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ELECTRODEPOSITION OF ZINC-IRON ALLOY

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Electrolytic parameters were optimised to get 12% to 21% iron content in the codeposition of zinc-iron alloy from a sulphate-chloride mixed electrolyte. The alloy deposits were better in corrosion resistance compared with pure zinc coatings. Microscopic studies and hardness data are also reported.

Key words: Electrodeposition, zinc-iron alloy, corrosion resistance

INTRODUCTION

In recent years, many developments have taken place in the production of galvanised coatings on steel and efforts have been made from time to time to enhance the corrosion resistance of the coating [1]. Zinc-iron alloy is one such development. These alloys were mainly deposited from sulphate or chloride baths [2]. It has been reported that a zinc alloy containing 15-25% iron has good weldability and corrosion resistance and is electroplated commercially on steel strip for automobile application. Further, zinc alloy containing 50% or more iron provided better paintability [3]. Zinc-iron alloys are also used in an environment in which zinc is attacked too rapidly, as for example, in hot water systems [4].

Deposition of zinc-iron alloy belongs to anomalous codeposition type in which less noble metal-zinc deposits preferentially and although various electrolytes have been reported in the literature for depositing zinc-iron alloys, the details on the effect of operating conditions on codeposition and the properties of the deposits were not described [2]. In this work, a detailed investigation was made to deposit zinc-iron alloy from a mixed sulphate-chloride electrolyte and to optimise the plating parameters. The properties and the microstructure of the deposit were also examined.

EXPERIMENTAL

The bath composition and plating conditions are given in Table I, following the conventional sequence of plating operations. The electrolyte was prepared and purified in the usual manner.

To judge the quality of the electrodeposit over a range of bath composition , pH and temperature, Hull cell experiments were carried out in a 267 ml cell for 3 minutes at 8 A current.

For the analysis of zinc and iron contents in the deposit, plating was carried out onto a stainless steel sheet (5 cm x 5 cm) and the plated panel was weighed, stripped in 10% nitric acid and made up to 100 ml in a standard flask. Iron in this solution was determined volumetrically [5] and the % of zinc in the deposit was determined by difference.

The static electrode potential of the Zn-Fe alloy was measured in 3.5% sodium chloride solution against SCE. The corrosion resistance of the deposit was studied by weight loss method by immersion in 3.5% sodium chloride solution. After ten days, the rate of corrosion was calculated from the weight difference.

Microhardness of the alloy was measured in a Vickers tester at a load of 20 g. The surface structure of the alloy was observed under a Scanning Electron Microscope (SEM).

TABLE-I : Electrolyte composition and operating conditions

Ferrous ammonium sulphate (g/l)	:	350
Zinc chloride (g/l)	:	21-105
Glycine (g/l)	:	10
Citric acid (g/l)	:	2
pH	:	2 - 2.5
Temperature (K)	:	323 - 328
Current density (kA. m^{-2})	:	0.5 - 1.5
Anode	:	Equal areas of zinc and iron

RESULTS AND DISCUSSION

Hull cell studies

Fig. 1 refers to the code used for Hull cell patterns and the results are indicated in Figs. 2 to 4. Fig. 2 shows the effect of zinc content in the bath composition with brightness range. With rise in the zinc ion content, the brightness range was decreased and ceased after 20 gpl of Zn^{++}. The effect of pH and temperature on the bath composition is shown in Figs. 3 and 4 respectively. The bright range was present only at pH 2 and was wider at the temperature of 323K. Based on the above results, the pH 2 and temperature of 323K were selected for studying the effect of current density on the iron content of the alloy deposit. Also baths having a lower content of Zn^{++} (10 gpl) and a higher Zn^{++} content (40 gpl) were arbitrarily chosen for studying the effect of bath parameters on the composition of the alloy deposit.

