

Full Paper

Fabrication of Zn-Ni Alloy Coatings from Acid Chloride Bath and its Corrosion Performance

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Abstract- Optimization of acidic chloride bath containing triethanolamine and citric acid for deposition of a smooth and uniform Zn-Ni alloy coating over mild steel is discussed in the present work. Bath constituents and operating parameters were optimized by standard Hull cell method. Triethanolamine and citric acid were used as additives altered the phase content in the coatings, most likely as a result of their adsorption at the surface of the cathode. The effect of citric acid was more pronounced than that of triethanolamine. The composition of coatings was determined by using colorimetric method. The bath followed anomalous codeposition with preferential deposition of Zn over nobler metal Ni. The experimental results reveal that a bright Zn-Ni alloy coating having ~4.92 wt.%Ni was showing peak performance of the coating against corrosion. Deposition was carried out under different condition of current densities and molar ratio of $[\text{Ni}^{+2}]/[\text{Zn}^{+2}]$. No transition current densities at which codeposition behaviour changed from anomalous to normal type was observed. The cathode current efficiency was higher than 80%. As the current density was increased or the bath temperature was decreased, the concentration of the nobler metal in the coating was increased. The thickness and hardness of all coatings increased as the applied current density was increased. The throwing power and reflectance of the coating was increased with current density to a peak value, and then decreased. Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods were used to assess the corrosion

resistance of Zn-Ni alloy coatings at different current densities. Surface morphology of the coatings was examined using Scanning Electron Microscopy (SEM). A new and cheap Chloride bath, for bright Zn-Ni alloy coating on mild steel has been proposed, and results are discussed.

Keywords- Electrodeposition, Corrosion resistance, Anomalous coating, Triethanolamine, Cathode current efficiency

1. INTRODUCTION

Electrodeposition is a unique technique in which a variety of materials can be processed with metals, ceramics and polymers. Electrochemical strategies offer important advantages and unique potentials in the development of nanomaterial's and nanostructures. The development of Zn-M (where M=Ni, Co and Fe) alloys is of commercial interest due to its ability to protect steel substrates at low cost. A large number of binary and ternary alloys of Zn-M alloy have been electroplated from aqueous solutions for the purpose of surface coating and micro fabrication [1,2]. Electrodepositions of metals or alloys are widely used in many industries, with distinct advantages over other coating technologies [3]. The corrosion resistance of Zn-Ni alloy depends mainly on the wt. % of Ni in the deposit. The alloy coatings with 12-15% Ni ensures improved corrosion protection and meets automotive industries [4]. Hosseini et al. [5] performed the electrochemical studies of Zn-Ni alloy coatings from non-cyanide alkaline bath containing tartrate as complexing agent.

Amongst the zinc alloys, Zn-Ni alloys with varying nickel content have been successful for corrosion protection [6,7]. Gomez et al. [8] found that the presence of additives in the bath has improved the surface homogeneity and the corrosion resistance even for an alloy with low wt. % of Ni. The roles of amines such as triethanolamine have been tried. They are found to be good complexing agents for nickel, and their effects on the deposition process, and the composition of metal on the final plate were tested [9]. This leads to Ni enrichment of the alloy, which rises corrosion protection towards nobler values and offering less cathodic protection to the steel [10]. There are numerous reports pertaining to electrodeposition of Zn-Ni alloy, carried out in acidic baths such as chloride bath, sulfate bath, sulfate-chloride bath, and aqueous acetate bath, as well as in some alkaline baths, either cyanide bath or non-cyanide bath etc. [11]. It was found that the kinetics of deposition is governed by the interfacial pH. Hegde *et al.* [12] showed that transition of metal alloys shows anomalous co-deposition, occurring as a result of changes in the applied current density during electrodeposition of Zn-Ni, Zn-Fe and Zn-Co alloys in the acidic medium. Eliaz *et al.* [13] concluded that deposition of iron group metals shows good corrosion resistance compared to the single metal deposition. Electrodeposition of Zn-Ni alloys is generally classified as anomalous co-deposition method due to the preferential deposition of Zn as less noble metal [3]. Numerous hypotheses have been proposed to elucidate this anomalous co-deposition [2,14]. Several widespread research

works have been reported on deposition mechanism of Zn-Ni group metal alloys, on anomalous co-depositions. Not any work, yet, has been reported on electrodeposition of Zn-Ni alloy bath containing triethanolamine in conjunction with citric acid (CA) for obtaining bright Zn-Ni alloy coatings. The present work illustrates the optimization of stable chloride bath for electrodeposition of Zn-Ni alloy coatings over mild steel for peak performance against corrosion.

