Role of Cadmium on Corrosion Resistance of Zn-Ni Alloy Coatings

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Cadmium (Cd) catalyzed Zn-Ni alloy plating has been accomplished galvanostatically on mild steel (MS) using gelatin and glycerol as additives. The effect of addition of Cd into Zn-Ni bath has been examined in terms of nickel (Ni) content and corrosion resistance of Zn-Ni-Cd ternary alloy coatings. The process and product of electrolysis under different concentrations of additives and Cd have been investigated by cyclic voltammetry (CV). The effects of current density (c.d.) on Ni content of the alloy have been studied by spectrophotometric method, supported by EDX analysis. The deposition has been carried out under different concentrations of Cd ranging from 0.004 to 0.1M. The corrosion rates (CR) of Zn-Ni alloy coatings have been found to decrease drastically with addition of Cd. It has been also revealed that the CR of binary Zn-Ni alloy coatings decreased with the increase of Cd concentration only up to a certain optimal concentration, i.e., up to 0.02M, and then remained unchanged. An effort to change the anomalous type of codeposition into normal one by changing the molar ratios of the metal ions, i.e. $[Cd^{2+}]/[Ni^{2+}]$ as 0.01, 0.05 and 0.25 has remained futile. CV study demonstrated an important role of Cd in mutual depositions of Zn^{+2} and Ni^{+2} ions by its preferential adsorption, thus leading to the increased Ni content of the alloy. The bath composition and operating parameters have been optimized for deposition of bright and uniform Zn-Ni-Cd alloy coatings. Changes in the surface morphology and phase structure of Zn-Ni alloy coatings due to addition of Cd has been confirmed by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) study respectively. Experimental investigations so as to identify the role of Cd in codeposition Zn-Ni alloy coatings have been carried out and the results are discussed.

Keywords: Zn-Ni-Cd alloy, glycerol, corrosion study, XRD, SEM.

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INTRODUCTION

Electrodeposition of Zn-based alloys (both binary and ternary) are gaining interest in the automotive industry due to their higher corrosion resistance than pure Zn coating. Zn is a very active metal due to its low standard electrode potential [E^0 = -0.76V vs. Normal Hydrogen Electrode, NHE]. It is well known that proper alloying of any metal can improve its properties such as hardness, mechanical strength, wear resistance as well as corrosion resistance [1]. Zn-Ni alloy deposition is known for a peculiar anomalous type of codeposition, where the less noble Zn deposits more readily compared to the nobler Ni as explained by Brenner [2]. This unusual behavior was accounted for "*hydroxide suppression mechanism*". According to which $Zn(OH)_2$ precipitate at the cathode (due to local increase of pH) prohibits the deposition of nobler Ni [3, 4]. This phenomenon is found to be true in codepositions of all Zn-Fe group metal alloys and mutual alloys of Fe-group metals.

The Zn-Ni alloy coatings obtained by electrodeposition having higher percentage of Ni, varying between 8% and 14% by wt., was found to exhibit better corrosion protection (five to six times superior) compared to that of pure Zn coatings [5–8]. Additives are extremely important in electroplating of metals and alloys as they influence the grain size, deposition pattern and the composition of the alloy [9]. Soares et al. have studied electrodeposition of Zn-Ni alloy using gelatin [10]. They noticed that an increase in the concentration of gelatin heightened the deposition efficiency and the Ni content of the alloy. On the other hand, Pedrosa et al. used glycerol as an additive in the deposition of Zn-Ni alloy and studied the effect of glycerol content on cathode current efficiency (CCE) [11]. They declared that the CCE and corrosion stability of the coatings were found to be changed drastically with addition of more glycerol by hindering the hydrogen evolution during reduction of metal ions. Albalat et al. showed that Zn-Ni alloy coatings with even a low Ni content, but in the presence of particular additives, can improve the surface homogeneity and corrosion stability of the coatings to a large extent [12].

The presence of high percentage of nickel in Zn-Ni alloy provides higher barrier resistance. Howe-ver, these coatings with Ni content, i.e. 8–20% Ni, exhibit rough, non-uniform and unattractive finish. Hence certain brightener systems, either individually or in combination, need to be developed for bright and uniform coatings [13]. Attempts are still in progress to decrease the anomaly of codeposition observed in Zn-Ni alloys either by introducing some inert species in the deposits or by going for ternary alloy coatings [14]. The electrodeposited ternary alloys such as Zn-Ni-Co were found to exhibit higher corrosion protection compared to both binary Zn-Ni and Zn-Co alloy coatings [15–17]. Cadmium (Cd) has been widely used in aerospace, electrical and fastener industries due to its excellent corrosion resistance and other engineering attributes. But environmental concerns on its toxicity and the failure in the structure, due to hydrogen embrittlement phenomenon, made it to go for some alternative met-hods.

The Cd coating developed on the hard steel was found to enhance the cathodic current efficiency and retard the Zn deposition with increasing current density and temperature [18]. Addi et al. attempted to reduce the anomalous codeposition of Zn-Ni alloy using boric acid and Cd. CV study demonstrated that the presence of boric acid and Cd in sulfate bath reduced the Zn deposition by shifting the reduction peak of Ni to more negative potentials and increasing the peak height. By reducing the Zn-Ni ratio with the addition of Cd, the barrier property of the steel surface has been increased drastically. A large reduction in the corrosion current, due to increase in the Ni content of the deposit, was achieved [19–21]. The corrosion resistance of alloy was found to be dependent on the noble metal content of the deposit [22]. Kim et al. have developed an alkaline Zn-Ni-Cd bath for good coatings of high Ni content [23]. Hence in the light of the above investigations this paper considers the catalytic role of Cd in electrodeposition of Zn-Ni-Cd, in the presence of gelatin and glycerol as additives, while improving the Ni content and corrosion stability of the coatings. Comparison of binary and ternary alloy coatings in terms of surface morphology, phase structure and corrosion stability has been made and results are discussed.

