Electro deposition of Zn-Fe alloy from non-cyanide alkaline sulphate bath containing Tartarate

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Abstract

Electrodeposition of Zn-Fe alloy from an alkaline sulphate bath containing tartarate has been carried out. The effect of plating variables on the composition of alloy and on cathodic current efficiency was studied. The cyclic voltammetric studies carried out to know the mutual co-deposition of Zinc and Iron. Hardness and the surface morphology of the alloy deposits were found to be dependent on the Iron content in the alloy. An alloy containing 20% wt. Fe showed smooth, uniform and finer grained deposits. Under the optimum composition and operating conditions, Zn-Fe alloy deposition from alkaline sulphate bath containing tartarate followed anomalous depositing process.

Keywords   Electrodeposition, Cyclic voltammetry, Tartarate, Cathodic Current Efficiency, Scanning Electron Microscope

Introduction

Recently, large numbers of investigations have been made to develop high corrosion resistant steel for automotive industries [1-4]. 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]. Zn-Fe alloys are being deposited from an acid sulphate, chloride and sulphate-chloride baths [10-15].

Literature survey indicates that there is very little work reported on Zn-Fe alloy deposition from alkaline baths. The main disadvantage of such alkaline baths is the loss of ammonia at high temperature and difficulties in the effluent treatment of cyanide baths. In order to overcome these problems, few attempts have been made on the development of non - cyanide and ammonia free alkaline pyrophosphate and sulphate baths have been reported. However, there is a great need to develop a bath which is free from ammonia and cyanide. In this, an attempt is made to formulate non-cyanide alkaline sulphate bath containing tartarate as a complexing agent. The results reported here include the study of plating variables, cathodic current efficiency, properties, cyclic voltammetry and surface morphology.

Experimental

The plating solutions were prepared by using distilled water and laboratory grade chemicals. The bath solutions are purified as described elsewhere. The optimum bath composition and operating conditions used in this study are given in the table 1.

Table 1: Optimum bath composition and operating conditions

Component	Concentration
$ZnSO_4. 7 H_2O$	0.09 M
$FeSO_4. 7 H_2O$	0.01 M
Ascorbic acid	0.02 M
$Na_2 SO_4$	30 g/l
NaOH	100 g/l
Sodium tartarate	46 g/l
pH	>14
Temperature	25^0C
Current density	20 mA/cm^2
Agitation	-

Hull cell experiments were performed by using standard 267 ml capacity cell for 5 minutes at 1 ampere cell current. The test results were used to optimize the bath composition and operating conditions. Electrodeposition was carried out galvanostaticaly from 250 ml bath solution by using 1 cm^2 stainless steel as cathode and 2 cm^{2}zinc as anode. 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.

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 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. Cyclic voltammetric 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).

Result and Discussion

Effect of metal ion ratio

Figure 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]
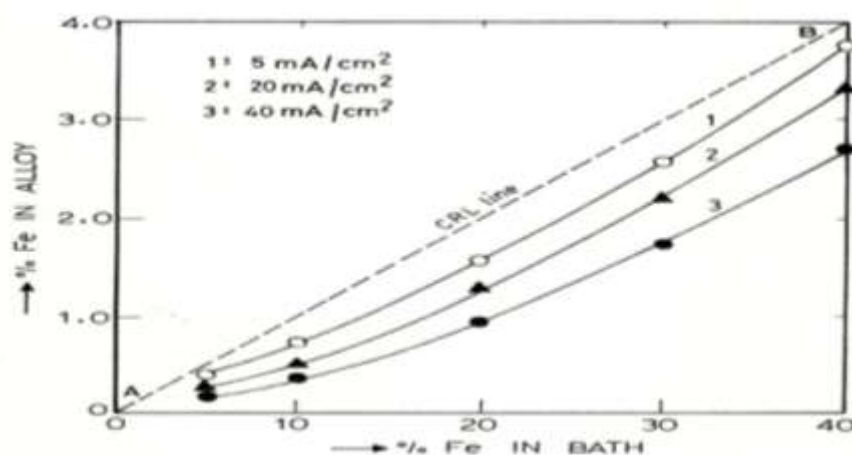

Figure 1.Effect of meal ion ration (Zn to Fe) in the plating bath on the composition of Zn-Fe alloy deposit.

