



A study on physico-chemical properties of Zn-Co alloy deposits from an acid sulphate bath containing Triethanolamine and Thiamine hydrochloride

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ABSTRACT

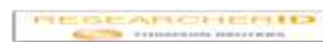
The composition, properties, structure and morphology of electrodeposited Zn-Co alloy deposits obtained from an acid sulphate bath containing TEA and Thiamine hydrochloride have been investigated. A bath solution containing 11 % Co produced an alloy deposit with 0.6 % Co indicating preferential deposition of zinc (anomalous process). The percentage of Co in the alloy increased with increase in current density and temperature. Cathodic current efficiency decreased with increase in current density and temperature. Static potentials of Zn-Co alloy were less negative to zinc and more negative to mild steel. Zn-Co alloy forms solid solution structure (η -phase). The morphology of the alloy varied with % Co in an alloy deposit.

Keywords

Electrode position, Zinc-Cobalt alloy, Triethanolamine (TEA), Thiamine hydrochloride, Cathodic Current Efficiency, X-ray powder diffraction ,Scanning Electron Microscope.

1. Introduction

In the recent years, many attempts have been made to develop a high corrosion resistant steel for automotive applications [1,2]. Electrodeposited Zinc alloyed with low percentage of cobalt (<1%) is a most commercially viable option from the point of low cost and better corrosion resistance than existing Zinc and Cadmium coatings [3]. Zn-Co alloys have been



electrodeposited from an alkaline sulphate baths [4-7], acid chloride baths [8-10] and sulphate baths [11-14].

The present work reports the results on the study of composition, properties, structure and morphology of electrodeposited Zn-Co alloy deposits obtained from an acid sulphate bath containing TEA and Thiamine hydrochloride.

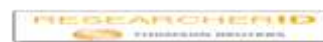
2. Experimental Methods

The plating bath solution was prepared using distilled water and laboratory grade chemicals. The bath solution was purified as described elsewhere. The optimum bath composition and plating conditions used in the present study are given in Table 1.

Table 1: Optimum bath composition and operating conditions for the electro deposition of 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 ₂ O	0.178 M
CoSO ₄ . 6H ₂ O	0.022 M
Triethanolamine	40 ml / l
Thiamine hydrochloride	0.4 g / l
Na ₂ SO ₄	30 g / l
H ₃ BO ₃	25 g / l
pH	5.0
Temperature	35 ⁰ C
Current density	10 Adm ⁻²
Stirring	Normal

Electrode position was carried out galvanostatically from 250 mL bath solution by using 1 cm² stainless steel as cathode and 2 cm² zinc as anode at 323 K under stirred conditions. The



panel so plated was weighted and stripped in 20% HNO₃, made up to 100 mL in a standard flask, the zinc and iron contents in the test solution was analyzed by atomic adsorption spectrometry (Varian spectra model AA 30). The cathodic current efficiencies and deposition rates were calculated in a conventional manner. The thickness of the alloy deposit was measured by Elicometer (Model 250 FN, England). The ductility alloy deposit and adhesion of the alloy deposit to the base metal (steel) was tested by a bending test. The porosity of the alloy deposit was determined by Ferroxy test. Static potentials of zinc and Zn-Fe alloy deposits dipped in 3.5% NaCl were measured with respect to saturated calomel electrode. Tensile strength of the alloy deposit (10 μm thick) was determined by a tensile strength testing machine (Tensiometer). Hardness of alloy deposits was determined on Vickers scale (load 50 g). Adhesion of the paint of Zn-Fe alloy deposit was evaluated by cross hatching method. Corrosion testing of zinc and zinc-iron alloy plated steel panels by accelerated neutral salt spray method was examined for 96 hours as per ASTM B117 specification in 5% NaCl at 35±2 °C.

The structure of Zn-Co alloy deposits was determined by X-ray powder diffraction (filter CuK_{α1}, 30 KV, 20 mA, 4000 counts). Surface morphology of alloy deposits were examined under scanning electron microscope (Model JEOL-JSM-840A).

3. Results and Discussion

3.1 Composition

Figure 1 shows the cathodic polarization curves for Zn-Co alloy deposition (curve 3) and the deposition of individual metals (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 explains why zinc deposits preferentially over cobalt *i.e.*, anomalous co-deposition.