Effect of zinc content in the bath on the composition of the deposit

The variation of zinc content in the bath of pH 2 at 323K against the zinc content of the alloy is shown in Fig. 5. It is seen that the less noble metal viz. zinc is deposited preferentially at all

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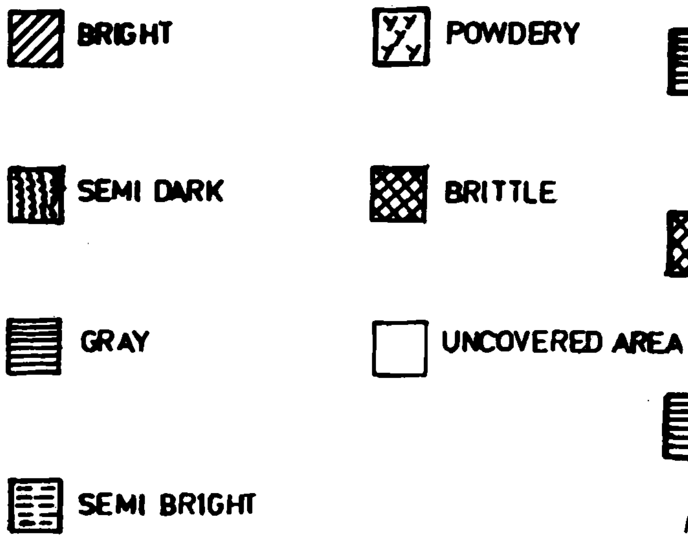

Fig. 1: Codes for recording Hull cell patterns

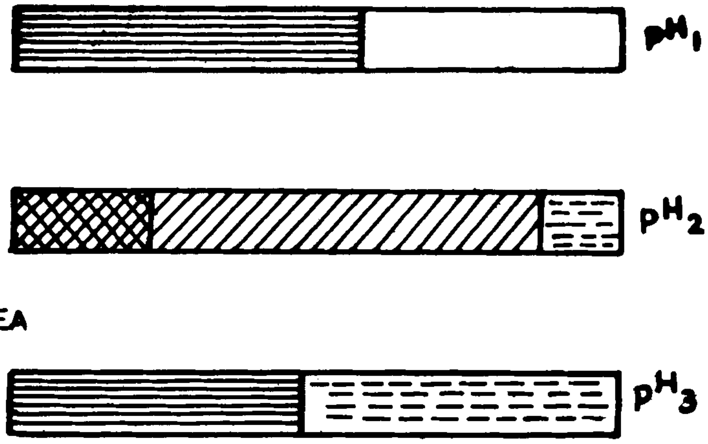

Fig. 3: Hull cell patterns at different pH values. Bath composition: 50 g/l Fe^{2+} + 10g/l Zn^{2+} : Cell current 8 A, Time 3 mts

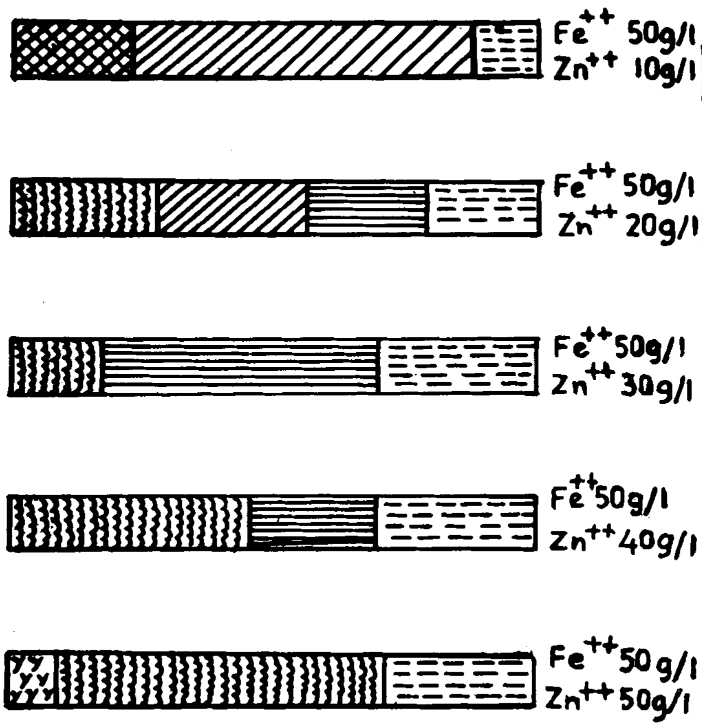

Fig. 2: Hull cell patterns at different bath compositions. Cell current 8 A, pH 2; Temperature 323K; Time 3 mts