MATERIALS AND METHODS

Acidic baths with $ZnCl_2$, $NiCl_2$, $CdCl_2$ (as metal salts), NH_4Cl (as conducting salt), boric acid (as buffer), gelatin + glycerol (as additives) were used. Gelatin and glycerol were used in combination in order to control the deposition rate, crystallization, leveling and brightness of the deposit. Due to a very high molecular weight of gelatin, its content in the plating baths in the present study is in concentrations that were several orders of magnitude smaller than the concentrations of metal ions. The plating solutions were freshly prepared with distilled water and filtered through Whatmann^{TM} laboratory grade filter paper. Electroplating of mild steel (MS) plates was done at pH = 4.0 and T = 303±2K, for either 10 min or 20 min (the former time – for corrosion study, the latter – for determination of chemical composition and CCE. The bath pH was monitored regularly and adjusted when necessary. The polished MS plates had an exposed surface area of either 7.5 or 25 cm^2 (the former – for the corrosion study) and served as a cathode. They were degreased with an alkali cleaner prior to coating. The gelatin being insoluble in cold water was dissolved in hot water and then poured into the bath. The gelatin was found to show significant effect on deposition process as proved by the CV study.

No nitrogen purging was done for electrolytic solution. The Hull cell method was used to examine the effect of additives and variation in molar concentration of Cd. The Hull cell study made it necessary to limit the applied current density (c.d.) within 1.0–4.0 Adm^{-2}, which yielded coatings with different appearance (porous/powdery/semi-bright/bright for Zn-Ni alloy and blackish/semi-bright/bright for Zn-Ni-Cd alloy). The bath composition and operating parameters of binary Zn-Ni and ternary Zn-Ni-Cd alloy baths were achieved by Hull cell method, and the data are given in Table 1. The CCE or Faradaic efficiency was calculated using the mass gained, the charge transferred and the chemical composition of the deposit:

$$\mathrm{CCE} = \frac{\text{measured mass gain}}{\text{theoretical mass gain}} \times 100 =$$

$$= \frac{w}{\frac{EW \times I \times t}{F}} \times 100 = \frac{wF}{It} \sum \frac{c_i}{M_i} \times 100.$$

Where w is the measured mass of the deposit in grams, t is the time of deposition, I is the current applied. EW is the equivalent weight of the alloy (g equiv^{-1}), c_i is the weight fraction of the element in the alloy deposit, n_i is the number of electrons transferred per atom of each metal, m_i is the atomic mass of that element and F is the Faraday constant (96,485C mol^{-1}).

All chemicals used in the present study are of Analytical Grade. Double distilled water was used for the preparation of electrolyte solutions. The effect of the additives (gelatin and glycerol) and Cd, at different molar concentrations, were studied by CV using a three-electrode cell. The deposition was carried out on a pure platinum foil as a working electrode to eliminate noise. It is confirmed that once several nanometers of coating material are deposited, the substrate no longer has any effect on the deposition process [24]. Before carrying out each experiment the electrodes were cleaned and activated by immersing in dil. HNO_3 solution for several minutes. The experiments were carried out in a still solution without disturbing. The saturated calomel electrode (SCE) was used as the reference electrode. The potential scan began at around +1.1V in the positive direction, upto +2.7V. Then, the scan rate reversed back in the negative direction, down to 2.5V whereas -3.5V, in the presence of Cd, finally reversing back in the positive direction up to +2.7V.

The thickness of the coating was estimated by Faraday's law and verified by measuring in Digital Thickness Meter (Coatmeasure Model M&C, AA Industries/Yuyutsu Instruments). The hardness of coatings was measured using Digital Micro Hardness Tester (CLEMEX). The compositions of alloys were evaluated by the spectrophotometric method as in [25]. The corrosion behavior of the coatings, having 7.5 cm^2 active surface area, has been studied in 5% NaCl at 298 K (ACM Instruments, Gill AC Series No-1480). The electrochemical impedance spectroscopy (EIS) study was made in the frequency range of 100 kHz-10 mHz, and corresponding Nyquist plots were analyzed. The potentiodynamic polarization study has been carried out at the scan rate of 1 mV/s, in a potential ramp of ± 250 mV from OCP. The corrosion resistance of coatings was evaluated by Tafel's extrapolation method [26]. The surface properties of the coatings were studied by means of SEM (Model JSM-6380 LA from JEOL, Japan) interfaced with EDX. The phase structures of alloy coatings were identified by XRD (JEOL JDX-8P), using Cu Kα (λ=1.5406 Å) radiation in a continuous scan mode at the scan rate of 2°min^{-1}.

RESULTS AND DISCUSSION

Hull cell study

The Hull cell method is the most elegant approach for optimization of the operating parameters like c.d., temperature, pH and bath composition in terms of salt concentration and additives for a bright and uniform deposit [27]. The optimal bath ingredients and operating parameters of binary Zn-Ni and ternary Zn-Ni-Cd alloy baths are given in Table 1.

Table 1. Bath composition and operating parameters for deposition of bright Zn-Ni and Zn-Ni-Cd coatings on MS

Bath ingredients (g/L)	Zn-Ni	Zn-Ni-Cd
$ZnCl_2$	27.2	27.2
$NiCl_2·6H_2O$	94.9	94.9
H_3BO_3	27.7	27.7
NH_4Cl	100	100
$CdCl_2$	–	2.2
Gelatin	5.0	5.0
Glycerol	2.5	2.5
Bath pH	4	4
Bath Temp.(K)	303	303

The deposit characters such as composition, hardness, thickness, appearance and corrosion behavior of binary Zn-Ni and ternary Zn-Ni-Cd alloy coatings deposited at different c.d.'s, from specified optimal baths are reported, respectively, in Table 2 and Table 3.

