Electrodeposition of ternary nickel–iron–cadmium alloys*

V. B. SINGH

Department of Chemistry, Banaras Hindu University Varanasi 221 005, India

Received 19 October 1977

Ternary nickel–iron–cadmium alloys have been electrodeposited from an acetate bath. The effect of bath composition current density, pH, temperature and duration of electrolysis on the deposit composition, quality and cathode current efficiency has been studied. The influence of some addition agents and cathodic polarization has also been studied. The iron and cadmium content decreased with an increase in current density or pH but did not alter significantly with respect to temperature, time or addition agents. X-ray studies confirmed the formation of a single-phase alloy within the composition range studied (84–88 wt% Ni).

1. Introduction

The electrodeposition of nickel–iron [1] and nickel–cadmium [2] alloys from an acetate bath has previously been reported, and the work was also extended to ternary alloy deposition [3]. A preliminary investigation on the electrodeposition of nickel–iron–cadmium alloys has also been reported by Ramachar and Dambal [4]. The present investigation relates to the electrodeposition of ternary nickel–iron–cadmium alloys from an acetate bath under different operating conditions.

2. Experimental

The general experimental details have been given in earlier publications [1–3, 5]. Each experiment was carried out in fresh solution, without agitation, at 35° C. Cathode potentials were measured against the saturated calomel electrode. The metal contents in the deposit were determined polarographically [6].

3. Results and discussion

3.1. Bath composition

The deposition electrolyte for the ternary alloy was prepared from the acetates of nickel and cadmium and ferrous sulphate. Boric acid and ascorbic acid were also added to the electrolyte. Ascorbic acid stopped the oxidation of iron (II)

and thus stabilized the bath without changing the composition of the deposit. The effect of the concentration of the electrolyte was studied in three different stages and the presentation of the results follows the guidelines laid down by Brenner [7]. Fig. 1 shows the effect of bath composition (curve I) on the composition of the deposits (curve II). Tie lines, drawn connecting the deposit compositions with the respective bath compositions, assist in the interpretation of the results. An increase in the concentration of iron or cadmium in the bath considerably increased their respective content in the deposit. The quality of the deposit deteriorated as the iron or cadmium content in the bath was increased beyond 3·34 and 1·32 per cent respectively. The cathode current efficiency (CCE) decreased significantly when the concentration of iron or cadmium in the bath increased beyond these values (CCE, 72–38 and 79–60 per cent respectively) and was also lowered by an increase in total metal content of the bath (Table 1). A low efficiency for the deposition indicates that good quality deposits are not obtained from the bath because of more hydrogen discharge. The iron and cadmium content in the deposit was always found to be higher than that in the bath.

3.2. Current density

The influence of current density between 0·5 and 4·5 A dm⁻² was studied. The quality of the deposit