2. EXPERIMENTAL PROCEDURE

All the chemicals used for electroplating were of laboratory reagent (LR) grade. The standard Hull cell of 267 ml capacity was used to optimize bath constituents. All depositions were carried out at 303 K except during temperature variation. The mild steel substrate as cathode (area 5 cm²) and zinc anode of same exposed area were used. Plating baths were adjusted to pH 3.0 with dilute solutions of H₂SO₄ and Na₂CO₃ whenever necessary. Mild steel substrates were smoothly polished and cleaned by anodic and cathodic electrolysis for 2 min in an aqueous solution of NaOH 35 g/L and Na₂CO₃ 25 g/L at 1 A/dm². Samples were then neutralized in a 10% HCl solution and rinsed with distilled water and were plated at required current density. After plating, the cathode was washed with tap water and rinsed with distilled water and dried.

A PVC cell of 200 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 behavior of electrodeposits were studied by DC/AC electrochemical techniques using CH instruments- Potentiostat with built-in software. The corrosion behaviour of the coatings was studied by the potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The corrosion current density and corrosion potential were determined based on Tafel's extrapolation. The exposed surface area of all samples was 1 cm². A standard three electrode cell containing 5% analytical grade sodium chloride (NaCl) at 30 °C was used. The reference electrode was calomel electrode and a platinum electrode was counter electrode. The corrosion behaviors of electroplated coatings were studied in 5% NaCl solution by potentiodynamic polarization method was carried out in a potential ramp of ±250 mV from an open circuit potential at the scan rate of 1 mVs⁻¹. Impedance behavior of Zn-Ni alloy deposits were studied by Nyquist plot in the frequency range from 100 KHz to 20 mHz using sine waves of 10 mV amplitude and the Nyquist plots were analyzed. the throwing power of the plating bath was measured using Haring-Blum cell.

$$\% \text{ Throwing power} = \frac{100(X-Y)}{X-Y} \quad (1)$$

Here X is the ratio of distance from the anode of farther and nearer cathodes, respectively, and Y is the ratio of deposit weights obtained on nearer and farther cathodes. Chemical composition of Zn-Ni alloy coating was estimated by colorimetric method. The known weight of deposit was dissolved in 5% HCl. The nickel content was precipitate, using dimethylglyoxime to get red coloured complex compound formed quantitatively in a solution. The complex compound was dissolved in alcohol and finally estimated calorimetrically [14, 15]. The surface morphology of the deposits were examined by Scanning Electron Microscopy (SEM, Model JSM-6380 LA from JEOL, Japan). The thickness of the deposits was calculated from Faradays law. The validity of measured thickness was cross examined using digital thickness tester (Coatmeasure M&C, ISO-17025/2005). The hardness of the deposit (~20 μm thickness) was measured by Vickers method using Micro Hardness Tester (CLEMEX). The cathode current efficiency of deposition was determined by knowing the mass and composition of the deposit [3]. The reflectivity of the deposit was measured using gloss meter (Nova-Elite, 60⁰, ASTM D2457).

3. RESULTS AND DISCUSSIONS

3.1. Hull cell studies

Acid chloride bath containing ZnCl_2 , NiCl_2 was optimized by conventional Hull cell method [3]. Addition of small amount (1 g/L) of triethanolamine was found to show substantial influence on the brightness of deposit. The citric acid (CA) was used as a buffer, to suppress the hydroxide formation. Deposits having greyish white/bright/porous appearance were obtained over wide current density, 1.0–6.0 A/dm^2 . Sodium acetate was used as conducting salt for improving the homogeneity of the deposit. Effect of each constituent was examined in terms of their influence on appearance, brightness and surface morphology of the coatings. Bath constituents and operating parameters arrived after optimization is shown in Table 1.