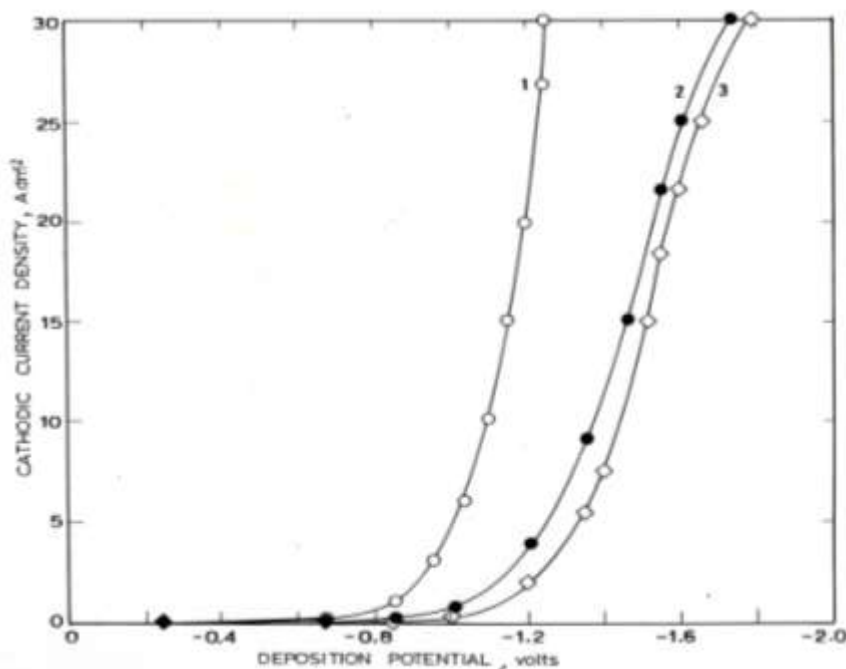


Figure 1. Cathodic polarization curves for the deposition of zinc, cobalt and Zn-Co alloy from an acid sulphate bath. All solution contained TEA 40 ml/l, H_3BO_3 25 g / l, stirred conditions

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.

In order to study the effect of metal ion ratio in the bath on alloy composition, zinc to cobalt ratio varied from 86:14 to 98:2 in the bath. Figure 2 shows the variation of alloy composition with bath composition obtained for three different current densities ($2.5, 10$ and 30 Adm^{-2}). A bath containing 11 % Co produced an alloy deposit with 0.6 % Co. This indicates preferential deposition of zinc (i.e. Anomalous process).

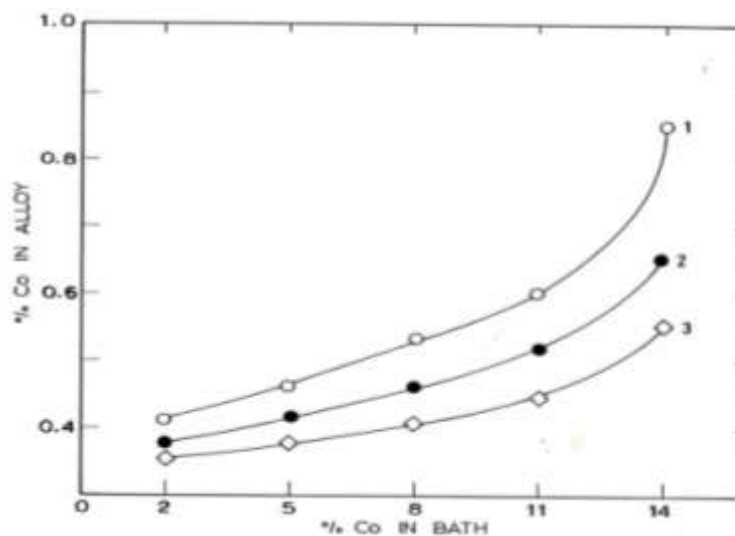


Figure 2. Dependence of the % of Co in an alloy with the % of Co in the bath.

