Electrodeposition of Zn-Co alloy from an acid sulphate bath containing Triethanolamine and Thiaminehydrochloride

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Abstract

Electrodeposition of Zn-Co alloy from an acid sulphate bath has been carried out. The effects of metal ion ratio in the bath, pH current density, temperature, stirring, thickness and concentrations of triethanolamine and thiaminehydrochloride on the alloy composition and on cathodic current efficiency have been investigated. The deposition potentials of Zn-Co alloy are less noble of zinc and cobalt. The structure of Zn-Co alloy was investigated by X-ray diffraction indicates zinc structure. The surface morphology of alloy deposits is found to depend on the percentage of cobalt in the alloy. Under the optimum operating conditions, Zn-Co alloy deposition follows anomalous co-deposition.

Keywords: Electrodeposition, Zinc, Cathodic Current Efficiency, Scanning Electron Microscope, Triethanolamine, Thiaminehydrochloride

1.Introduction

In the recent years, many efforts have been made to develop high corrosion resistant steel for automotive and body building works [1, 2]. Extensive work has been reported [3-5] in the area of development of zinc alloys to provide high degree of corrosion resistance. Among several zinc alloys electroplated, zinc alloyed with low percentage of cobalt (<1%) is the most commercially viable option for cost effectiveness and for better corrosion resistance than conventional zinc system.

Zn-Co alloys have been electrodeposited from acid chloride [6-8] and sulphate [9, 10] baths. Current density, temperature and pH were found to increase the percentage of cobalt in the alloy. Zn-Co alloy deposition was found to follow anomalous type of co-deposition [11, 12]. The presence of some of the additives like Germanium, Arsenic and Antimony reduces the anomalous behavior to a small extent [13, 14]. Literature survey on Zn-Co alloy plated from acid sulphate baths indicates that baths exhibit poor throwing power and low cathodic current efficiencies. An attempt has been made in this study to formulate a suitable bath and to determine an optimum operating conditions required for the deposition of Zn-Co alloy containing 0.4-1.2 % Co having high cathodic current efficiency.

2.Experimental Methods

Plating bath solutions were prepared from laboratory grade chemicals using distilled water. The bath solution was filtered and purified as described by elsewhere. Copper foil (1 cm^2, and 0.4 mm thick) was used as a cathode and a stainless steel anode (2 cm^2) was used as an auxiliary electrode. Electrodeposition was carried out galvanostatically. To determine the composition of alloy, alloy deposits were dissolved in 20 % HNO_3 and analyzed for metal content by atomic absorption spectrometry (Varian spectra model AA 30).

Deposition potentials were measured w.r.t. SCE with the help of a scanning potentiostat [Elico (India) CL 35]. The adhesion of alloy to base metal was tested by a standard bending test. Porosity of alloy deposits was determined by Ferroxyl test.

Phase structure of Zn-Co alloy deposits was determined by X-ray powder diffraction (filter Cukα_1, 30 KV, 20 mA, 4000 counts). Scanning electron microscopy was used to study surface morphology of alloy deposits coated over polished copper surface.

3.Results and Discussion

3.1.Composition

3.1.1.Cathodic polarization characteristics

Figure 1 shows the cathodic polarization curves for Zn-Co alloy deposition on copper cathode (curve 3). Figure also shows the polarization characteristics for the deposition of individual metals as well (curves 1 and 2). The deposition potential for cobalt was around -1.0V, whereas for Zinc, it is -1.20 V and the deposition potential for Zn-Co alloy (curve 3) was at -1.40V. The position of Zn-Co alloy deposition potential curve is shown to be more negative to less noble zinc. This clearly indicates why zinc deposits preferentially over cobalt *i.e.*, anomalous co-deposition.

