ELECTRODEPOSITION OF TERNARY NICKEL-IRON-COBALT ALLOY FROM ACETATE BATH*

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(Received 4 October 1976; and in revised form 22 November 1976)

Abstract—Ternary nickel-iron-cobalt alloys of wide range composition have been deposited from acetate baths under a variety of conditions and the optimum conditions established are: nickel acetate 0.2828 M. ferrous sulphate 0.0359 M. cobalt acetate 0.2828 M. boric acid 0.1617 M. ascorbic acid 0.0056 M, pH 5.0, cd 1.5 A/dm² and temperature 30°. The bath gave bright, smooth and adherent deposits. Iron and cobalt contents decreased with an increase in cd and pH. X-ray studies of the deposits revealed *fcc* structure within the composition range studied (43.6-54.0% Ni). The results indicate that acetate bath can be successfully employed for plating purposes.

INTRODUCTION

In view of the known better buffering capacity of acetates[1, 2], the present investigations were undertaken to study the electrodeposition of mutual alloys of iron group metals (Ni, Fe and Co). Electrodeposition of nickel-iron and nickel-cobalt alloys from acetate bath has been successfully carried out[1, 2].

The present work relates to the electrodeposition of ternary alloys of nickel iron cobalt from an acetate bath under different operating conditions.

EXPERIMENTAL

The general experimental details have been described earlier [1, 2]. The plating solutions contained nickel and cobalt acetates, ferrous sulphate, boric acid (0.1617 M) and ascorbic acid (0.0056 M). The pH was adjusted using acetic acid. All the reagents were of E. Merck extra-pure grade. Each experiment was carried out in a fresh bath without agitation and mostly at 30°.

The cathode potentials were measured against a saturated calomel electrode.

The metal contents in the deposits were determined polarographically using ammonium oxalate and ammonia[3] as supporting electrolyte.

RESULTS AND DISCUSSION

The plating variables had a marked influence on the quality and composition of the deposits and also on the cathode current efficiency (*cce*).

Concentration of electrolyte

The ratio between the contents of two metals and the total metal content in the bath was kept constant and the content of third metal was varied. Subsequently, the ratio between the three metals was kept constant while the total metal content was varied (Table 1c). It is seen that alloy deposits with higher nickel content are very bright, uniform and satisfactory. As the iron or cobalt concentration in the bath is increased the content of either metal in the deposit goes up considerably (Table 1a and b). An increase in iron and cobalt content is observed with an increase in total metal content of the bath (Table 1c).

Cathode current efficiency decreased as the iron or total metal content increased while it increased considerably with an increase in cobalt content in the bath.

It is clear that nickel, though nobler than iron and cobalt, is always found to be in lower percentage in the deposit than in the bath. This implies that the percentages of iron and cobalt in the deposit are higher than those in the bath. Thus the deposition is of anomalous type as has been found in other baths [4, 5].

Current density

Current densities ranging from 0.5 to 4.0 A/dm^2 were used. The quality of the deposits improved as the current density was increased up to a certain value (1.5 A/dm^2) but further increase of *cd* resulted in inferior deposits. Of course, bright deposits were obtained at higher *cds* (>2 A/dm²) but a tendency to peel off was noticed.

Iron and cobalt content was found to decrease while nickel content and *cce* increased with current density (Fig. 1a). Decrease in the less noble metal contents in the deposits at higher *cds*, probably indicates the impoverishment of diffusion layer with respect to the codepositing metal (Fe and Co) and thus causing the system to come under diffusion control. Such a trend of variation in iron and cobalt contents in deposits with respect to current density has also been observed by other investigators in binary [1, 6, 7] and ternary [4, 5] alloys of nickel.

pН

The influence of pH on the deposits was studied in the pH range 3.8 to 6.0 using baths of optimum composition at cd 1.5 A/dm². At low pH the deposits were dull, loose and porous. Satisfactory deposits

^{*} Dedicated in honour of late Dr. D. Singh, D.Sc., Reader in Chemistry, Banaras Hindu University.

0	6 Metal in bai	th	% M			
Ni	Fe	Co	Ni	Fe	Co	% CCE
(a) Effect of 1	FeSO ₄ 7H ₂ O	concentration				
Total met	al content (21.	.943 g/l) and 🗅	Ni:Co (4.98:1)	kept constan	t	
75.00	9.0	16.00	46.0	22.0	32.0	55.5
68.07	18.2	13.60	33.5	40.5	25.5	42.5
60.00	27.9	11.88	32.0	45.0	23.0	41.3
52.83	36.5	10.61	24.0	57.0	18.5	35.5
(b) Effect of	Co(CH ₁ COO)	, concentratio	n			
Total me	tal content (21	943 g/l) and 1	Ni:Fe (8.25:1)	kept constan	t	
75.65	9.17	15.1	45.0	21.0	34.0	56.0
62.25	7.54	30.2	33.6	15.2	50.2	67.8
48.70	5.90	45.4	23.0	16.3	59.7	76.6
35.68	4.32	60.0	22.5	13.0	63.6	89.2

Table 1. Effect of concentration of electrolyte on the metal content and cce of Ni-Fe-Co deposit

Total metal content 21.943 g/l, Boric acid 0.1617 M, ascorbic acid 0.0056 M, cd 1.5 A/dm², pH 5.0, Temp. 30°.