Bath composition: total metal content 0.1 M, $[Zn^{2+}]$ 0.06-0.095 M, $[Fe^{2+}]$ 0.005-0.04 M, tartarate 0.2 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/l, NaOH 100 g/l, temperature 25 ^0C, pH > 14, thickness ~ 6 μm, unstirred condition.

Curve 1: 5 mA/cm^2,   Curve 2: 20 mA/cm^2,   Curve 3: mA/cm^2

Effect of current density

Figure 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 flow discharge of iron ions at higher current densities.
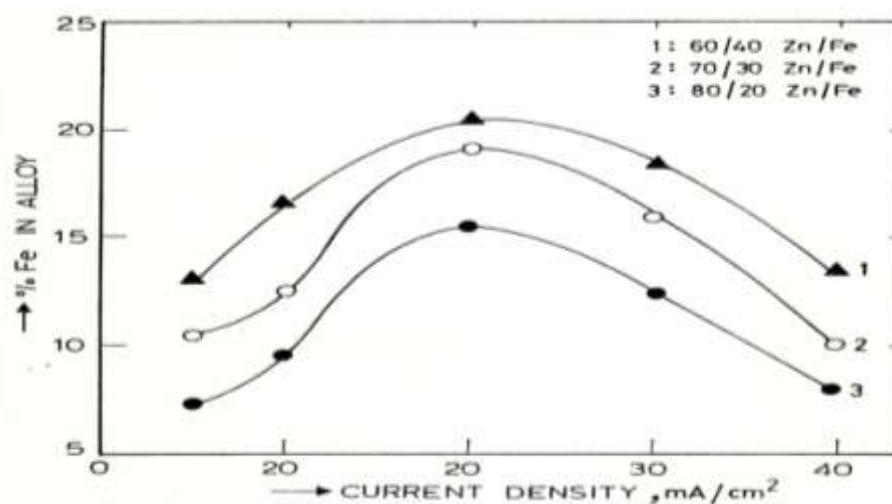

Figure 2.Effect of Current density on the composition of Zn-Fe alloy deposit.

Bath composition: total metal content 0.1 M, $[Zn^{2+}]$ 0.06 M-0.08 M, $[Fe^{2+}]$ 0.02M-0.04 M, tartarate 0.2 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/l, NaOH 100 g/l, temperature 25 ^0C, pH > 14, thickness ~ 6 μm, unstirred condition.

Curve 1: 60/40 Zn/Fe, Curve 2: 70/30 Zn/Fe,Curve 3: 80/20 Zn/Fe

Effect of temperature

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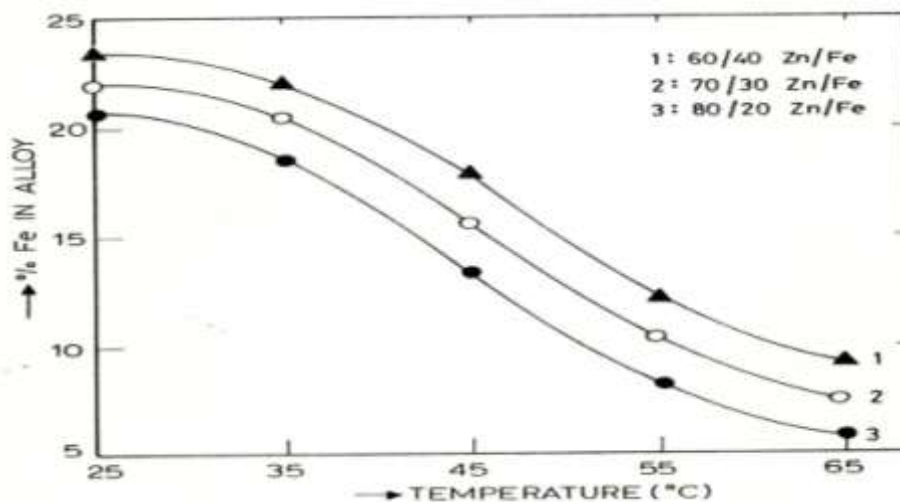
Figure 3.Effect of temperature on the composition of Zn-Fe alloy deposit.