Cyclic voltammetry study

The CV study was carried out so as to get the preliminary information about the deposition and dissolution process of the alloy in the presence/absence of additives and Cd. Fig. 1 shows the CV for deposition and dissolution of the alloy under various conditions mentioned therein. It may be observed that cathodic peaks are profoundly influenced by the presence of additives and of Cd at different concentrations. The preliminary CV study with only additives revealed that they are electrochemically inactive. The CV for only metal ions, the potential scan started at around 2.7 V signaled the deposition of Zn(II)-Zn(0) at -1.15 V followed by an evolution of hydrogen at still negative potential. No specific dissolution peak was observed in cyclic voltammogram corresponding to an alloy without additives (Fig. 1a).

However, on addition of additives, a distinct anodic peak was observed as shown in Fig.1b, corresponding to the dissolution of Zn-Ni alloy having γ-Zn (411, 330), Zn (101) and Zn (103) phase structures. Further, addition of a small amount of Cd (0.004M) into the electrolytic bath has changed the nature of CV by shifting the peak anodic potential to a more noble side as shown in Fig. 1c, indicating the formation of Zn-Ni-Cd alloy having different XRD patterns. This observation is supported by increased Ni content of the ternary alloy as depicted in Table 3.

Increase of Cd concentration in the bath, i.e. to 0.02M, resulted in decrease of the anodic current corresponding to the dissolution of the alloy having 11.95% wt. Ni. However, further addition of Cd into the bath led to the coating showing lowest corrosion protection, signaled by a shorter anodic peak as shown in Fig. 1e. Hence, a ternary Zn-Ni-Cd alloy corresponding to 0.02M Cd, demonstrating the least CR, was taken as optimal concentration as shown in Table 1. The CV response was found to be discouraging on further addition of Cd into the bath (Fig. 1e). It may be attributed to an excessive adsorption of Cd, which blocks the active sites of the cathode surface and inhibits the electrocrystallisation of Ni as well as Zn ions [19, 24]. Thus CV study revealed that addition of gelatin + glycerol has improved the homogeneity and brightness of the deposit, while Cd ions catalyzed the deposition of Zn-Ni by increasing the Ni content only at minimal concentration. Thus addition of Cd into the bath plays a specific role in improving the corrosion resistance of the ternary alloy, consequent to its Ni content.

The CV study on electrodeposition of Zn-Ni-Cd alloy revealed that depositions of Zn and Cd are mass-transfer controlled while nickel is kinetically

Table 2. Deposit characters of binary Zn-Ni alloy coatings developed from optimized bath at different c.d.'s

C.d. (Adm^{-2})	Wt. % of Ni	CCE (%)	Hardness VHN	Nature of deposit	Thickness (μm)	E_{corr} (V/vs SCE	i_{corr} ($μAcm^{-2}$)	CR×10^{-2} (mmy^{-1})
1.0	2.62	90.1	146	Porous/powdery	5.8	1.019	17.62	23.42
2.0	4.05	91.5	153	Semi-bright	10.4	1.086	13.87	18.44
3.0	7.95	92.4	202	Bright	17.8	1.105	10.88	14.46
4.0	8.07	90.5	184	Semi bright	23.2	1.162	12.53	16.66

Table 3. Deposit characters of ternary Zn-Ni-Cd alloy coatings developed from optimized bath at different c.d.'s

C.d. (Adm^{-2})	Wt.% of Ni	Hardness (VHN)	CCE (%)	Nature of deposit	Thickness (μm)	E_{corr} (V/vs SCE)	i_{corr} ($μAcm^{-2}$)	CR×10^{-2} (mmy^{-1})
1.0	11.82	154	91.15	Black	7.3	1.098	2.71	3.93
2.0	6.15	169	92.10	Semi-bright	11.4	1.072	2.60	3.77
3.0	11.95	236	94.18	Bright	17.9	1.125	0.74	1.06
4.0	13.22	188	91.61	Semi-bright	21.8	1.145	2.69	3.90

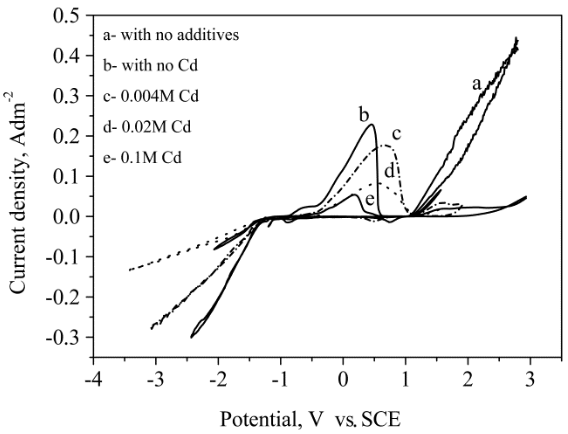

Fig. 1. Cyclic voltammetric study for deposition and dissolution of Zn-Ni alloy in presence of additives, and Cd ions at different molar concentrations at 303 K.

