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*Electroplating of Fe–Ni alloys: a sulphate–amine bath**

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Thin films of Fe–Ni alloys have been electroplated from acidic sulphate bath (0.06 mol dm^{-3} $NiSO_4$, 0.015 mol dm^{-3} $FeSO_4$, 0.005 mol dm^{-3} ascorbic acid, 20 g dm^{-3} boric acid and 1 g dm^{-3} saccharin) containing aliphatic amines. The percentage Ni in the alloy varied with bath composition (Fe/Ni), current density, stirring of the medium, nature and concentration of the amine. Increase of temperature and pH of the medium increased the percentage Ni in the deposit. The composition of the alloy remained constant with thickness of the film. The cathodic current efficiency depends on the plating variables. The plating potential in acidic sulphate bath was shifted in the less noble direction by the presence of amines. Smooth and bright films are obtained with small grain size when the Ni in the film is 75% or above. Electroplating conditions are optimized to get thin, magnetic 20:80 Fe–Ni films.

1. Introduction

In recent years, the study of the electrolytic preparation and properties of Fe–Ni alloys has become a subject of practical importance because of their extensive applications in the micro-electronic [1] and metal finishing [2, 3] industries. A review on the electroplating of binary magnetic alloys from our laboratory should be noted [4]. Electroplating techniques have the unique advantage of producing alloy films of varying magnetic properties by manipulating the plating conditions [5]. In micro-electronic applications, proper functioning of the magnetic films require uniform magnetic properties over the entire wafer surface which in turn is critically related to the compositions of the films [6].

In recent years there has been a trend towards bath solutions containing lower concentration of electrolytes operating at low temperatures. Thin films of 20:80 Fe–Ni magnetic alloys have been electroplated from acidic and alkaline complex baths by using pulse current [7] and also by superimposing alternating current on direct current [8–10]. Triethanolamine [11] has been used as a complexing agent during the electroplating of Ni–Co alloys from an alkaline bath. A review of the literature, however, reveals the absence of comprehensive studies of the electroplating of thin films of Fe–Ni permalloy using amines as complexing agents. The present communication deals with the effect of aliphatic amines on the electroplating of thin films of Fe–Ni alloys from acid sulphate bath.

2. Experimental procedure

The solutions were prepared using distilled water and reagent grade chemicals. All experiments were carried out at 50° C and pH 4.8 to a constant thickness, 0.4 μm, under unstirred conditions with a molar ratio of Fe/Ni in the bath solution of 20/80. The bath had the composition 0.015 mol dm^{-3} $FeSO_4$, 0.06 mol dm^{-3} $NiSO_4$, 0.005 mol dm^{-3} ascorbic acid, 20 g dm^{-3} boric acid, 1 g dm^{-3} saccharin and amines 0.03–0.30 mol dm^{-3}.

Freshly prepared copper coated platinum foil (2 cm × 2 cm) and cylindrical platinum foil were used as cathode and auxiliary electrode respectively. Deposition potentials were recorded with reference to the saturated colomel electrode using a Systronics digital multimeter (Model 435). The surfaces of the electroplated Fe–Ni alloys were observed under a metallurgical microscope of high

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Table 1. Effect of bath composition on the composition of Fe–Ni alloys in the presence of amines. Temperature, 50° C; pH, 4.8; Current density, 0.5 A dm^{-2}; amine concentration 0.15 mol dm^{-3}.

*Bath composition** (% Ni)	*Percentage Ni in the deposit*					
	None	*EA*	*DEA*	*TEA*	*BA*	*EDA*
60	48	50	52	50	43	65
70	50	69	65	63	59	80
80	59	80	74	73	67	87
90	72	85	78	80	80	94
95	80	94	95	90	88	98

* Boric acid concentration 20 g dm^{-3}, saccharin 1 g dm^{-3}, ascorbic acid concentration 0.005 mol dm^{-3}; layer thickness = 0.4 μm.

resolution. After each experiment, the alloy was stripped in an HNO_3 solution (1 : 4). The composition of the alloy was obtained by analysing the solution using an atomic absorption spectrometer. The detailed experimental procedure has been given elsewhere [12].