Bath composition: total metal content 0.1 M, $[Zn^{2+}]$ 0.06 M-0.08 M, $[Fe^{2+}]$ 0.02-0.04 M, tartarate 0.2 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/l, NaOH 100 g/l, temperature 25 ^0C, pH > 14, thickness ∼ 6 μm, current density 20 Adm^{-2}.

Effect of tartarate concentration

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

Table 2: Effect of tartarate concentration on deposition rate of Zn-Fe alloy from alkalinesulphate bath

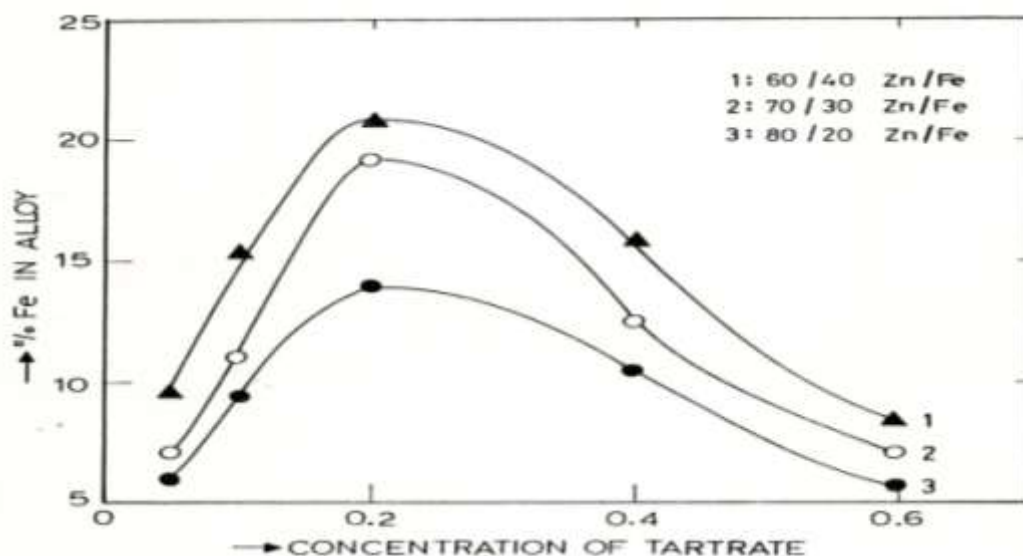| Tartarate Concentration (moles)	Deposition rate (mg / cm^2 / sec)		
	80/20 Zn/Fe	70/30 Zn/Fe	60/40 Zn/Fe
0.05	3.8	4.4	5.6
0.1	7.3	8.5	8.9
0.2	10.3	12.0	14.7
0.4	7.4	9.2	12.3
0.6	5.1	6.3	7.9

Figure 4.Effect of tartarate 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, tartarate 0.5 M – 0.6 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/l, NaOH 100 g/l, temperature 25^0C, pH > 14, thickness ~ 6 μm, current density 20 mA/cm^{-2}, unstirred condition.

Effect of stirring

Stirring of the plating bath solution increased the % wt. Fe compared to unstirred solution (Table 3).

Table 3, Composition of Zn-Fe alloy with stirring and without stirring of the plating bath solution at 50^0C

	% 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)

Bath composition: total metal content 0.1 M, $[Zn^{2+}]$ -0.07 M, $[Fe^{2+}]$ -0.03 M, ascorbic acid 0.019 M, tartarate 0.2 M, Na_2SO_4 30 g/l, NaOH 100 g/l, pH > 14, thickness ~6 μm, within parenthesis CCE are given.