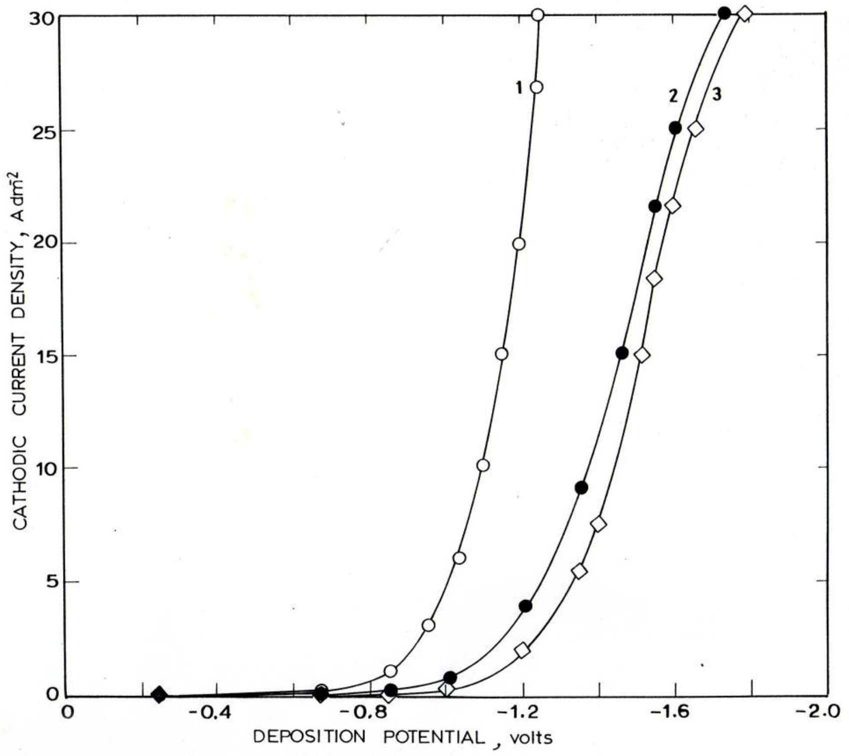


Figure 1.Cathodic polarization curves for the deposition of zinc, cobalt and Zn-Co alloy from an acid sulphate bath. All solution contained TEA 40 ml/l, H_3BO_3 25 g / l, stirred conditions

Curve 1: Deposition of cobalt

Curve 2: Deposition of zinc

Curve 3: Deposition of zinc-cobalt alloy

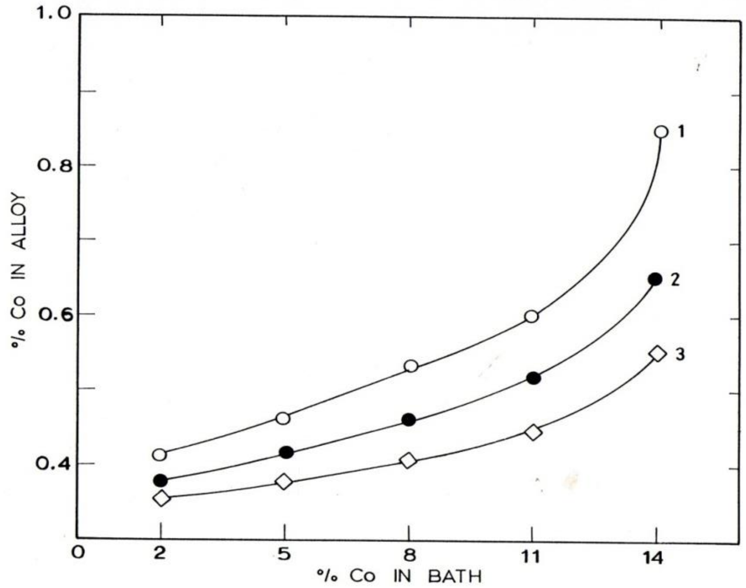
The bath solution contained same concentration of cobalt and zinc as those in the individual baths.

3.1.2.Effect of metal ion ratio in the bath

To study the effect of metal ion ratio in the bath on alloy composition, the bath contained zinc to cobalt ratio varied from 86:14 to 98:2. Figure 2 shows the variation of alloy composition with bath composition obtained at three different current densities (2.5, 10 and 30 Adm^{-2}). A bath solution containing 11 % Co produced an alloy deposit with 0.6 % Co indicating preferential deposition of zinc (anomalous process).

3.1.3.Effect of pH

Increase in the bath pH resulted in increase in the percentage of cobalt in the alloy deposit (Figure



3).