3. Results

3.1. *Effect of plating variables*

A series of experiments were carried out to study the effect of plating variables namely; metals ratio in the bath, pH, temperature, current density, agitation of the bath and addition agents (amines) on the composition of the Fe–Ni alloys. In all these experiments, proper care was taken to maintain constant pH by using a boric acid buffer. Saccharin was used to minimise the stress in the deposit. Ascorbic acid was also added to the bath solution to prevent any precipitation and subsequent incorporation of ferric hydroxide into the deposit.

Fe–Ni alloys were electroplated at 0.5 A dm^{-2} to a constant thickness (0.8 μm) at 50° C and pH 4.8 from acid sulphate bath of various metals ratio with and without different amines (ethylamine-EA, diethylamine-DEA, triethylamine-TEA, butylamine-BA and ethylene diamine-EDA) of known concentration (0.15 mol dm^{-3}). Under these plating conditions and in the absence of amines, iron was more readily deposited than nickel. However, in the presence of amines, the extent of preferential deposition of iron was reduced considerably. Table 1 gives the values of the percentage of Ni both in the bath and in the deposit with and without known amounts of various amines. Fe–Ni alloy containing 48% Ni, electroplated from the bath solution containing 60% Ni was increased to 65% by the presence of 0.15 mol dm^{-3} EDA. The extent of the increase of the percentage of Ni in the deposit by the presence of a specific amount of various amines at constant pH and temperature was in the order

$$\text{EDA} > \text{EA} \approx \text{DEA} \approx \text{TEA} > \text{BA}$$

In order to know the influence of current density on the composition of the Fe–Ni alloys, the plating experiments were carried out at various current densities (0.05–2.0 A dm^{-2}) using bath solution containing constant molar ratio of Fe/Ni (20/80) and 0.15 mol dm^{-3} various amines at 50° C. The variation in the composition of the alloy was very small at the range of current densities studied. The proportion of nickel in the alloy deposited from a bath solution containing EDA, increased slightly with an increase of the current density (Fig. 1). Similar variation was observed with other amines.

Fe–Ni alloys were also electroplated from bath solutions containing amines with different pH and temperatures to study their effects on the composition of alloys. The amount of nickel in the deposit was slightly enhanced either with increase of pH or temperature of the bath solution. The values of the percentage of Ni in the deposit at various pH and temperatures are given in Table 2.

In order to obtain further information concerning the part played by diffusion of the electrolyte

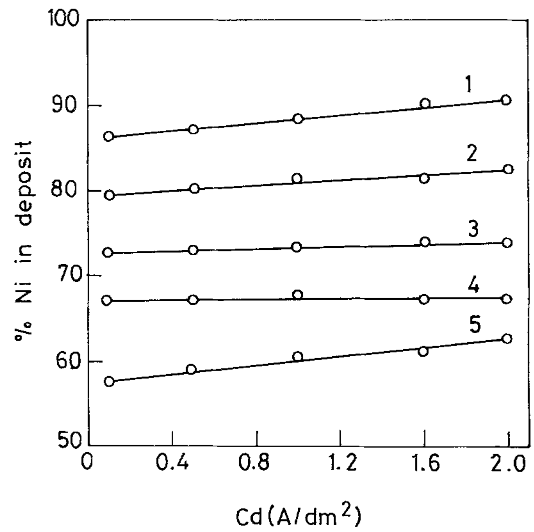

Fig. 1. Effect of current density on percentage Ni in deposit at 50° C and pH 4.8. 1, EDA; 2, EA; 3, TEA; 4, BA and 5, no amine. Bath: 0.06 mol dm^{-3} NiSO$_4$, 0.015 mol dm^{-3} FeSO$_4$, 0.005 mol dm^{-3} ascorbic acid, 20 g dm^{-3} boric acid, 1 g dm^{-3} saccharin and 0.15 mol dm^{-3} amine.

