

Effect of bath composition and operating parameters on deposit character and corrosion behaviour of Zn-Ni alloy

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Electrodeposited Zn-Ni alloys are extensively used as protective coatings for steel substrates and hence the studies on the factors which enhance corrosion resistance are of considerable significance. The present work details the optimization of acid chloride bath for bright Zn-Ni alloy over mild steel and study of the parameters which influence Ni content in the deposit. Use of sulphanic acid and gelatin was found to show significant effect on brightness of the deposit. The effect of molar ratio of $\text{Ni}^{+2}/\text{Zn}^{+2}$ in the bath on limiting current density of nickel deposition was emphasized. Under no conditions of bath compositions and operating parameters studied, the change in codeposition behaviour from anomalous to normal type was observed. The wt. %Ni in the deposit was found to be the independent factor of its corrosion resistance. The photomicrograph of electroplates confirmed that superior corrosion resistance is due to good surface morphology. The effect of bath composition, current density (c.d.), pH and temperature on appearance, hardness and corrosion resistance of deposits were studied and discussed. Corrosion behaviour of electroplates has been studied by Tafel's extrapolation method. Electrochemical impedance spectroscopy analysis revealed that superior corrosion resistance of Zn-Ni alloy coatings at optimized current density is due to barrier resistance at the interface of deposit and medium. Formation of n-type semiconductor film at the interface was confirmed by Mott-Schottky plot. Addition of small amount of cadmium chloride did not increase corrosion resistance.

Keywords: Zn-Ni alloy, Chloride bath, Corrosion resistance, Surface morphology, Electrochemical impedance

Anomalous codeposition of Zn-Fe group metal (Ni, Co and Fe) alloys is widespread in its application as protective coatings for steel substrates to prevent corrosion¹. Corrosion resistance along with other mechanical and physical properties of these coatings such as hardness and ductility depends on the specific procedure used for its preparation. It has been shown that the corrosion resistance of electrodeposited Zn-Ni alloy with about 12-16 wt. %Ni is 5-6 times better than for pure zinc of equal thickness². Improvements in corrosion resistance of Zn-M (where M = Ni, Co, Fe and Mn) alloys is believed due to the introduction of slightly nobler metal into the crystal lattice. Amongst the Zn-M alloys, electrodeposition and characterization of Zn-Ni alloys has been the most important one because of its excellent corrosion resistance and many studies have been attempted to understand the characteristics of the deposition process of Zn-Ni alloy³⁻⁵. The electrodeposition of Zn-Ni alloys is classified by Brenner⁶ as an anomalous codeposition where zinc the less noble metal, is preferentially deposited. Although this phenomenon⁷ has been known since 1907, the codeposition mechanisms of zinc and nickel are not well

understood^{8,9}. However, there have been some attempts^{10,11} to explain the anomalous codeposition of the Zn-Ni alloys. The first attributes the anomalous codeposition to a local pH increase, which would induce zinc hydroxide precipitation and would inhibit the nickel deposition. It was, however, found later that anomalous codeposition occurred even at low current densities¹², where hydrogen formation is unable to cause large alkalization effects. Another proposition is based on the under potential deposition of zinc on nickel-rich zinc alloys or on nickel nuclei¹³. Matlosz¹⁴ used a two-step reaction mechanism involving adsorbed monovalent intermediate ions for electrodeposition of iron and nickel, as single metals, and combined the two to develop a model for codeposition. Anomalous effects are assumed to be caused by preferential deposition of Zn as proposed by Sasaki and Talbot¹⁵. This model extends the one-dimensional diffusion modeling of Grande and Talbot¹⁶, a supportive or interpretive, rather than a predictive, model of electrodeposition. A main contribution of this model is the inclusion of hydrogen adsorption and its effects on electrodeposition. Zech *et al.*¹⁷ concluded that deposition of iron group metals

leads to a reduction of the reaction rate of the more noble component and an increase of reaction rate of the less noble component compared to single metal deposition.