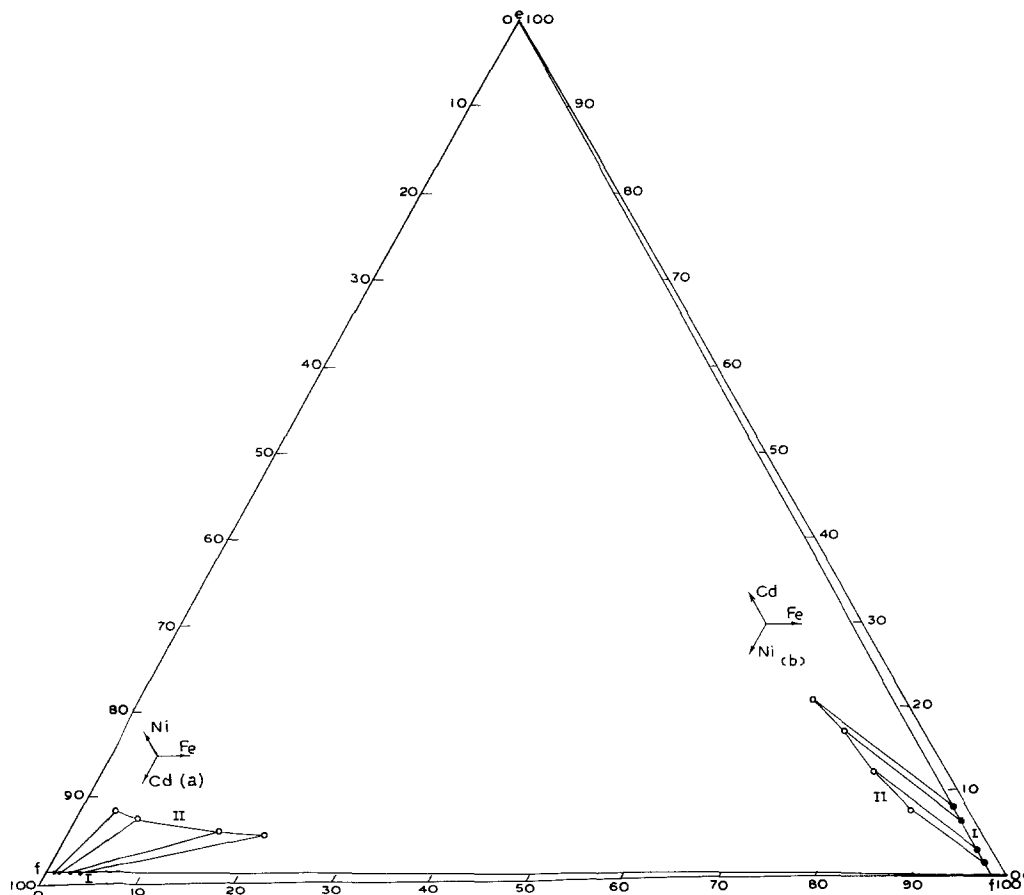Fig. 1. Effect of concentration of electrolyte on the metal content of the Ni–Fe–Cd deposit. Total metal content 24 g l^{-1}, pH 5·1, current density 2·0 A dm^{-2}, temperature 35° C, time 25 min (optimum conditions). Curves I and II represent the bath and deposit composition respectively. (a) Effect of Cd(CH$_3$COO)$_2$·2H$_2$O concentration. Total metal content and Ni:Fe (57·85:1) kept constant. (b) Effect of FeSO$_4$·7H$_2$O concentration. Total metal content and Ni:Cd (73·5:1) kept constant.

at low or high current densities was unsatisfactory. Shining, uniform and adherent deposits were obtained between 0·5–2·5 A dm^{-2} but above this range the deposits were modular and slightly dull.

A marked tendency to peel off was also observed. The iron and cadmium content in the deposit decreased with an increase in current density but beyond 1·5 A dm^{-2} the variation was insignificant.

Table 1. Effect of total metal content on the metal content and CCE of Ni–Fe–Cd deposit. (Ratio of all the metals kept constant. Conditions: boric acid 0·2426 M, ascorbic acid 0·0056 M, current density 2·0 A dm^{-2}, pH 5·1, temperature 35° C, time 20 min)