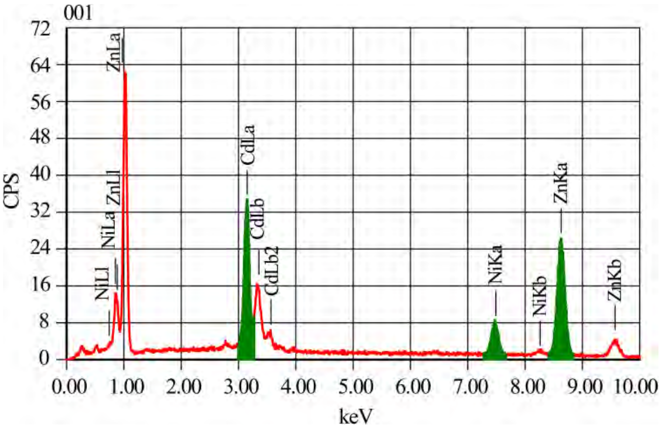

Fig. 2. EDX spectrum showing relative amount of M (Zn, Ni and Cd) in Zn-Ni-Cd coatings, deposited at 3.0 Adm^{-2} under condition of 0.02M $CdCl_2$.

controlled [28]. Therefore, addition of Cd into the bath has a significant effect on the nature of cyclic voltammogram represented by curves *b*, *c*, *d* and *e* in Fig. 1, in terms of anodic peak currents/potentials. This may be explained by low reduction potential of Cd compared to that of Zn, and by a low equilibrium potential (or high activation over potential) of Ni for depositing at room temperature. Hence, Cd and Ni content (in the deposit) dominates over Zn at low concentrations [24]. For the same reason, the deposition c.d. and concentrations of Cd^{+2} ions largely affect the composition of the deposit and hence its properties.

Compositional analysis of coatings

The composition of Zn-Ni and Zn-Ni-Cd alloy coatings deposited at different c.d's were analyzed by colorimetric method by stripping the deposit in dil. HCl [29]. This was further confirmed by Energy Dispersive X-ray analysis (EDXA) shown in Fig. 2.

Effect of Cd on Ni content of the ternary alloy

Bright and uniform Zn-Ni coatings having 7.95% Ni were obtained at 3.0 Adm^{-2}. The Ni content of binary Zn-Ni alloy was found to increase with applied c.d., i.e., from 1.0 Adm^{-2} through 4.0 Adm^{-2}, showing an anomalous type of codeposition (Table 2). In addition, the Ni content of Zn-Ni-Cd coatings over a wide range of c.d. (under optimal bath condition) has been studied and results are reported in Table 3. It may be noticed that the ternary bath showed similar behavior as binary bath, except for an increase of Ni content in the deposit. It may be attributed to the codeposition of Zn and Ni catalyzed by Cd^{+2} ions.

The effect of addition of $CdCl_2$, over a range of c.d., on the composition of Zn-Ni-Cd alloy has been studied. The [$CdCl_2$] varied from 0.004M through 0.1M, while concentration of $ZnCl_2$ and $NiCl_2·6H_2O$ were fixed as 27.2 and 94.9 g/L, respectively. The bath pH was maintained at 4.0, and depositions were carried out at 303 K. Variations in Ni content with Cd concentration, i.e. 0.004M, 0.02 and0.1M $CdCl_2$ including the one without Cd, are shown in Fig. 3.

It may be noted that wt. % Ni in the deposit increased with the addition of Cd only up to a certain level (0.02M) and then decreased. Further, under no

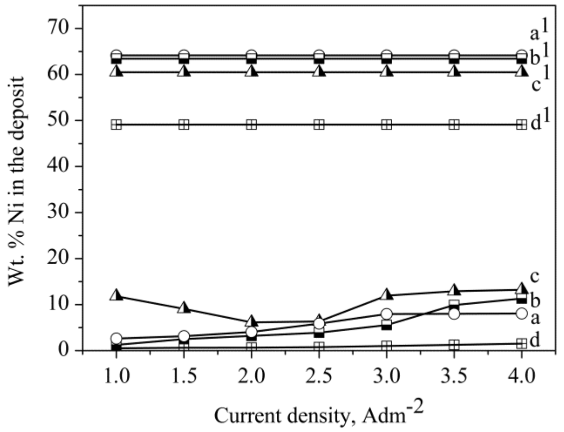

Fig. 3. Variation of Ni content at different molar concentrations of Cd: (a) without Cd;(b) 0.004M;(c) 0.02M and (d) 0.1M (horizontal lines represented by a^1, b^1, c^1 and d^1 show corresponding Ni content in the bath as calculated from bath composition).

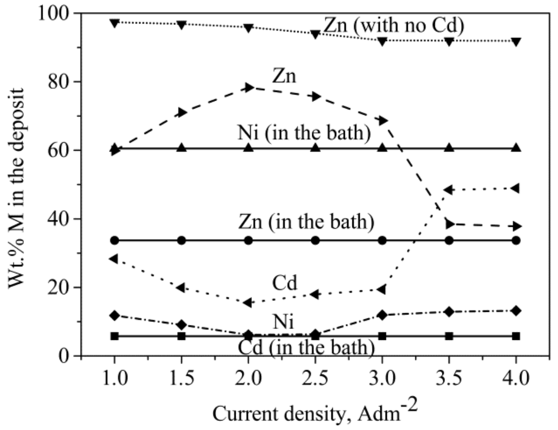

Fig. 4. Variation in metal content, M (Zn, Ni and Cd) in Zn-Ni-Cd alloy with current density under optimal bath conditions.

conditions of c.d.’s and $CdCl_2$ concentrations, the Ni content of the deposit has reached that in the respective baths (represented by horizontal lines) as shown in Fig.3. Addition of a tracer amount of $CdCl_2$ increased the Ni content of the alloy at high c.d. in relation to the one without Cd as shown in Fig. 3. It can be accounted by the fact that adsorbed Cd^{+2} ions inhibited the preferential deposition of Zn, thereby suppressing the anomalous codeposition (or favoring the normal deposition).Thus Cd^{+2} ions suppressed the anomalous type of codeposition by retarding the deposition of Zn. In other words, Cd^{+2} ions catalyzed the Ni deposition.

