

# Electrodeposition and Characterization Zn–Co Alloy<sup>1</sup>

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**Abstract**—The present work details optimization of a stable acid chloride bath for electroplating of bright Zn–Co alloy on mild steel using gelatin and glycine as additives. It was found that the addition of gelatin along with glycine changed the deposition pattern markedly. A suitable bath has been formulated using conventional Hull cell experiments. The bath under plating conditions were found to exhibit anomalous codeposition with preferential deposition of less noble (zinc) over more noble (cobalt) as characterized by Zn–Fe group metal alloys. Investigation revealed that the current density (c.d.), temperature, and pH of the bath have strong effect on the composition of the deposit. Influence of bath constituents and operating parameters on appearance and composition of deposits were studied as measure of their performance against corrosion. A variety of deposits were obtained and their corrosion resistances were measured by Tafel method with/without chrome passivation. Experimental results demonstrated the fact that the corrosion resistances of Zn–Co alloys increased with percent of Co in the deposit except at very high c.d. This is due to the fact at very high c.d. the deposit becomes very porous and thick as evidenced by SEM image. The formation of Zn–Co alloy is confirmed by EDAX analysis. A stable chloride bath for Zn–Co alloy deposition has been proposed and discussed. The formation of passive film on chromatization is indicated by almost same  $E_{\text{corr}}$  value of all Zn–Co electroplates irrespective of the current densities at which they have been deposited.

**Key words:** electrodeposition, Zn–Co alloy, composition, corrosion behavior

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## INTRODUCTION

Normal zinc electroplates plays an important corrosion-protection role that will certainly never be completely achieved, but the alloys perform better in certain critical applications. The materials being used include alloys with iron, cobalt, nickel, and tin. The improvement in corrosion resistance from these alloys is possible because the introduction of the alloy component causes the alloy to become slightly nobler than zinc, thus slowing the corrosion rate [1, 2]. If the alloy composition is low enough, the deposit remains sacrificial with respect to the steel substrate. Thus, the same thickness of an alloy has the ability to protect the underlying steel for a longer time than conventional zinc. The iron group metals Fe, Co, and Ni exhibit a so-called anomalous codeposition behavior during plating, i.e. the less noble metal is deposited preferentially to the more noble one [3]. The phenomenon has been explained in the literature as an inhibition of the deposition of the more noble metal by the codepositing less noble metal [4, 5]. The inhibiting effect is generally strongest when the reaction rate of the less noble metal is kinetically controlled and it diminishes as the limiting c.d. is reached. In this direction Zn–Co alloy plating has become more popular because of its relatively lower

cost of operation, exceptional brightness and leveling ability. Even though enormous amount of literature is available on the production and properties of zinc-cobalt alloy plating using many hydroxy acid compounds [6–9], the present work demonstrates the optimization of a stable and very economic acid chloride bath for electrodeposition of a bright Zn–Co alloy on mild steel using glycine and gelatin in combination.

## EXPERIMENTAL

Polished mild steel cathode panels of standard size and pure zinc anode were used for Hull cell experiment. A cell current of 1 A for duration of 5 min were used. The nature of the deposits obtained under different conditions was examined for their appearance and accordingly a bath has been optimized for smooth and uniform deposit of Zn–Co alloy showing peak performance against corrosion. The composition of the deposit was measured by colorimetric method [10] by stripping the deposit in dilute HCl and by EDAX. The variation in the microstructure of deposit with c.d. and pH of the bath was analyzed through scanning electron microscope (SEM), (JEOL, Model JSM-6390, Japan). Current efficiencies were determined from standard equations knowing the mass and composition of alloy [3]. The Zn–Co deposit of about 20  $\mu\text{m}$  thickness were plated over mild steel specimens (20  $\times$  20  $\times$  1 mm) and were tested for their corrosion resistance using Electrochemical Work Station (AutoLab, Model PGSTAT 30,

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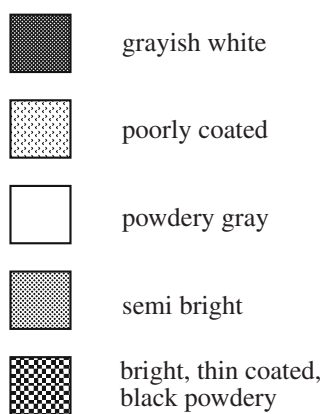


