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Physico-Chemical Properties of Zn-Ni Alloy from Alkaline Sulphate Bath Containing Tartrate

V. Narasimhamurthy[1,*], M.N. Srinivasa[2], L.H. Shivashankarappa[3]

[1]*Government First Grade College and Post Graduate Study Center, Shivamogga – 577 201, Karnataka, India.*
[2]*Maharani Science College for Women (Autonomous), J.L.B. Road, Mysore – 570 005, Karnataka, India.*
[3]*Maharani Science College for Women, Palace Road, Bengaluru – 560 001, Karnataka, India.*

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ABSTRACT

The composition, properties, voltammetry studies and morphology of electrodeposited Zn-Fe alloy deposits obtained from an alkaline sulphate bath containing tartrate have been investigated. A bath containing high percentage of iron (20% wt.) produced an alloy with less percentage of iron (12% wt.) i.e. anomalous co-deposition process. The percentage of iron in an alloy decreased with temperature of the plating bath and thickness of the alloy deposit. The cathodic current efficiency depends on plating variables. Cyclic voltammetry studies indicate the mutual co-deposition of zinc with iron. Zn-Fe alloy showed a superior corrosion resistance than zinc coatings. Hardness of the alloy deposits increased with increase in iron content in the alloy. Smooth, uniform and fine grained deposits were obtained for the Zn-Fe alloy containing 20% Fe.

1. Introduction

In the past couple of decades many attempts have been made on developing a high corrosion resistance steel especially for an automotive body panels [1-4]. Recently electrodeposited Zn-Fe alloy has been found to be suitable for this purpose. Electrodeposited Zn-Fe alloy containing 15-25% wt. Fe on steel can provide sacrificial protection to steel and serve as a viable substitute for Zinc and Cadmium coatings [5-9]. An alloy containing 15-25% Fe shows an excellent corrosion resistance, formability, weldability, workability, adaptability to phosphating and chromating and an alloy deposit containing 40% Fe or more shows an excellent paintability. The Zn-Fe alloys have been deposited from various types of baths like sulphate-chloride, chloride, sulphate, acetate [10-15] and alkaline sulphate baths [6-8].

The literature survey reveals the absence of comprehensive work on the electrodeposition of Zn-Fe alloy from an alkaline sulphate bath containing tartrate. The aim of the present investigation is to develop the optimum plating bath with suitable composition and plating conditions for obtaining good quality Zn-Fe alloy deposit with 15 -25% Fe and to study properties, voltammetry studies and morphology of Zn-Fe alloy deposit.

2. Experimental Methods

The plating bath solution was prepared using distilled water and laboratory grade chemicals. The bath solution was purified as described earlier [16]. The optimum bath composition and plating conditions used in the present study are given in Table 1.

Electrodeposition was carried out Galvano-statically from 250 mL bath solution by using 1 cm^2 stainless steel as cathode and 2 cm^2 zinc as anode at 323 K under stirred conditions. The panel so plated was weighted and stripped in 20% HNO_3, 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 Ferroxyl 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 cathodic current efficiencies and deposition rates were calculated in a conventional manner.

Cyclic voltametric studies of the plating bath solutions were carried out by using Potentiostat (Model CL-95, Elico, India). Morphology of the alloy deposits were examined under scanning electron microscope (Model JEOL-JSM-840A).

Table 1 Optimum bath composition and operating conditions to electroplates zinc-iron alloy having the composition 15-25%

Bath composition	Optimum composition and conditions
$ZnSO_4.7H_2O$	0.09 M
$FeSO_4.7H_2O$	0.01 M
Ascorbic acid	0.02 M
Na_2SO_4	30 g/L
NaOH	100 g/L
Sodium tartrate	46 g/L
pH	14
Temperature	25 °C
Current density	20 mA/cm^2

3. Results and Discussion

3.1 Composition

Fig. 1 shows the variation of the alloy composition with the bath composition. In the graph, the line AB is the composition reference line (CRL) represents the metal contents in the bath solution and in alloy deposit are of the same composition. A bath solution with high percentage of iron (20% wt.) produced an alloy with less percentage of iron (12% wt.) indicating that the less noble metal (zinc) depositing preferentially and leading to anomalous co-deposition process. This might be due to the formation of zinc hydroxide film at the cathode surface, which facilitates the discharge of more zinc at the cathode surface and suppresses the iron deposition [12].

*Corresponding Author: drvnm123@gmail.com(V. Narasimhamurthy)

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Fig. 2 illustrates the dependency of the alloy composition with the current density for three different zinc to iron ratios in the bath. With increase in the current density, the % wt. Fe in the alloy increased up to 20 mA/cm^2. Further increase in current density, the % wt. Fe decreased. This might be due to the poor discharge of iron ions at higher current densities.