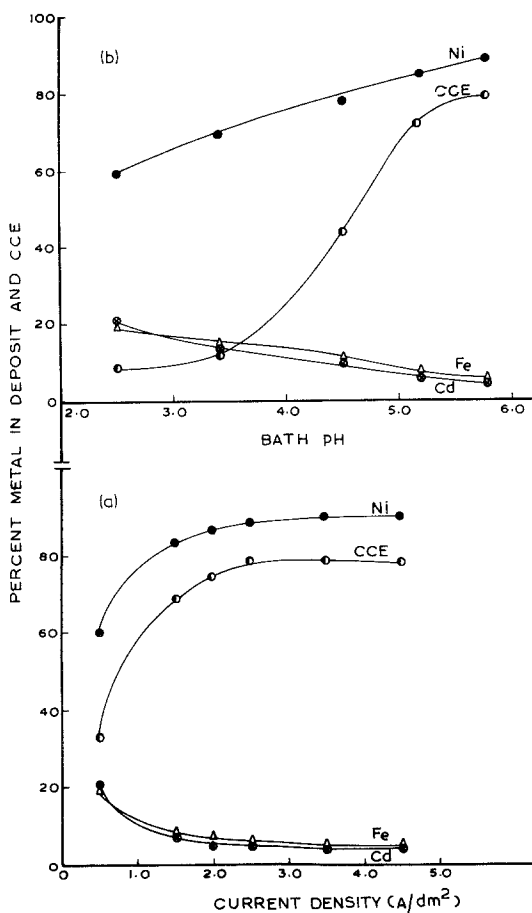| Concentration of electrolyte (moles l^{-1})			Metal in the deposit (wt%)			CCE (%)
Ni(CH$_3$COO)$_2$	FeSO$_4$·7H$_2$O	Cd(CH$_3$COO)$_2$·2H$_2$O	Ni	Fe	Cd	
0·1779	0·003 59	0·001 40	94·0	3·0	2·5	74·1
0·3559	0·007 19	0·002 81	85·5	7·5	6·3	72·8
0·7118	0·014 38	0·005 62	78·5	8·9	12·0	36·5

Fig. 2. (a) Effect of current density on the metal content and CCE of the Ni–Fe–Cd deposit. Bath composition, temperature (35° C), pH and duration of electrolysis optimum. (b) Effect of bath pH on the metal content and CCE of the Ni–Fe–Cd deposit. Bath composition, temperature, time as in (a); at current density $2 \cdot 0$ A dm^{-2}.

The deposit contained almost equal content of iron and cadmium. The nickel content and CCE increased but above $1 \cdot 5$ A dm^{-2} the increase is small (Fig. 2a). The composition of the deposit was found not to depend on the current density; this was also observed during the electrodeposition of nickel–iron [8], nickel–cadmium [4, 9] and nickel–cobalt–cadmium [3] alloys. The variation in composition of the deposits with current density does not show whether the process is under diffusion control.

The following bath compositions and current densities were found to be the optimum: nickel acetate, $0 \cdot 395\,90$ M; boric acid, $0 \cdot 2426$ M; ferrous sulphate $0 \cdot 007\,19$ M; ascorbic acid,

$0 \cdot 0056$ M; cadmium acetate $0 \cdot 002\,81$ M; current density, $2 \cdot 0$ A dm^{-2}.

3.3. Effect of pH

The effect of pH on the quality, composition and CCE was studied between pH $2 \cdot 5$–$5 \cdot 8$ using a bath of optimum composition at optimum current density. Dull, semi-bright and porous deposits were obtained up to pH $4 \cdot 5$ and also at pH $5 \cdot 8$. Satisfactory deposits were obtained in the pH region 5–$5 \cdot 8$. There was a decrease in the iron and cadmium contents in the deposit with an increase in the pH of the bath. The nickel content increased steadily with pH while CCE was seen to increase sharply (Fig. 2b). Such a trend of variation in composition of the deposit with pH is very general during the alloy deposition of iron group metals from this type of bath.
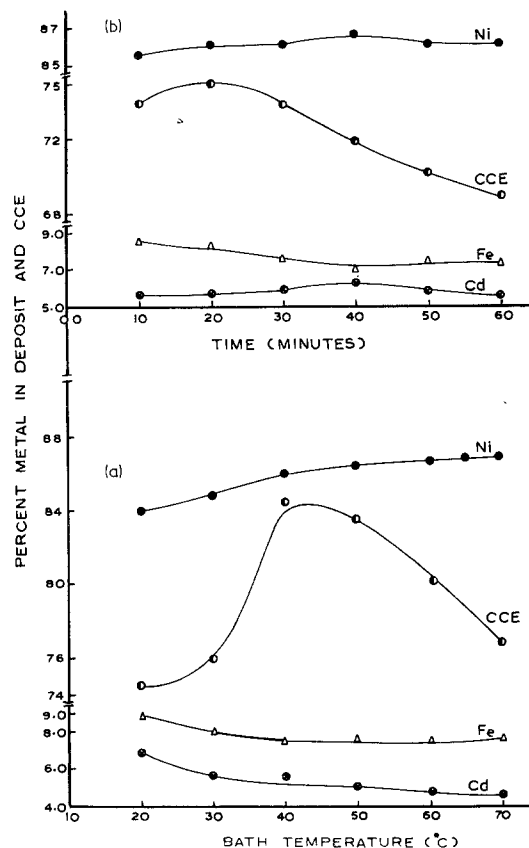