Bath composition: Total metal content 0.2 M, $[Zn^{2+}]$ 0.172 – 0.196 M, $[Co^{2+}]$ 0.022 M, TEA 40 ml / l, Thiamine hydrochloride 0.4 g / l, Na_2SO_4 30 g / l, H_3BO_3 25 g / l, pH 5.0, temperature 35°C, 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}

Increase in the bath pH resulted in increase in the % Co in the alloy deposit. Increase in current density increased the % Co in the alloy deposit (Figure 3). This is because of the preferential deposition of zinc in the cathode diffusion layer. The experiments were conducted at different temperatures (25-30°C) to study the effect of temperature on alloy composition.

Figure 4 shows the dependence of alloy composition on temperature of the plating bath. An increase in temperature increased the percentage of cobalt in the alloy deposit. Increase in the thickness of alloy deposit decreased the percentage of cobalt in the alloy deposit. This might

be due to the depletion in concentration of cobalt metal in the cathode diffusion layer. The percentage of cobalt in the alloy deposit was found to be more under stirred conditions compared to unstirred conditions (Table 2).

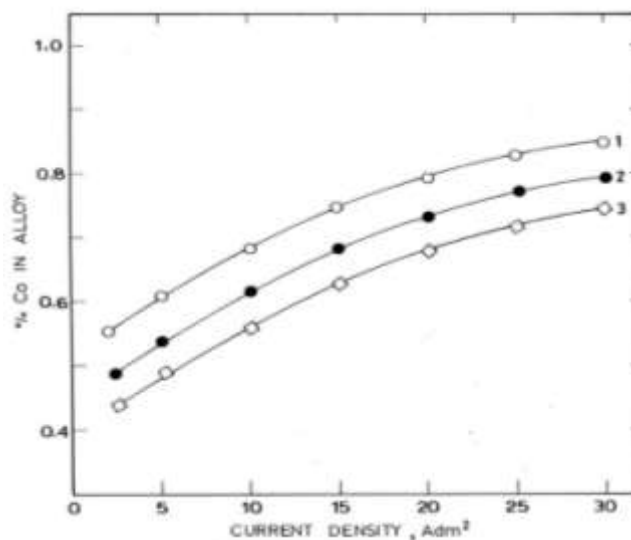


Figure 3. Variation of % of Co in the alloy with the current density.

Bath composition: Total metal content 0.2 M, $[\text{Zn}^{2+}]$ 0.172 – 0.196 M, $[\text{Co}^{2+}]$ 0.004 – 0.028 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°C , current density $2.5\text{-}30 \text{ Adm}^{-2}$, pH 5.0, thickness $\sim 6 \mu\text{m}$, stirred condition.

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

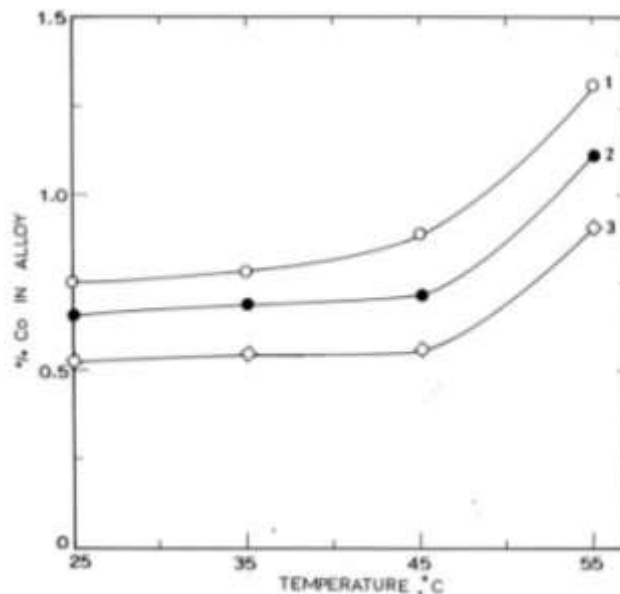


Figure 4. Variation of the % Co in alloy with temperature of the operating bath.