Table 1. Composition and operating parameters of optimized bath for electroplating Zn-Fe alloy on mild steel

Bath composition	Amount in g/L	Operating parameters
Zinc chloride	120	pH : 3.0
Nickel chloride	100	Temperature : 303 K
Sodium acetate	70	Anode : Pure zinc
Triethanolamine	1.0	Current density: 4.0 A/dm^2
Citric acid	4.0	

3.2. Effect of current density

3.2.1. Wt. % Ni in the deposit

The effect of current density on wt. % Ni was studied using optimized Zn-Ni bath. It was found that current density plays a significant role on both appearance and corrosion performance of the deposit. Increase in the wt. % Ni with increase in current densities was found. The change in appearance of the coatings, and wt. % Ni in the deposit over a wide range of c.d., 1.0–6.0 A/dm² is shown in Table 2. The bath produced slate white deposit at low current density side with ~1.08 wt % Ni and porous bright with ~6.93 wt. % Ni deposit at high current density side. A sound deposit with ~4.92wt. % Ni was found at 4.0 A/dm². Increase in Ni content with current density is attributed to the rapid depletion of more readily depositable Zn²⁺ ions at the cathode coating [3].

Table 2. Effect of current density on pH, Ni content, CCE, thickness, throwing power, hardness, glossiness and appearance of Zn-Ni electrodeposited from optimized bath at 303 K

Current density (A/dm ²)	pH of bath	Wt. %Ni in deposit	CCE (%)	Throwing power %	Vickers Hardness V ₂₀₀	Thickness μm	Glossiness or Reflectivity	Appearance of deposit
1.0	4.0	1.08	81	14	145	17.2	154	Slate white
2.0	4.0	2.67	90	24	168	21.3	180	Grayish white
3.0	4.0	3.49	93	29	178	23.6	365	Bright
4.0	4.0	4.92	98	34	212	29.7	339	Bright
5.0	4.0	6.87	96	31	236	37.2	317	Porous bright
6.0	4.0	6.93	91	28	241	38.1	298	Blackish
4.0	2.0	3.36						Grayish white
4.0	4.0	4.92						Bright
4.0	5.0	5.32						Porous bright

3.2.2. Cathode current efficiency and throwing power

Cathode current efficiency and throwing power of optimized bath solution were measured at different current densities from 1 to 6 A /dm² as shown in table 2.

The cathode current efficiency [16] is given by:

$$CCE = \frac{\Delta W \left(\frac{wt.\%Ni}{M_{Ni}} + \frac{wt.\%Zn}{M_{Zn}} \right) \times 2F}{IAT} \times 100 \quad (2)$$

Where: *CCE* cathode current efficiency, (%), ΔW change in weight after plating, (g), *wt. %Ni*, *wt.%Zn* weight percentages of Ni and Zn in the deposit, *wt.%Ni+wt.%Zn=100 %*, M_{Ni} , M_{Zn} atomic weight of Ni and Zn (g/mol), *F* - Faraday constant (96500 C/mol), *I*- applied current density (A/dm²), *A* -effective cathode surface area (dm²), *T* -plating duration (second). At lower current density, (1 A/dm²), the cathode current efficiency was found to be 81%. The

highest efficiency of 98% was observed at 4 A/dm². Further increase in current density, reduces efficiency to 91% at 6 A/dm².

Throwing power of optimized bath at low current density, 1A/dm² was found to be 14%. Throwing power was improved to 34% at 4 A/dm². Further increase in current density above 4 A/ dm², decreases throwing power to 28% at 6A/ dm².

3.2.3. Hardness, Thickness and Glossiness of deposit

Hardness of Zn-Ni alloy coating was found to increase with current density as shown in Table 2. This may be ascribed by the high density of Ni, compared to Zn ($d_{Zn}= 7.14 \text{ g cm}^{-3}$ and $d_{Ni}=8.90 \text{ g cm}^{-3}$). The applied current density was found to show direct dependency on thickness of deposit as shown in Table 2. The observed linear dependency of deposit thickness with applied c.d. may be due to the adsorbed metal hydroxide at the cathode, caused by the steady increase of pH due to cathodic evolution of hydrogen gas. The glossiness of Zn-Ni alloy coatings at different current densities was also tested and it was found that the deposit formed at low current density showed least glossiness, whereas at the optimum current density, the glossiness was found maximum. At higher current density, glossiness decreased due to increased porosity.