Effect of thickness

The variation of the alloy composition with the thickness of the alloy deposit is shown in figure 5. With increase inthickness, the % wt. Fe in the alloy deposited decreased.
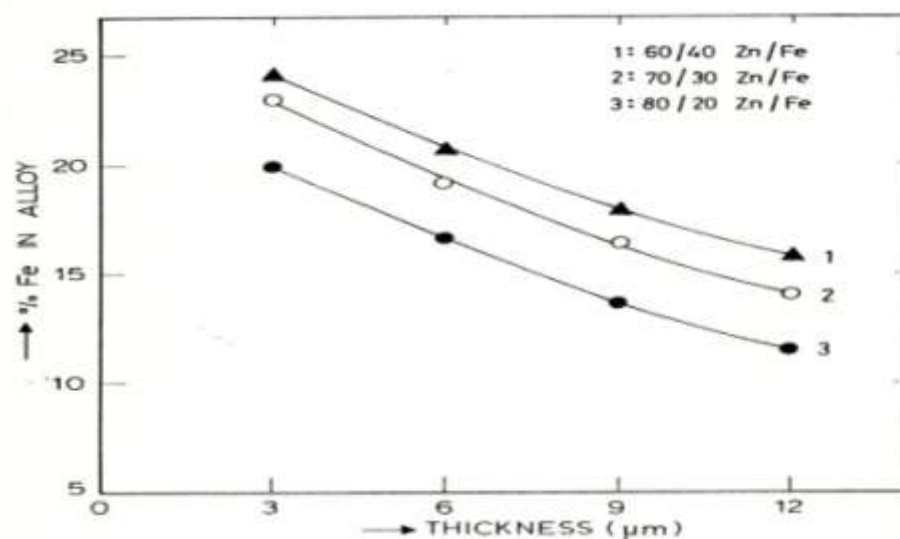

Figure 5.Effect of thickness on the composition of Zn-Fe alloy.

Bath composition: total metal content 0.1 M, $[Zn^{2+}]$ 0.06 M-0.08 M, $[Fe^{2+}]$ 0.02-0.04 M, tartarate 0.2 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/l, NaOH 100 g/l, temperature 25^0C, current density 20 mA/cm^{-2}, pH > 14, unstirred condition, thickness 3-12μm.

Curve 1: 60/40 Zn/Fe, Curve 2: 70/30 Zn/Fe,Curve 3: 80/20 Zn/Fe

Cathodic current efficiency (CCE)

Figure 6 shows the dependence of the cathodic current efficiencies (CCE) on the current density. With increase in current density, the CCE increased at a current density of 20 mA/cm^2. With further increase in current density, the CCE was found to decrease. Increase in bath temperature (Table 4) decreased the CCE. Stirring of the bath solution increased the CCE (Table 3).

Table 4: Effect of temperature oncathodic current of Zn-Fe alloy deposited from an alkalinesulphate bath containing tartarate

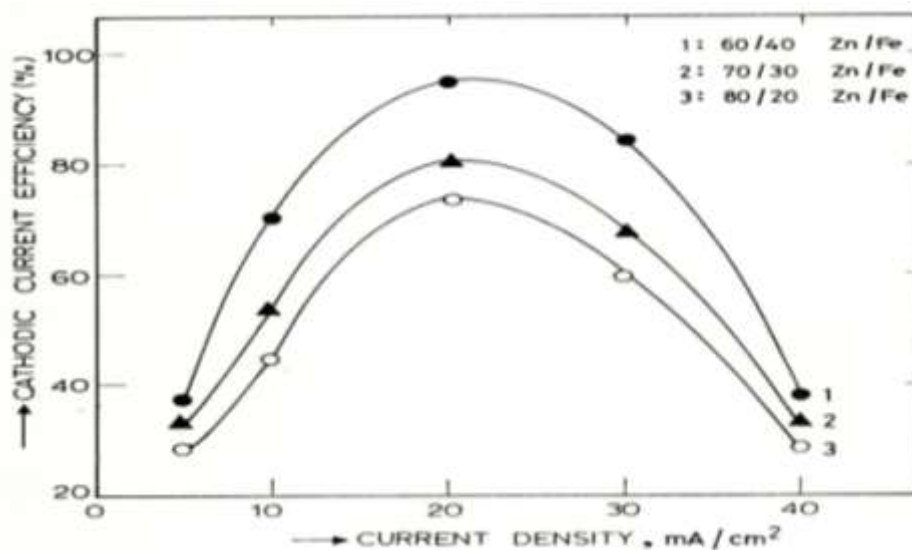| Temperature ^{0}C	% CCE		
	60/40 Zn/Fe	70/30 Zn/Fe	80/20 Zn/Fe
25	93.7	90.8	87.3
35	90.6	86.8	82.6
45	87.4	84.4	77.5
55	85.1	80.1	74.9
65	60.9	57.2	46.8

