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*Electrodeposition of ternary nickel-iron-molybdenum alloys from an acetate bath**

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Ternary nickel–iron–molybdenum alloys containing 0·5–8·5% molybdenum, 18–48% iron and balance nickel were electrodeposited from an acetate bath under a variety of conditions. Satisfactory deposits were obtained from the bath containing 0·3394 M nickel acetate, 0·02878 M ferrous sulphate, 0·0015 M sodium molybdate at current density 2·0 A dm^{-2}, pH 5·0 and temperature 20°C without agitation for plating times up to 30 min. The alloy deposits were examined for their crystal structure by X-ray diffraction and microstructure by metallography.

1. Introduction

Since acetates show better buffering capacity than other simple salts, e.g. sulphates and chlorides, and since the electrodeposition of nickel–iron [1] and nickel–molybdenum alloys [2] had been successfully carried out earlier, it was of interest to extend the work to the electrodeposition of ternary nickel–iron–molybdenum alloys using an acetate bath. The present investigation deals with the electrodeposition of ternary nickel–iron–molybdenum alloys from an acetate bath under varying conditions such as concentration of electrolyte, current density, pH, temperature and duration of electrolysis.

2. Experimental

The experimental details regarding preparation of baths, deposition apparatus and structural studies have been outlined in earlier publications [1, 2]. The plating solutions contained nickel acetate, sodium molybdate, ferrous sulphate and ascorbic acid. Each experiment was conducted in fresh solution without agitation generally at 20° C. Cathode potential was measured using a saturated calomel electrode. Copper and platinum plates were employed as base metals for qualitative and quantitative electrodeposition studies respectively.

The metal contents in the deposits were determined polarographically [3] using ammonium oxalate and ammonia as supporting electrolyte and iron and molybdenum contents were subsequently confirmed spectrophotometrically [4].

3. Results and discussion

The effect of plating variables on the composition, appearance and cathode current efficiency (CCE) has been studied.

3.1. *Electrolyte concentration*

This was studied in three phases. Firstly, the ratio between the contents of two of the metals and also the total metal content in the bath were maintained constant while the content of the third metal was varied (Table 1a and b). Subsequently, keeping the ratio of all the three metals constant the total metal content in the bath was changed (Table 1c). When the concentration of iron in the bath was increased, its content in the deposits also increased appreciably but the quality of the deposits deteriorated. Higher iron content in the bath (14·5%) or its corresponding content in the deposit (42%) resulted in dark and powdery deposits. An increase in molybdenum content in the bath also considerably increased its content in the deposit (Table 1b). Bright, uniform and adherent deposits were obtained from the bath containing 0·66% molybdenum but above this concentration the deposits turned dull, cracked and

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Table 1. Effect of concentration of electrolyte on the metal content and CCE of the Ni–Fe–Mo deposit. Total metal content 21·68 g l^{-1}, Ascorbic acid 0·0056 M cd 2·0 A dm^{-2}, pH 5·0; Temperature 20° C.

% Metal in bath			*% Metal in the deposit*			*%CCE*
Ni	*Fe*	*Mo*	*Ni*	*Fe*	*Mo*	
(a) *Effect of $FeSO_4 \cdot 7H_2O$ concentration* *Total metal content (21·68 g l^{-1}) and Ni : Mo kept constant*						
94·52	4·8	0·68	73·3	23·0	3·2	68·1
91·44	7·2	0·66	66·0	30·5	3·1	66·0
89·76	9·6	0·64	62·2	33·8	3·0	63·5
84·89	14·5	0·61	54·5	42·0	2·7	51·6
(b) *Effect of $Na_2MoO_4 \cdot 2H_2O$ concentration* *Total metal content (21·68 g l^{-1}) and Ni : Fe kept constant*						
92·29	7·44	0·27	77·6	19·8	1·6	68·6
92·03	7·42	0·55	74·0	21·8	3·2	62·5
91·78	7·40	0·82	70·2	23·0	6·3	57·1
91·62	7·38	1·00	68·5	22·0	8·5	57·7
(c) *Effect of total metal content* *Ratio of all the metals kept constant*						
Concentration of electrolyte (M/l)			*% Metal in the deposit*			*%CCE*
$Ni(CH_3COO)_2$	*$FeSO_4 \cdot 7H_2O$*	*$Na_2MoO_4 \cdot 2H_2O$*	*Ni*	*Fe*	*Mo*	
0·1697	0·01439	0·0007	73·0	22·8	3·0	64·5
0·3394	0·02878	0·0015	66·0	29·5	3·7	66·3
0·6788	0·05756	0·0030	50·3	44·0	4·7	62·3