Recently, a new Zn-Ni-Cd alloy plating process was developed by Popov *et al.*¹⁸ from a bath solution containing 0.5M NiSO₄ + 0.2M ZnSO₄ + 0.015M CdSO₄ and 1 g/L nonyl phenyl polyethylene oxide(NPPO). Zn-Ni-Cd ternary alloy showed superior corrosion resistance compared to Zn-Ni alloy deposit obtained from conventional Zn-Ni baths. The present paper presents the experimental results of optimization of chloride bath for production of Zn-Ni alloy for better corrosion resistance applications. The influence of bath composition and operating parameters on deposit characters and their corrosion behaviours were examined and discussed.

Experimental Procedure

Plating solutions were prepared from reagent grade chemicals and distilled water. All deposition was carried out at 303K except during temperature variation. The mild steel panels as cathode (area 5 cm²) and zinc anode were used. Plating baths were adjusted to pH 3.0 with hydrochloric acid. Solution pH was monitored frequently and adjusted when necessary. Mild steel panels were smoothly polished with emery cloths, then grease if any was removed from the surface by anodic and cathodic electrolysis for 2 min in an aqueous solution of NaOH 35 g/L and Na₂CO₃ 25 g/L at 6 A/dm². Samples were then neutralized in a 10% HCl solution and rinsed with distilled water and were plated at required current density. After deposition, the cathode was washed with tap water and rinsed with distilled water and dried. A PVC cell of 500 mL in capacity was used for electroplating with cathode - anode space of about 5 cm. Polished mild steel cathode panels of standard size and pure zinc anode were used for Hull cell study. The corrosion and semiconductor behaviour of electrodeposits were studied by dc/ac electrochemical techniques using Electrochemical Work Station (Metrohm PGSTAT 30). The polarization measurements were made at 298K in aerated 5% NaCl solution prepared with distilled water and analytical grade reagents. The reference electrode was saturated calomel electrode and a platinum electrode was counter electrode. The polarization curves were obtained by cathodic and anodic potentiodynamic polarizations at the scan rate of 1 mVs⁻¹. Impedance behaviour of Zn-Ni alloy

deposits were studied by Nyquist plot in the frequency range from 100 KHz to 5 mHz. To determine the compositions of the coatings, the electrodeposits were stripped in 1:3 HCl solutions and wt. %Ni was estimated colorimetrically¹⁹. The microstructure of alloy deposits were examined by scanning electron microscopy (SEM), (JEOL, Japan). The thickness of the deposits were calculated from Faradays law using equation:

$$t = E \times I_C \times C.E. \times \Delta t / (d.F)$$

where t is the thickness of the deposit, E is an electrodeposit coating equivalent, I_C is a film deposition current density, C.E. is a current efficiency, Δt is a time interval, and d is the density of the deposit and F is Faraday's constant (96500 Coulombs). The validity of measured thickness was cross examined using digital thickness tester (Coatmeasure M& C, ISO-17025/2005). The hardness of the deposit (25 μ m thickness) was measured by Vickers method using micro Hardness Meter (CLEMEX). The cathode current efficiency of deposition was determined by knowing the mass and composition of the deposit⁶.

Results and Discussion

Hull cell studies

Acid bath having ZnCl₂, NiCl₂, sulphanilic acid, and gelatin has been optimized by conventional Hull cell method at 1A cell current, pH 3.0 and temperature 303K. Varieties of deposits having grayish white/bright/semi-bright/porous/black powdery appearance were obtained over the wide c.d. of 1.0-5.0 amp/dm². Effect of each bath constituents on Hull cell panels were examined in terms of their surface morphology. NH₄Cl and KCl were used as conducting salts for improvement of bath conductance and homogeneity of the deposit. Amount of each constituent in the bath solution and operating parameters to develop bright Zn-Ni alloy coatings was optimized (Table 1). Studies of the factors which influence the wt. %Ni in the deposit and its dependence on hardness and corrosion resistance were made using optimized bath.