Figure 2. Dependence of the % of Co in alloy with the % of Co in the bath.

Bath composition: Total metal content 0.2 M, $[Zn^{2+}]$ 0.172 – 0.196 M, $[Co^{2+}]$ 0.022 M, TEA 40 ml / l, Thiaminehydrochloride 0.4 g / l, Na_2SO_4 30 g / l, H_3BO_3 25 g / l, pH 5.0, temperature 35^0C, current density 2.5-30 Adm^{-2}, thickness ~ 6 µm, stirred condition.

Curve 1: 30 Adm^{-2}, Curve 2: 10 Adm^{-2}, Curve 3: 2.5 Adm^{-2}

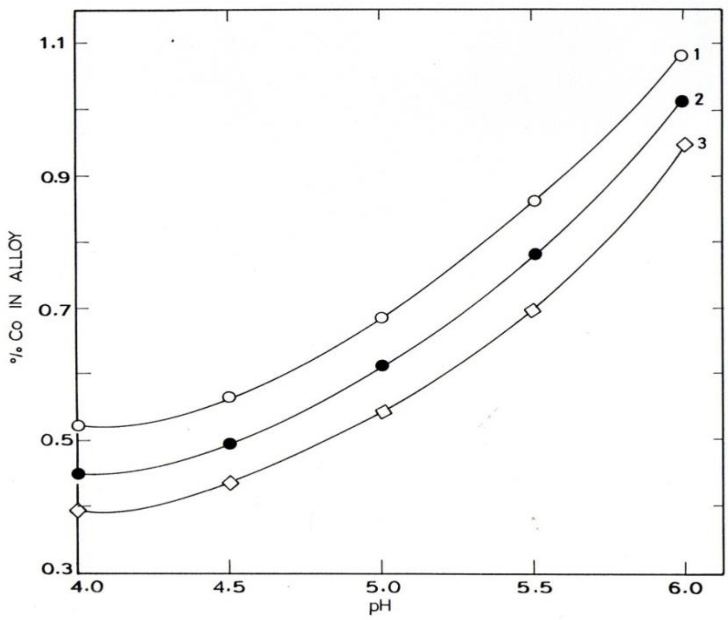


Figure 3. Variation of % Co in the alloy with the pH of the plating bath.

Bath composition: Total metal content 0.2 M, $[Zn^{2+}]$ 0.172 – 0.196 M, $[Co^{2+}]$ 0.004 – 0.028 M, TEA 40 ml / l, Thiaminehydrochloride 0.4 g / l, Na_2SO_4 30 g / l, H_3BO_3 25 g / l, temperature 35^0C, current density 10 Adm^{-2}, pH 4-6, thickness ~ 6 µm, stirred condition.

Curve 1: 86/14 Zn/Co, Curve 2: 89/11 Zn/Co, Curve 3: 92/8 Zn/Co

3.1.4.Effect of current density

Increase in current density increases % Co in the alloy deposit (Figure 4). This is attributed to the preferential deposition of zinc in the cathode diffusion layer due to its rapid depletion than cobalt, *i.e.*, diffusion controlled.

3.1.5.Effect of temperature

To study the effect of temperature on alloy composition, experiments were conducted at different temperatures (25-30 ^{0}C). Figure 5 illustrates the dependence of alloy composition on temperature of the plating bath. An increase in temperature increased the percentage of cobalt in the alloy deposit.

3.1.6.Effect of Triethanolamine (TEA) and Thiamine hydrochloride

Variation of Zn-Co alloy composition with concentrations of TEA and Thiaminehydrochloride is shown in figure 6. Increase in TEA concentration, increases % Co in the alloy, whereas increase in the concentration of Thiaminehydrochloride decreased the percentage of cobalt in the alloy deposit.

3.1.7.Effect of thickness

Increase in the thickness of alloy deposit decreased the percentage of cobalt in the alloy deposit (Figure 7). This might be due to the depletion in concentration of cobalt metal in the cathode diffusion layer.

3.1.8.Effect of stirring

The percentage of cobalt in the alloy deposit was found to be more under stirred conditions compared to unstirred conditions (Table 1).