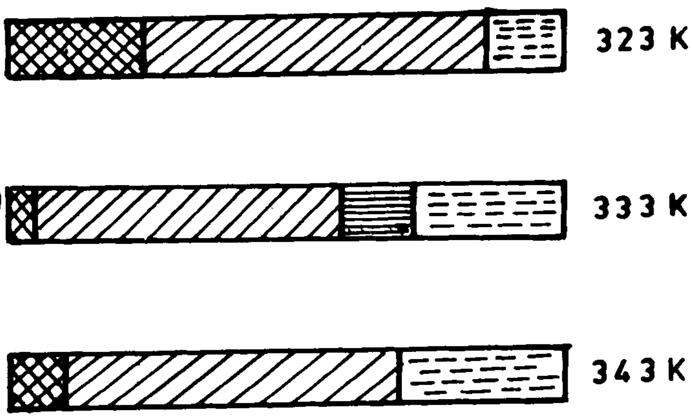

Fig. 4: Hull cell patterns at different temperatures. Bath composition: 50 g/l Fe^{2+} + 10 g/l Zn^{2+} ; pH 2; Cell current 8 A, Time 3 mts.

concentrations of iron and zinc in the bath. A bright deposit has been observed at low concentration of zinc in the bath, namely, 16.65% zinc and 83.35% iron. The cathode efficiency for this bath is maximum and it decreases with zinc content of the bath. Similar type of anomalous behaviour has been observed [3,6] during the deposition of zinc-iron alloys from sulphate and chloride baths.

Effect of current density on the composition of the alloy deposit

The effect of current density on the iron content of the deposit in two different bath combinations, 50 g/l iron + 10 g/l zinc and 50 g/l iron + 40 g/l zinc is shown in Fig. 6 along with their current efficiencies. The iron content of the alloy deposit increases with current density suggesting the deposition of the more noble metal. In other anomalous plating systems also such trends have been reported [7-9]. The current efficiency of alloy deposition has been observed to decrease with current density.

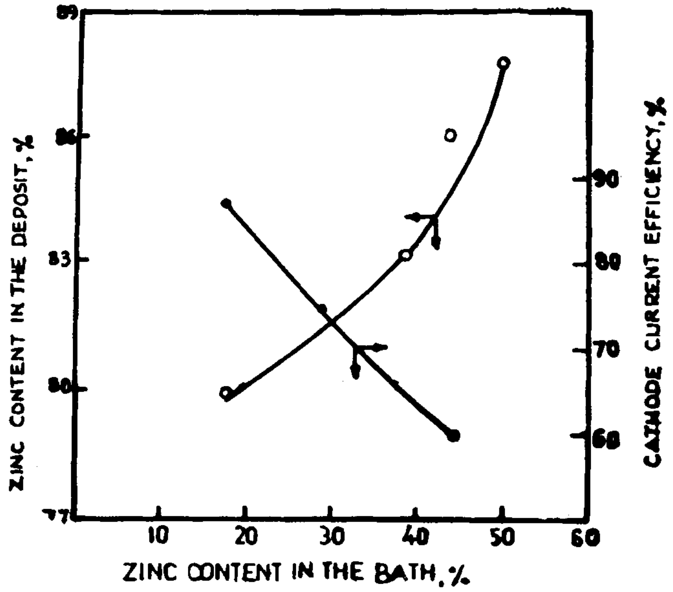

Fig. 5: Effect of zinc content in the bath on the zinc % in the alloy Fe^{2+} 50 g/l, pH 2, Current density 1.5 kA. m^{-2}, Temp. 323K