Effect of current density

Wt. %Ni in the deposit

Factors that enhance the corrosion resistance of electrodeposited Zn-Ni alloys were studied by varying c.d., pH, and temperature of the bath. It was found

that c.d. plays an important role on appearance and corrosion performance of the deposits. Variation in the appearance and corresponding wt. %Ni of deposits over a wide range of 1.0-5.0 amp/dm² using optimized bath is given in Table 2. The bath produced grayish white deposit with about 6%Ni at low c.d. side and produces a porous bright deposit at high c.d. with about 10%Ni. A sound deposit of Zn-Ni alloy was found at 3.0 Amp/dm² with about 3.8%Ni. The increase of %Ni in the deposit at low c.d. side is attributed to the tendency of the system to follow normal codepositon with preferential deposition of nickel. However, at high c.d. side increased %Ni is due to rapid depletion of more readily depositable (mrd) Zn⁺² ions at cathode film.

Thickness of deposit

The thickness of Zn-Ni deposit was found to increase drastically with c. d. as shown in Table 2. The linear dependency of thickness of the deposit with c.d. may be explained by the fact that at very high c.d., adsorbed metal hydroxide film at cathode (due to local decrease of pH by evolution of hydrogen) is likely to get occluded in the crystal lattice of deposits^{10,11}.

Hardness of deposit

Generally, the hardness of the Zn-Ni alloy having more nickel content is high due to inherent property of nickel ($d_{Zn} = 7.14 \text{ g cm}^{-3}$ and $d_{Ni} = 8.90 \text{ g cm}^{-3}$). At

low c.d. side (Table 2) inspite of high nickel content, the deposit showed less hardness. It may be due to the fact that the diamond tip must have touched the substrate during measurement. However at high c.d. side, the deposit has shown less hardness due to increased porosity. The constancy of cathode current efficiency (CCE) of the bath (Table 2) over the entire range of c.d. is supported by the factors responsible for nickel content in the alloy as discussed above.

Effect of pH

The pH of the bath was varied from 2 to 5 and corresponding data is shown in Table 2. At low pH, the deposit was semi-bright and powdery with a drastic increase in pH of the bath after plating. At high pH, no much change in the appearance of the deposit was observed and pH remained unaltered after plating. In present bath conditions, a increase of wt. %Ni in the deposit with pH indicates that the metal ions are in complex form due to additives (sulphanilic acid and NH⁺⁴ ions), and was not sufficient enough to inhibit the deposition of more noble nickel.

Effect of molar ratio of Ni⁺²/Zn⁺²

Normally Zn-Ni alloy coatings follow anomalous codeposition with preferential deposition of less noble zinc. By proper formulation of molar ratio of Ni⁺²/Zn⁺² in the bath, it is possible to change anomalous type of codeposition into normal type codeposition. Hence molar ratio of Ni⁺²/Zn⁺² was varied over a range of 0.1 to 10.0. The variation in the nickel content in the deposit at different molar ratio of Ni⁺²/Zn⁺² with c.d. is shown in Fig. 1. It was found that under no conditions of the bath, the deposition was normal type with same nickel content as in the bath (and hence it is anomalous type of codeposition). However at 0.1 molar ratio of Ni⁺²/Zn⁺², the system was tending towards normal type at lower c.d. side. But at 10.0 molar ratio of Ni⁺²/Zn⁺², the system was found to be perfect anomalous type over the entire

Table 1—Composition and operating parameter of optimized bath for electrodeposition of bright Zn-Ni alloy on mild steel

Bath composition	Amount (M)	Operating parameters
Zinc chloride	0.37	pH: 3.0
Nickel chloride	0.34	Temperature: 303 K
Ammonium chloride	2.24	Anode: Pure zinc
Potassium chloride	1.61	Current density: 3.0 Amp/dm ²
Sulphanilic acid	0.03	
Gelatin	7 g/L	

Table 2—Effect of current density and pH on wt. %Ni, hardness, thickness and deposit patterns of electroplates at 303K

Current density (A/dm ²)	pH of bath	Wt. %Ni in deposit	Vickers hardness V ₂₀₀	Thickness (μm)	Appearance of deposit
1.0	3.0	6.0	172	7.6	Grayish white
1.5	3.0	4.5	176	10.5	Semi bright
2.0	3.0	3.4	197	15.9	Bright
3.0	3.0	3.8	220	20.5	Bright
4.0	3.0	5.4	214	25.0	Bright
5.0	3.0	10.0	205	27.8	Porous bright
3.0	2.0	3.0	179	10.5	Semi bright
3.0	3.0	3.8	220	20.5	Bright
3.0	5.0	4.5	228	20.5	Bright

