.**—Cyclic voltammograms (CVs) were obtained at a scan rate of  $1$  mV/s. The potential was swept from  $-0.40$  to  $-1.2$  V vs. SCE and back to  $-0.4$  V. This potential range covered the hydrogen evolution and metal dissolution reactions and is representative of the processes occurring at the surface of the coating under normal corroding conditions. Figure 4 shows the CV of pure cadmium coating and that of a Zn-Ni alloy coating produced with  $2$  and  $3$  g/L of CdSO<sub>4</sub> additive in the plating bath, respectively. The CVs are characterized by the presence of two processes in the forward and reverse scans. The cathodic current at  $-1.0$  V vs. SCE corresponds to hydrogen evolution occurring at Cd and on the coating surfaces. As shown in Fig. 4a decrease of the hydrogen evolution occurs on Zn-Ni-Cd alloy coating deposited from a bath, which contains  $3$  g/L CdSO<sub>4</sub>.

The second reduction process occurs  $-0.8$  V. As shown in Fig. 4, in both pure cadmium coating and Zn-Ni alloy coating with CdSO<sub>4</sub> additives, this peak arises due to the reduction of cadmium oxides to elemental cadmium. According to Pourbeaux<sup>21</sup> the cadmium oxides reduce to cadmium at this potential. The anodic sweep showed the cadmium oxidation at  $-0.7$  V and metal dissolution reactions dis-

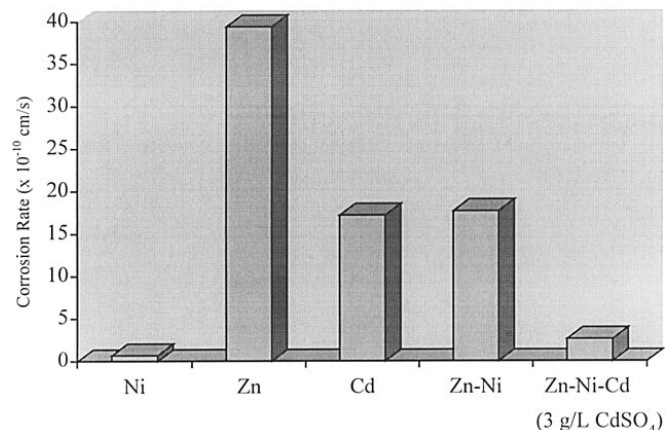
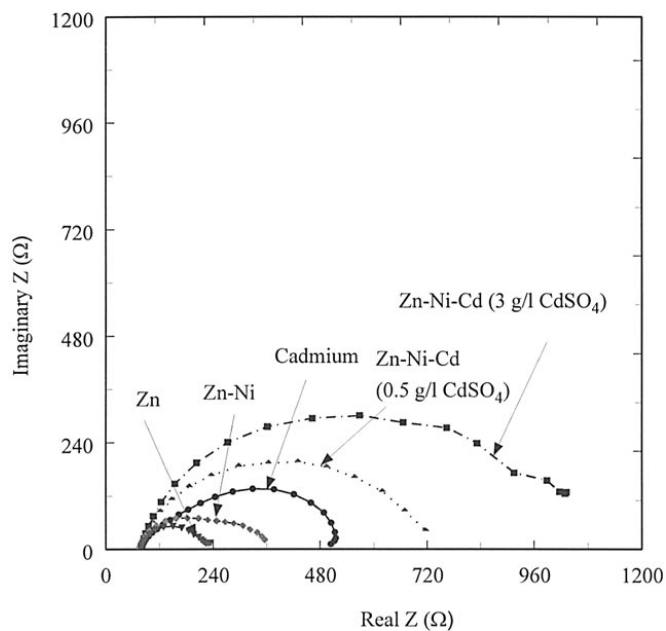


**Figure 5.** CVs of Zn, Ni, Zn-Ni, and Zn-Ni-Cd coatings. The metal dissolution currents are smaller in the case of Zn-Ni-Cd deposits indicative of the slower dissolution rate. This is also due to the increase in the nickel content in these coatings.

tinctly. The enormous difference between Cd dissolution current and the Zn-Ni-Cd alloy dissolution currents indicates the excellent barrier properties of Zn-Ni-Cd ( $3$  g/L CdSO<sub>4</sub>) alloy. Also, it appears that the addition of CdSO<sub>4</sub> not only alters the Zn-Ni ratio, but also includes Cd in the deposit.

