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# Effect of Current Density on Deposit Characters of Zn-Co Alloy and their Corrosion Behaviors

S. Yogesha, K. Udaya Bhat, and A. Chitharanjan Hegde

National Institute of Technology Karnataka, Surathkal, Srinivasnagar, India

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**Electrodeposition of Zn-Co alloy on mild steel has been studied, using thiamine hydrochloride (THC) as an additive. The effect of current density on deposit characters, such as chemical composition, thickness, hardness, phase structure, and surface morphology has been investigated. The electrochemical corrosion study revealed that the coating with 1.69 wt. % Co, deposited at 3.0 A dm<sup>-2</sup> exhibited the best corrosion stability. Scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX), and X-ray diffraction (XRD) analyses were used to study the surface morphology, chemical composition, and phase structure of the coatings. The results were discussed focusing the effect of THC on coating characters.**

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**Keywords** corrosion resistance, cyclic voltammetry, SEM, thiamine hydrochloride, XRD, Zn-Co alloy

## INTRODUCTION

Electroplating of Zn-M (where, M = Ni, Co and Fe) alloys has been applied to the production of highly corrosion resistant coatings on steel. They are found to be a good substitute for cadmium, due to their high toxicity.<sup>[1–5]</sup> Among zinc-iron group metal alloys, Zn-Co alloy is known for its excellent brightness and good corrosion resistance.<sup>[6,7]</sup> Furthermore, compared with Zn and other Zn alloys, it has other superior properties, namely hardness, ductility, internal stresses, paintability, and weldability.<sup>[7,8]</sup> Zn-Co alloys are widely used as replacement for zinc in appliances, bicycle parts, lighting fixtures, and some hand tools as well as furniture, plumbing, and window hardware.<sup>[8]</sup> In addition, the cobalt content in the alloy is low, usually 1.0 wt. %<sup>[9,10,11]</sup>, when compared to 10–12 wt. % Ni in Zn-Ni deposits, which makes Zn-Co alloy less expensive to operate. Electrodeposition of Zn-Co alloy falls under the category of anomalous codeposition, envisaged by Brenner.<sup>[12]</sup> Extensive

research has been reported on deposition of Zn-Co alloys, concentrating on anomalous codeposition mechanism and dependency of deposit characters on bath constitutions and operating parameters. Generally, the electrodeposition of Zn-Co alloy at higher values of cathodic current follows anomalous codeposition (the less noble zinc is deposited preferentially than more noble cobalt), whereas at very lower values of cathodic current densities, they were found to follow normal codeposition. Hence, in the case of Zn-M alloy coatings, cathodic current density (c.d.) plays an important role on composition, homogeneity, porosity, phase structure, and consequently, the corrosion resistance of the coatings.<sup>[13–16]</sup>

It is well known that surface modification can significantly improve the stability of a metal system against corrosion. Hence, in the present work, an attempt has been made to develop bright zinc-cobalt alloy coating on mild steel using thiamine hydrochloride (THC) as an additive for its better corrosion stability. Standard Hull cell method was followed to optimize the deposition conditions and bath chemistry. The role of THC, and the effect of cathode c.d. on chemical composition, hardness, thickness, phase structure, surface morphology, and corrosion resistances of the deposit were analyzed, in view of the role of THC on plating process.

## EXPERIMENTAL

To begin with, the optimization of the electrolytic bath, in terms of bath chemistry and operating parameters, was made through standard Hull cell method. Thiamine hydrochloride (THC) was used as additive. It is a water-soluble B-complex vitamin, and is reportedly compatible with many metal ions. Compatibility is dependent upon factors such as pH, concentration, and temperature. Addition of small amounts of THC was found to show a significant improvement on brightness and homogeneity of the deposit. Electrolyte was prepared using LR-grade chemicals and distilled water. Polished mild steel panels (0.063% C, 0.23% Mn, 0.03% S, 0.011% P, 99.6% Fe) with 7.5 cm<sup>2</sup> active surface area were used as a cathode after pretreatment. The cathode was mechanically polished with progressively finer grade emery coated mops prior to deposition, and the cathode was washed by alkali cleaning. Before