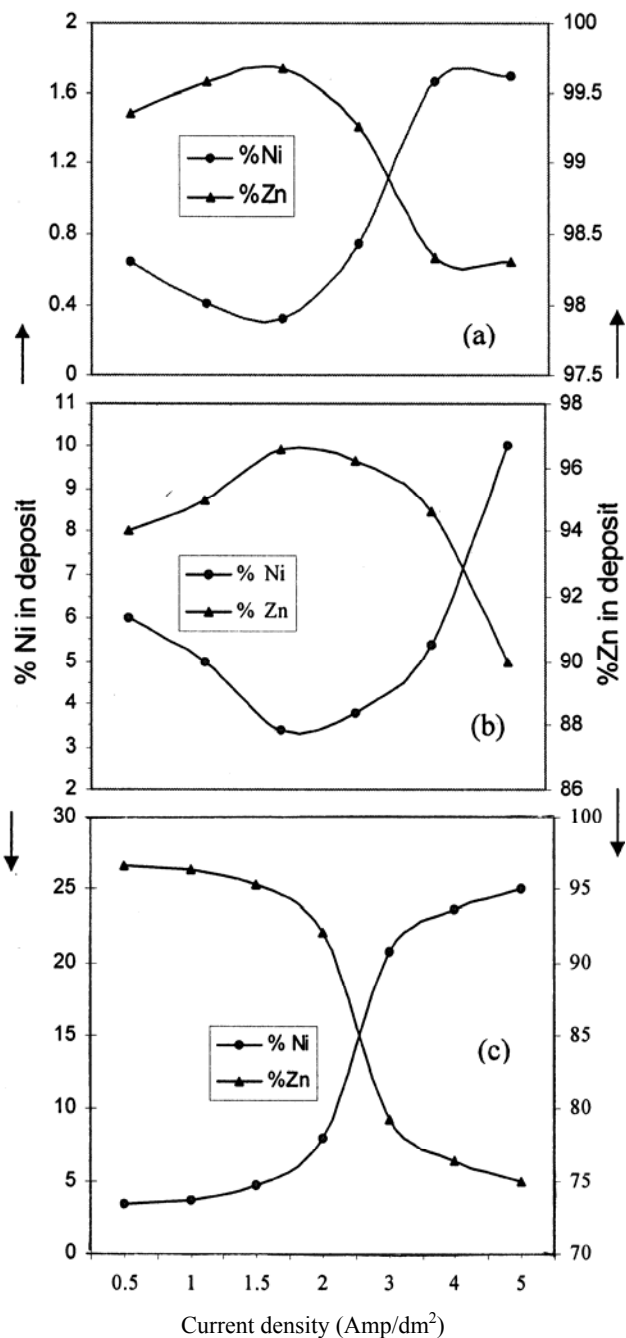


Fig. 1— Variation of wt. %Ni in the deposit with current density at different molar ratio of Ni^{+2}/Zn^{+2} in bath keeping other variables constant at 303 K (a) $Ni^{+2}/Zn^{+2} = 0.1$, (b) $Ni^{+2}/Zn^{+2} = 1.0$ (c) $Ni^{+2}/Zn^{+2} = 10.0$

current density range as shown Fig. 1c. Hence under conditions of temperature and pH employed in the present study, it is not possible to observe normal codeposition just by changing the molar ratio of Ni^{+2}/Zn^{+2} in the bath. However, the increase of molar ratio of Ni^{+2}/Zn^{+2} in the bath decreased the limiting current density for deposition of nickel drastically as

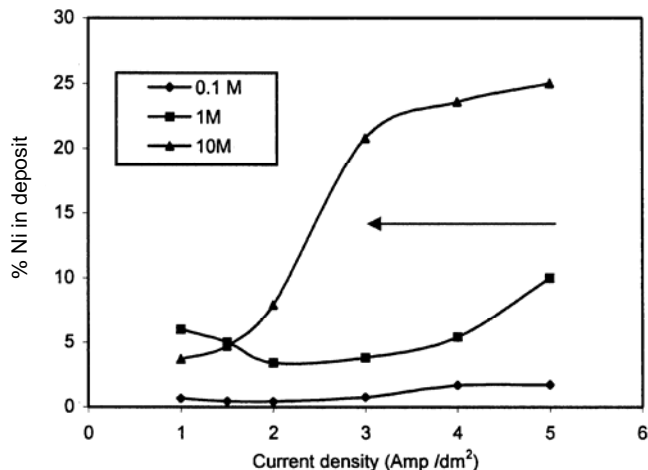


Fig. 2— Shifting of limiting current density of nickel deposition towards lower current density with increase molar ratio of Ni^{+2}/Zn^{+2} in the bath at 303K