Bath composition: Total metal content 0.2 M, [Zn²⁺] 0.178 M, [Co²⁺] 0.022 M, TEA 40 ml/l, Thiamine hydrochloride 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

Table 2:Composition of Zn-Co alloy with and without stirring of the bath solution at 35⁰ 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 [Zn²⁺] 0.178 m, [Co²⁺] 0.022 M, TEA 40 ml/l, Thiamine hydrochloride 0.4 g / l, Na₂SO₄ 30 g / l, H₃BO₃ 25 g / l, temperature 35 °C, Cd 2.5-30 Adm⁻², pH 5.0, thickness ~ 6 μm.

Dependence of Zn-Co alloy composition with concentrations of TEA and Thiamine hydrochloride is shown in figure 5. Increase in TEA concentration, increases % Co in the alloy, whereas increase in the concentration of Thiamine hydrochloride decreased the % Co in the alloy deposit.

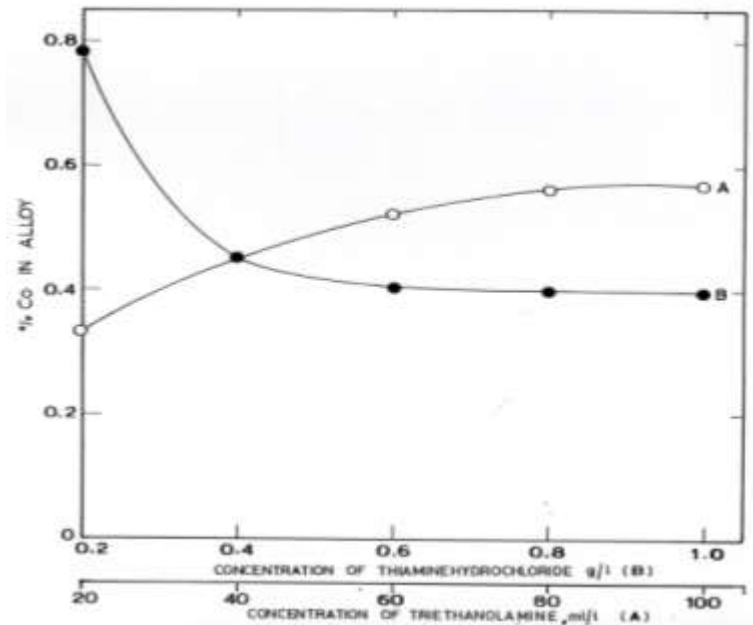


Figure 5. Effect of TEA and Thiamine hydrochloride concentrations on the composition of Zn-Co alloy. Bath composition: Same as in figure 5. TEA 20-100 ml/l, Thiamine hydrochloride 0.2-1.0 g/l, Temperature 35⁰ C, Cd 10 Adm⁻², thickness ~6 μm, stirred condition.

Cathodic current efficiencies (CCE) were calculated for each experiment at any given temperature, current density and stirring of the bath solution. Increase in current density decreases CCE of alloy plating. This is because of more hydrogen discharge at higher current densities. Increase in temperature of plating bath decreases CCE (Table 3). It was also observed that CCE was higher under stirred conditions when compared to unstirred conditions (Table 2).



Table 3: Effect of temperature on cathodic current efficiency of Zn-Co alloy deposition

Temperature (°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° 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. Microhardness of alloy deposits was determined on Vickers scale (load 50 gm). Hardness of the alloy increases with an increase in the amount of cobalt in the deposit (Table 4).

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 Zn-Co alloy were less negative to zinc and more negative to mild steel (Table 4). Zn-Co alloy deposits were found to protect steel much more effectively than pure zinc coatings.

Table 4: 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

3.3. Structure and morphology

The phase structure of electrodeposited Zn-Co alloy from an acid sulphate bath containing TEA and thiamine hydrochloride was determined by X-ray powder diffraction. It was observed that Zn-Co alloy forms zinc structure of solid solution type η -phase (Figure 6). The surface morphology of Zn-Co alloy deposits were examined under scanning electron microscopy. Figure 7 shows how the surface morphology of deposits changes with % Co in the alloy deposits.