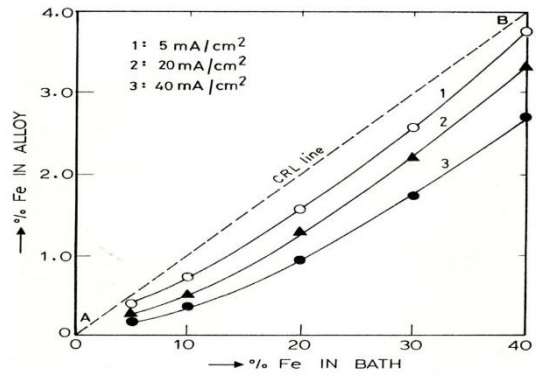

Fig. 1 Effect of meal ion ration (Zn to Fe) in the plating bath on the composition of Zn-Fe alloy. Bath composition: total metal content 0.1 M, [Zn^{2+}] 0.06-0.095 M, [Fe^{2+}] 0.005-0.04 M, tartrate 0.2 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/L, NaOH 100 g/L, temperature 25 °C, pH > 14, thickness ~ 6 μm, unstirred condition. Curve 1: 5 mA/cm^2, Curve 2: 20 mA/cm^2, Curve 3: 40 mA/cm^2

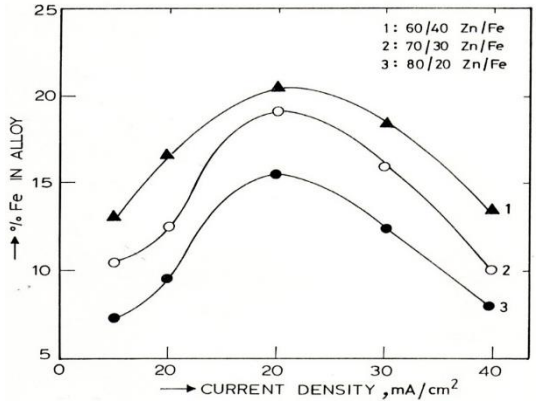

Fig. 2 Effect of current density on the composition of Zn-Fe alloy deposit. Bath composition: Total metal content 0.1 M, [Zn^{2+}] 0.06 M-0.08 M, [Fe^{2+}] 0.02M-0.04 M, tartrate 0.2 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/L, NaOH 100 g/L, temperature 25 °C, pH 14, thickness ~ 6 μm, unstirred condition.

Increase in temperature of bath, decreased the % wt. Fe, indicating that the deposition process is under diffusion controlled (Fig. 3). This is because an elevation of bath temperature might increase the concentration of preferentially depositing metal (zinc). Hence the process is anomalous.

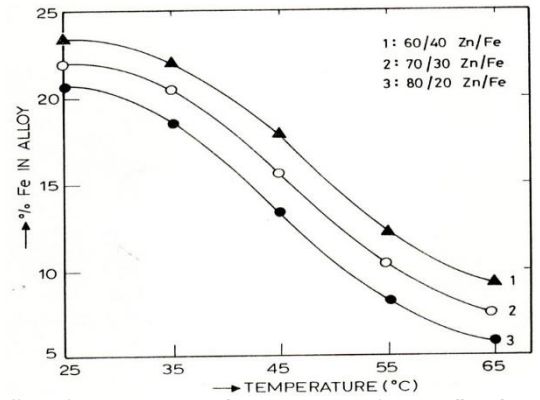

Fig. 3 Effect of temperature on the composition of Zn-Fe alloy deposit. Bath composition: Total metal content 0.1 M, [Zn^{2+}] 0.06 M – 0.08 M, [Fe^{2+}] 0.02 – 0.04 M, tartrate 0.2 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/L, NaOH 100 g/L, temperature 25 °C, pH 14, thickness ~ 6 μm, current density 20 Adm^{-2}.

Fig. 4 shows the dependence of the alloy composition on the concentration of tartrate in the bath solution. Increase in the concentration of tartrate in the bath, increased the % wt. Fe in the alloy, maximum deposition rate was obtained at 0.2 M concentration of tartrate (Table 2). Further increase in the concentration of tartrate, decreased the % wt. Fe in the alloy.