Figure 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, tartarate 0.2 M, ascorbic acid 0.019 M, Na_2SO_4 30 g/l, NaOH 100 g/l, temperature 25^0C, pH > 14,thickness 6 μ,current density 5-40 mA/cm^{-2}, unstirred condition.

Cyclic voltammetry studies

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 rat 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 ^{0}C. Figure 7(a) represents the cyclic voltammogram of pure $ZnSO_4$ with KCl as the supporting electrolyte in the absence tartarate. The existence of the cathodic peak was observed at the potential of -1.2 V, which corresponds to the reduction of zinc ion. Figure 7 (b) shows the cyclic voltammogram of pure $ZnSO_4$ with KCl in the presence of tartarate. The complexation of zinc ion with tartarate shifted the cathodic peak slightly to -1.2 V. Figure 7 (c) represents the cyclic voltammogram for the bath containing $ZnSO_4$, $FeSO_4$, KCl and tartarate. 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 at -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, which explains why the mutual co-deposition of zinc with iron occurs.
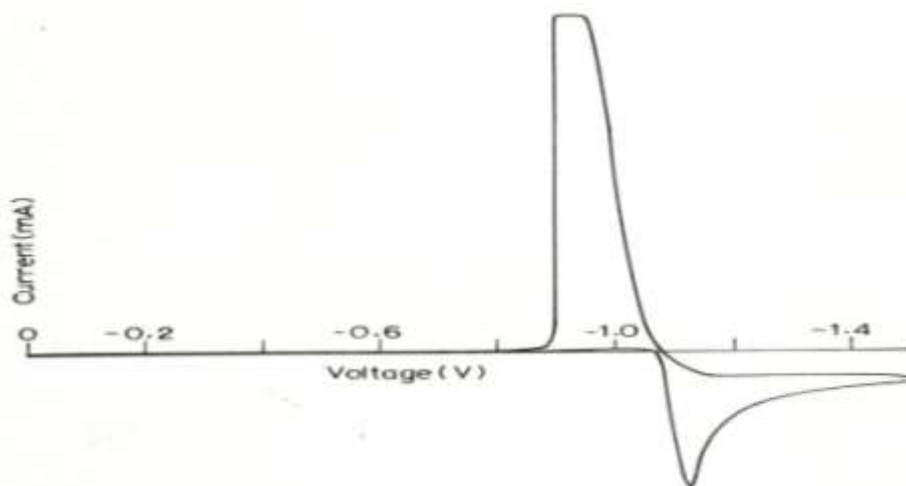