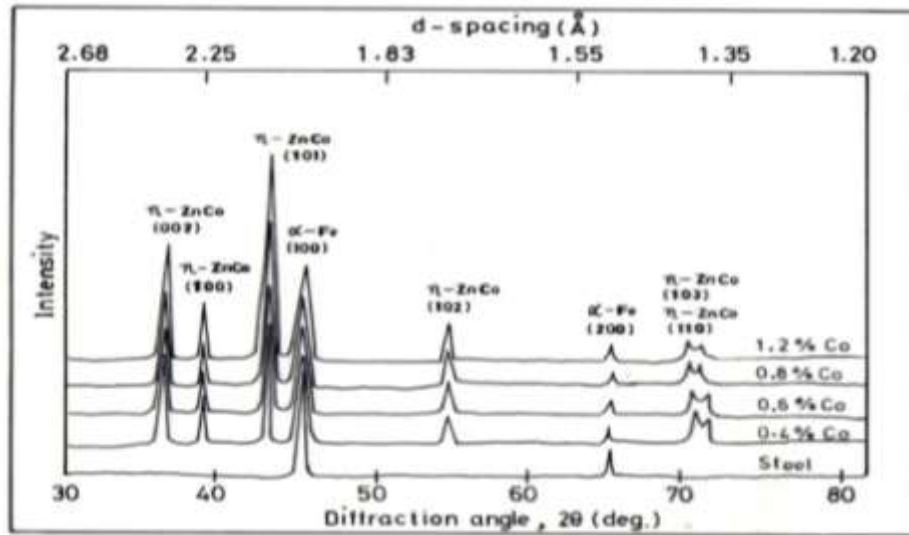
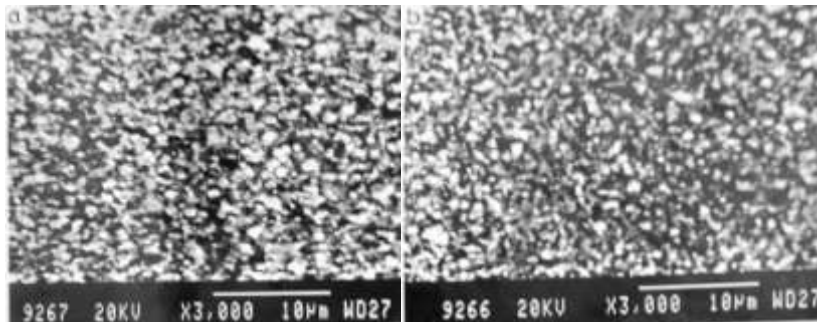


Figure 6. X-ray powder diffraction patterns for electrodeposited zinc and Zn-Co alloy deposits obtained from an acid sulphate bath.



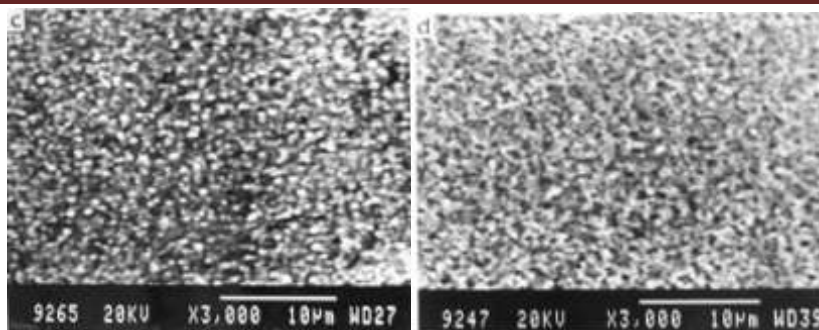


Figure 7. Scanning electron micrographs of zinc and zinc-cobalt alloy deposits containing different % of Co from an acid sulphate bath containing TEA and Thiaminehydrochloride ($\times 3000-4000$).

(a) 0 % Co (b) 0.4 % Co (c) 0.8 % Co (d) 1.0 % Co

4. Conclusion

Electrodeposition of Zn-Co alloy from an acid sulphate bath containing TEA and Thiaminehydrochloride follows anomalous co-deposition. A bath solution containing 11 % Co produced an alloy deposit with 0.6 % Co indicating preferential deposition of zinc (anomalous process). The percentage of Co in the alloy increased with an increase in current density and temperature. Cathodic current efficiency decreased with increase in current density and temperature. Static potentials of Zn-Co alloy were less negative to zinc and more negative to mild steel. Zn-Co alloy forms solid solution structure (η -phase) as Zinc. The morphology of the alloy varied with % Co in an alloy deposit.

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