(c) Effect of total metal content. Ratio of all the metals kept constant

Co	ncentration of electro (moles/litre)	% N				
Ni(CH ₃ COO) ₂	FeSO ₄ ·7H ₂ O	Co(CH ₂ COO) ₂	Ni	Fe	Co	% CCE
0.1414	0.0178	0.0282	52.3	18.4	28.5	58.5
0.2828	0.0359	0.0564	45.5	22.0	32.0	55.0
0.5656	0.0718	0.1128	36.8	28.0	34.5	48.5

were obtained in the pH region 5-5.5 but beyond this value again inferior deposits were obtained.

There was a decrease in iron and cobalt contents in the deposit with an increase in pH of the bath.



Fig. 1(a) Effect of current density on the metal content and *cce* of the Ni–Fe–Co deposits. Bath composition, temperature, pH and duration of electrolysis optimum.

However, the decrease is more evident in lower pH region (<pH 5). Cobalt content remained almost constant above pH 5.0. There was an increase in nickel content and also a sharp increase in the *cce* with pH of the bath (Fig. 1b). The change in the composition of the deposit with respect to pH is similar to that reported by Marikar and Vasu[5].



Fig. 1(b). Effect of bath pH on the metal content and cce of the Ni-Fe-Co deposit. Bath composition, temperature, time as in Fig. 1(a); at cd 1.5 A/dm².



Fig. 2(a). Effect of temperature on the metal content and cce of the Ni-Fe-Co deposit. Bath composition, cd and pH optimum.

(b) CCE ದ್ದ * 20 Fe ы **Metal** in deposit and CCI 10 Time, min (...) CCE Ni 50 Co 30 Fa 20 30 40 50 60 Both temperature, ۰C

Fig. 2(b). Effect of duration of electrolysis on the metal content and *cce* of the Ni-Fe-Co deposit. Conditions as in Fig. 2(a) at 30°.

Temperature

The temperature range covered was $20-80^{\circ}$ under optimum conditions of bath composition, cd and pH. Mirror bright, finegrained and smooth deposits were obtained up to 50° but thereafter slightly dull and nonuniform deposits were obtained. The deposits turned loose and dark at elevated temperatures (>60°C). Iron content in the deposits decreased with an increase in temperature of the bath while cobalt content increased up to 40° and thereafter remained more or less constant. *Cce* was found to increase consistently with temperature. Such improvement in the *cce* with temperature is probably due to the decrease in polarization of deposition of iron group metals (Fig. 2a). Trend of variation in composition of the deposits with respect to temperature is similar to that reported earlier[4].

Duration of electrolysis

Under optimum conditions, the duration of electrolysis was varied from 10 to 60 min. Deposits obtained up to 40 min duration of time were dense, adherent, bright, and satisfactory but beyond this a tendency to peel off was observed. The composition of the deposits remained almost unchanged beyond 40 min. However, iron content decreased while nickel content increased with increased duration up to 40 min. *Cce* and cobalt content also did not change appreciably (Fig. 2b).

Table 2.	Effect	of	addition	agent	on	the	metal	content	and	CCE	of	the	Ni-Fe-Co	deposit	under
						0	ptimur	n conditi	ons						

	Amount	%	Metal in th deposit	ı¢	
Addition agent	(per litre)	Ni	Fe	Co	% CCE
Formic acid	0.2 ml	46.0	20.5	33.0	55.0
Formamide	0.3 ml	48.0	20.2	31.0	57.5
Dimethylformamide (DMF)	0.2 ml	45.0	20.5	34.0	56.2
n-methylformamide (NMF)	0.3 ml	46.0	23.3	30.0	58.0
Tetraethylammonium bromide (TEABr)	0.1 g	47.0	21.3	31.0	59.5
Tetraethylammonium iodide (TEAI)	0.1 g	45.5	25.2	28.5	53.7
Tetramethylammonium bromide (TMABr)	0.2 g	42.3	27.8	29.2	52.5
Tetramethylammonium iodide (TMAI)	0.1 g	48.0	21.0	30.5	58.5
Teepol	0.3 ml	47.2	20.2	32.0	57.3
Glycerine	0.4 ml	46.5	22.3	30.5	56.0
Thiourca	0.1 g	49.0	20.5	29.5	48.5