Stirring of the plating bath solution increased the % wt. Fe compared to unstirred solution (Table 3), indicating that the deposition process is under diffusion controlled. The variation of the alloy composition with the thickness of the alloy deposit is shown in Fig. 5. With increase in thickness, the % wt. Fe in the alloy deposited decreased. Fig. 6 shows the dependence of the cathodic current efficiencies (CCE) on the current density. With increase in current density, the CCE increased up to current density of 20 mA/cm^2. With further increase in current density, the CCE was found to decreased. Increase in bath temperature (Table 4) decreased the CCE. Stirring of the bath solution also increased the CCE (Table 3).

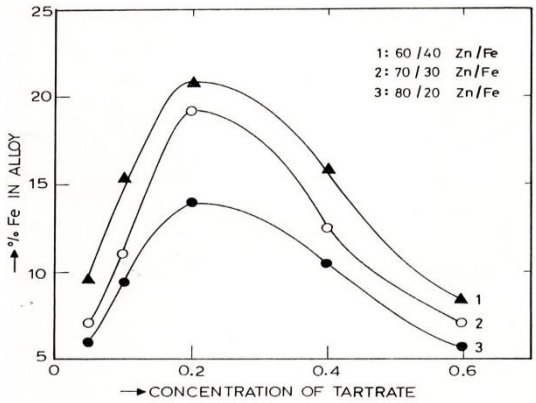

Fig. 4 Effect of tartrate concentration on the composition of Zn-Fe alloy. Bath composition: Total metal content 0.1 M, [Zn^{2+}] 0.06 M - 0.08 M, [Fe^{2+}] 0.02 - 0.04 M, tartrate 0.5 M – 0.6 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/L, NaOH 100 g/L, temperature 25 °C, pH 14, thickness ~ 6 μm, current density 20 mA/cm^2, unstirred condition.

Table 2 Effect of tartrate concentration on deposition rate of Zn-Fe alloy from alkaline sulphate bath

Tartrate Concentration (moles)	Deposition rate (mg/cm^2/sec)		
	80/20 Zn/Fe	70/30 Zn/Fe	60/40 Zn/Fe
0.05	3.8	4.4	5.6
0.1	7.3	8.5	8.9
0.2	10.3	12.0	14.7
0.4	7.4	9.2	12.3
0.6	5.1	6.3	7.9

Table 3 Composition of Zn-Fe alloy with stirring and without stirring of the plating bath solution at 50 °C

	% Fe in alloy		
	5 mA/cm^2	20 mA/cm^2	40 mA/cm^2
With stirring	12.2 (92.4)	21.5 (97.5)	11.3 (88.1)
Without stirring	10.5 (88.0)	19.3 (93.7)	10.0 (85.2)

CCE are given in parenthesis

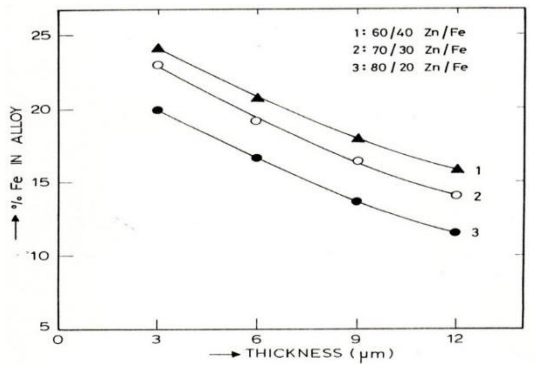

Fig. 5 Effect of thickness on the composition of Zn-Fe alloy. Bath composition: Total metal content 0.1 M, [Zn^{2+}] 0.06 M - 0.08 M, [Fe^{2+}] 0.02 - 0.04 M, tartrate 0.2 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/L, NaOH 100 g/L, temperature 25 °C, current density 20 mA/cm^2, pH 14, unstirred condition, thickness 3-12 μm. Curve 1: 60/40 Zn/Fe, Curve 2: 70/30 Zn/Fe, Curve 3: 80/20 Zn/Fe

Table 4 Effect of temperature on cathodic current of Zn-Fe alloy deposited from an alkaline sulphate bath containing tartrate

Temperature °C	% CCE		
	60/40 Zn/Fe	70/30 Zn/Fe	80/20 Zn/Fe
25	93.7	90.8	87.3
35	90.6	86.8	82.6
45	87.4	84.4	77.5
55	85.1	80.1	74.9

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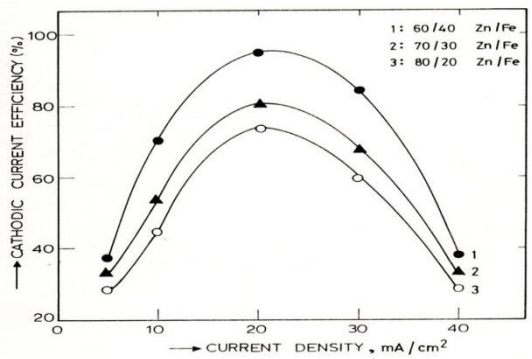