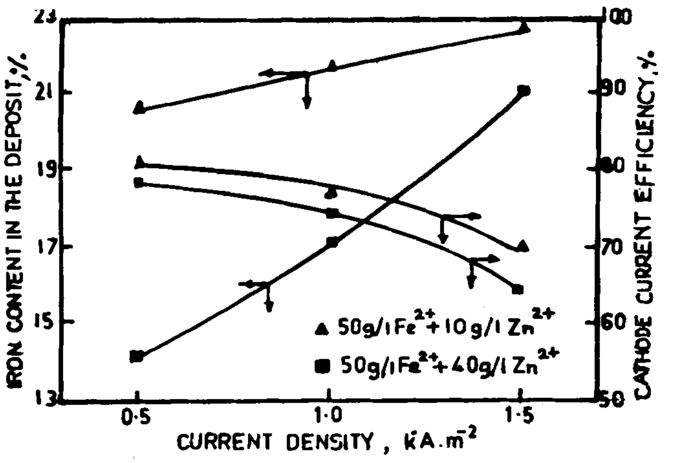

Fig.6: Effect of current density on the iron (%) content in the alloy pH2, Temp. 323K

Effect of temperature on the composition of alloy deposit

Fig. 7 shows that the percentage of iron in the alloy and the current efficiency decrease with temperature. When temperature is raised in the case of Zn-Ni (8-13%) anomalous codeposition system [8], the anomalous behaviour got relieved and zinc content in the deposit diminished; but in the case of Zn-Fe alloys, the opposite trend is observed.

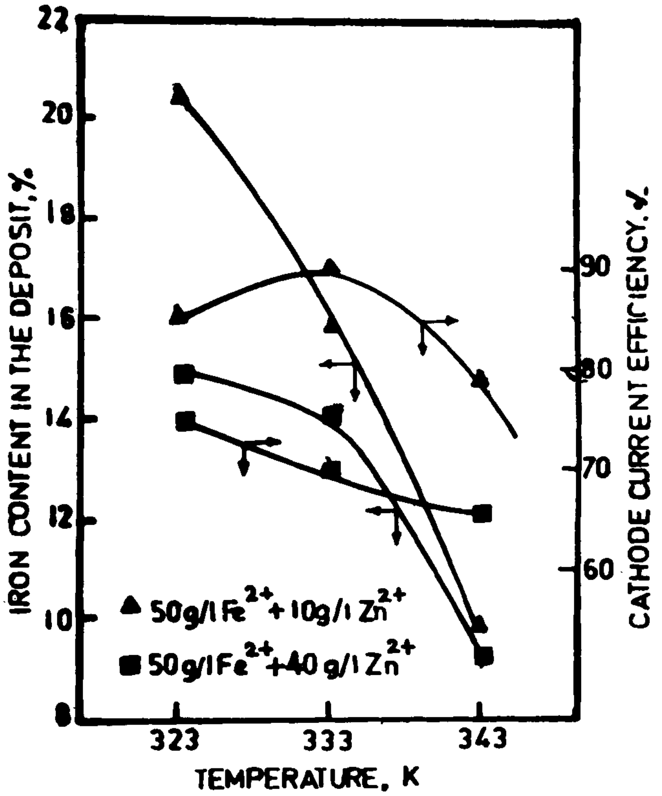

Fig.7: Effect of temperature on the iron (%) content in the alloy, pH2, Current density 1.5 kA.m^{-2}

Effect of pH on the composition of alloy

As seen in Fig. 8, the percentage of iron increased with pH. Bright deposit was obtained at pH 2 and at pH beyond this, the bright range was very much reduced. Unlike the influence of current density and temperature on cathode efficiency, the current efficiency increased with pH. These effects are difficult to explain and there is no definite set pattern of occurrence with plating conditions [2].