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Address correspondence to A. Chitharanjan Hegde, Electrochemistry Research Laboratory, Department of Chemistry, Surathkal, Srinivasnagar - 575 025, India. Email: ahegde@rediffmail.com

TABLE 1  
Effect of current density on deposit characters of monolithic Zn-Co alloy

Current density (A/dm <sup>2</sup> )	pH of bath	Wt.% Co	CCE (%)	TP (%)	VHN V <sub>100</sub>	Thickness (μm)	CR (×10 <sup>-2</sup> mm/y)	Nature of the deposit
1.0	3.0	17.0	41.1	18	138	6.2	30.16	Blackish
2.0	3.0	1.77	81.2	25	151	6.8	20.22	Semi bright
3.0	3.0	1.69	93.1	31	154	11.1	19.51	Bright
4.0	3.0	2.10	94.0	33	168	12.1	22.22	Bright
5.0	3.0	2.21	90.6	35	179	14.9	24.47	Bright
6.0	3.0	2.24	85.9	31	163	16.3	27.41	Bright
7.0	3.0	1.93	81.4	28	160	17.0	30.92	Porous bright
3.0	2.0	1.40	—	—	—	—	—	Grayish bright
3.0	4.0	1.75	—	—	—	—	—	Semi bright
3.0	5.0	1.98	—	—	—	—	—	Grayish bright

immersion, the surface was neutralized in a 10% HCl solution. After deposition, coatings were washed with distilled water, then dried with hot air. A PVC cell of 250 cm<sup>3</sup> capacity was used for electroplating with cathode-anode space of ~ 5 cm. All depositions were carried out galvanostatically using sophisticated power source (N6705A, Agilent Technologies). All depositions were carried out at pH = 3 (±0.05) and temperature 30 ± 2°C for same time (10 minutes), for comparison purposes.

The corrosion behavior of the coatings was evaluated by electrochemical AC and DC techniques using VersaSTAT<sup>3</sup> Potentiostat/Galvanostat (Princeton Applied Research), interfaced with ZSimpWin software for circuit fitment. The corrosion study was carried out in a three-electrode cell, containing 5% NaCl solution. All potentials expressed in this study are with reference to Ag/AgCl/KCl<sub>sat</sub> electrode. Potentiodynamic polarization study was carried out in a potential limit from -250 mV to +250 mV around open circuit potential (OCP), at scan rate of 1.0 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) study was carried out in frequency range from 100 kHz to 10 mHz, using a perturbing voltage of 10 mV. The experimental impedance data were fitted to an appropriate equivalent circuit using ZSimpWin software, interface with potentiostat/ galvanostat. To identify the effect of THC on deposition process, cyclic voltammetry (CV) studies have been made using electrolyte (having optimal bath composition) at scan rate 50 mV s<sup>-1</sup>. Pure platinum foil with a surface area of 1 cm<sup>2</sup> was used as working electrode. Before each experiment, the electrode was activated by immersion in 1:1 HNO<sub>3</sub>. The CV experiments were conducted in a quiescent solution without purging, and scanning was done from left to right starting from 0 V, and then reversed.

An X-ray diffraction (XRD) investigation of Zn-Co electrodeposits was carried out using an X-ray diffractometer D8 (Bruker AXS). Cu Kα (λ = 0.15405 nm) radiation, and a continuous scan mode with a scan rate of 1° min<sup>-1</sup> was used. The surface morphology of the deposited coatings was studied using scanning electron microscopy (SEM), model JSM-6380 LA

from JEOL, Japan. The composition of the coatings was determined colorimetrically using standard<sup>[17]</sup> method and cross examined by using EDX. While the thickness of the deposits was assessed through Faradays law, it was cross-examined using digital thickness tester (Coatmeasure M&C, ISO-17025/2005). Mechanical properties such as adhesion and micro-hardness of the coatings were studied using adhesion tester (CC2000, DIN ISO 2401) and Hardness Meter (CLEMEX), respectively.