Figure 7(a). Cyclic voltammogram of $ZnSO_4$ + KCl, Scan rate: 50 mV/sec, potential range: 0 to o-1.5 V.
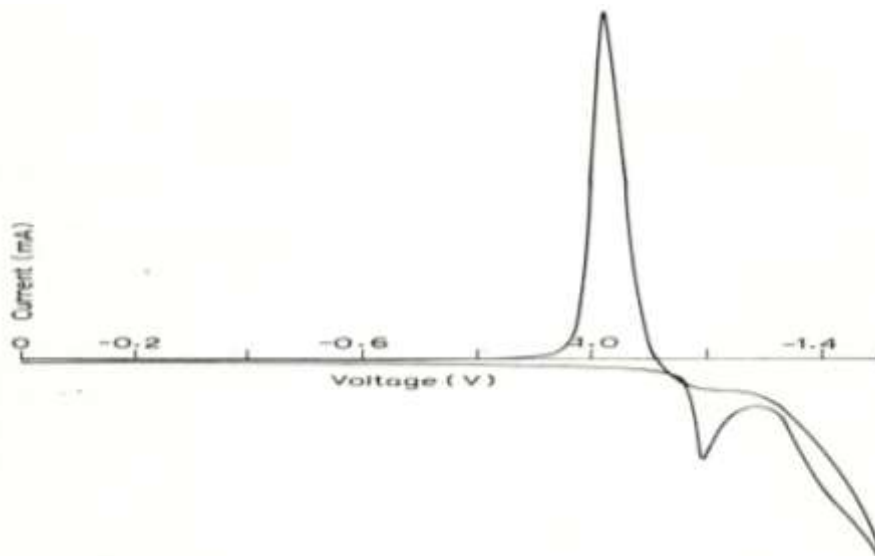
Figure 7(b). Cyclic voltammogram of $ZnSO_4$ + $FeSO_4$ +KCl + tartarate, Scan rate: 50 mV/sec, potential range: 0 to o-1.5 V.

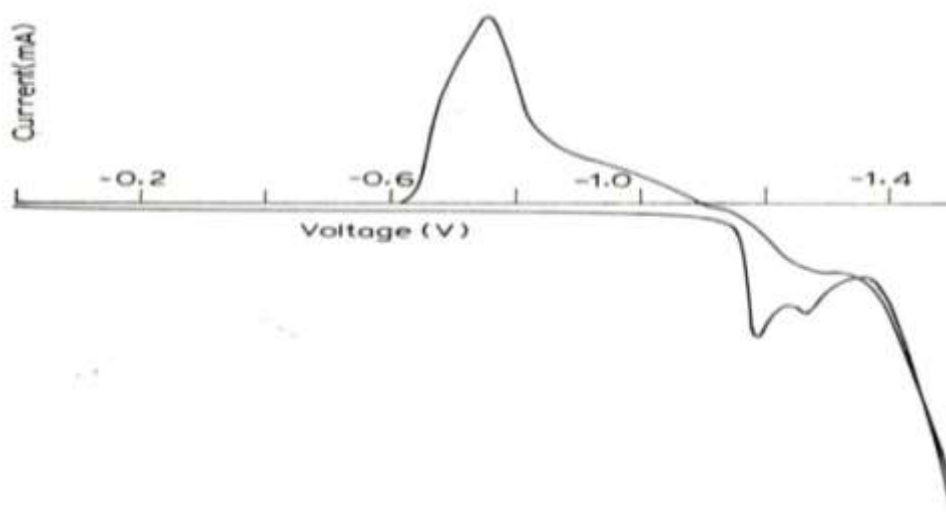
Figure 7(c). Cyclic voltammogram of $ZnSO_4$ + $FeSO_4$ +KCl + tartarate, Scan rate: 50 mV/sec, potential range: 0 to o-1.5 V.

Properties

The adhesion of alloy deposit to the base metal (steel) was tested by a bending test. Alloy deposits did not develop any cracks even after bending to 180^0, this indicates the good adhesion of alloy to the steel.

Porosity tests were carried out on alloy coated steel (4 × 4 sq. inch) to a thickness 3 to 12 µm. Filter paper soaked in the potassium ferricyanide (1 %) solution was placed over the alloy coated steel panel and the appearance of number of blue spots on the filter paper with time was noticed. The alloy deposits were pore free at sufficient thickness (> 6 µm).

Microhardness of 6 µm thick Zn-Fe alloy coated steel panels was determined on Vickers scale (load-50gm). Hardness of the alloy increased with increase in iron content (Table 5). The static potentials of zinc and zinc-iron alloy plated on steel were measured in 3.5 % NaCl solution with respect to saturated calomel electrode. Table 5 lists the static potential values for zinc-iron alloy, which were significantly more positive to zinc and more negative to steel under the same conditions. This shows that Zn-Fe alloy protects steel from corrosion more efficiently than pure zinc coatings.