Fig. 1. Hull Cell Code

Ecochemie, Netherland). Deposits were given passivation in a potassium dichromate solution, 200 g/l, at pH 1.8 and dried for 24 h in a clear and clean atmosphere. Corrosion behavior of alloy deposits were studied and compared with/without passivation. The Hull cell experiments were carried out by introducing polished mild steel panels into the plating bath having the composition: zinc chloride (100 g/l), cobalt chloride (5 g/l), potassium chloride (50 g/l), ammonium chloride (100 g/l), glycine (3 g/l), gelatin (5 g/l). Effect of various constituents on deposit patterns were experimented upon using Hull cell at pH 4 and temperature 303 K.

The electrolytic bath was maintained at pH 4 and was frequently checked and variations found were adjusted using dilute HCl and dilute  $\text{NH}_4\text{OH}$ .

The same procedure was followed during variation of concentrations of  $\text{ZnCl}_2$  and  $\text{CoCl}_2$  in Hull Cell study.

Hull cell code is as given in Fig. 1. The effect of bath constituents on Hull cell patterns are shown in the Figs. 2 and 3.

## RESULTS AND DISCUSSION

### *Effect of zinc chloride*

The effect of zinc chloride on Hull cell panels is shown in the Fig. 2. At lower concentration, a very thin deposit was observed at a wide c.d. of 1.0–6.0 A/dm<sup>2</sup>. The increase of  $\text{ZnCl}_2$  increased the brightness of the deposit uniformly up to 80 g/l. But the further increase of zinc chloride concentration decreased the brightness as shown in the Figs. 2f and 2g. Hence 80 g/l of  $\text{ZnCl}_2$  is fixed as its optimum concentration.

### *Effect of cobalt chloride*

The effect of adding cobalt chloride into bath is given in the Fig. 3. It was observed that as the cobalt content of the solution increased, bright region becomes prominent on the Hull cell plates, indicating

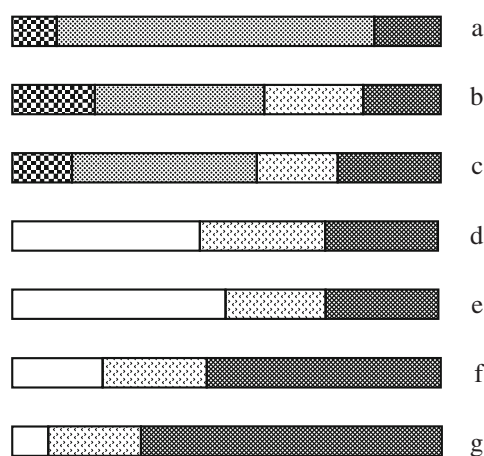


Fig. 2. Effect of  $\text{ZnCl}_2$  on Hull cell patterns at 303 K and pH 4 and 5 g/l  $\text{CoCl}_2$ , 50 g/l KCl, 100 g/l  $\text{NH}_4\text{Cl}$ , 3 g/l glycine, 5 g/l gelatin at 1 A cell current for duration of 5 min (a) no  $\text{ZnCl}_2$ , (b) 10 g/l, (c) 30 g/l, (d) 50 g/l, (e) 80 g/l, (f) 100 g/l, (g) 130 g/l.

that this is the region corresponding to zinc-cobalt alloys. At lower cobalt concentrations, the bright region becomes prominent at high c.d. and but it tends to reduce with excessive cobalt as shown in Fig. 3f.

### *Effect of glycine*

The effects of glycine on the Hull cell panels were studied. Without glycine the deposits were bright only at a narrow range of about 4 A/dm<sup>2</sup>. The addition of 7 g/l glycine showed very bright deposition in the range of 3–6 A/dm<sup>2</sup>. Further increase of glycine has not altered the deposition characters considerably and hence 7 g/l of glycine is fixed for optimized bath.