## RESULTS AND DISCUSSION

### Deposition of Zn-Co Alloy

The bath composition and operating conditions for deposition of Zn-Co alloy coatings were optimized by means of a standard Hull cell.<sup>[18]</sup> The effect of bath chemistry on the appearance and surface morphology of the coatings was evaluated. The effect of CoCl<sub>2</sub> additions was also studied. The composition and operating conditions of optimized baths are given in Table 1. A wide spectrum of Zn-Co alloys (having varying composition) formed on Hull cell panel showed that c.d. plays an important role in deciding the properties of the deposit. Deposits ranging from semi-bright to bright, and then to porous bright were observed in the range of 1.0–7.0 A dm<sup>-2</sup>. The optimal cathode c.d., pH, and concentration of each constituent in the bath were arrived, based on the brightness (visual observation), homogeneity, and adhesion (tape test) of coatings. The electrolytic bath consisting of 10 g L<sup>-1</sup> ZnO, 30 g L<sup>-1</sup> CoCl<sub>2</sub>.6H<sub>2</sub>O, 200 g L<sup>-1</sup> NH<sub>4</sub>Cl, 20 g L<sup>-1</sup> boric acid, 10 g L<sup>-1</sup> citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>.H<sub>2</sub>O), and 3 g L<sup>-1</sup> THC (C<sub>12</sub>H<sub>17</sub>N<sub>4</sub>O<sub>5</sub>Cl.HCl) has been proposed for development of bright and smooth Zn-Co coatings on mild steel. The coatings at different c.d. are developed, and subjected to various tests. The effects of c.d. on wt. % Co, hardness, thickness, and corrosion resistance of the coatings were reported in Table 1. The corrosion data showed that corrosion protection ability of the coatings decreases with increase of c.d.

### Variation in wt. % Co.

It was observed that the wt. % Co in the deposit has increased with c.d., as shown in Table 1. It is due to the fact that at high c.d., more readily depositable metal (zinc) is depleted at the cathode film, as characteristic feature of anomalous codeposition, observed in Zn-M alloys.<sup>[12]</sup> However, at very low c.d., the wt. % Co in the deposit was found to increase (Table 1), due to tendency of the bath to follow the normal codeposition. It may be ascribed to the less hydrogen formation at low c.d., which in turn causes less of an alkalization effect at the cathode film (hydroxide suppression mechanism).<sup>[19]</sup>

### Cathode current efficiency and throwing power measurements

The cathode current efficiency (CCE) and throwing power (TP) of the bath (optimal) was determined by conventional method.<sup>[18]</sup> The CCE was found to be about 41.1% at low current density, and at 4.0 A dm<sup>-2</sup> it increased to about 94%, but further increase of current density resulted in decrease of CCE, shown in Table 1. It may be noted that CCE was found to increase and then decreased with current density. This decrease of CCE at high current density may be attributed to the excessive hydrogen evolution.

The TP value can be used to define the behavior of bath, and to identify the most suitable cell current for good deposition. The TP of the optimal bath at different current density has been evaluated using Haring-Blum cell, and is shown in Table 1. It may be observed that TP remains almost constant at bright plate range, indicating right current density, responsible for bright deposition.

### Hardness of deposit

The hardness of Zn-Co coatings, developed at different c.d., is shown in Table 1. At low c.d. side, in spite of high cobalt content, the deposit showed less hardness. It may be due to thin coating, where the diamond tip must have touched the substrate during measurement. It was found that hardness of the coatings decreased with increase in c.d. It may be attributed to the occlusion of metal hydroxide into the crystal lattice, due to excessive liberation of hydrogen, during plating. Hence, even though thick deposit is formed at high c.d., it was found to exhibit less hardness as reported in Table 1. Further, the coatings at high c.d., namely at 7.0 A dm<sup>-2</sup>, the deposits are found to be porous bright, as shown in Table 1.