Table 5: Effect of iron content on microhardness and static potentials of Zn-Fe alloy

% Fe in alloy	Microhardness on Vickers scale in VHN (load-50 g)	Static potential values in mV versus SCE measured in 3.5% NaCl solution
Zinc	85.20	-1013
10	126.50	-975
15	140.61	-913
20	147.34	-900
24	155.12	-852
30	159.54	-802
Mile steel	--	-570

Morphology

The surface morphology of zinc and zinc-iron alloy deposits obtained from an alkaline sulphate bath containing tartaratewere examined under scanning electron microscope. Morphology of the alloy deposit varied with the % wt. Fe. The alloy deposit containing 20% wt. Fe showed uniform, smooth and finer grained deposit (Fig. 8)
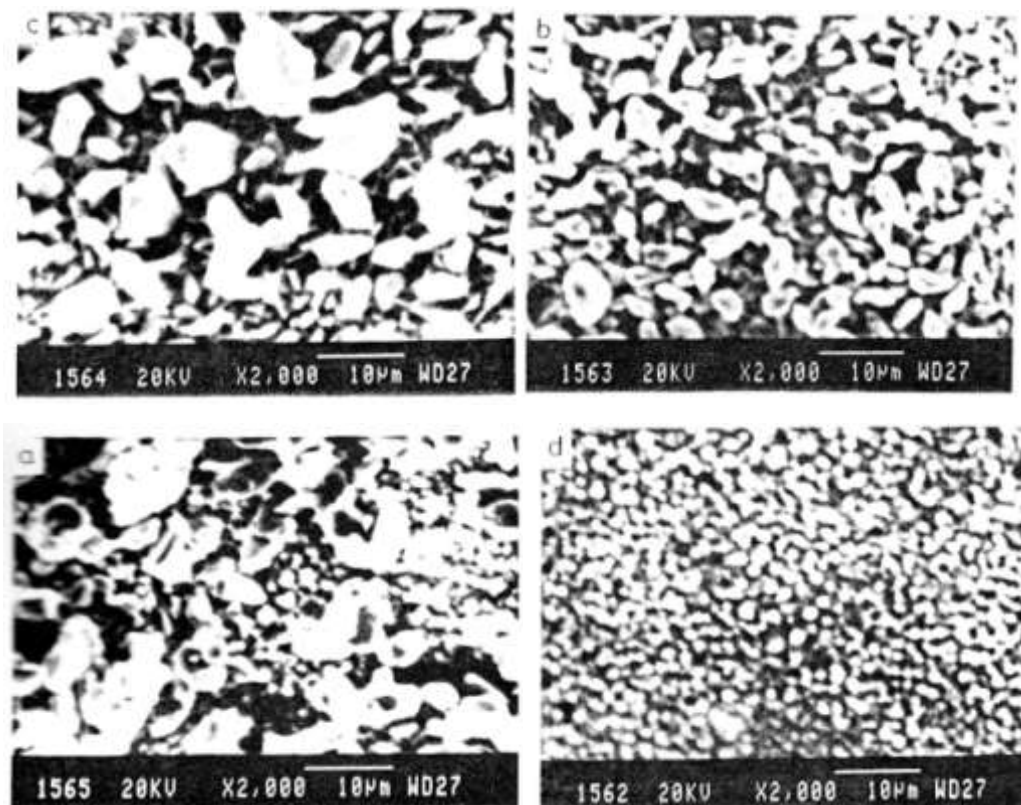
Figure 8. Scanning electron micrographs of Zn-Fe alloy containing different percentage of iron from alkaline sulphate bath containing tartarate.

(a) 0% Fe   (b) 100% Fe   (c) 15% Fe   (d) 20% Fe

Conclusion

Zinc-iron alloy containing 15-25% wt. Fe electrodeposited from non-cyanide alkalinesulphate bath containing tartarate were bright, smooth, uniform and finer grained in size morphologically, the alloy deposition showed the characteristics of anomalous co-deposition. Increase in current density and stirring of the bath solution increased the percentage of iron in the alloy deposit. Increase in temperature and thickness of the deposit decreased the percentage of iron in the alloy deposit.

Acknowledgement

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