Fig. 3. (a) Effect of temperature on the metal content and CCE of the Ni–Fe–Cd deposit. Bath composition, current density and pH optimum. (b) Effect of duration of electrolysis on the metal content and CCE of the Ni–Fe–Cd deposit. Conditions as in (a) at 35° C.

Table 2. Effect of addition agents on metal content and CCE of the Ni–Fe–Cd deposit under optimum conditions

Addition agent	Amount (l^{-1})	Metal in the deposit (wt%)			CCE (%)
		Ni	Fe	Cd	
formic acid	0·2 ml	86·0	7·5	6·0	74·0
formamide	0·3 ml	85·0	8·7	5·7	72·5
dimethylformamide (DMF)	0·2 ml	84·7	8·0	6·8	73·0
N-methylformamide (NMF)	0·3 ml	84·3	9·0	6·2	76·0
tetraethylammonium bromide (TEABr)	0·1 g	84·0	9·5	5·8	75·5
tetraethylammonium iodide (TEAI)	0·2 g	86·5	7·5	5·5	74·2
tetramethylammonium bromide (TMABr)	0·2 g	86·3	8·0	5·2	73·5
tetramethylammonium iodide (TMAI)	0·2 g	85·2	7·3	6·6	73·0
teepol	0·2 ml	84·0	8·0	7·3	70·5
glycerine	0·3 ml	85·8	7·2	6·5	71·0
thiourea	0·1 g	85·0	8·5	6·0	60·5
thiolactic acid	0·2 ml	86·2	7·5	5·5	45·2

3.4. *Temperature*

The effect of temperature was studied in the temperature range 20–70° C under optimum conditions of bath composition, current density and pH (5·1). The quality of the deposit was seen to improve by increasing the temperature up to 40° C and to deteriorate at higher temperatures (> 50° C). The deposits were very bright, uniform and adherent up to 50° C but beyond this temperature tended to turn more and more nodular and dull. The composition of the deposit remained insensitive to the temperature of the bath. An insignificant variation in composition of the deposit with temperature confirmed that the deposition is not diffusion controlled. CCE increased initially and then decreased at above 40° C (Fig. 3a).

3.5. *Duration of electrolysis*

Under optimum conditions the period of electrolysis was varied from 10–60 minutes. Smooth bright and uniform deposits were obtained for up to 40 minutes of electrolysis but they deteriorated after longer deposition. An increased duration of

electrolysis resulted in dull and cracked deposits. The composition of the deposit did not vary appreciably with time, the maximum change in composition being one per cent (Fig. 3b). The CCE remained more or less the same.