### Thickness of deposit

The c.d. employed was found to show direct dependency on the thickness of deposit as shown in Table 1. The observed linear dependency of thickness with c.d. may be due to the adsorbed metal hydroxide at the cathode (caused by steady increase of pH due to evolution of hydrogen gas).

### Adhesion

The adherence of Zn-Co alloy coatings at different c.d. was tested. It was found that all coatings, except at high c.d., are hard

adherent with completely smooth cut edges, and none of squares of the deposit are detached from the substrate, indicating that optimized coatings have excellent adhesion.

### Effect of pH

The pH of the bath was varied from 2.0 to 5.0 and effect of pH on deposit characters are shown in Table 1. At low pH, the deposit was semi-bright and powdery. It was observed that there exists a slight increase in pH of the bath after plating, due to depletion of H<sup>+</sup> ions. Further, it was observed that both appearance and cobalt content of the deposit remained unaltered with change in the pH of the bath.

### Effect of temperature

Temperature was also found to play a prominent role on the process and product of electrolysis, as observed in other Zn-M alloys. Electrodeposition at temperature range of 283–323K revealed that a black deposit with high proportion of zinc content is formed at low bath temperature than a silver bright deposit (with more cobalt) formed at high bath temperature (Table 2). It may be ascribed by the fact that, at elevated temperatures, more readily depositable metal (zinc) are favored to be replenished fast at the cathode film resulting to cause more wt. % Co in the deposit.

### Tafel's Polarization Study

The potentiodynamic polarization curves in Figure 1 show the corrosion current densities of Zn-Co alloy coatings in the presence and absence of THC. The low  $i_{\text{corr}}$  value exhibited by Zn-Co alloy deposits in presence of additive indicated that they are less susceptible for the corrosion than compared to deposits obtained without THC. The  $i_{\text{corr}}$  value of Zn-Co deposit obtained in the absence of THC is 73.47  $\mu\text{A cm}^{-2}$ . The smallest corrosion current density value (13.15  $\mu\text{A cm}^{-2}$ ) was obtained for Zn-Co alloy deposited in presence of THC in the bath solution. Thus, the above result shows that the added THC had increased the corrosion resistance of Zn-Co alloy coatings. It may be concluded that during corrosion, zinc dissolves preferentially, leaving a top layer enriched with cobalt and acts as a barrier to further attack, as envisaged by many workers.<sup>[20,21]</sup>

TABLE 2  
Effect of temperature on wt. % Co in the deposit at 3.0 A dm<sup>-2</sup> and pH 3.0

Temp. (K)	wt. % Co in the deposit	Appearance of the deposit
283	1.33	Blackish
293	1.58	Semi bright
303	1.69	Semi bright
313	2.32	Silver bright
323	2.93	Silver bright