Figure 5 compares the CVs of pure Zn, Ni, Zn-Ni, and Zn-Ni-Cd coatings. The CVs were carried out under the same conditions as in Fig. 4. The forward sweep as well as the reverse sweep shows the presence of hydrogen evolution and metal dissolution reactions on the coating surface. The additional peak that is due to cadmium reaction is discussed in Fig. 4. Both zinc and Zn-Ni deposits are characterized by the absence of any cathodic peaks. However, the metal dissolution currents during the anodic sweep are larger in the case of pure Zn and Zn-Ni coatings compared to Zn-Ni-Cd coatings. This is due to the improved barrier properties of Zn-Ni-Cd alloy coatings, which have corrosion potential very close to the substrate corrosion potential. Thus, in the case of Zn-Ni-Cd deposits, an effective barrier film forms on the surface.

**Electrochemical impedance spectroscopy (EIS).**—EIS was used to evaluate the barrier properties of the coatings and to determine the polarization resistance and the corrosion rates without modifying the surface. Figure 6a presents a comparison of Nyquist responses obtained for Zn, Zn-Ni, and various Zn-Ni-Cd coatings. The solution



**Figure 6.** (a, top) Nyquist responses of Zn, Cd, Zn-Ni, and various Zn-Ni-Cd coatings. (b, bottom) Comparison of corrosion rates of various alloy coatings.

resistance remains the same for all deposits. This is to be expected since the studies were done under similar conditions in pH 7.0.  $R_p$  values can be approximately determined by fitting the Nyquist response to a simple equivalent circuit consisting of ohmic resistance, double layer capacitance, and polarization resistance. Nickel coatings possess a high  $R_p$  value of 5800  $\Omega$  (not shown in Fig. 6a). This is obvious owing to the high barrier properties of nickel coatings. The polarization resistance of Zn-Ni-Cd alloy coatings improved with an increase in the CdSO<sub>4</sub> content in the plating bath. Zn-Ni coating with 3 g/L additive offers a barrier resistance of 1200  $\Omega$ , which is three times higher than the typical Zn-Ni deposit. The curves shown in Fig. 6a are composed of two (in some cases three) overlapping semicircles. Further, studies are to be done to evaluate these individual depressed semicircles.

**Energy dispersive analysis (EDAX).**—EDAX was used to analyze the Zn-Ni ratio of the electrodeposits. The concentration of the constituent elements was determined by comparing the intensities of the X-ray spectrum to the standard intensities of the pure element. The alloy composition was estimated at 50 different spots randomly selected throughout the area of the deposit. The standard deviations were estimated for deposits, which were obtained for different concentrations of CdSO<sub>4</sub> in the plating bath. In case of Cd they varied between  $\pm 1.3$  and  $\pm 1.8$ . For Zn content in the alloy, the standard deviations were between  $\pm 2.4$  and  $\pm 4.3$ . The standard deviation for nickel content was estimated to be between  $\pm 1.1$  and  $\pm 1.6$ . Also, the surface concentration analyses were carried out on three different deposits obtained under similar plating conditions. The Zn, Ni, and Cd content in the alloy varied within  $\pm 6.7$ ,  $\pm 4.3$ , and  $\pm 5.3\%$ , respectively.