Fig. 6 Effect of current density on cathodic current efficiency. Bath composition: Total metal content 0.1 M, [Zn^{2+}] 0.06 M - 0.08 M, [Fe^{2+}] 0.02 - 0.04 M, tartrate 0.2 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/L, NaOH 100 g/L, temperature 25 °C, pH 14, thickness 6 μ,current density 5-40 mA/cm^{-2}, unstirred condition

A series of voltammetry experiments were performed with the bath solution having the composition given in the Table 1. A potential range of 0.0 V to -1.5 V was scanned at a different scan rates (10 mV/Sec to 500 mV/sec). A 50 mV/sec scan rate was chosen for the detailed studies. A saturated calomel electrode, a platinum working electrode and a platinum foil counter electrode were used in these measurements at 25 °C. Fig. 7 represents the cyclic voltammogram of pure $ZnSO_4$ with KCl as the supporting electrolyte in the absence of tartrate. The existence of the cathodic peak was observed at the potential of -1.2 V, which corresponds to the reduction of zinc ion.

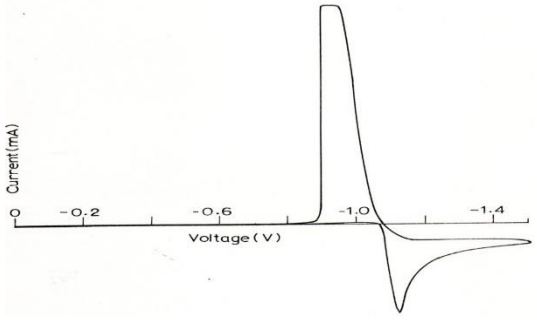

Fig. 7 Cyclic voltammogram of $ZnSO_4$ + KCl, Scan rate: 50 mV/sec, potential range: 0 to -1.5 V

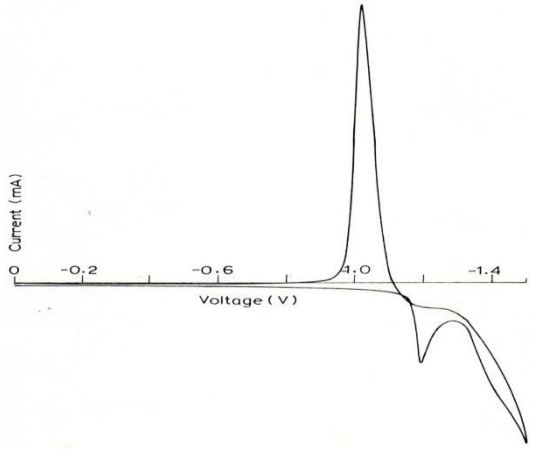

Fig. 8 Cyclic voltammogram of $ZnSO_4$ + KCl + tartrate , Scan rate: 50 mV/sec, potential range: 0 to -1.5 V

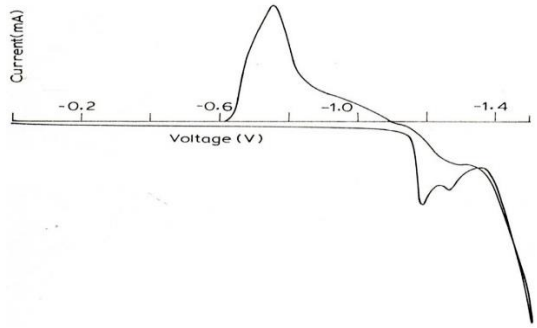

Fig. 9 Cyclic voltammogram of $ZnSO_4$ + $FeSO_4$ + KCl + tartrate, Scan rate: 50 mV/sec, potential range: 0 to -1.5 V

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Fig. 8 shows the cyclic voltammogram of pure $ZnSO_4$ with KCl in the presence of tartrate. The chelation of zinc ion with tartrate shifted the cathodic peak slightly to -1.2 V. Fig. 9 indicates the cyclic voltammogram for the bath containing $ZnSO_4$ and $FeSO_4$ with KCl and tartrate. In this graph there are two cathodic peaks observed, one peak at the potential of -1.19 V, which corresponds to zinc ion reduction and the other peak at the potential of -1.265 V, which corresponds to iron reduction. These two potentials are more negative than that of pure metals and found to lie in a range so close to each other, this explains the reason for the occurrence of mutual co-deposition of zinc with iron.