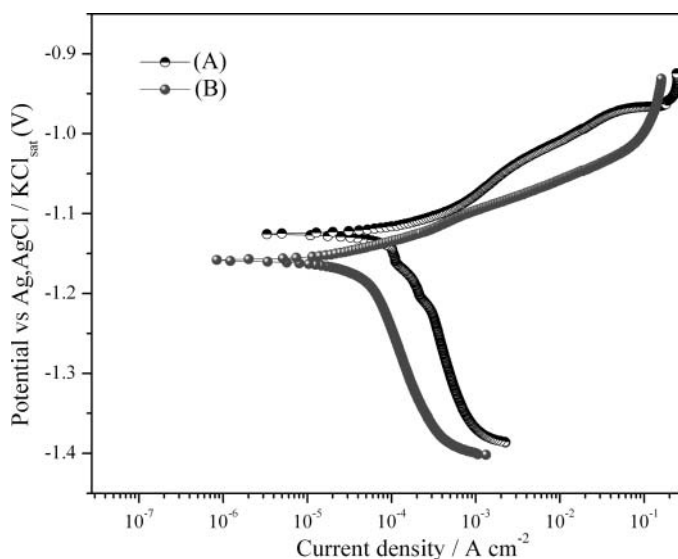


FIG. 1. Potentiodynamic polarization behavior of Zn-Co alloys in 5 wt% NaCl solution. The deposits obtained at current density  $3.0 \text{ A dm}^{-2}$ : (A) in absence of THC, and (B) in the presence of THC.

### Electrochemical Impedance Spectroscopy (EIS)

Though potentiodynamic polarization technique is used to study the kinetics of an electrode reaction, the result is often corrupted by side effects such as the charging currents of the double layer observed on a time-scale of the order of a millisecond, or by the ohmic drop associated to the experimental setup.<sup>[22]</sup> The response of reversible electrochemical systems studied in the presence of an ohmic drop unfortunately resembled the response of kinetically slow systems. The best way of differentiating the kinetics of an electrode reaction from experimental side effects is to use an excitation function covering a large time domain. Thus, EIS was used to evaluate the barrier properties of the electrical double layer capacitance and to determine the polarization resistance.<sup>[23]</sup> Electrochemical Nyquist responses of Zn-Co alloy deposits obtained at optimized c.d. ( $3.0 \text{ A dm}^{-2}$ ), in the presence and absence of THC, are shown in Figure 2. The capacitive loops at high frequency limit indicate that the corrosion resistance is due to double layer capacitance ( $C_{dl}$ ). Maximum diameter of the capacitive loop, shown in Figure 2(B) (at optimal c.d. of  $3.0 \text{ A dm}^{-2}$ ), in presence of THC shows that the deposit is most corrosion resistant than one without THC, shown in Figure 2(A). Thus, added additive (THC) is found to improve the polarization resistance of the deposit.

Electrified interface between electroplate and medium is fit to a simple equivalent circuit. The experimental impedance data at  $3.0 \text{ A dm}^{-2}$  was fitted to an appropriate equivalent circuit LR(C(R(QR)))(CR) using ZSimpWin software, and is shown in Figure 3. A close agreement was found between the calculated values and the measured values of circuit elements, namely, 'L' is the inductor, 'C' the capacitor, 'R' the resistor and 'Q' the constant phase element (CPE).

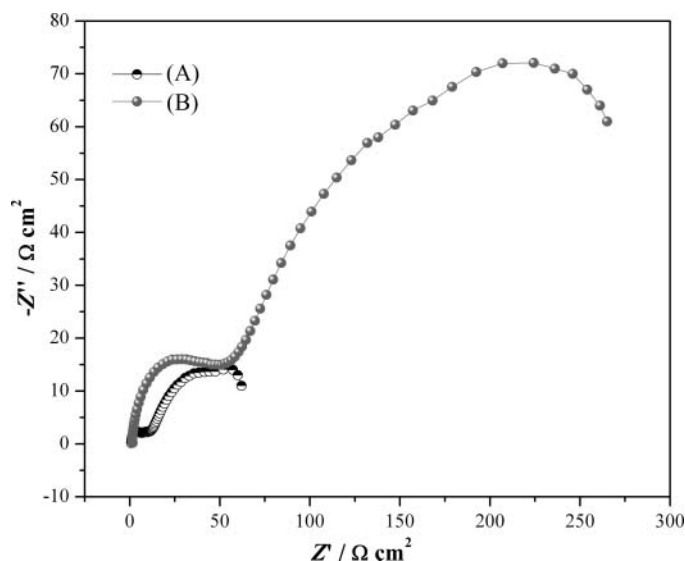


FIG. 2. Nyquist plots of Zn-Co alloys deposits obtained at current density  $3.0 \text{ A dm}^{-2}$ : (A) in absence of THC, and (B) in presence of THC.