3.1.9.Cathodic current efficiency

Cathodic current efficiencies (CCE) were calculated for each experiment at any given temperature, current density and stirring of the bath solution. Dependency of CCE on current density is shown in figure 8. Increase in current density decreases CCE of alloy plating. This is probably due to more hydrogen discharge at higher current densities. Increase in temperature of plating bath decreases CCE (Table 2). It was also noticed that CCE was higher under stirred conditions compared to unstirred conditions (Table 1).

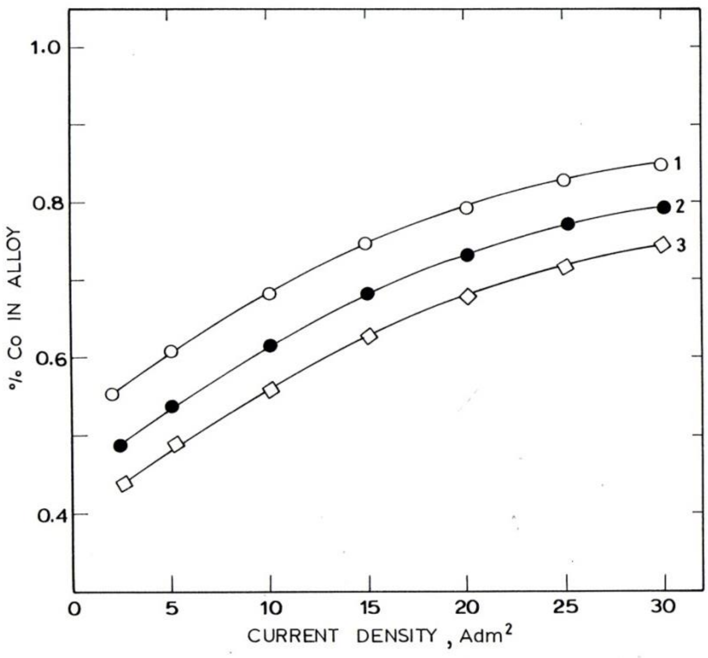


Figure 4. Variation of % of Co in the alloy with the current density.
Bath composition: Total metal content 0.2 M, [Zn^{2+}] 0.172 – 0.196 M, [Co^{2+}] 0.004 – 0.028 M, TEA 40 ml / l, Thiaminehydrochloride 0.4 g / l, Na_2SO_4 30 g / l, H_3BO_3 25 g / l, temperature 35^0C, current density 2.5-30 Adm^{-2}, pH 5.0, thickness ~ 6 μm, stirred condition.

Curve 1: 86/14 Zn/Co, Curve 2: 89/11 Zn/Co, Curve 3: 92/8 Zn/Co

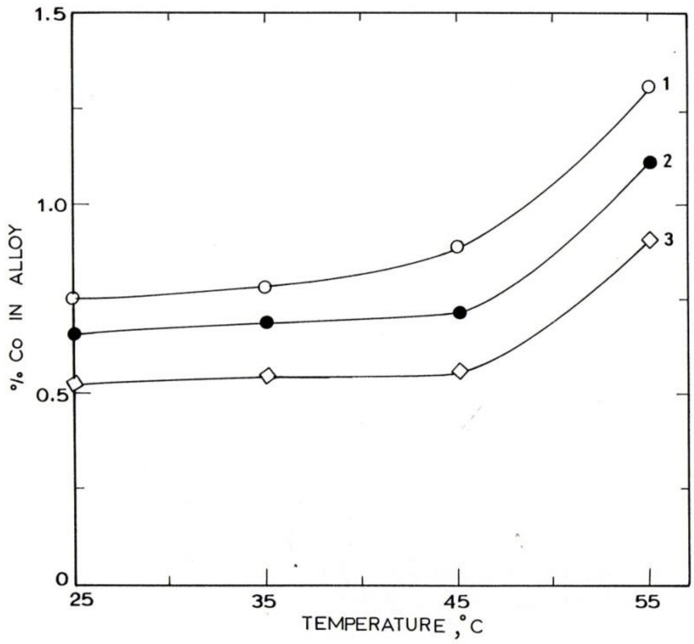


Figure 5.Variation of the % Co in alloy with temperature of the operating bath.
Bath composition: Total metal content 0.2 M, [Zn^{2+}] 0.178 M, [Co^{2+}] 0.022 M, TEA 40 ml/l, Thiaminehydrochloride 0.4 g / l, current density 2.5-3.0 Adm^{-2}, pH 5.0, thickness ~ 6 μm, stirred condition.