3.3. Effect of pH

The pH of the bath was varied from 2 to 5 and related data are shown in Table 2. At low pH, the deposit was grayish white with a drastic increase of pH after plating. At high pH, a porous bright deposit was observed and pH remained almost unchanged after plating. Under the bath conditions studied, almost constant wt. %Ni with variation of pH indicates that the metal ions are in complex form due to triethenolamine and citric acid.

3.4. Effect of temperature

Temperature also found to play a most important role on wt.%Ni and appearance of the coating as observed clearly in Zn-M (where Ni, Co and Fe) alloys. The coating was found to be slate white at high temperature with more proportion of zinc compared to blackish with high wt.% Ni at low temperature as shown in Table 3. It may be approved by the fact that, at elevated temperature more readily depositable metal (zinc) are favored to be replenished at the cathode film and hence decrease the nickel content in the alloy was found.

In this work it was observed that the Zn-Ni alloy coating system, the wt.% Ni content was decreased as the bath temperature was increased. This behaviour indicates that the electrodeposition in this study is, at least partially, mass transport controlled (which is more likely at high current densities). Brenner [3] noted that, as the bath temperature is increased, cathodic polarization would favour a decrease while diffusion would favour an increase in the

content of the less noble metal (Zn). However, it should be born in mind that the enthalpy of activation for diffusion-controlled processes is usually smaller than for common chemical reactions (~12–20 versus 40–100 kJ mol⁻¹, respectively). Consequently, at high temperatures the rate constant *k* would be more leading than the diffusion coefficient *D*. Therefore, it is possible that the temperature affects either the distribution of complexes of the iron-group metals (either with triethanolamine or with citric acid) or, more likely based on other results obtained in this study-the adsorption of citric acid on the surface of the cathode.

Zn-Ni alloy coating specimens were subjected to corrosion study with variation in temperature, while performing the corrosion tests in 5% NaCl solution, as corrosive medium. The corrosion rates with variation in temperature are shown in Table 3. It was observed that corrosion rate was decreased with increase in temperature (303 K) to a peak value, and then increased the corrosion rate because of porosity in the deposit at higher temperature.

Table 3. Effect of Temperature on wt. %Ni in the deposit at 4.0 A/dm² and pH 3.0 and corrosion rate of Zn-Ni alloy coatings under variation in temperature using aerated 5% NaCl

Temperature (K)	wt. %Ni in the deposit	CR (×10 ⁻² mm/y)	Appearance of the deposit
283	9.4	5.91	Blackish
293	6.4	5.70	Blackish grey
303	4.9	2.39	Bright
313	2.8	11.20	Grayish white
323	0.9	13.17	Slate white

3.5. Variation of molar ratio of Ni⁺²/Zn⁺²

Zn-M (M=Ni, Co, and Fe) alloy coatings are well known for anomalous codeposition with preferential deposition of less noble zinc deposited under most plating conditions. [3]. The change of anomalous type of codeposition into normal type was examined by accurate formulation of molar ratio of metal ions, i.e. [Ni⁺²]/[Zn⁺²]=0.1, 1.0 and 10.0. The corresponding wt. %Ni in the bath are found to be 6.7, 48.4 and 85.0%, respectively, and are shown by horizontal dotted lines in Fig. 1. It may be noted that all three baths having molar ratio of ions equal to 0.1, 1.0 and 10.0, the wt. %Ni in the deposit is found to be much less than in the bath at every conditions of current densities are investigated. Further, it may be noted that in all three baths, wt. % Ni in the deposit was tend to increase at high current densities, but never reached to that in bath as may be seen in Fig. 1. It indicates that the bath follows anomalous types of codeposition under all conditions of current densities, and all molar ratios of metal ions in the bath.

The variation in wt. % Ni with current density at different molar ratio of Ni⁺² and Zn⁺² ions in the bath are shown in Fig. 1. It may be noted that at 0.1 and 1.0 molar ratios, the system was tending towards normal type; but at higher (10.0 M) molar ratio of metal ions increased

drastically, it tended towards anomalous type. However, the increase in molar ratio of metal ions in the bath has decreased the limiting current density, i_L drastically, as shown by the arrow mark in Fig. 2. The i_L is the maximum current density that is required to achieve a desired electrode reaction before hydrogen or other ions are discharged simultaneously. In case of direct current electrolysis, the current efficiency of metal deposition decreases as soon as the limiting current density is exceeded [1]. Hence it may be inferred that the current efficiency of the bath can be increased by increasing the molar ratio of the ions in the bath. Further, the proposed bath under no conditions of temperature and pH can follow the normal type of codeposition.