The superior corrosion resistance of the Zn-Co alloy deposit may be explained by the barrier protection mechanism theory.<sup>[24]</sup>

### Cyclic Voltammetry Study

Cyclic voltammogram of Zn-Co bath in presence and absence of THC is shown in Figure 4. Preliminary electrochemical study has been carried out using optimized bath without metal ions and corresponding cyclic voltammogram, shown by curve (a), indicates that THC is not electrochemically active. Two small dissolution peaks (at  $-0.614 \text{ V}$  and  $-0.292 \text{ V}$ ) were observed in the case having only metal ions without THC, curve (b). This indicates that Zn-Co alloy, having two different phase structures are stripped into solution. However, on addition of THC, a large potential span was observed between two dissolution peaks, as seen in curve (c). The first peak ( $-0.926 \text{ V}$ ) within the anodic

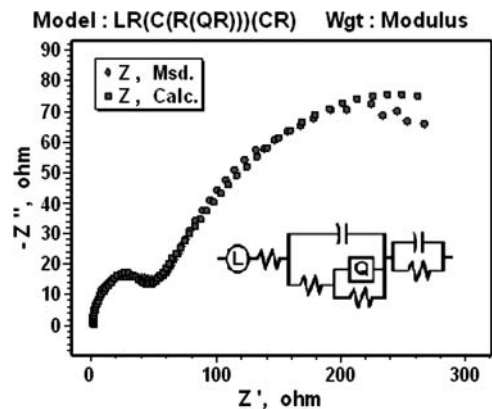


FIG. 3. Equivalent circuit fit for corrosion circuit, corresponding to Zn-Co coating at optimal current density ( $3.0 \text{ A dm}^{-2}$ ), using ZSimpwin Software.

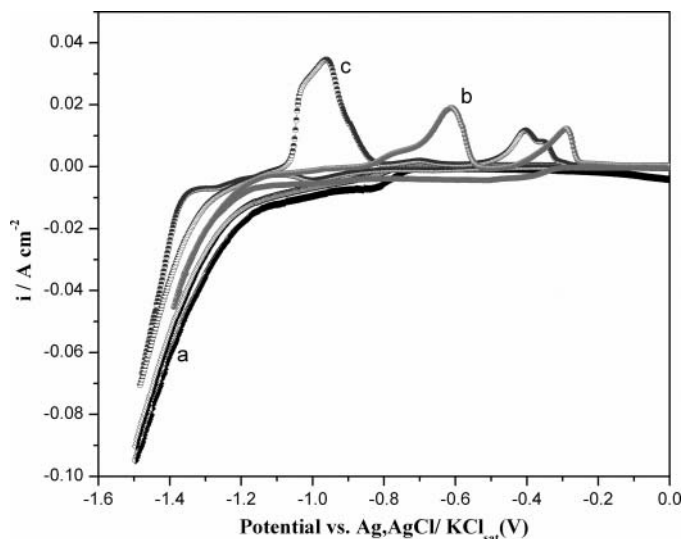


FIG. 4. Cyclic voltammograms of Zn-Co deposition process: (a) blank, (b) without THC, and (c) with THC. Working electrode: Pt, pH = 3.0, T = 30° C, scan rate = 50 mV s<sup>-1</sup>.

regime corresponds to the selective dissolution of Zn and steep cathodic curve, implies that corrosion process is cathodic controlled. Thus, it may be inferred that THC has a prominent role in shifting the deposition potential of Zn by 0.348 V towards negative side by complexing with metal ions. Thus, addition of small amount THC shifted the deposition potential of the Zn-Co alloy, which in turn, has improved the homogeneity of the coating.