Structure of the deposit

When the plated alloys are observed under S E M , fine grained deposits are obtained (Fig. 9). Uniform structure indicates the homogeneous composition of the alloy deposited. With increase in current density, the alloy deposits become more fine grained (Fig.10). The right hand side of the photographs shows the topography of the deposited alloy and left hand side of the same shows the microstructure of the alloy.

Hardness

The microhardness of 40 μm thick alloy deposits is shown in Table II. As the iron content in the alloy increases, the hardness also increases, as anticipated.

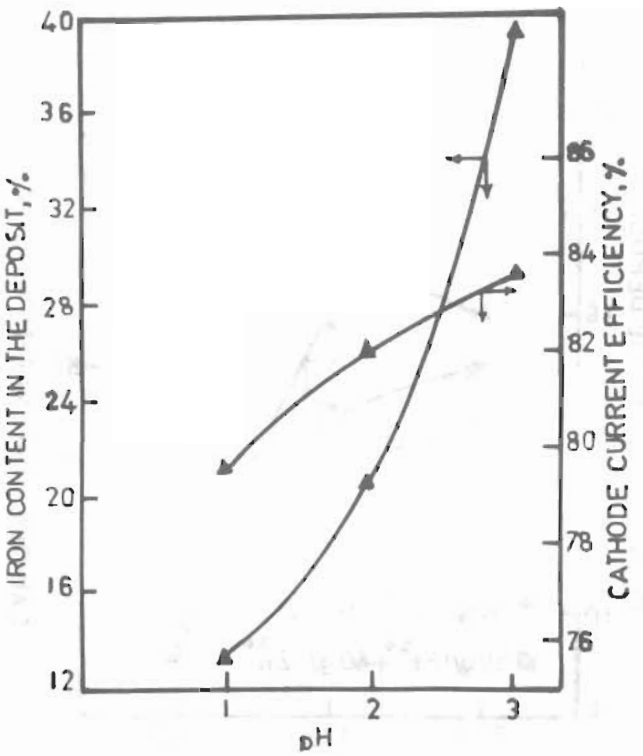

Fig.8: Effect of pH on the iron (%) content in the alloy. Fe^{2+} 50 g/l + Zn^{2+} 10 g/l, Current density 1.5 kA. m^{-2}, Temp. 323K

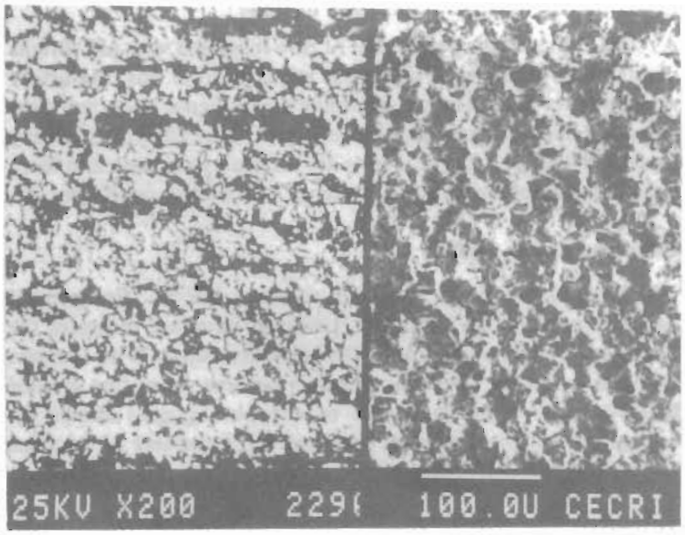

Fig.9: Microstructure of zinc-iron (14%) alloy deposited: 0.5 kA. m^{-2}, Fe^{2+} 50 g/l + Zn^{2+} 40 g/l. pH 2, temperature 323K