3.6. *Addition agent*

Some addition agents (Table 2) were introduced separately and singly to the bath under optimum conditions. Tetramethylammonium iodide, teepol and glycerine showed little beneficial effect, although formic acid and formamide led to a slight improvement in the quality of the alloy deposited. Quaternary ammonium salts, dimethylformamide and N-methylformamide also considerably improved the brightness and grain size of the deposit. In contrast, thiourea and thiolactic acid were found to cause deterioration in the quality of the deposits. The stability of the electrolyte was not affected by the use of the above addition agents. The deposit composition and CCE, however, remained more or less the same except in the case of the thio compounds where the CCE was lowered appreciably.
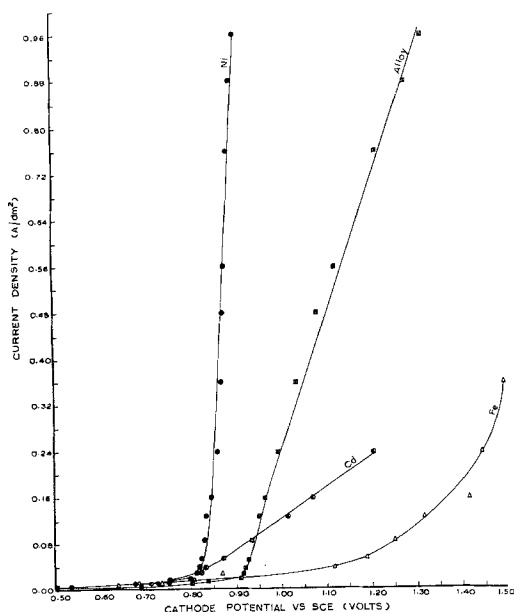
Fig. 4. Current density–cathode potential curves for the electrodeposition of the Ni–Fe–Cd alloy at pH 5·1 and temperature 35° C. For each curve optimum concentration of the respective electrolyte has been taken.

3.7. *Cathodic polarization*

Cathodic polarization curves for the different metals and the alloy are shown in Fig. 4. The deposition potential for the alloy was more than that for nickel or cadmium. The cathode potential became more negative with increasing current density.

3.8. *Structure of the deposits*

The alloy deposits obtained were shiny under most conditions tried. Deposits with a higher cadmium content were non-adherent and coarse.

Ni–Fe–Cd alloy deposits were not uniform and fine-grained like the nickel–cadmium [2] and nickel–cobalt–cadmium [4] alloys and cadmium was randomly distributed in the matrix. X-ray powder patterns of the deposits (in the as-deposited condition) showed a single phase and f c c structure and the lattice parameter for the alloys was close to that of nickel (Table 3).

The variation in the composition of the deposits with respect to different plating variables reveals that the iron and cadmium content in the deposit is always higher than in the bath and thus the deposition shows anomalous behaviour.

Acknowledgements

References

[1]   D. Singh and V. B. Singh, *Ind. J. Tech.* **13** (1975) 520.
[2]   *Idem, ibid* **14** (1976) 189.
[3]   V. B. Singh and P. K. Tikoo, *Electrochim. Acta* **22** (1977) 1201.
[4]   T. L. Ramachar and R. P. Dambal, *Plating* **59** (1972) 1145.
[5]   V. B. Singh and P. K. Tikoo, *J. Appl. Electrochem.* **8** (1978) 41.
[6]   L. Meites, 'Polarographic Techniques', 2nd Edition, Interscience Publishers, John Wiley and Sons (1965) p. 656.
[7]   A. Brenner, 'Electrodeposition of Alloys', Vol. I, Academic Press, New York (1963) p. 114.
[8]   N. V. Korovin, *Zh. Neorg. Khim.* **2** (1957) 2259.
[9]   E. Raub and W. Wittum, *Chem. Abstr.* **33** (1939) 7204.

Table 3. X-ray studies of the alloy deposits

Metal in the deposit (wt%)			Lattice	Lattice parameter	Conditions
Ni	Fe	Cd		Å (a)	
100	–	–	f c c	3·530	Ni(CH$_3$COO)$_2$ (0·5000 M), boric acid (0·3000 M), pH 5·0, current density 1·5 A dm^{-2} temperature 30° C
88·0	6·5	5·5	f c c	3·535	bath composition, pH and temperature optimum; current density 2·5 A dm^{-2}
84·4	8·8	6·8	f c c	3·536	bath composition, current density and pH optimum; temperature 20° C.