### Phase Structure of the Deposit

An identification of phase structures of the deposits can be made using X-ray diffraction (XRD) study and equilibrium phase diagram of the binary Zn-Co system.<sup>[25]</sup> The XRD patterns of Zn-Co alloy deposits, obtained at optimized c.d. (3.0 A dm<sup>-2</sup>), in absence and presence of THC, are shown in Figure 5. Pure Zn and low-alloyed coatings with Co electrocrystallize with a distorted form of hexagonal close packing.<sup>[26]</sup> The electrodeposited Zn-Co coatings demonstrated the sharp peaks corresponding to Zn and Fe (base metal). However, two different phases of Zn can be identified for all the deposited low-alloyed Zn coatings. The first peak, corresponding to Zn (100), is referring to  $\alpha$ -phase or the solid solution of Co in Zn. The above statement is reasoned in Figure 5, where some fragments of XRD patterns for Zn-Co coatings are presented. The maxima of XRD peaks of Zn (100) and Zn (101) are shifted with respect to the position of these peaks for the pure Zn (PDF 04-0831). Figure 5(A) shows the XRD patterns of Zn-Co alloy without the addition of THC. Among them Zn (100) reflection was strongest of zinc compared to Zn (101), indicating its preferred orientation in the deposit. After adding THC, shown in Figure 5(B), the reflections corresponding to Zn (101), Zn (102), and Zn (103), are intensified along with the suppression of Zn(100), Fe(110), and

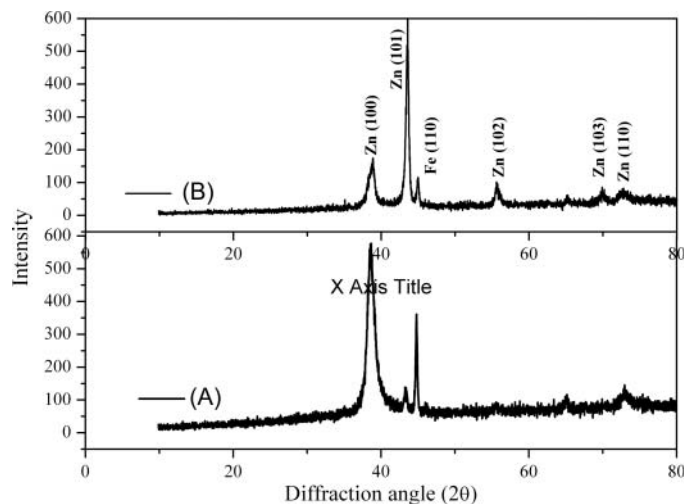


FIG. 5. X-ray diffraction patterns of the Zn-Co alloys deposited at current density 3.0 A dm<sup>-2</sup> : (A) in the absence of THC, and (B) in the presence of THC.

Zn(110), corresponding to the deposit obtained without THC. The XRD study revealed that the electrodeposited Zn-Co alloy is a mixture of two phases; one is  $\alpha$ -phase and the other pure zinc, or the  $\alpha$ -phase with a significantly lower proportion of Co.<sup>[27]</sup>

### Surface Morphology Study

The SEM micrographs of the Zn-Co alloy deposits at optimal c.d. (3.0 A dm<sup>-2</sup>), with and without THC is shown in Figure 6. Figure 6 (A) shows that the coating in the absence of THC looks like regularly branched acicular (needle like) structure. In the presence of THC, the crystal size regulated with uniform arrangement of crystals, which resulted in fine grained deposits, shown in Figure 6(B). Thus, SEM images confirmed the inclusion of THC, as brightener in Zn-Co alloy deposition.

### CONCLUSIONS

The following conclusions were drawn from the present study:

1. A stable electrolytic bath has been proposed for electrodeposition of bright Zn-Co alloy on mild steel using THC as additive.
2. Under worked conditions, 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.
3. THC was found to play a prominent role during deposition, by imparting the homogeneity to the coatings. Cyclic voltammetry study revealed that THC has changed the deposit characters by shifting the deposition potential of the Zn-Co alloy.