nodular. A high concentration of molybdenum (> 0·0015 M) in the bath inhibits the deposition. This may be ascribed to the fact that at high concentrations of MoO$_4^{2-}$, the cathode becomes covered with a thin insoluble film of molybdenum in some oxidation state or states intermediate between the free metal and Mo(VI) resulting in the inhibition of metal deposition. The total metal content of the bath has little effect on the appearance of the deposits, but at high concentrations the deposits obtained were not very coherent. There was an increase in the iron and molybdenum content in the deposit with total metal content (Table 1c). It can be seen from the Tables 1a and b that the contents of iron and molybdenum in the deposits are always far higher than in the bath. Cathode current efficiency decreased with an increase in either the iron or molybdenum content but remained almost constant with total metal content in the bath.

3.2. *Current density*

Using the bath of optimum composition (nickel acetate 0·3394 M, ferrous sulphate 0·02878 M, sodium molybdate 0·0015 M and ascorbic acid 0·0056 M), the effect of current density over the range 0·5 to 4·0 A dm^{-2} was studied. Deposits obtained between 1–2·0 A dm^{-2} were very bright, uniform, fine-grained and adherent. At current densities higher than 2·0 A dm^{-2} the deposits were, of course, mirror bright but were nodular and cracked with a marked tendency to peel off. The molybdenum content in the deposits decreased slightly whereas the iron content was found to decrease appreciably. The nickel content and CCE increased with current density (Fig. 1A). Such a variation of deposit composition with respect to current density has been reported by Frantsevich-Zabludovskaya *et al.* [5].

3.3. *pH*

The influence of the bath pH was studied from pH 3·5 to 6·2 under optimum conditions of composition and current density (2 A dm^{-2}). Deposits obtained below pH 5 were dull and loose, but

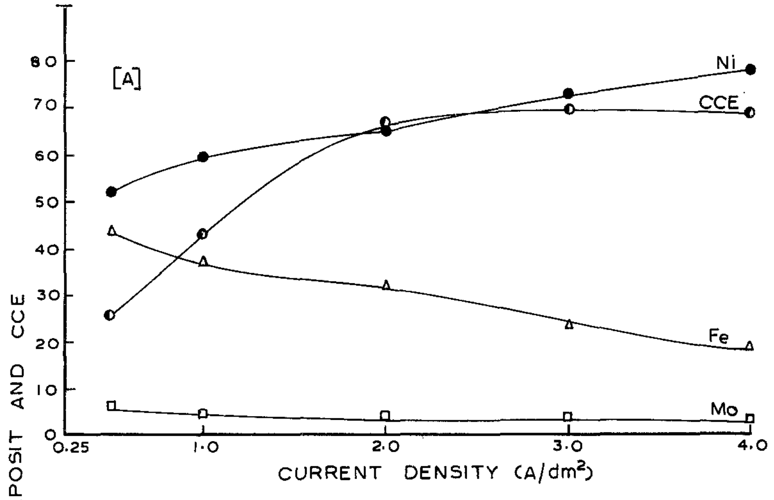

Fig. 1A. Effect of current density on the metal content and CCE of the the Ni–Fe–Mo deposits. Bath composition, temperature, pH and duration of electrolysis optimum.