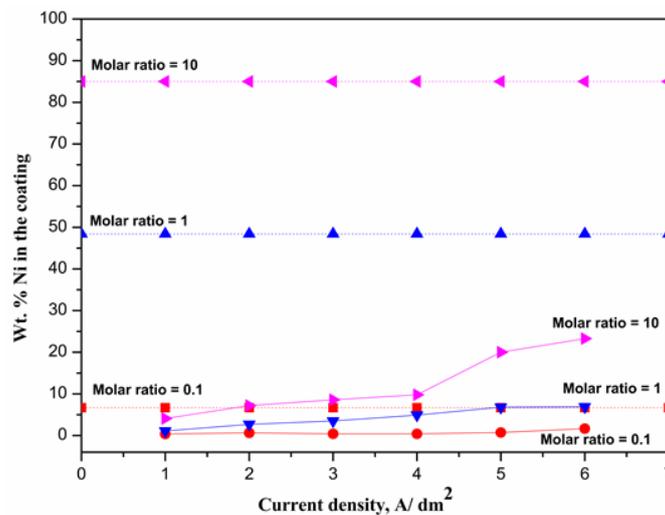


Fig. 1. Variation of wt. %Ni in the deposit with current density from Zn-Ni baths having molar ratio of ions, i.e. $[\text{Ni}^{+2}]/[\text{Zn}^{+2}] = 0.1, 1.0$ and 10.0 , shown by solid lines against those in the bath, represented by horizontal dashed lines

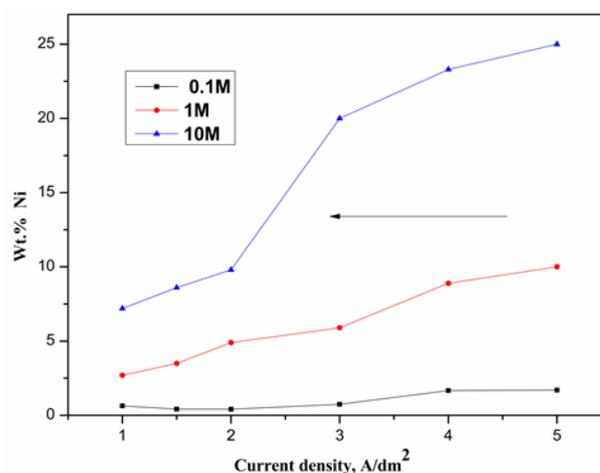


Fig. 2. Shifting of limiting current density for nickel deposition with increase in molar ratio of ions, i.e. $[\text{Ni}^{+2}]/[\text{Zn}^{+2}]$ in the bath while keeping other variables constant

3.6. Corrosion study

3.6.1. Potentiodynamic polarization study

Electrodeposited specimens were subjected to corrosion study in 5% NaCl solution, as corrosive medium, and experimental data are given in Table 4. Corrosion rates of Zn-Ni alloy coatings at different current densities were determined by Tafel's extrapolation method and Tafel's plots (only four representatives) are shown in Fig. 3. Potentiodynamic polarization study was carried out in a potential ramp of ± 250 mV from an open circuit potential at the scan rate of 1 mVs^{-1} . Observed E_{corr} and i_{corr} at different current densities are shown in Table 3. It was observed that the deposit at 4.0 A/dm^2 with ~ 4.9 wt. %Ni showed least corrosion rate ($2.39 \times 10^{-2} \text{ mm/y}$). Hence it is inferred that at 4.0 A/dm^2 , added triethenolamine and citric acid has reduced the availability of free Ni^{+2} ions in the solution by proper complexation, and improved the homogeneity of coatings and reduced the corrosion rate.