Table 3. X-ray studies of the alloy deposits

Percent	metal in the	deposit		Lattice			
Ni	Fe	Co	- Lattice	(a)	Conditions		
100	_		fec	3.530	Ni(CH ₃ COO) ₂ 0.5000 M, Boric acid 0.3000 M, pH 5.0, CD 1.5 A/dm ² , Temperature 30°.		
54.0	14.5	31.5	fec	3,539	Bath composition, CD and tempera- ture optimum; pH 5.5.		
43.6	24.2	32.2	fcc	3.568	Bath composition, CD and pH opti- mum; Temperature 20°.		

Addition agent

A number of organic and inorganic addition agents were added separately and singly to the bath under optimum conditions and the results are summarized in Table 2.

It is seen that formamide, *dmf* and quaternary ammonium compound except tetraethyl ammonium iodide improved the quality of the deposits considerably and are also helpful in prolonged operation of the bath. Other addition agents have little beneficial effect. The composition of the deposits remained practically almost unchanged but *cce* changed slightly. In presence of thiourea unsatisfactory deposits were obtained and *cce* was also reduced appreciably.

Cathode potential

Cathodic polarization increases with current density (Fig. 3). Although nickel is the noblest amongst iron group metals, it is seen from Fig. 3 that it de-



Fig. 3. Current density-cathode potential curves for the electrodeposition of Ni Fe-Co alloy at pH 5.0 and Temp. 30°. Curve Ni Ni(CH₃COO)₂ 0.2828 M, Borie acid 0.1617 M, borie acid 0.1617 M, ascorbic acid 0.0056 M. Co 0.0359 M, borie acid 0.1617 M, ascorbic acid 0.0056 M. Co Co(CH₃COO)₂ 0.0565 M, borie acid 0.1617 M. Alloy Ni(CH₃COO)₂ 0.2828 M, FeSO₄ 7H₂O 0.0359 M, Co(CH₃COO)₂ 0.0565 M, borie acid 0.1617 M and ascorbic acid 0.0056 M. Photomicrograph of Ni Fe-Co deposit containing 45% Ni, 21.5% Fe and 33% Co taken under coptimum conditions (100 × 1)

posited with higher polarization. The cathode polarization curve for the alloy lies between Ni and Fe curves. Preferential deposition of iron and cobalt over nickel is also indicated by cathodic polarization.

It is seen that content of less noble metals in the deposit is always higher than that in the bath and the process of deposition follows anomalous behaviour.

In light of the kinetic interpretation of anomalous codeposition outlined by Giuliani and Lazzari[8,9], certain trends seen during present investigations can be explained. The observed increase in nickel content at high *cds* and high pH (Fig. 1a, b) can thus be attributed to the increased concentration of Ni(OH)⁺ under these conditions. The role of cobalt ions in maintaining a stable hydroxyl ion gradient in the cathode layer and thus ensuring high *cce* is seen from the fact that, other conditions being same, the *cce* increases with Co²⁺ concentration in the bath (Table 1b).

Structure of the deposits

The deposits obtained were generally very bright, adherent, fine grained and smooth. Deposits rich in nickel were more bright and adherent while iron rich alloys contained some non-metallic inclusions and tarnished in air.

X-ray diffraction studies of the deposits (in as deposited condition) showed formation of solid solution with face centred cubic structure like nickel and the lattice parameter was higher than nickel (Table 3).

Acknowledgement—Thanks are due to Professor O. P. Malhotra, Head of the Department of Chemistry for providing necessary facilities.

REFERENCES

- D. Singh and V. B. Singh, Ind. J. Tech. 13(11), 520 (1975).
- V. B. Singh and V. N. Singh, Plating Surf. Finish. 63(7), 35 (1976).
- L. Meites, 'Polarographic Techniques', 2nd edn, p. 623. John Wiley, Interscience, New York (1965).
- R. P. Dambai and T. L. Ramachar, *Plating* 59, 861 (1972).
- Y. M. F. Marikar and K. I. Vasu, Electrodep. Surf. Treat. 2, 281 (1973/74).
- 6. N. V. Korovin, Zh. neorg. Khim. 2, 2259 (1957).
- C. B. F. Young and C. Egerman, *Trans. electrochem.* Soc. 72, 447 (1937).
- 8. L. Giuliani and M. Lazzari, Electrochim. Metal 3, 45 (1968).
- 9. L. Giuliani and M. Lazzari, Electrochim. Metal 3, 397 (1968).