Variation in M content at different concentrations of $CdCl_2$

The concentrations of Cd^{+2} ions and applied c.d. were found to largely affect the composition, i.e., Ni content, and properties of the coatings. With this incentive, the M content (Zn, Ni and Cd) of Zn-Ni-Cd alloy over a range of c.d. has been studied, keeping $CdCl_2$ as 0.02M. The variation of M content as a function of deposition c.d. is shown in Fig. 4. It may be noted that due to preferential adsorption of Cd^{+2} ions, even a small amount of $CdCl_2$ (2.2 g/L) decreased the Zn content of the alloy by allowing the normal codeposition (with no *hydroxide suppression mechanism*) [2]. This is evidenced by high Cd content of the alloy over the entire range of c.d., compared to that in the bath as shown in Fig. 4. This is not observed in relation to the codeposition of Ni and Cd, instead, it followed anomalous type of codeposition. Hence it may be concluded that the preferential deposition of Cd is due to inherent deposition overpotential of Ni. Thus in presence of Cd, an increase of Ni content in the deposit was observed, which increased with c.d. as shown in Fig. 4.

It may be noted that at low c.d., the wt. % Zn in Zn-Ni-Cd alloy increased with c.d., while its Ni and Cd content was decreasing. This increase of Zn is due to deposition of more readily depositable metal, M (Zn). However, as c.d. increased, i.e. at 2.0 Adm^{-2}, the Zn content started decreasing indicating the onset of normal codeposition. At extremely high c.d., i.e. above 3.0 Adm^{-2}, the Zn content of the alloy was found to be less than that of Cd, leaving Ni to increase slightly, as shown in Table 3. The decrease of Zn content at very high c.d. is due to the suppression of more readily depositable Zn leading to coating having more Cd and Ni. This observation once again supports the fact that deposition of Zn and Cd are mass-transport controlled driven by the applied c.d., whereas Ni is kinetically controlled due to high activation overpotential [24]. The wt. % Zn in binary alloy (deposited without Cd) was found to be much higher compared to the one with Cd as shown in Fig. 4. It shows that Cd^{+2} ions catalyze the deposition of Ni by suppressing deposition of Zn.

Thickness and hardness of coatings

The thickness of the coatings increased significantly with c.d. in both Zn-Ni and Zn-Ni-Cd coatings as reported in Tables 2 and 3. The thickness was found to have a linear dependency with c.d., employed for its deposition as required by Faraday’s law. The appearance and composition of the coatings were found to be largely influenced by the c.d., as exhibited in other Zn-Fe group metal alloys, namely Zn-Ni, Zn-Co, Zn-Fe and less commonly in Zn-Mn. Similarly, the hardness of deposits were found to be increased with c.d. up to a certain level, and then decreased. This decrease is due to local alkylation caused by high hydrogen discharge at cathode.

CORROSION STUDY

Polarization behavior

The electroplated coatings were subjected to the corrosion study in 5% NaCl solution. The corrosion data of Zn-Ni and Zn-Ni-Cd alloy coatings deposited at different c.d.’s, from specified baths, are reported in Tables 2 and 3, respectively. Tafel's extrapolation method was used to evaluate the corrosion rate (CR), expressed in mmy^{-1}. The polarization behaviors of Zn-Ni-Cd alloy coatings (only representative) at different c.d.'s are shown in Fig. 5.

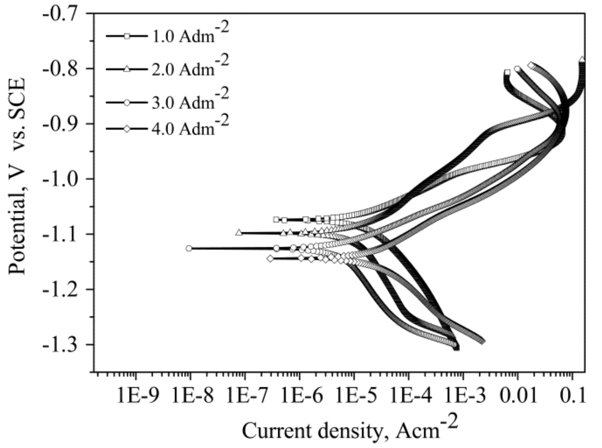

Fig. 5. Potentiodynamic polarization behavior of Zn-Ni-Cd alloy coatings at different current densities deposited from optimized bath at 303 K.

The CR of the coatings decreased with c.d. up to 3.0 Adm^{-2} and then increased as evidenced by corresponding i_{corr} values. The decrease in E_{corr} value with the increase in c.d. showed the corrosion protection to be anodic in nature. Thus, the Zn-Ni-Cd ternary alloy at optimal c.d., i.e, 3.0 Adm^{-2}, exhibited the least CR (1.06×10^{-2} mmy^{-1}), which is about 14 times better than Zn-Ni binary alloy coating. The relative polarization behavior of binary Zn-Ni and ternary Zn-Ni-Cd alloy coatings deposited from respective optimal baths are shown in Fig. 6.

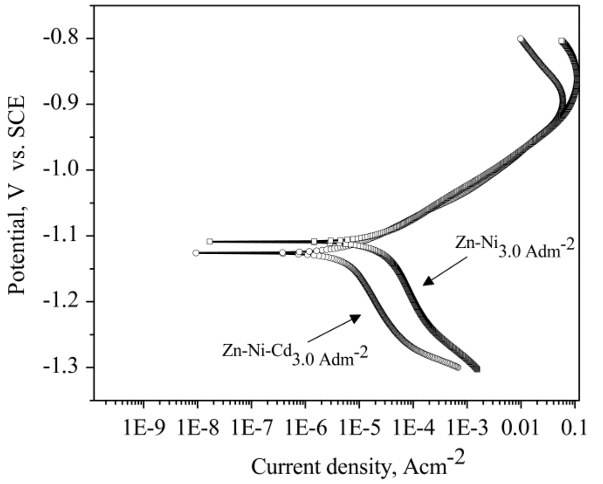

Fig. 6. Potentiodynamic polarization behavior of binary Zn-Ni and ternary Zn-Ni-Cd alloy coatings deposited from respective baths under optimal conditions.