These composition values of Zn-Ni-Cd alloys deposited from the plating bath containing different concentrations of CdSO<sub>4</sub> and their corrosion rates are compared with those of Zn-Ni alloy and Zn, Ni, and Cd plates in Table I. As shown in Table I, by increasing the CdSO<sub>4</sub> concentration in the plating bath from 0 to 10 g/L, the zinc content in the alloy decreases while the nickel content increases. The cadmium content increases from 3.57 wt % in Zn-Ni-Cd ternary alloy deposited from electrolyte containing 0.5 g/L CdSO<sub>4</sub> to approximately 30 wt %, deposited from a bath containing 3 g/L CdSO<sub>4</sub>. Further increase in CdSO<sub>4</sub> concentration up to 10 g/L does not cause any change in the cadmium content in the deposit. Thus, using CdSO<sub>4</sub> in the Zn-Ni sulfate bath and introducing Cd in the alloy, the Zn/Ni ratio decreases, which accounts for the observed increase in the corrosion potential of the alloy, inhibited hydrogen evolution reaction, and slow dissolution rate.

According to our previous studies,<sup>21</sup> the composition of the Zn-Ni alloy is controlled by the pH at the interface, the equilibrium concentrations of zinc and nickel ions and the charge and mass transfer of the electroactive species. In order to understand the influence of Cd on the codeposition reaction mechanism, electrochemical kinetic studies are currently being carried out for different concentrations of cadmium ions in the sulfate electrolyte. These studies will correlate the deposit composition with the concentration of the electroactive species in the bath.

The linear polarization technique was used to determine the corrosion rates presented in Table I and Fig. 6b. The estimated corrosion rates of Zn-Ni-Cd alloy reported in Table I are one order of magnitude smaller than those of the Zn-Ni. As shown in Table I, the corrosion rates of the Zn-Ni-Cd alloy depend upon the Cd content in the alloy. They stabilize at  $2.6 \times 10^{-10}$  cm/s for alloys with Cd content of 29% (CdSO<sub>4</sub> concentrations in the sulfate bath higher than 3 g/L). This ensures the longevity of the coating for industrial applications. A much thinner coating can be used to achieve the same protection that will be obtained using a thicker cadmium coating.

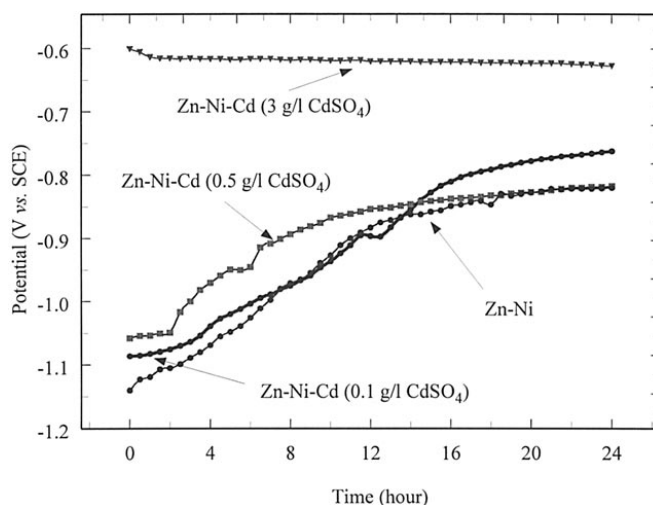
**Thin film studies.**—**Film dissolution studies.**—It is critical to understand the influence of the CdSO<sub>4</sub> on the rate of dissolution of the sacrificial metal. In order to examine the complete dissolution of the zinc-rich coating under corroding conditions, thinner coatings were studied. Thin films of a Zn-Ni-Cd alloy, approximately 2  $\mu\text{m}$ , were

deposited by decreasing the deposition time to 15 min. Our previous studies indicated that this deposition time is sufficient to cover the substrate surface completely.<sup>17</sup> The deposit thickness as mentioned above was estimated by dividing the weight of a unit area of the coating with the average density of the alloy. Thus, the estimated value of the thickness of 2  $\mu\text{m}$  is an average value.