Curve 1: 30 Adm^{-2}, Curve 2: 10 Adm^{-2} , Curve 3: 2.5 Adm^{-2}

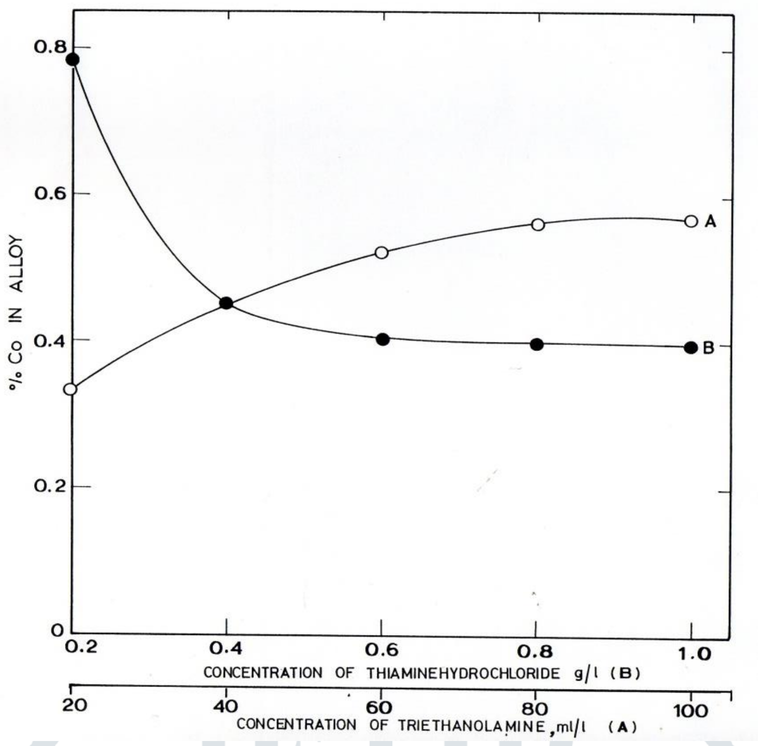


Figure 6. Effect of TEA and Thiaminehydrochloride concentrations on the composition of Zn-Co alloy.Bath composition: Same as in figure 5. TEA 20-100 ml/l, Thiaminehydrochloride 0.2-1.0 g/l, Temperature 35^0 C, Cd 10 Adm^{-2}, thickness ~6 µm, stirred condition.

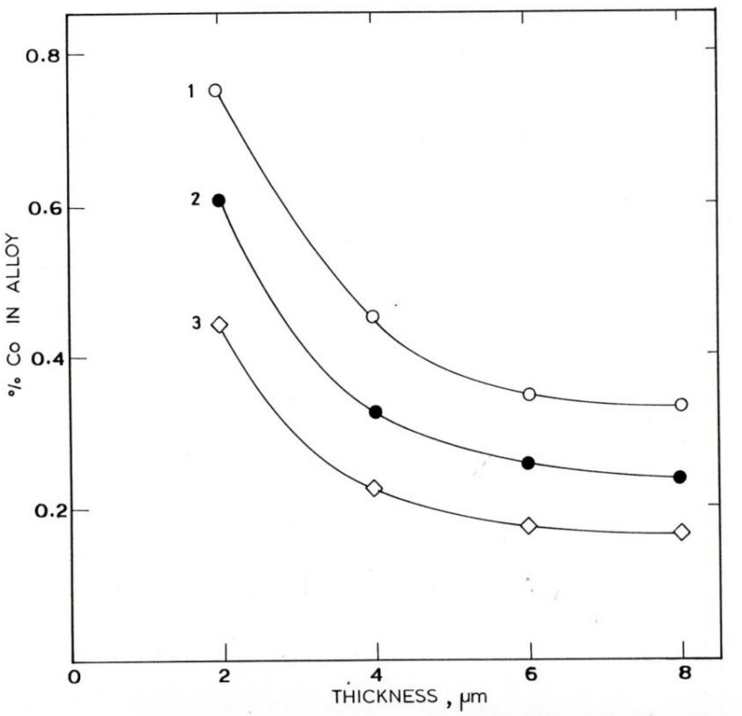


Figure 7. Dependence of composition of alloy with thickness of the alloy deposit.