Electrochemical impedance spectroscopy study

EIS or AC impedance method is a very popular technique to acquire the valuable information regarding electrode processes like double layer capacitance for the enhanced corrosion protection and role of inhibitors etc. EIS study considers the response of test specimen for AC signals of small amplitude. The most versatile tool is the Nyquist plot that commonly displays the data as imaginary impedance, Z_{img}, vs real impedance, Z_{real}, with the provision to distinguish the contribution of polarization resistance (R_p) verses solution resistance (R_s) [30]. The Nyquist response of Zn-Ni-Cd coatings deposited at different c.d. is shown in Fig. 7. The impedance responses indicate that the polarization resistance, R_P increased progressively with c.d.'s, and reached maximum at 3.0 Adm^{-2} i.e., the real component of the impedance Z_{real} is more comparable to other c.d's. Comparison of impedance responses of Zn-Ni-Cd coatings developed at different c.d's reveals that coating at 3.0 Adm^{-2} is most corrosion resistant, and is shown in inset of Fig. 7.

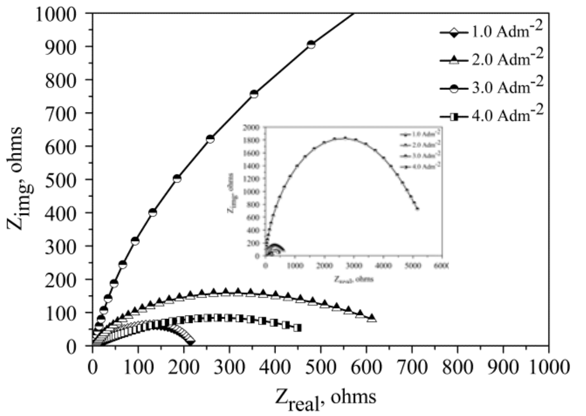

Fig. 7. Electrochemical impedance response (Real vs Imaginary reactance values) displayed by Zn-Ni-Cd coatings at different c.d.'s from optimized bath.

Surface morphology

The surface morphology of Zn-Ni-Cd at different c.d.'s deposited from the optimal bath is shown in Fig. 8.

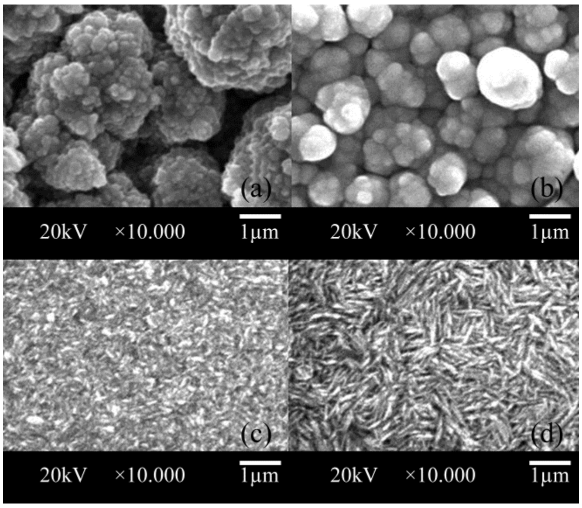

Fig. 8. SEM image of Zn-Ni-Cd coatings deposited using optimized bath at different c.d.'s: (a) 1.0 Adm^{-2}; (b) 2.0 Adm^{-2}; (c) 3.0 Adm^{-2}and (d) 4.0 Adm^{-2}.

A significant change in the surface structure of the coatings was found as c.d. was changed. The cauliflower type surface structure has changed to a well defined granular one when c.d. was changed from 1.0 to 2.0 Adm^{-2} as shown in Figs. 8a and 8b. The granular structure formed at 3.0 Adm^{-2} tends to form a needle-like structure at high c.d., i.e. 4.0 Adm^{-2}, as shown in Figs. 8c and 8d, respectively.

XRD Study

The surface morphology and XRD peaks of binary Zn-Ni and ternary Zn-Ni-Cd coatings deposited at optimal c.d., i.e., at 3.0 Adm^{-2}, is shown in Fig. 9.

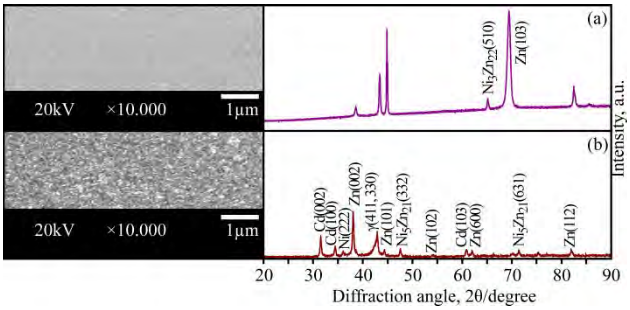

Fig. 9. Surface morphology and corresponding XRD patterns of alloy deposited from respective baths at 303 K: (a) Zn-Ni and (b) Zn-Ni-Cd.