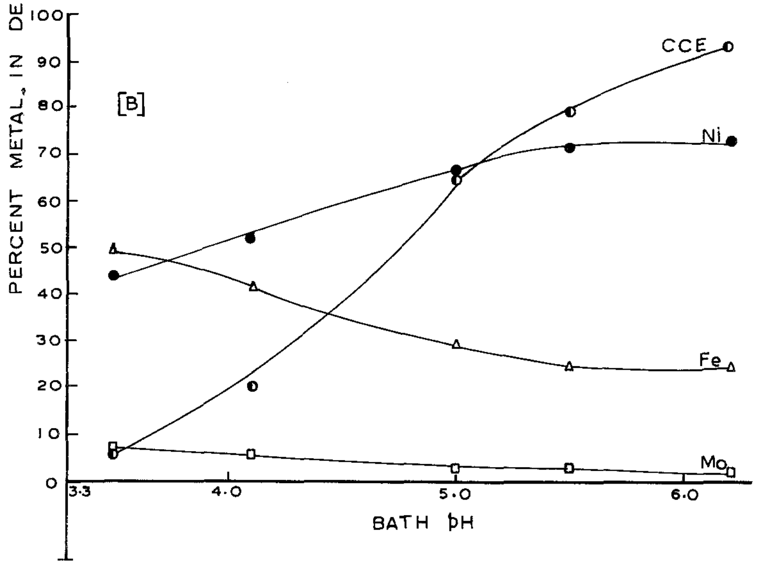

Fig. 1B. Effect of bath pH on the metal content and CCE of the Ni–Fe–Mo deposit. Bath composition, temperature, time as in Fig. 1A; at current density 2·0 A dm^{-2}.

were lustrous, uniform and adherent between pH 5–5·5. Semi-bright and nodular deposits containing some dull spots were found above pH 5·5. A decrease in the iron and molybdenum content in the deposits was noted while the nickel content and CCE were found to increase sharply with an increase in pH of the bath (Fig. 1B).

3.4. *Temperature*

With the bath at otherwise optimum conditions, the effect of temperature between 20–75° C was studied. Mirror bright, smooth, adherent and fine-grained deposits were obtained up to 40° C but above this temperature the quality of the deposits turned slightly inferior. Dark dull deposits with nonmetallic inclusions were obtained at 75° C. The molybdenum content of the deposit increased slightly but the iron and nickel contents remained more or less constant with an increase in the temperature. CCE was seen to remain constant up to 40° C but beyond this it increased considerably (Fig. 2A). The variations in composition of the deposits obtained in the present investigations with respect to pH and temperature are similar to those reported by other investigators during the electrodeposition of nickel–molybdenum alloys [2, 6].

3.5. *Duration of electrolysis*

Electrolysis was continued for 10–60 min under optimum conditions. Satisfactory deposits were obtained up to 30 min but at longer times a marked tendency for the deposits to peel off was

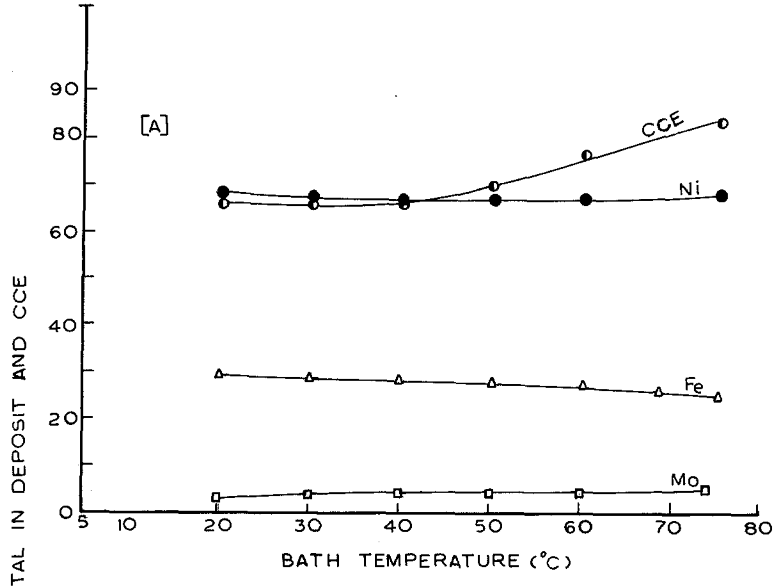

Fig. 2A. Effect of temperature on the metal content and CCE of the Ni–Fe–Mo deposit. Bath composition, c.d. and pH optimum.