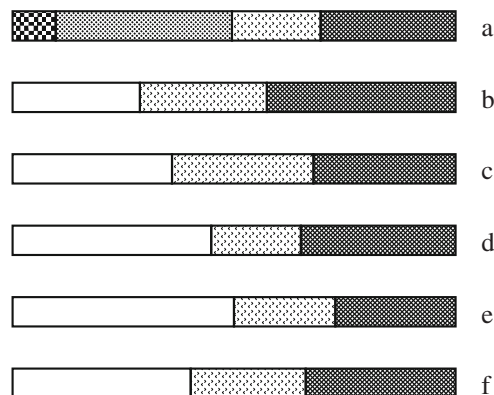


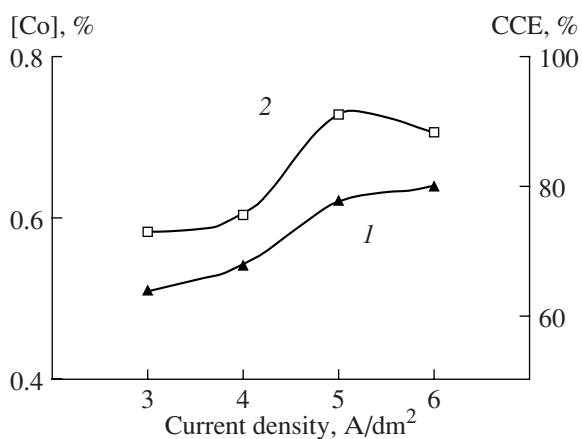
Fig. 3. Effect of  $\text{CoCl}_2$  on Hull cell patterns at 303 K and pH 4 and 100 g/l  $\text{ZnCl}_2$ , 50 g/l KCl, 100 g/l  $\text{NH}_4\text{Cl}$ , 3 g/l glycine, 5 g/l gelatin at 1 A cell current for duration of 5 min (a) no  $\text{CoCl}_2$ , (b) 1 g/l, (c) 3 g/l, (d) 5 g/l, (e) 7 g/l, (f) 10 g/l.

**Table 1.** Effect of c.d. and pH on composition and appearance of the Zn–Co deposit

c.d., A/dm <sup>2</sup>	pH of bath	(%) Co	Appearance of the deposit
3.0	4.0	0.51	Grayish white
4.0	4.0	0.57	Semi bright
5.0	4.0	0.62	Bright
6.0	4.0	0.64	Porous bright
5.0	2.0	0.43	Thin bright
5.0	3.0	0.55	Thin bright
5.0	5.0	0.68	Porous bright
5.0	6.0	0.70	Porous bright

#### Effect of gelatin

Addition of gelatin has significant effect on the smoothness of deposit. In the absence of the gelatin a semi-bright deposits were observed in range of 1.0–4.0 A/dm<sup>2</sup> with grayish white zinc deposit at high c.d. side. The effect of gelatin was studied at 2.0 g/l, 5.0 g/l, 8.0 g/l, 10.0 g/l, 12.0 g/l, and 15 g/l. At 2.0 g/l of gelatin a bright deposit was observed only at high c.d. side. Further additions of gelatin increased the bright region and tended to the maximum at 10.0 g/l between 3.0–6.0 A/dm<sup>2</sup>.



**Fig. 4.** Plot of % Co and CCE vs. current density at 303 K, pH 4, and 80 g/l ZnCl<sub>2</sub>, 7 g/l, CoCl<sub>2</sub>, 70 g/l KCl, 75 g/l NH<sub>4</sub>Cl, 7 g/l glycine, 10 g/l gelatin.

#### Effect of potassium chloride and ammonium chloride

To increase the conductivity of the bath, KCl and NH<sub>4</sub>Cl were used. Concentration of KCl was varied from 10 g/l to 130 g/l. The appearance of deposit has improved only up to 70 g/l. Further addition of KCl had no effect on the nature of the deposit. At much higher concentration of KCl, the deposit has become grayish white. Further, NH<sub>4</sub>Cl found to increase the smoothness of the deposit and was optimized at 75 g/l in the similar manner. It was observed that the operating Hull cell voltage decreased with increase of salt concentration in the bath.