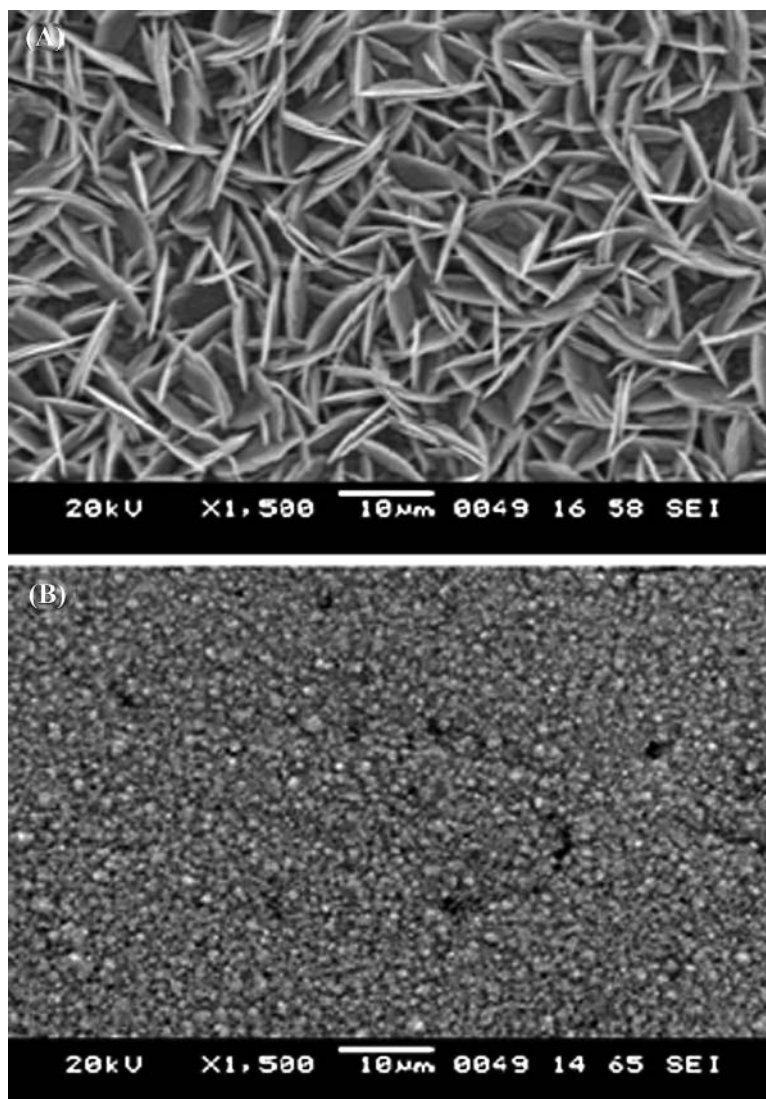


FIG. 6. SEM Micrographs of Zn-Co coatings obtained at current density  $3.0 \text{ A dm}^{-2}$ : (A) in the absence of THC, and (B) in the presence of THC.

4. The Zn-Co alloy coating developed at  $3.0 \text{ A dm}^{-2}$ , having about 1.69 wt. % Co, was found to exhibit the highest corrosion stability, compared to coatings at other current densities.
5. The EIS study revealed that superior corrosion resistance of Zn-Co coating, under optimal c.d., is due to dielectric barrier of the coating. The Nyquist responses fit well into the equivalent circuit, represented by LR(C(R(QR))) (CR).
6. Under optimal c.d., the surface morphology of the coating was found to be uniform, and hence they exhibit better appearance and corrosion resistance.
7. Corrosion study, XRD, and SEM analyses have revealed that the deposit characters have changed significantly when the coating is carried out in the presence of THC.

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