The surface morphology of binary alloy coatings was changed when Cd was added into the bath. Though XRD reflection corresponding to γ-Zn (411, 300) phase was observed in both binary and ternary alloy coatings, the dominant Zn (101), Zn (103), Ni_3Zn_{22} (510) and Zn (112) peaks, observed in Zn-Ni alloy (Fig. 9a) were suppressed in ternary Zn-Ni-Cd coatings. However, addition of Cd into an electrolytic bath resulted in the coatings having distinct Cd (002), Cd (100), Ni (222), Ni_5Zn_{21} (332), Zn (102), Cd (103), Zn (600) and Ni_5Zn_{21} (631) reflections as shown in Fig. 9b. A significant difference in the surface structure of Zn-Ni alloy (having 7.95 wt. % Ni) and Zn-Ni-Cd alloy (having 11.95 wt. % Ni) coatings was found as shown in Figs. 9a and 9b, respectively. Thus XRD study revealed that the enhanced corrosion protection of Zn-Ni-Cd is due to unique phase structure of the coating having specific composition.

CONCLUSIONS

Based on experimental investigations on electrodeposition of Zn-Ni alloy using Cd as a catalyst, the following observations were made as conclusions:

1. A stable Zn-Ni-Cd bath has been proposed for electrodeposition of bright coatings on MS using gelatin and glycerol as additives.

2. The CV study revealed that addition of gelatin and glycerol has improved the homogeneity and brightness of the deposit, while Cd ions catalyzed the deposition of Ni by suppressing the anomalous codeposition.

A small amount of Cd is good enough to bring significant increase in the Ni content, and hence corrosion resistance of the ternary alloy. The added Cd enhanced the Ni nucleation process by suppressing the anomalous codeposition.

A small amount of $CdCl_2$ decreased the Zn content of the alloy by allowing the normal codeposition. But it was not observed with referring to codeposition of Ni and Cd, due to inherent deposition overpotential of Ni.

However the effect is diminishing with the excess addition of Cd due to the adsorbed Cd that blocks the active sites of the cathode and inhibits the electrocrystallisation of Zn and Ni.

The applied cathode current density and $[Cd^{+2}]$ ions largely affect the composition, and hence the properties of the Zn-Ni-Cd alloy by decisively changing Ni content of it.

The decrease of Zn content at a very high c.d. is due to suppression of more readily depositable Zn, leading to deposition of coatings having more Cd and Ni. This observation confirms the fact that depositions of Zn and Cd are mass-transport controlled driven by the applied c.d., whereas Ni is kinetically controlled due to its high activation overpotential.

Both the SEM and XRD studies demonstrated that the peak corrosion protection of Zn-Ni-Cd coatings is due to their unique surface morphology and phase structure conditioned by the Ni and Cd content.

Zn-Ni-Cd alloy coating at optimal c.d., i.e, 3.0 Adm^{-2}, exhibited the least CR (1.06×10^{-2} mmy^{-1}), which is about 14 times better than Zn-Ni binary alloy coating, evidenced by potentiodynamic polarization and electrochemical impedance study.

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REFERENCES

1. Albalat R., Gomez E., Muller C., Sarret M. and Valles E. Electrodeposition of Zinc-nickel Alloy Coatings: Influence of a Phenolic Derivative. *J App Electrochem*. 1990, **20**, 635–639.
2. Brenner A. *Electrodeposition of Alloys-Principles and Practice*. Vol. 1 & 2. New York: Academic Press, 1963.
3. Ishihara M., Yumoto H., Akashi K. and Kamei K. Zinc-nickel Alloy Whiskers Electrodeposited from a Sulfate Bath. *Mater Sci Eng. B*. 1996, **38**, 150–155.
4. Zech N., Podlaha E.J. and Landolt D. Anomalous Codeposition of Iron Group Metals: I. Experimental Results. *J Electrochem Soc*. 1999, **146**, 2886–2891.
5. Bhat R.S., Bhat K.U. and Hegde A.C. Corrosion Behavior of Electrodeposited Zn-Ni, Zn-Co and

Zn-Ni-Co Alloys. *Anal Bioanal Electrochem*. 2011, **3**, 302–315.