#### Effect of current density

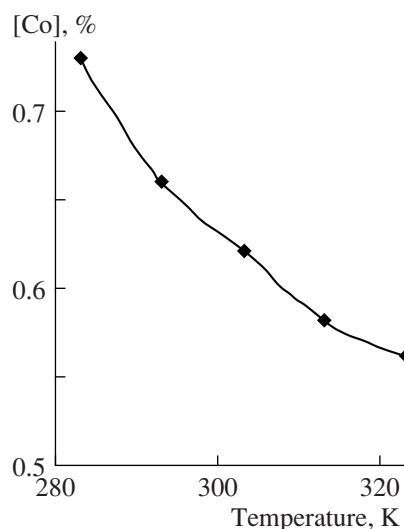
The current density (c.d.) has significant effect on the nature and composition of the deposit as shown in Table 1 and Fig. 4. The bath produces a grayish white deposit with less % Co at low c.d. side and produces a porous bright deposit at high c.d. with about 0.62% Co. The deposit becomes more porous and flakey with increased thickness at higher c.d. Further, it was found that at all current densities studied, % Co in the deposit is much less than that in the bath (about 7% Co) demonstrating anomalous type of codeposition as expected for Zn–Fe group metal alloys. The variation in the appearance of the deposit with c.d. and pH was studied and is shown in Table 1. Variation of cathode current efficiency (CCE) and % Co in the deposit with c.d. is as depicted in Fig. 4. It was found that the CCE of the bath increases with c.d. and tended to a maximum at 5.0 A/dm<sup>2</sup> and then started decreased due to excessive evolution of hydrogen at cathode.

#### Effect of temperature

The variations in appearance and composition of Zn–Co deposit with temperature from the optimized bath have been studied. It was observed that at 323 K the deposit is almost gray in color indicating high % Zn (less noble) deposited preferentially as per anomalous codeposition. The variation of % Co content of the deposit with temperature is as shown in Fig. 5.

#### Morphology

Figure 6 shows the metallographic structure of Zn–Co alloy deposit at different current densities and pH. The deposit was found to be grayish white at low c.d. of 3 A/dm<sup>2</sup> and 4 A/dm<sup>2</sup> (Figs. 6a and 6b). A very smooth and fine grained deposit was obtained at optimum c.d. of 5 A/dm<sup>2</sup> (Fig. 6c). Deposit was found to be very porous at higher c.d. of 6.0 A/dm<sup>2</sup> (Fig. 6d). Further, the deposit was uniform at pH 3 and porous at pH 6. The surface structure of zinc–cobalt alloy at 5 A/dm<sup>2</sup> and pH 4 was found to be very smooth and uniform with fine grained structure.



**Fig. 5.** Variation of % Co in the deposit with temperature at pH 4 and 80 g/l ZnCl<sub>2</sub>, 7 g/l, CoCl<sub>2</sub>, 70 g/l KCl, 75 g/l NH<sub>4</sub>Cl, 7 g/l glycine, 10 g/l gelatin.