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

Current density (A/dm^2)	$-E_{\text{corr}}$ in V, vs. Ag/AgCl/Cl _{sat}	I_{corr} ($\mu\text{A}/\text{cm}^2$)	CR ($\times 10^{-2} \text{ mm/y}$)
1.0	1.056	11.60	17.02
2.0	1.047	9.89	14.51
3.0	1.057	6.57	9.64
4.0	1.055	1.63	2.39
5.0	1.058	4.92	7.22
6.0	1.071	13.44	19.73

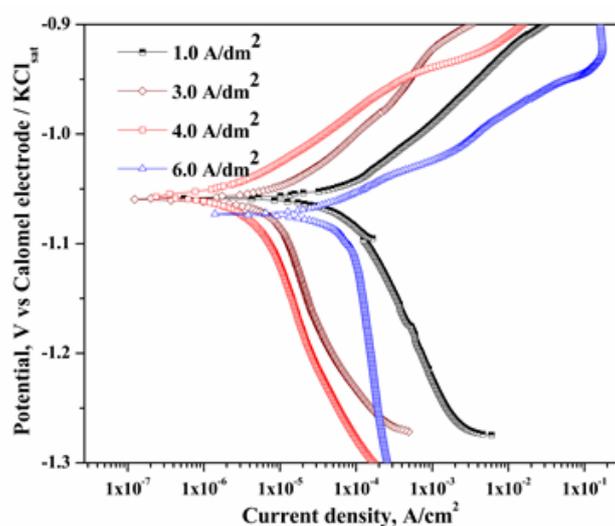


Fig. 3. Tafel plots for Zn-Ni alloy coatings formed at different current densities from the optimal bath at scan rate of 1 mV s^{-1}

3.6.2. Electrochemical impedance spectroscopy (EIS)

The better corrosion resistance of Zn-Ni alloy coatings may be explained by theory of barrier protection mechanism. EIS was used to assess the barrier properties of the coatings and to determine its polarization resistance, R_p . Nyquist responses of Zn-Ni alloy deposits under different conditions of current densities were shown in Fig. 4. It may be observed that the radius of the semicircle largely depends on the current densities employed indicating its most important role in alloy deposition. The highest diameter of the capacitive loop at optimal c.d. (4.0 A /dm²) shows that the coating is most corrosion resistant. Impedance study revealed that superior corrosion resistance of electroplates at optimal current density (4.0 A /dm²) is due to improved barrier resistance which is higher than that of Zn-Ni alloy deposits at other current densities. The solution resistance remains the same for all deposits since the studies were done under similar conditions.

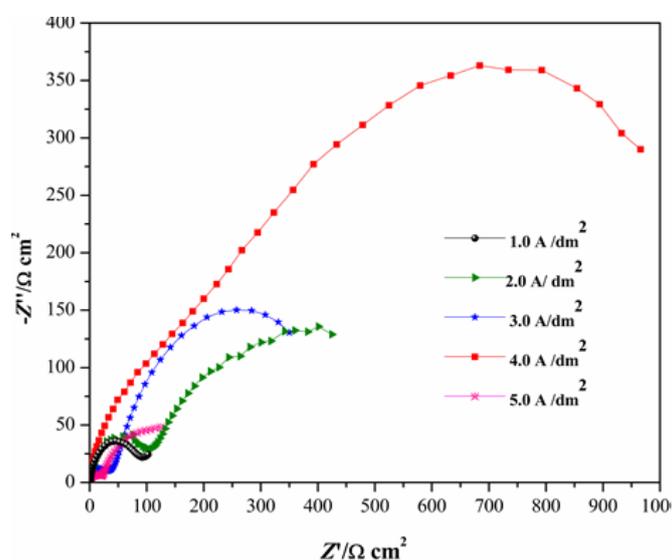


Fig. 4. Electrochemical impedance spectra (100 kHz–20 mHz) of Zn-Ni coatings electrodeposited at different current densities

3.6.3. Surface study

The SEM image of Zn-Ni alloy deposit showed that current density plays a significant role in the phase structure of the deposit. The variation in the surface morphology of the deposit with current density is shown in Fig. 5. It was found that coatings is dull and non-uniform at low current density with grayish spots likely due to nickel (Fig. 5a) and very smooth and bright at optimum c.d. of 4.0 A/dm² (Fig. 5b). But at high current density the deposit was very rough, porous and very thick as shown in Fig. 5c. Hence, the brightness and surface homogeneity of the coatings are determined mainly by deposition current density, as a function of its Ni content, and hence the phase structure. The corroded specimens were washed with distilled water and examined under SEM. Figure 5(d) and 5(e) shows a sample

with Zn-Ni alloy deposition at two different current densities, after corrosion tests was used to understand the reason for improved corrosion resistance. In Figure 5(d) the coating was uniform with high composition of Nickel content, which prevents the destruction and Figure 5(e) shows the coating was thin with low content of Nickel and completely getting degraded during corrosion.