6. Fratesi R. and Roventi G. Corrosion Resistance of Zn-Ni Alloy Coatings in Industrial Production. *Surf Coat Technol*. 1996, **82**,158–164.
7. Younan M.M. Surface Microstructure and Corrosion Resistance of Electrodeposited Ternary Zn-Ni-Co Alloy. *J Appl Electrochem*. 2000, **30**, 55–60.
8. Yogesha S. and Hegde A.C. Optimization of Bright Zinc-nickel Alloy Bath for Better Corrosion Resistance. *T Indian I Metals*. 2010, **63**, 841–846.
9. Boto K. Organic Additives in Zn Electroplating. *Electrodep Surf Treat*. 1975, **3**, 77–95.
10. Soares M.E., Souza C.A.C. and Kuri S.E. Characteristics of a Zn–Ni Electrodeposited Alloy Obtained from Controlled Electrolyte Flux with Gelatin. *Mater Sci Eng. A*. 2005, **402**, 16–21.
11. Pedroza G.A.G., de Souza C.A.C., Carlos I.A. and de Andrade Lima L.R.P. Evaluation of the Effect of Deposition Bath Glycerol Content on Zinc–nickel Electrodeposits on Carbon Steel. *Surf Coat Technol*. 2012, **206**, 2927–2932.
12. Albalat R., Gomez E., Muller C., Pregonas J., Sarret M. and Valles E. Zinc-nickel Coatings-relationship between Additives and Deposit Properties. *J Appl Electrochem*. 1991, **21**, 44–49.
13. Muller C., Sarret M. and Benballa M. Some Peculiarities in the Codeposition of Zinc–nickel Alloys. *Electrochim Acta*. 2001, **46**, 2811–2817.
14. Venkatakrishna K., Hegde A.C. and Eliaz N. Electrodeposition of Zn-Ni, Zn-Fe and Zn-Ni-Fe Alloys. *Surf Coat Technol*.2010, **205**, 2031–2041.
15. Younan M.M., Oki T. Electrodeposition of Zn-Ni-Fe Alloy in Acidic Chloride Bath with Separated Anodes. *J Appl Electrochem*. 1996, **26**, 537–541.
16. Abou-Krisha M.M., Rageh H.M. and Matter E.A. Electrochemical Studies on the Electrodeposited Zn–Ni–Co Ternary Alloy in Different Media. *Surf Coat Technol*. 2008, **202**, 3739–3746.
17. Abou-Krisha M.M. Influence of Ni^{2+} Concentration and Deposition Potential on the Characterization of thin Electrodeposited Zn–Ni–Co Coatings. *Mater Chem Phys*. 2011, **125**, 621–627.
18. Abd El Rehim S.S., Fouad E.E., Abd El Wahaab S.M. and Hassan H.H. Electrodeposition of Zn-Ni-Cd Ternary Alloys from Acetate Bath. Indian. *J Chem Technol*. 1998, **5**, 387–392.
19. Addi Y. and Khouider A. Zinc-nickel Codeposition in Sulfate Solution Combined Effect of Cadmium and Boric Acid. *Int J Electrochem*. 2011, 1–7, (doi: 10.4061/2011/742191).
20. Durairajan A., Haran B.S., White R.E. and Popov B.N. 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. *J Electrochem Soc*. 2000, **147**(5), 1781–1786.
21. Ganesan P., Kumaraguru S.P. and Popov B.N. Development of Zn–Ni–Cd Coatings by Pulse Electrodeposition Process. *Surf Coat Technol*. 2006, **201**, 3658–3669.
22. Felloni L., Fratesi R., Quadrini E. and Roventi G. Electrodeposition of Zinc-nickel Alloys from Chloride Solution. *J Appl Electrochem*. 1987, **17**, 574–582.
23. Kim H., Popov B.N. and Chen K.S. A Novel Electrodeposition Process for Plating Zn-Ni-Cd Alloys. *J Electrochem Soc*. 2003, **150**(2), C81–C88.
24. Eliaz N., Venkatakrishna K. and Hegde A.C. Electroplating and Characterization of Zn–Ni, Zn–Co and Zn–Ni–Co Alloys. *Surf Coat Technol*. 2010, **205**, 1969–1978.
25. Thangaraj V., Udayashankar N.K. and Hegde A.C. Development of Zn-Co Alloy Coatings by Pulsed Current from Chloride Bath. *Indian J Chem Technol*. 2008, **15**, 581–587.
26. Jones D.A. *Principles and Prevention of Corrosion*. New York: Prentice Hall, 1996.
27. Pardhasaradhy N.V. *Practical Electroplating Hand Book*. New Jersey: Prentice Hall Incl. Pub, 1987.
28. Ashassi-Sorkhabi H., Hagrah A., Parvini-Ahmadi N. and Manzoori J. Zinc–nickel Alloy Coatings Electrodeposited from a Chloride Bath using Direct and Pulse Current. *Surf Coat Technol*. 2001, **140**, 278–283.
29. Vogel A.I. *Quantitative Inorganic analysis*. Third ed. London: Longmans Green & Co, 1951.
30. Yuan X., Song C., Wang H. and Zhang J. *Electrochemical Impedance Spectroscopy in PEM Fuel Cells-Fundamentals and Applications*. London: Springer Publications, 2010.

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Реферат

Электроосаждение цинк-никелевых сплавов с использованием кадмия в качестве катализатора проводилось гальваностатически на низкоуглеродистой (мягкой) стали, с добавлением желатина и глицерина. Изучено влияния кадмия на свойства цинк-никелевой ванны с точки зрения содержания никеля и устойчивости к коррозии покрытий из сплавов цинк-никель-кадмий. Циклическая вольтамперометрия была главным методом при анализе процесса и продуктов электролиза при различных концентрациях кадмия и других добавок. С помощью спектрометрии и энергорассеивающего рентгеновского анализа было изучено влияние плотности тока на содержание никеля. Осаждение было выполнено при концентрации кадмия в пределах 0,004–0,1M. Как оказалось, скорость коррозии покрытий из цинк-никелевого сплава значительно снижается при добавлении кадмия. Однако, следует отметить, что такое снижение скорости коррозии происходит только при определенных концентрациях кадмия, то есть вплоть до концентрации 0,02M, а при более высокой величине эта скорость остается неизменной. Все попытки изменить тип совместного осаждения из нетипичного в типичный путем изменения молярного соотношения ионов металла, то есть $[Cd^{2+}]/[Ni^{2+}]$ как 0,01; 0,05 и 0,25 оказались безрезультатными. С помощью циклической вольтамперометрии удалось показать важную роль кадмия, то есть его избирательную адсорбцию при совместном осаждении ионов Zn^{+2} и Ni^{+2}, результатом чего стало увеличение содержания никеля в сплаве. Химический состав и рабочие характеристики цинк-никелевой ванны были оптимизированы для получения однородных светлых покрытий из сплава Zn-Ni-Cd. Для анализа морфологии поверхности покрытий из сплава Zn-Ni с добавлением никеля был использован метод рентгеновской дифракции, (XRD), а сканирующая электронная микроскопия (SEM) позволила исследовать фазовую структуру таких покрытий. В работе представлены результаты экспериментов, проведенных для установления роли кадмия при совместном осаждении покрытий из Zn-Ni сплавов.

Ключевые слова: сплав Zn-Ni-Cd, глицерин, исследование коррозии, рентгеновская дифракция (XRD), сканирующая электронная микроскопия (SEM).