shown by the direction of arrow mark in Fig. 2. No transition current density, at which the codeposition behaviour changed from the anomalous to normal type, was observed over the whole range of molar ratio of Ni^{+2}/Zn^{+2} (0.1-10.0).

Effect of temperature

Bath temperature also has prominent role on the composition and appearance of the deposit as in the cases of other Zn-Fe group metal alloys. The deposit was found to be slate white at high temperature with more proportion of zinc compared to silver bright at low temperature with less zinc as shown in Table 3. At elevated temperature, more readily depositable metal (zinc) ions are favoured to be replenished at the cathode and hence a decrease in the nickel content in the alloy was found.

Corrosion study

Tafel plots

Electroplated specimens were subjected to corrosion study in aerated 5% NaCl solution and experimental data are given in Table 4. Corrosion rates of the deposits were determined by Tafel’s extrapolation method and Tafel’s plots are shown Fig. 3. The polarization studies have been made at a scan rate of 1 mV/s in a potential ramp of + 0.5V cathodic and -1.5V anodic from open circuit potential (OCP). The anodic polarization was studied up to -1.5V from OCP to see the possibility of passive film formation to inhibit the corrosion under certain conditions of applied potential. But under no conditions of c.d. studied, the deposit has shown

passive film formation. Observed E_{corr} and Tafel's slopes at different current densities are shown in Table 4. The values of Tafel slope indicate that the corrosion rate is controlled more by cathodic reaction. Observed results showed that, the deposit at 3.0 Amp/dm² is more nobler with high $E_{\text{corr}} = -1.142\text{V}$ (versus SCE) and least $i_{\text{corr}} = 14.91 \mu\text{Amp cm}^{-2}$ as shown in Table 4. Zn-Ni alloy at 3.0 Amp/dm² having about 3.8 %Ni was found to show least corrosion rate. It is believed that during corrosion, zinc dissolves preferentially, leaving a top layer enriched with nickel and acts as a barrier to further attack as envisaged by earlier workers^{3,5}.

Electrochemical impedance spectroscopy (EIS)

EIS was used to evaluate the barrier properties of the coatings and to determine the polarization resistance. Nyquist responses of Zn-Ni alloy deposits at different current densities are shown in Fig. 4. The semicircle in all cases corresponds to a capacitive loop. The semicircle radii depend on the c.d. employed for deposition. Maximum diameter of the capacitive loop at optimized c.d. (3.0 Amp/dm²) shows that the deposit is most corrosion resistant. Electrified interface between electroplate and medium is fit to a simple equivalent circuit consisting of ohmic resistance (R_s), double layer capacitance (C_{dl}), and polarization resistance (R_p) as shown in Fig. 5.

The superior corrosion resistance of the Zn-Ni alloy deposit may be explained by the barrier

protection mechanism theory. The time constants at high frequencies in general have been attributed to the formation of a surface film²⁰. Formation of a passive film at the interface was confirmed by Mott-Schottky's plot as shown in Fig. 6. It was found that the structural and electronic properties of passive

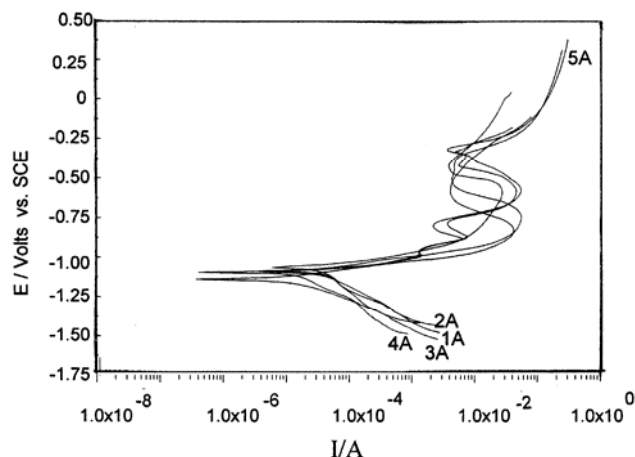


Fig. 3— Tafel plots for Zn-Ni alloy deposits at current density as specified on the curves from the optimized bath at scan rate of 1 mV/s versus SCE in a potential ramp of -0.5V and +1.5V from OCP.

