Electrodeposition of Iron-Zinc and Nickel-Zinc Alloys: Cathode Potentials and Structure

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INTRODUCTION

ALLOYS of iron and zinc have been deposited from sulphate[1-6] and chloride[4] solutions. Nickel-zinc alloys have been deposited from sulphate[7-10], chloride[11], sulphate-chloride[12] and sulphamate[13] solutions. It has been shown in this laboratory that the pyrophosphate bath can be used for the plating of iron[14], nickel[15] and zinc[16]. The preliminary work on the deposition of iron-zinc[17] and nickel-zinc[18] alloys from this bath has been briefly reported earlier. The results on cathode potentials and structure in the two systems will be presented here.

EXPERIMENTAL RESULTS

The plating solutions consisted of: (*a*) iron-zinc: ferric chloride, zinc pyrophosphate and potassium pyrophosphate, (*b*) nickel-zinc: nickel chloride, zinc pyrophosphate and potassium pyrophosphate. The cathodes were of platinum or copper, and the anodes were of platinum in both cases. Nickel and zinc anodes can, however, be used for nickel-zinc. The experimental details were the same as described in a previous paper on brass plating from this bath[19]. The optimum conditions for obtaining satisfactory deposits of iron-zinc in the composition range 50-80 per cent zinc are: composition of solution—iron 5·6, zinc 19·6, pyrophosphate 174·0 g/l; pH 9·5, 60°C, cathode current density 0·35-8·4 amp/dm^2, cathode efficiency 42-85 per cent. Nickel-zinc alloys in the composition range 16-79 per cent zinc can be plated under the following optimum conditions: composition of solution—nickel 17·6, zinc 19.6, pyrophosphate 260·6 g/l; pH 9, 60° C, cathode current density 0·25-15 amp/dm^2, cathode efficiency 9-49 per cent Satisfactory deposits of both the alloys with a wide composition range can be produced by varying the operating conditions.

The effect of current density on alloy composition, *i.e.* increase in the zinc content with increase in current density, was significant only at low values; in the high current density range the composition was practically constant. There were sudden jumps in composition and cathode potential in the lower current density range. These observations are well illustrated in the data presented in Table I[20,21]. Similar observations have been made in earlier reports on iron-zinc[5] and nickel-zinc[9-11] from other baths. The deposition potentials for iron, nickel, zinc, iron-zinc and nickel-zinc in pyrophosphate solutions under optimum conditions are 0·64, 0·63, 1·02, 0·68 and 0·77 v respectively. An alloy deposit with a high iron or nickel content is to be expected at low current densities, as is borne out by the experimental results.

DISCUSSION

The sudden changes in plate composition and cathode potential corresponded more or less to the deposition of alloys of different phases from high iron or nickel to high zinc: (*a*) iron-zinc: alpha (2, 14% Zn), alpha plus epsilon (45, 69% Zn) and zeta (77, 84% Zn); (*b*) nickel-zinc: alpha (14% Zn), gamma (67, 75% Zn), gamma plus delta (83% Zn) and delta plus eta (92% Zn). The beta and delta phases were missing in nickel-zinc, as also observed by Raub and Elser[12] who got only the alpha and gamma phases. The composition limits in the deposited state are somewhat different from those in the thermal diagram. For a small variation in the current density, the composition and cathode potential changes were quite sharp (Table I). The current density at which the potential changes occurred depended on the experimental conditions. Foerster[5] has reported potential jumps of about 0·24 v for iron-zinc, the same order as in the present work, at 2·2 amp/dm^2 corresponding to a change of 42 per cent zinc in the deposit. Jumps of the order of 0·2-0·3 v have been noticed during deposition of nickel-zinc alloys from sulphate[9,10], chloride[11] and sulphamate[22] baths.

TABLE I

Deposit Composition and Cathode Potential during the Deposition of Iron-Zinc and Nickel-Zinc Alloys.

Conditions: (a) Fe 5·6, Zn 19·6 g/l, 60°C; (b) Fe 8·4, Zn 19·6 g/l, 60°C; (c) Fe 5·6, Zn 19·6 g/l, 70°C; (d) Fe 5·6, Zn 19·6, molybdic acid 1 g/l, 60°C; (e) Ni 17·6, Zn 19·6 g/l, 60°C; (f) Ni 3·0, Zn 32·7 g/l, 60°C; (g) Ni 5·9, Zn 32·7 g/l, 60°C; (h) Ni 11·8, Zn 32.7 g/l, 60°C. Molar ratio of P_2O_7 to metal 2·5; cathode potential (-ve sign) on hydrogen scale.

Alloy		*c d., amp/dm²*	*Deposit Composition, % Zn*	*Cathode potential, v*
Iron-zinc	(a)	0·35–2·1	50–75	0·99–1·23
		2·1 –8·4	75–80	1·23–1·35
	(b)	0·7 –1·4	30–68	1·05–1·18
		1·4 –8·4	68–72	1·18–1·33
	(c)	0·7 –1·4	38–73	0·97–1·18
		1·4 –8·4	73–79	1·18–1·33
	(d)	0·7 –1·4	11–73	0·93–1·21
		1·4 –8·4	73–79	1·21–1·35
Nickel-zinc	(e)	0·25–4·0	16–58	0·74–1·04
		4·0 –6·0	58–79	1·04–1·33
		6·0 –15·0	79	1·33–1·54
	(f)	0·25–0·5	24–90	0·79–1·13
		0·5 –8·0	90–91	1·13–1·38
	(g)	0·5 –1·0	26–85	0·84–1·19
		1·0 –10·0	85–87	1·19–1·45
	(h)	1·0 –2·0	49–84	0·94–1·21
		2·0 –12·0	84–85	1·21–1·49

Glasstone[9] has explained that the jump in potential occurs simultaneously with a decrease in the iron or nickel ion concentration in the vicinity of the cathode, so that a zinc rich alloy with a high hydrogen overvoltage is deposited. The behaviour during the deposition of iron-zinc alloys from sulphate solutions has been explained in a similar way by Foerster[3]. Lustman[11] found that the potential arrests corresponded to the change in structure of the nickel-zinc deposit from the alpha solid solution to the gamma phase, and then from gamma to delta or eta phase. He has suggested that the non-deposition of the beta phase may be due to the energy for the formation of its lattice being greater than that for the gamma-lattice, resulting in a more negative deposition potential for the former phase in spite of the higher zinc content of the gamma-phase. In the high current density region where the plate composition was practically constant, the potential changes were comparatively very little over a wide current density range. This has also been observed by Glasstone[9] for nickel-zinc. In this region the potential values are very close to those of zinc, and a high zinc deposit of more or less constant composition is obtained. Similar changes in plate composition and cathode potential have been observed during the deposition of alloys of different phases in tin-copper[21] from the pyrophosphate bath.

The cathode potential curves for iron and zinc, and nickel and zinc, are far apart, zinc being the baser metal in both systems. Even then alloy deposition is possible because of the mutual influence of the two metals. From the alloy composition and potential it is possible to reconstruct the single metal potential curves and compare them with the experimental single metal curves. Calculations of this type have been made for both the alloy systems[20],[41]. The relative position of the reconstructed curves indicate the possibility of codeposition. After a certain current density the alloy and the reconstructed curves tend to straighten out. Under these conditions the alloy deposit will have more or less a constant composition.

It is seen that studies of this type will help in establishing a reasonable correlation between the operating conditions of electrodeposition, the cathode potentials at which the alloy is deposited

and the structure of the deposited phase. The experimental data obtained in this manner will go a long way in clarifying the mechanism of alloy deposition.

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