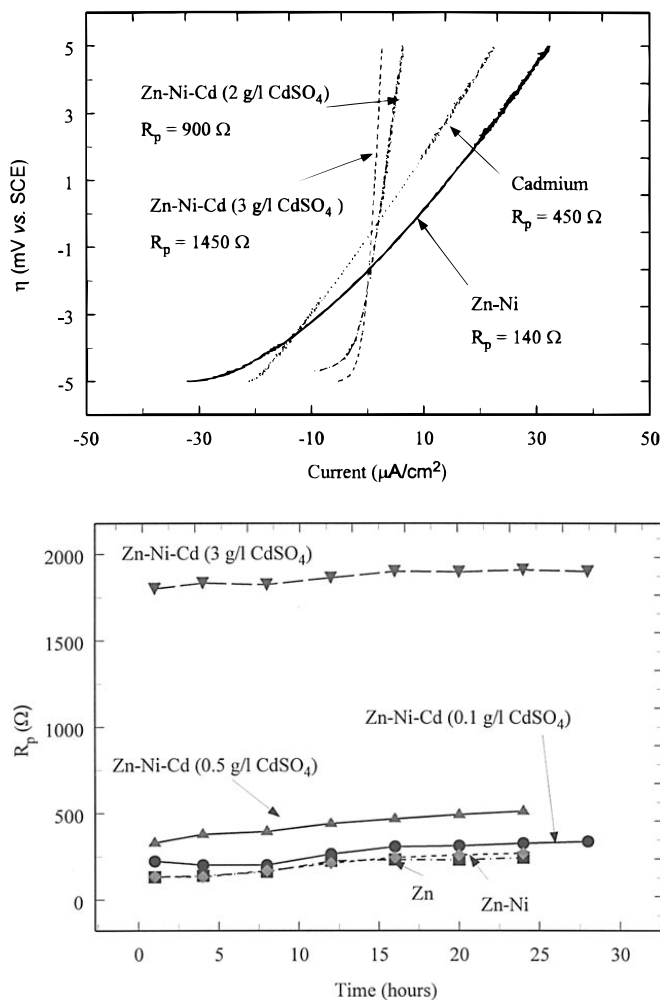
A sample of known surface area was exposed to the corroding media and the rest potential was monitored. Zn-Ni alloys deposit in three phases: a Zn-rich phase called eta ( $\eta$ ) phase ( $E_{\text{corr}} = -1.050$  V vs. SCE), an intermediate gamma phase, ( $\gamma$ ), ( $E_{\text{corr}} = -0.780$  V vs. SCE), and a nickel-rich alpha ( $\alpha$ ) phase, ( $E_{\text{corr}} = -0.450$  V vs. SCE) phase.<sup>17</sup> The  $\eta$  phase has a rest potential comparable to that of pure zinc as it is mostly composed of zinc.  $\eta$  phase deposits exhibit homogenous hexagonal shaped crystals, but once a galvanic couple is formed, they dissolve rapidly and the surface becomes enriched in the  $\gamma$  phase. The intermediate phase or the  $\gamma$  phase has a Zn-Ni ratio of 4:1, is a body-centered cubic structure, and usually represents a good barrier resistance against dissolution. But the thickness of this layer is so small that it vanishes in a short time. Dissolution of  $\beta$  phase would expose the nickel-rich phase to the 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 life of the protective coating would simply depend on the life of the more electronegative phase, which is a Zn-rich  $\eta$  phase in the case of Zn-Ni coatings and a Zn-Ni-Cd-rich phase in case of Zn-Ni-Cd coatings. The dissolution studies were carried out until the potential of the coating shifted to positive values thus indicating a phase change.