#### *Properties of electrodeposited zinc–cobalt alloys*

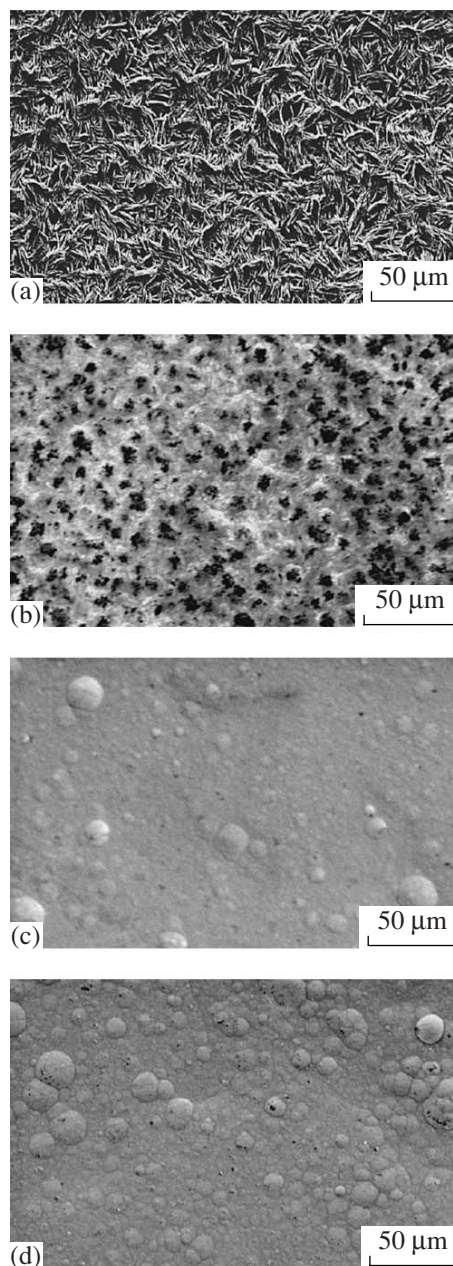
It was found that % of cobalt increased with c.d. and tended to a maximum at 6.0 A/dm<sup>2</sup>. This steady increase of % Co (more noble) with c.d. is due to the fact that less noble zinc is ineffective in inhibiting the deposition of more noble cobalt. It was observed that the cathode current efficiency of alloy deposition was maximum at optimum c.d. compared to that at other c.d. The composition of the deposit was determined by standard colometric method, confirmed further by the EDAX analysis as shown in Fig. 7.

#### *Corrosion behavior of alloy deposits*

Corrosion behavior of electroplated deposits of Zn–Co alloy at different conditions was studied in 5% NaCl solution with and without chrome passivation. Polarization plots for Zn–Co deposits after passivation are given in Fig. 8 and corresponding data are given in the Table 2. From the data it is seen that the deposit at optimized c.d. (5 A/dm<sup>2</sup>) showed least corrosion current. The deposits obtained at all other conditions record high  $I_{\text{corr}}$  value showing that they are more susceptible for corrosion. It was found that the corrosion resistance of all Zn–Co deposits has

increased drastically after passivation. Almost same  $E_{\text{corr}}$  with respect saturated calomel electrode (SCE) value in Fig. 8 shows that irrespective of the current densities at which they are deposited, a passive film is formed on chromatization has decreased the corrosion of the deposits considerably.

It was found that Zn–Co alloy deposited at c.d. of 5 A/dm<sup>2</sup> and pH 4 shows peak performance against corrosion in both conditions, i.e. with and without passiva-



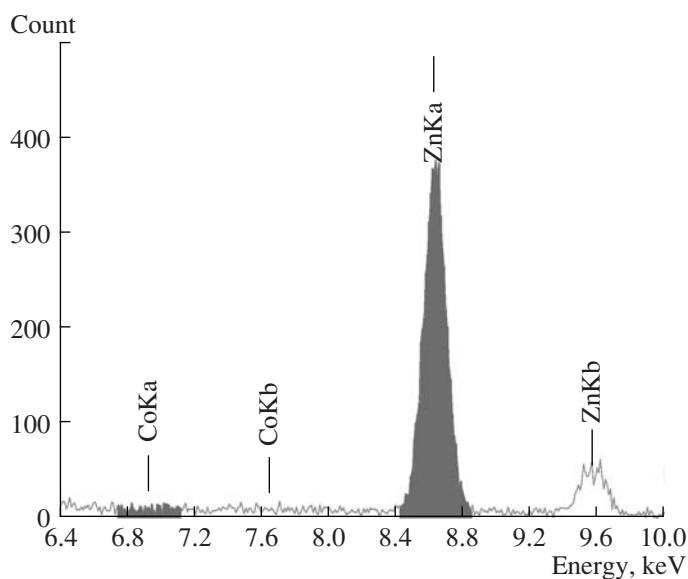
**Fig. 6.** SEM image (500 magnification) of Zn–Co alloy at 303 K (a) c.d. 3 A/dm<sup>2</sup>, (b) c.d. 4 A/dm<sup>2</sup>, (c) c.d. 5 A/dm<sup>2</sup>, (d) c.d. 6 A/dm<sup>2</sup> (all at pH 4).

tion. Thus on the basis of the investigation made a suitable bath for electrodeposition of bright and smooth zinc–cobalt alloy for good corrosion resistance has been and is given in Table 3.