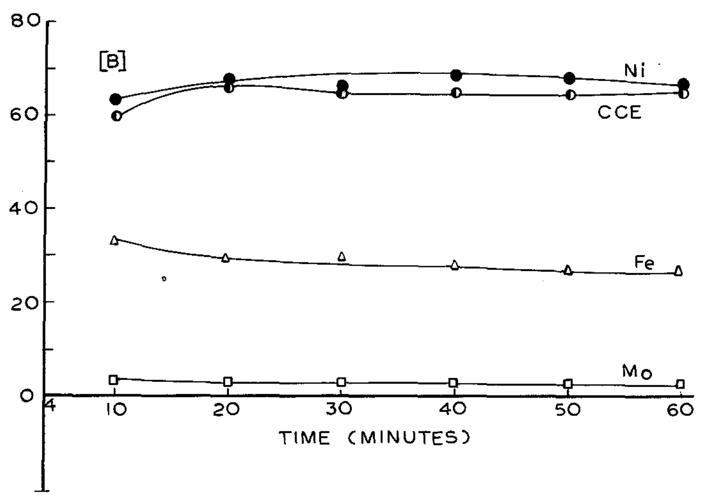

Fig. 2B. Effect of duration of electrolysis on the metal content and CCE of the Ni–Fe–Mo deposit. Conditions in Fig. 2A at 20° C.

observed. Black and cracked deposits were obtained when the duration of electrolysis was 60 min. The compositions of the deposits and the CCE remained almost the same for different periods (Fig. 2B).

3.6. *Addition agent*

Some addition agents listed in Table 2 were separately introduced into the bath. It was found that quaternary ammonium compounds improved the brightness and grain size and also suppressed the cracking of the deposits which appeared at higher current densities and after prolonged operation of the bath. Brighter and smoother deposits were obtained in the presence of Teepol, *N*-methyl-formamide and hydrogen peroxide whereas dull and unacceptable deposits were obtained when thiourea and thiolactic acid were used. The other addition agents did not show any apparent effect. The compositions of the deposits remained almost practically unchanged and CCE was also more or less the same except in the case of hydrogen peroxide, thiourea and thiolactic acid where it was lowered effectively (Table 2).

3.7. *Cathode potential*

Current density versus cathode potential studies showed that the alloy deposited initially at a more noble potential than those of the parent metals (Fig. 3). The curve obtained for molybdenum appears to result mainly from cathodic hydrogen evolution.

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

Addition agent	*Amount (Per litre)*	*% Metal in the deposit*			*% CCE*
		Ni	*Fe*	*Mo*	
Formic acid	0·2 ml	65·0	31·0	3·2	65·2
Formamide	0·3 ml	64·4	32·0	3·0	67·0
Dimethylformamide (DMF)	0·2 ml	67·4	28·5	3·5	66·5
N-methylformamide NMF	0·3 ml	67·0	29·5	2·8	69·5
Tetraethylammonium bromide (TEABr)	0·1 g	66·0	30·7	2·7	61·2
Tetraethylammonium iodide (TEAI)	0·1 g	64·0	33·0	2·5	62·4
Tetramethylammonium bromide (TMaBr)	0·2 g	64·0	31·5	3·7	67·5
Tetramethylammonium iodide (TMAI)	0·1 g	63·0	32·8	3·5	66·0
Teepol	0·3 ml	66·0	30·5	2·9	66·7
Glycerine	0·5 ml	64·7	31·5	3·1	64·5
Hydrogen peroxide	0·3 ml	64·4	31·7	2·9	55·7
Thiourea	0·1 g	65·3	31·0	2·8	39·3
Thiolactic acid	0·2 ml	67·5	28·5	3·0	32·5

Table 3. X-ray studies of the alloy deposits

Percent metal in the deposit			*Lattice*	*Lattice Parameter (Å)* (a)	*Conditions*
Ni	*Fe*	*Mo*			
100	–	–	f.c.c.	3·530	$Ni(CH_3COO)_2$ 0·5000 M, Boric acid 0·3000 M, pH5·0, cd 1·5 A dm^{-2} temperature 30° C
61·0	35·4	3·60	f.c.c.	3·532	Bath composition, pH and temp.optimum; cd 1·3 A dm^{-2}.
67·1	28·1	4·80	f.c.c.	3·560	Bath composition, pH and cd optimum; temp. 60° C.

3.8. *Structure of the deposits*

The deposits obtained were generally very bright, fine-grained and adherent. Deposits with high molybdenum contents (> 5%) were slightly cracked and also contained some nonmetallic inclusions. Deposits obtained under optimum conditions were very bright, adherent and fine-grained but showed slight dendritic growth on the surface. Uniformity of the deposits was also evidenced by electron micrographs as hardly any holes in the deposits were located.