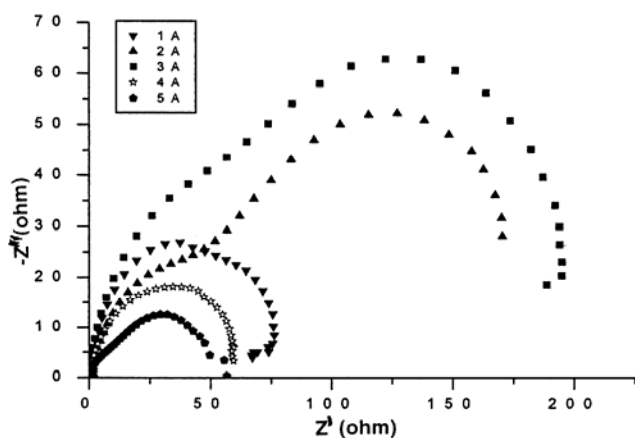


Fig. 4— Nyquist behaviour of Zn-Ni alloy coatings at different current densities from the optimized bath at 303K

Table 3— Effect of temperature on wt. %Ni in the deposit at 3.0 Amp/dm² and pH 3.0

Temp. (K)	wt. %Ni in the deposit	Appearance of the deposit
283	4.8	Bright
293	4.2	Bright
303	3.8	Bright
313	3.5	Grayish white
323	3.2	Slate white

Table 4— Corrosion parameters of Zn-Ni alloy deposits under different current densities using aerated 5% NaCl

Current density (Amp/dm ²)	Wt. %Ni in deposit	CCE (%)	E_{corr} (V) versus SCE	β_a (V/dec)	β_c (V/dec)	i_{corr} ($\mu\text{Amp cm}^{-2}$)	Corrosion rate (mm/year)
1.0	6.0	92.5	-1.063	0.101	0.208	39.54	0.567
1.5	5.0	92.6	-1.109	0.081	0.168	35.36	0.507
2.0	3.4	95.4	-1.083	0.057	0.269	31.69	0.455
3.0	3.8	95.3	-1.142	0.063	0.172	14.91	0.214
4.0	5.4	94.0	-1.097	0.061	0.216	17.98	0.258
5.0	10.0	92.8	-1.089	0.062	0.217	36.38	0.522

layers under optimized bath conditions has brought great influence on the corrosion behaviour of alloys. Further, the positive slope of graph reveals that the interface layer is of n-type semiconductor.

Surface study

The SEM image of Zn-Ni alloy deposit showed that c.d. plays a significant role in the phase structure of the deposit. The variation in the surface morphology of the deposit with c.d. is shown in Fig. 7. It was found that coatings is dull at low c.d. with black spots likely due to nickel (Fig. 7a) and very smooth and bright at optimum c.d. of 3.0 Amp/dm² (Fig. 7c). But at high c.d. the deposit was very rough, porous and very thick as shown in Fig. 7d.

Effect of CdCl₂

Having inspired by work of Papov *et al.*¹⁸, effect of addition of CdCl₂ (1 - 10 g/L) to the present optimized bath was tested (Table 1). It was found that addition of CdCl₂ did not show any influence on either appearance or corrosion performance of electroplates. Deposit was found to be very powdery and black at high concentration of Cd⁺². Experimental results showed that the bath is incapable of producing ternary alloy of Zn-Ni-Cd for improved corrosion resistance.