## CONCLUSIONS

The addition of glycine greatly increased the polarization of deposition of a more noble cobalt metal with-



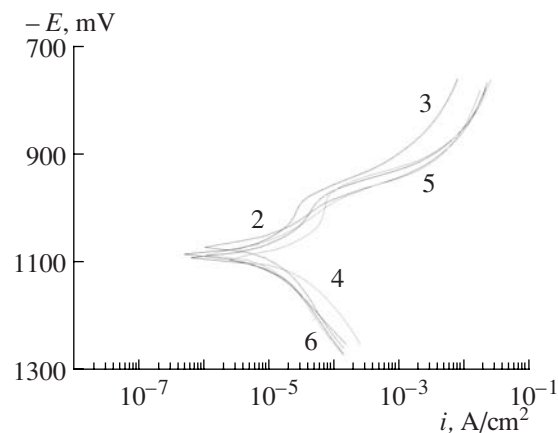


**Fig. 7.** EDAX diagram of the Zn–Co alloy deposit at c.d. 5 A/dm<sup>2</sup>, 303 K, and pH 4.

out appreciably affecting the deposition potential of the less noble zinc. Thus the deposition potentials of two metals are brought close together and making co-deposition possible. Anomalous codeposition Zn–Co alloy was found at very low c.d. and elevated temperature with preferential deposition of less noble metal (zinc) as characterized by Zn–Fe group metal alloy. At high c.d. range high % Co in the deposit is due to the fact that less noble zinc is ineffective inhibiting more noble cobalt. The bath produces a grayish white deposit with less % Co at low c.d. side and produces porous bright deposit at high c.d. with about 0.65 %Co. The pH has also significant effect on composition and morphology of the deposit. It was observed that the deposit is bright with high % Co at low temperature and becomes grayish white having low % Co at high temperature. A very

**Table 2.**  $I_{\text{corr}}$  value of Zn–Co alloy at different c.d. and pH

Plating c.d., A/dm <sup>2</sup>	Without passivation		With passivation	
	$E_{\text{corr}}$ , –mV	$I_{\text{corr}}$ , A/cm <sup>2</sup>	$E_{\text{corr}}$ , –mV	$I_{\text{corr}}$ , A/cm <sup>2</sup>
2	1050	62.03	1084	22.50
3	1070	58.78	1086	17.19
4	1080	50.62	1081	15.29
5	1040	33.25	1075	13.78
6	1010	39.46	1062	20.22



**Fig. 8.** Polarization curves of Zn–Co alloy after passivation in 5% NaCl at scan rate 5 mV/s, (number on the curves represents c.d.).

smooth and fine grained deposit was obtained at optimized c.d. of 5 A/dm<sup>2</sup>. Deposits were found to be porous at about 6.0 A/dm<sup>2</sup> and uniform at low c.d. Zn–Co alloy deposited at 5 A/dm<sup>2</sup> and pH 4 was found to be less susceptible for corrosion with least  $I_{\text{corr}}$  value. Corrosion resistance of Zn–Co deposits obtained at different conditions was found to be increased drastically after passivation. A suitable bath consisting of zinc chloride, cobalt chloride, potassium chloride, ammonium chloride, gelatin, and glycine has been identified for plating smooth and bright zinc–cobalt alloy over mild steel for better performance against corrosion.

#### ACKNOWLEDGMENTS

The authors are grateful to National Institute of Technology Karnataka, Surathkal for extended the sup-

**Table 3.** Composition and operating parameters of optimized bath for electrodeposition of zinc–cobalt alloy on mild steel

Zinc chloride, g/l	80
Cobalt chloride, g/l	7
Potassium chloride, g/l	70
Ammonium chloride, g/l	75
Gelatin, g/l	10
Glycine, g/l	7
pH	4
c.d., A/dm <sup>2</sup>	4–5
Temperature, K	303
Anode	Pure Zinc

port in carrying out this work and awarded Institute fellowship to TV.

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