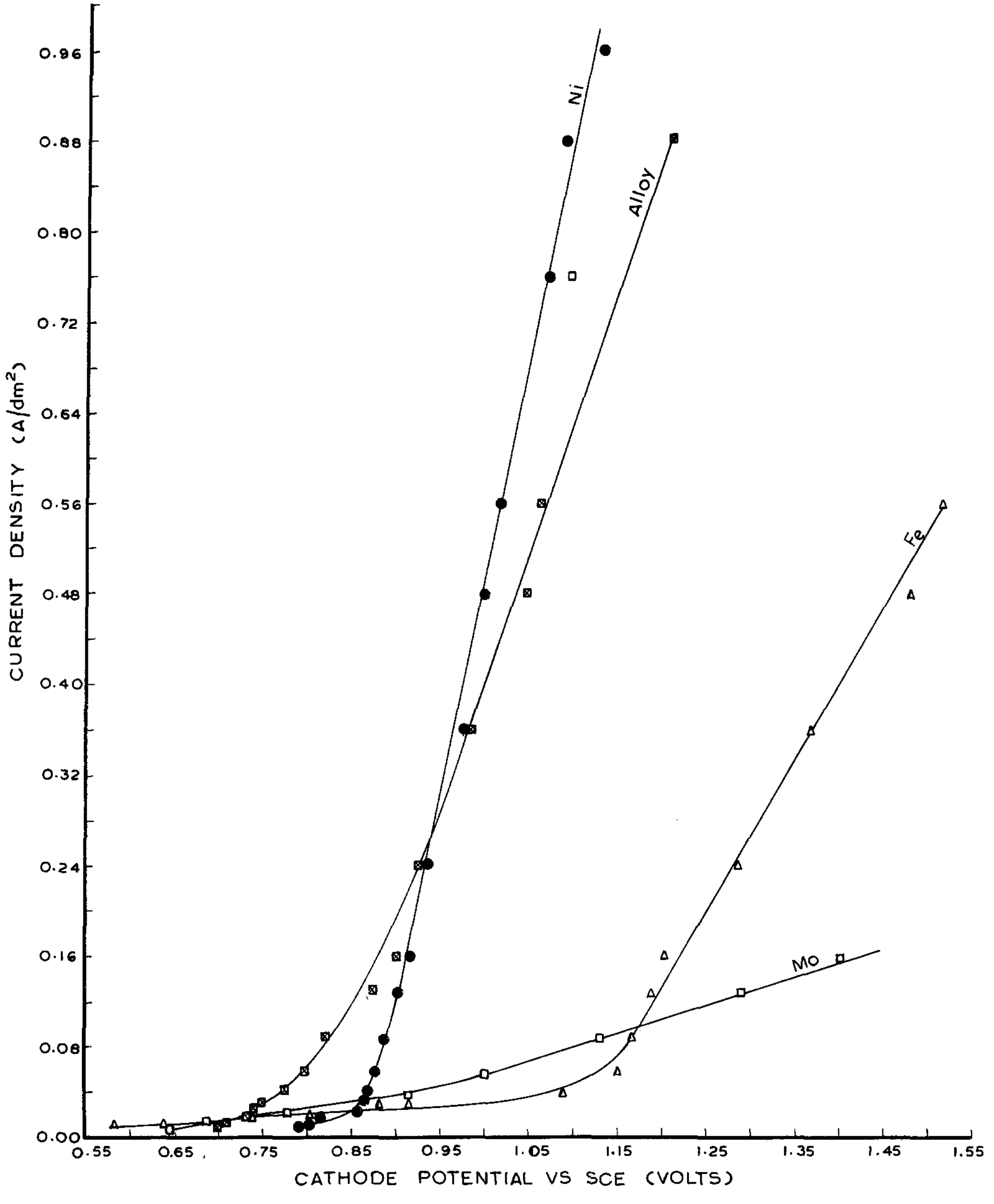

Fig. 3. Current density–cathode potential curves for the electrodeposition of Ni–Fe–Mo alloy at pH 5·0 and temperature 20° C. For each curve the optimum concentration of respective electrolyte has been taken.

The microstructure of the alloy deposits (after deposition) was further confirmed by X-ray diffraction which showed the presence of only a single phase. The alloy was a solid solution with f.c.c. structure and the lattice parameter was slightly higher than that of Ni (Table 3). Frantsevich-Zabludovskaya *et al.* [5] also reported the formation of a solid solution of iron and molybdenum in nickel.

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