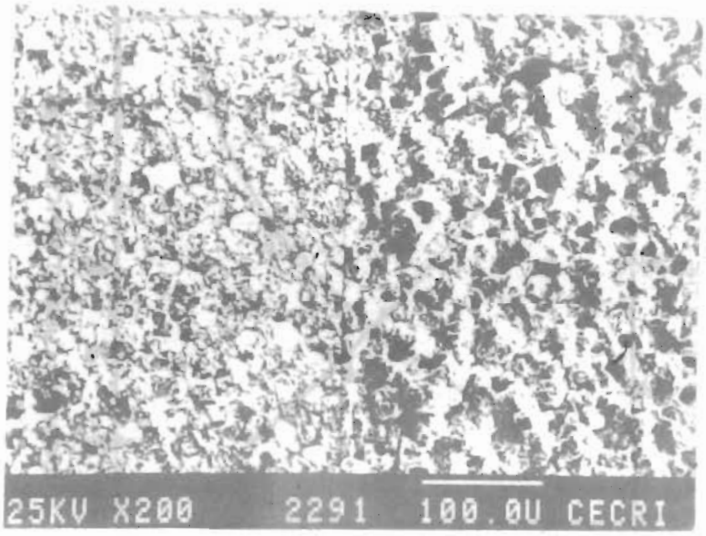

Fig. 10: Microstructure of zinc-iron (21%) alloy deposited at 1.5 kA. m^{-2} Fe^{2+} 50 g/l + Zn^{2+} 40 g/l, pH 2, temperature 323K

TABLE-II: Microhardness of Zn-Fe specimens

% Fe in the deposit	Hardness, VHN (load 20 g)
12	69
14	73
21	81

Studies on corrosion resistance

Table III shows that the static potential of the alloy is considerably more positive to zinc and more negative to steel under identical experimental conditions. This shows that the Zn-Fe alloy can electrochemically protect the steel substrate.

TABLE-III: Static electrode potential of Zn-Fe alloys vs SCE in 3.5% sodium chloride solution

Mild steel	...	...	-550 mV
Zinc -iron (21%)	...	...	-784 mV
Zinc -iron (12%)	...	...	-803 mV
Zinc	...	...	-1026 mV

The weight loss of the coating in 3.5% sodium chloride solution (Table IV) shows that high iron-bearing alloy has more resistance to corrosion. In fact there are more corrosion resistant coatings up to 25% iron content alloys, as reported [3].

TABLE-IV: Weight loss of Zn-Fe alloy in 3.5% sodium chloride solution

Alloy	Weight loss (mdd)
Zinc-iron (21%)	2.82
Zinc-iron (18%)	4.73
Zinc-iron (16%)	6.26
Zinc-iron (14%)	9.24

CONCLUSION

Under optimum conditions of deposition, the current efficiency of the alloy deposition was between 68 and 90% and the alloy showed good corrosion resistance in 3.5% sodium chloride solution.

REFERENCES

1. T Adaniya and M Chmura, *Interfinish '76,* Amsterdam (1976)
2. *Electrodeposition of alloys*, (Ed) A Brenner (Vol. II), Academic Press, New York (1963)
3. T Adaniya, T Hara, M Sagiyama, T Homa and T Watanabe, *Plat Surf Finish* **72**-8 (1985) 52
4. K Nishimura, *J Iron Steel Inst, Japan,* **69** -5 (1983) 334
5. *Modern Analysis of Electroplating* (Ed) W W Peter, Finishing Publication Ltd. , England (1974)
6. N Nakamura and T Hayashi, *Plat Surf Finish,* **72** -8 (1985) 42
7. G N K Ramesh Bapu, J Ayyapparaju and G Devaraj, *B Electrochem,* **3** (1987) 139
8. G N K Ramesh Bapu, J Ayyapparaju and G Devaraj, *Metal Finish,* **85** -2 (1987) 49
9. K C Tripathi and H V Udupa, *J Sci Research,* **8** (1957-58) 94.