Bath composition: Total metal content 0.2 M, $[Zn^{2+}]$ 0.172 – 0.196 M, $[Co^{2+}]$ 0.004 – 0.028 M, TEA 40 ml / l, Thiaminehydrochloride 0.4 g / l, Na_2SO_4 30 g / l, H_3BO_3 25 g / l, temperature 35^0C, pH 5.0, current density 10 Adm^{-2}, thickness 2-8 µm, stirred condition.

Curve 1: 86/14 Zn/Co, Curve 2: 89/11 Zn/Co, Curve 3: 92/8 Zn/Co

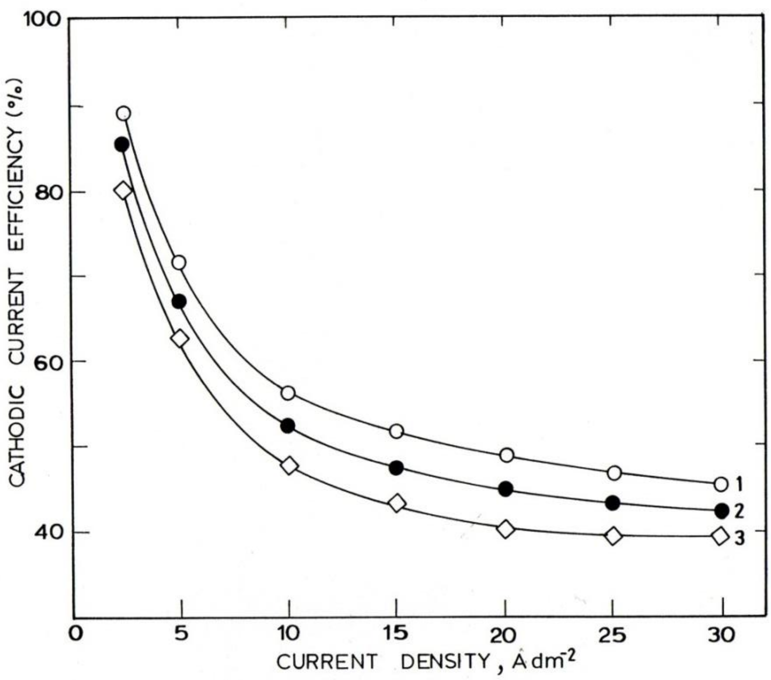


Figure 8. Dependence of cathodic current efficiency with current density.

Bath composition. Same as in Figure 4.

Curve 1: 86/14 Zn/Co, Curve 2: 89/11 Zn/Co, Curve 3: 92/8 Zn/Co

Table 1 :Composition of Zn-Co alloy with and without stirring of the bath solution at 35^0 C

	% Co in alloy		
	2.5 Adm^{-2}	10 Adm^{-2}	30 Adm^{-2}
With stirring	0.55 (86.29)	0.70 (52.54)	0.78 (42.20)
Without stirring	0.62 (78.64)	0.79 (45.62)	0.85 (27.44)

The cathodic current efficiency is given in parenthesis.

Bath composition: Total metal content 0.2 M [Zn^{2+}] 0.178 m, [Co^{2+}] 0.022 M, TEA 40 ml/l, Thiamine hydrochloride 0.4 g / l, Na_2SO_4 30 g / l, H_3BO_3 25 g / l, temperature 35 ^{0}C, Cd 2.5-30 Adm^{-2}, pH 5.0, thickness ~ 6 μm.