Figure 7 shows a plot of the corrosion potential  $E_{\text{corr}}$  vs. time for the Zn-Ni alloys deposited with and without CdSO<sub>4</sub> in the plating bath. The depositions were carried out under similar conditions. The deposits were approximately 2  $\mu\text{m}$  thick. The alloy dissolution rate was very fast in case of pure Zn-Ni, which is due to a large potential difference between Zn-rich phase ( $E_{\text{corr}, \eta \text{ phase}} = -1.050$  V vs. SCE) and the underlying steel ( $E_{\text{corr}, \text{steel}} = -0.550$  V vs. SCE). Addition of CdSO<sub>4</sub> in amounts greater than 0.1 g/L in the plating bath has a beneficial effect on the alloy dissolution rate. Zinc concentration in the deposit reduces with an increase in the CdSO<sub>4</sub> concentration, which results, as discussed above, in a drastic decrease of the Zn-Ni-Cd alloy corrosion potential. Thus, using CdSO<sub>4</sub> in the Zn-Ni sulfate bath and introducing Cd in the alloy, the Zn/Ni ratio decreases drastically which accounts for the observed increase in the corrosion potential of the alloy and the very slow alloy dissolution rate observed in Fig. 7.

**Linear polarization studies.**—Linear polarization studies were carried out on pure Cd plate, Zn-Ni, and Zn-Ni-Cd alloy coatings deposited from electrolytes containing 2 and 3 g/L CdSO<sub>4</sub> in the plating bath.



**Figure 7.**  $E_{\text{corr}}$  vs. time plot for various Zn-Ni-Cd composite coatings of thickness 2  $\mu\text{m}$ .



**Figure 8.** (a, top) Linear polarization plots for Zn-Ni, and Zn-Ni-Cd coatings in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub> at pH 7.0. (b, bottom) Plot of polarization resistance vs. time for Zn-Ni and Zn-Ni-Cd coatings in 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M H<sub>3</sub>BO<sub>3</sub> at pH 7.0

The potential was swept linearly from +5 to -5 mV vs.  $E_{\text{corr}}$  at a scan rate of 0.5 mV/s. The resulting graphs of overpotential vs. current density for Cd and various Zn-Ni alloy coatings are shown in Fig. 8a. The slope of these lines yields the value of the polarization resistance. The slopes of  $\eta$  vs.  $i$  plots are very high for Zn-Ni-Cd alloys suggesting that they have excellent barrier properties. The low polarization resistance in case of the Zn-Ni alloy suggests a high corrosion rate in these alloys. Figure 8b shows the plot of the resistance values as a function of time for various Zn-Ni alloy coatings. The corrosion resistance was smaller for the Zn-Ni alloy without any cadmium for the entire period of study. However, the resistance value increased with time owing to the depletion of the zinc-rich phase from the coating and the exposure of an intermediate phase with more nickel content. The resistance values in the case of Zn-Ni with 3 g/L CdSO<sub>4</sub> was ten times higher than those of the Zn-Ni alloy.

### Conclusion

Effective control of the zinc-nickel ratio in composite alloy coatings was achieved by plating from sulfate Zn-Ni deposition bath in

the presence of small amounts of CdSO<sub>4</sub> (3 g/L) and 1 g/L of nonyl phenyl polyethylene oxide. Material characterization studies done on the resulting deposit showed the codeposition of Cd along with Ni and Zn. A new Zn-Ni-Cd (29.56 wt % Cd) ternary alloy was synthesized which has higher nickel content compared to that in Zn-Ni obtained from ordinary Zn-Ni baths. The nickel content increases with increasing amounts of CdSO<sub>4</sub> in the bath. The observed increase in nickel content and presence of Cd in the alloy improves the corrosion resistance of the deposit. EIS analysis carried out on these coatings shows a barrier resistance that is ten times higher than a typical Zn-Ni coating. Polarization studies on these deposits show a large reduction in the corrosion current of these alloys compared to the Zn-Ni alloy. This is due to the increase in the barrier properties of the surface due to higher nickel content.

The new Zn-Ni-Cd plating process offers a unique way of controlling and optimizing the Ni and Cd contents in the final deposit. The coatings exhibit corrosion resistance and barrier properties much higher than those of the typical Zn-Ni and cadmium coatings.

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