3.2 Properties

The adhesion Zn-Fe alloy deposit to the base metal (steel) was tested by a standard bending test. Zn-Fe alloys were electroplated for different thickness (2-12 μm) on mild steel panels (1 × 4 sq. inch). Each sample was subjected to bending test., the alloy coating did not show visually any cracks even after 180° bending. This indicates a good adhesion of the alloy to the base metal.

The Zn-Fe alloy coated on steel panels (3 × 3 sq. inch) to a thickness of 2-12 μm were used to measure the porosity of the alloy deposit. A filter paper soaked in potassium ferricyanide (1%) solution was placed over the alloy plated steel panels and the number of blue spots developed on the filter paper with time was taken as the measure of the porosity of the deposit. The alloy deposits were pore free at sufficiently higher thickness (>8 μm).

The ductility of the Zn-Fe alloy was measured by a simple bending test. The alloy deposits coated on mild steel panels (1 × 4 sq. inch) to a thickness of 12 μm were subjected to a bend test up to 180°. The alloy deposits did not show any visual cracks at the point of bending. The microhardness of 25 μm thick alloy deposits was measured on Vickers hardness tester (50 g load). As expected, increase in the percentage of iron in the alloy deposit enhanced the hardness (Table 3). The static potentials of Zn-Fe alloy and zinc were measured in 5% NaCl solution. The static potentials of alloys which were significantly more positive to pure zinc and more negative to mild steel under identical experimental conditions.

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, pH 7.0. The Zn-Fe alloy sample were compared with pure zinc plated on steel panels. A white corrosion product (rust) was observed after 35 hours. It was followed by red corrosion product (red rust) of steel after 45 hours. Moreover, none of these panels with stood corrosion for more than 50 hours of the test. In the Zn-Fe alloy plated steel panels, blisters of white and red rust appeared only after 90 hours indicating that Zn-Fe alloy can protect steel from corrosion more efficiently than pure zinc.

3.3 Surface Morphology

The surface morphology of Zn-Fe alloy deposits was examined under scanning electron microscope. Fig. 10 shows the change in the surface morphology of the deposit with increase in the percentage of iron in alloy deposit. Morphology of the alloy deposit containing 20% Fe was found to be uniform, smooth and finer grained.

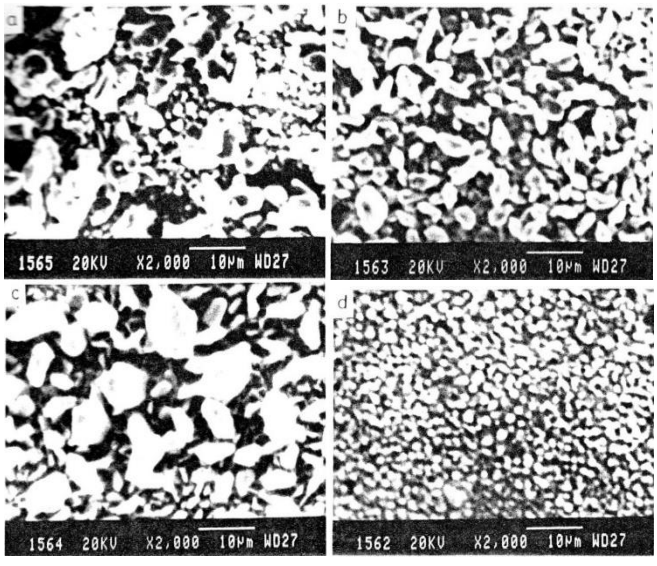

Fig. 10 Scanning electron micrographs of Zn-Fe alloy containing different percentage of iron from alkaline sulphate bath containing tartrate. (a) 0% Fe; (b) 10% Fe; (c) 15% Fe and (d) 20% Fe

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4. Conclusion

Electrodeposition of Zn-Fe alloy having 15-25% Fe from an alkaline sulphate bath containing tartrate follows anomalous co-deposition. A bath containing high percentage of iron (20% wt.) produced an alloy with less percentage of iron (12% wt.). Increase in temperature and thickness of the deposit decreased the percentage of iron in the alloy deposit. Bath composition and operating conditions were optimized to electrodeposit Zn-Fe alloy containing 15-25% Fe. The shift in deposition potentials of Zn-Fe alloy is a chief cause in the co-deposition process to produce alloy of varying composition. Zn-Fe alloy shows a superior corrosion resistance than zinc coatings. Cyclic voltammetric studies of the plating bath indicates the mutual co-deposition of zinc with iron. Hardness of the alloy deposits increased with increase in iron content in the alloy. Smooth, uniform and fine grained deposits were obtained for the Zn-Fe alloy containing 20% Fe.

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