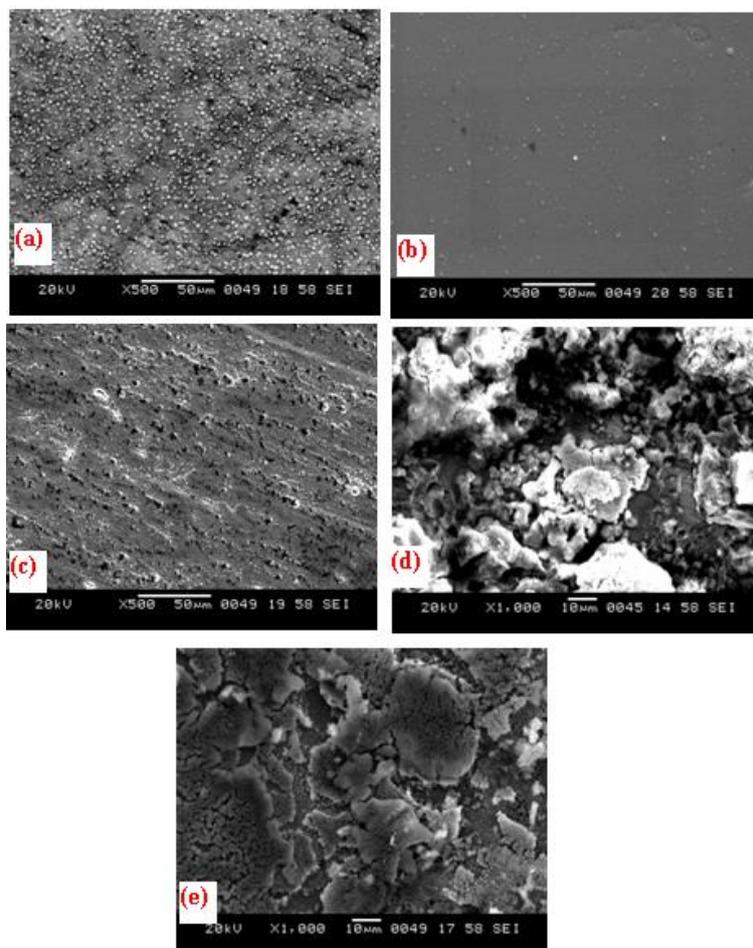


Fig. 5. Surface morphology of Zn-Ni alloys deposited at (a) 2.0 A/ dm²; (b) 4.0 A/ dm² and (c) 6.0 A/ dm² and Surface morphology of Zn-Ni coating after corrosion test; (d) 4.0 A/ dm²; (e) 1.0 A/ dm²

4. CONCLUSION

A stable acid Chloride bath has been proposed for deposition of bright Zn-Ni alloy coating onto mild steel using direct current (DC). All conditions of electroplating, (temperature, pH and molar ratio of [Ni⁺²]/[Zn⁺²]) the bath followed anomalous codeposition with preferential deposition of zinc. The effect of temperature on the plating process showed that the codeposition of metals is diffusion controlled. The Zn-Ni alloy coating developed at 4.0 A /dm² having about 4.92 wt. % Ni was found to exhibit the highest corrosion resistance (least C.R 2.39×10⁻² mm/ y) compared to those at other c.d.'s. The complexing agent triethanolamine gave smooth, uniform Zn-Ni alloy coating at 4.0 A/dm². The triethanolamine

improves bath properties like cathode current efficiency and throwing power to 98% and 34%, respectively. The thickness, reflectance and hardness of the deposit have direct dependency with wt. %Ni in the deposit. The SEM images of Zn-Ni alloy deposited at different current densities before and after the corrosion confirmed the structure-property relationship of the coatings.

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