Conclusions

A suitable bath for electroplating of bright Zn-Ni alloy over mild steel has been proposed. Under working conditions of the bath, the bath followed anomalous codeposition with preferential deposition of nickel. No transition current density, at which the codeposition behaviour changed from the anomalous to normal type, was observed over the range (0.1-10.0) of molar ratio of Ni⁺²/Zn⁺². However, drastic decrease of limiting current density for deposition of nickel was observed when molar ratio of Ni⁺²/Zn⁺² in the bath increased. The effect of temperature on the plating process showed that the codeposition of metals is diffusion controlled. The corrosion resistance of each electroplate is found to be independent of its nickel content and dependent of surface morphology. The electrodeposits having about 3.8%Ni was found to be very smooth and uniform showing good performance against corrosion. The use of the additives has played a significant role in improving homogeneity and grain size. The thickness of the deposit was found to increase drastically with current density due to increased porosity. The SEM

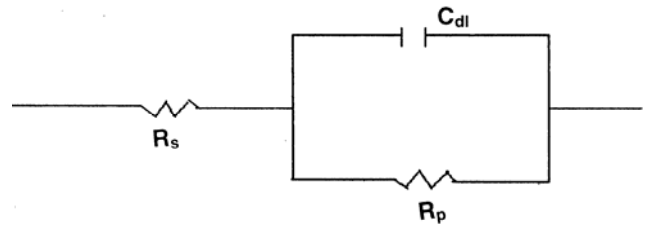


Fig. 5—Equivalent circuit of the studied system

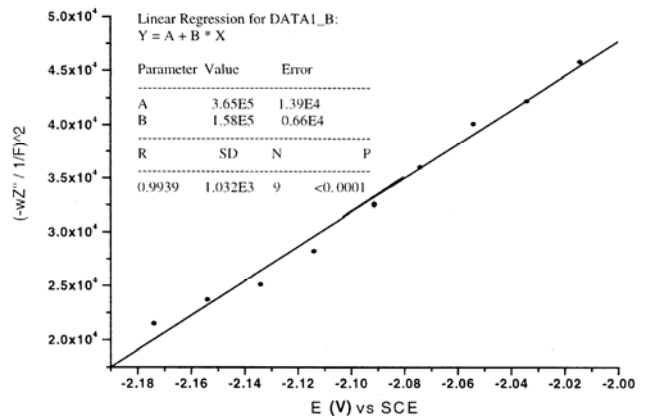


Fig. 6—Mott-Schottky plot showing n-type semiconductor film at the interface under optimized condition

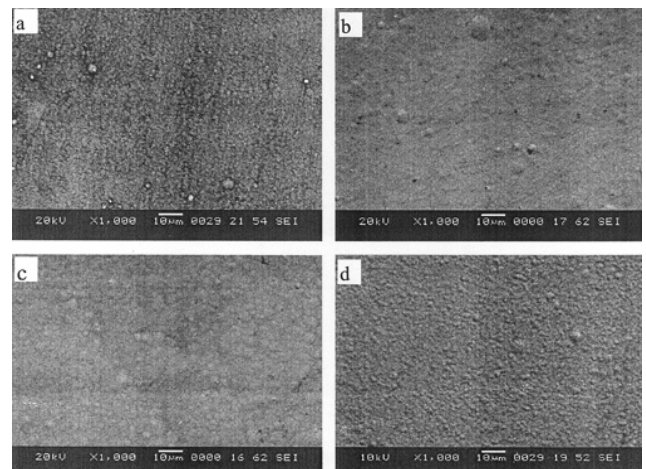


Fig. 7—SEM image of Zn-Ni alloy deposit at current densities (a) 1.0, (b) 2.0, (c) 3.0 and (d) 4.0 Amp/dm²

images of electroplates confirmed that superior corrosion resistance is due to improved homogeneity of the deposits. The polarization studies and electrochemical impedance analysis revealed that superior corrosion resistance of Zn-Ni coatings at optimized current density is due to barrier resistance at the interface of the metal and medium. Nyquist responses are fitting into a simple equivalent circuit consisting of ohmic resistance (R_s), double layer

capacitance (C_{dl}), and polarization resistance (R_p). The structural and electronic properties of passive layers developed under optimized bath conditions bring out significant influence on the corrosion behaviour of the alloy. Formation of a n-type semiconductor film at the interface was also confirmed.

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