Table 2:Effect of temperature on cathodic current efficiency of Zn-Co alloy deposition

Temperature (^{0}C)	Cathodic current efficiency (%)		
	2.5 Adm^{-2}	10 Adm^{-2}	30 Adm^{-2}
25	89.30	84.15	67.21
35	86.29	80.35	64.18
45	85.17	76.63	55.67
55	85.17	67.81	42.10

3.2.Properties

The adhesion of alloy deposits to the base metal was tested by a bending test. Alloy deposits did not show any visual cracks even after 180^0 bending. This shows good adhesion of Zn-Co alloy deposits to the substrate. Ferroxyl test was conducted for Zn-Co alloy coated on steel. Alloy deposits with sufficient thickness (> 6μm) were free from pores.

Microchardness of alloy deposits was determined on Vickers scale (load50 gm). Hardness of the alloy increases with an increase in the amount of cobalt in the deposit (Table 3)

The static potentials of zinc and Zn-Co alloy coated on steel panels were measured *w.r.t.* SCE in 3.5 % NaCl solution. Static potentials of alloy were less negative to zinc and more negative to mild steel (Table 3). Zn-Co alloy deposits were found to protect steel much more effectively than pure zinc coatings.

3.3.Structure and morphology

The phase structure of electrodeposited Zn-Co alloy from an acid sulphate bath containing TEA and thiaminehydrochloride was determined by X-ray analysis. It is found that Zn-Co alloy forms zinc structure of solid solution type η-phase (Figure 9).

The surface morphology of Zn-Co alloy deposits were examined by scanning electron microscopy. Figure 10 shows the changes in surface morphology of deposits with % Co in the alloy deposits.

Table 3: Effect of cobalt content on microhardness and static potentials of Zn-Co alloy

% Co in alloy	Microhardness in VHN (load – 50 gm)	Static potential in mV versus SCE measured in 3.5% NaCl solution
Zinc	90	-1036
Zn-0.4% Co	185	-1001
Zn-0.6% Co	206	-991
Zn-0.8% Co	220	-984
Zn-1.0% Co	229	-976
Zn-1.2% Co	234	-955
Mild Steel	-	-582

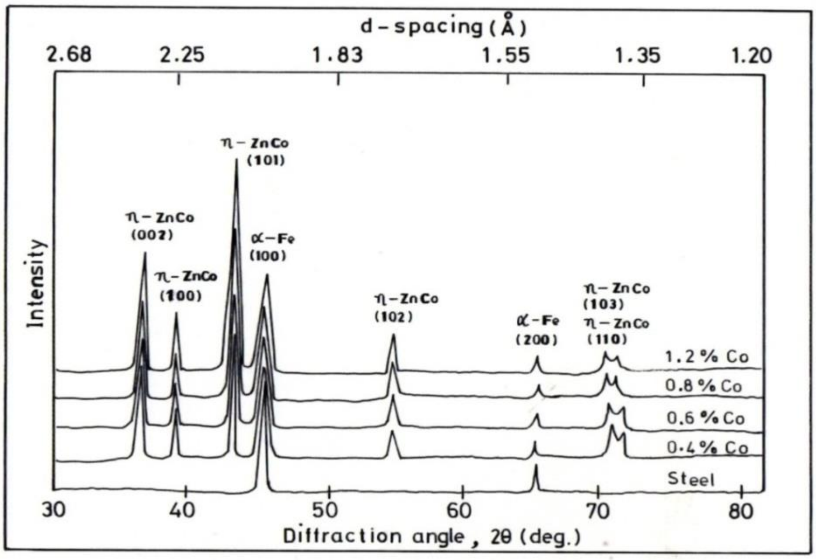


Figure 9. X-ray powder diffraction patterns for electrodeposited zinc and Zn-Co alloy deposits obtained from an acid sulphate bath.

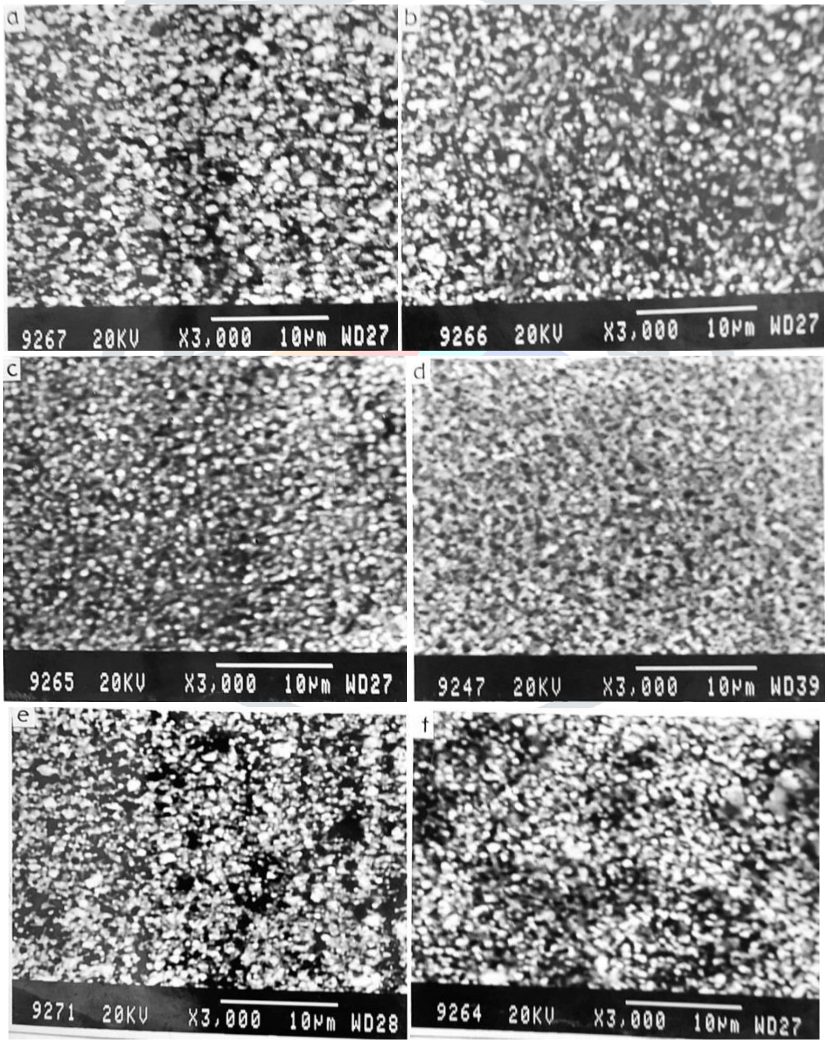


Figure 10.Scanning electron micrographs of zinc and zinc-cobalt alloy deposits containing different % of Co from an acid sulphate bath containing TEA and Thiaminehydrochloride (× 3000-4000). a) 0% Co (b) 0.4 % Co (c) 0.9 % Co (d) 0.8 % Co (e) 1.0 % Co (f) 1.2% Co

Table 4: Optimum bath composition and operating conditions for the electrodepositionof Zn-Co alloy having 0.4 -1.2%

Bath Component	Optimum bath composition and operating conditions
Total metal content	0.2M
$ZnSO_4 . 7 H_2O$	0.178 M
$CoSO_4 . 6H_2O$	0.022 M
Triethanolamine	40 ml / l
Thiaminehydrochloride	0.4 g / l
Na_2SO_4	30 g / l
H_3BO_3	25 g / l
pH	5.0
Temperature	35^0 C
Current density	10 Adm^{-2}
Stirring	Normal

4.Conclusion

Eletrodeposition of Zn-Co alloy from an acid sulphate bath containing TEA and Thiaminehydrochloride follows potential curve for alloy was formed to lie in the right of Zinc deposition potential curve. Increase in pH, current density, concentration of TEA and stirring of bath solution increased % Co in the alloy. The CCE was found to decrease with current density temperature and increase with stirring of the bath solution. The phase structure of Zn-Co alloy is a solid solution (η-phase). The surface morphology of the alloy changed with the amount of cobalt in the deposit. The optimum bath composition and operating conditions for electrodeposition of Zn-Co alloy containing 0.4-1.2% Co is given in Table 4.

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