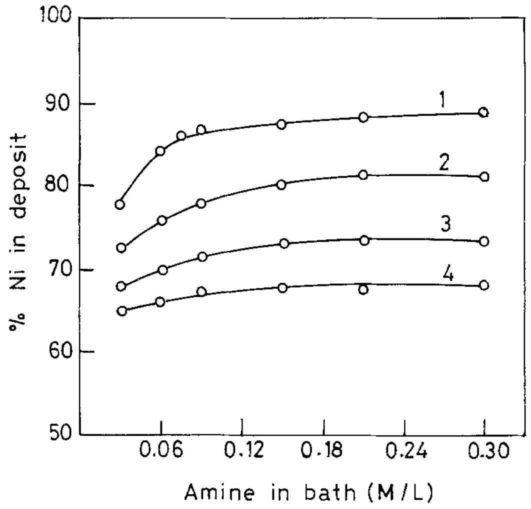

Fig. 2. Dependence of percentage Ni in the deposit on amine concentration at 50° C and pH 4.8. 1, EDA; 2, EA; 3, TEA and 4, BA. Bath: 0.06 mol dm^{-3} NiSO$_4$, 0.015 mol dm^{-3} FeSO$_4$, 0.005 mol dm^{-3} ascorbic acid, 20 g dm^{-3} boric acid, and 1 g dm^{-3} saccharin.

in determining the composition of the Fe–Ni alloy, some experiments were carried out under stirred conditions. The effect of agitation of the bath on the composition of electroplated Fe–Ni alloys appeared to be significant at a given current density, pH, temperature and the concentration of amine. The percentage Ni in Fe–Ni alloy, electroplated at 0.5 A dm^{-2} from the bath solution containing 0.15 mol dm^{-3} EA under unstirred condition was decreased from 80% to 48% by just agitating the bath solution. Under the stirred condition, the composition of Fe–Ni alloys electroplated in the presence of various amines attained nearly the same composition (Table 3) except in the case of EDA.

Experiments were conducted at 0.5 A dm^{-2} in the presence of various amines with different concentrations (0.03–0.3 mol dm^{-3}) at 50° C. Figure 2 illustrates the dependence of the nickel content of the alloy on the amine concentration. The amount of nickel in the deposit increased slightly with increase of the amine concentration and finally attained the limiting value at the higher concentration range. The trend in the variation of the amount of nickel in the deposit with amine concentration was the same for all the

Table 2. Effect of temperature and pH on the amount of nickel (%) (bath composition and operating conditions as Table 1).

Amines	*Percentage Ni*						
	*pH**			*Temperature*†			
	3.0	4.8	6.0	30° C	40° C	50° C	60° C
EA	74	80	88	73	76	80	85
DEA	69	74	81	69	72	74	80
TEA	67	73	78	68	70	73	74
BA	58	67	74	62	65	67	71
EDA	75	87	96	75	80	87	92

* Temperature, 50° C.
† pH, 4.8
concentration, 0.15 mol dm^{-3}

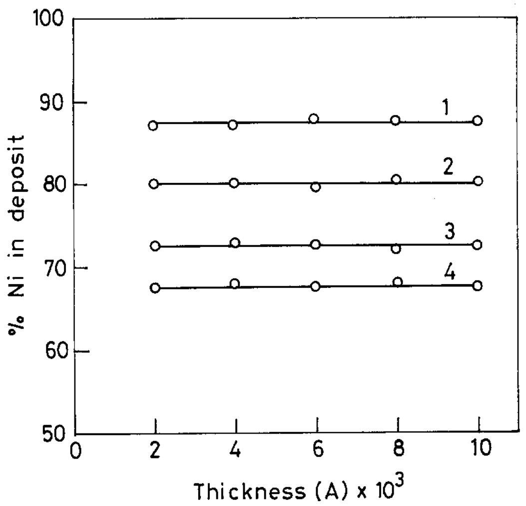

Fig. 3. Amount (%) of Ni in deposit as a function of film thickness at 50° C. 1, EDA; 2, EA; 3, TEA and 4, BA. Bath: 0.06 mol dm^{-3} $NiSO_4$, 0.015 mol dm^{-3} $FeSO_4$, 0.005 mol dm^{-3} ascrobic acid, 20 g dm^{-3} boric acid and 1 g dm^{-3} saccharin.

amines but the effect being more pronounced with EDA and EA.

The distribution of the composition across the thickness of Fe–Ni alloys affects its magnetic properties. Therefore to know the dependence of the composition of Fe–Ni alloys on thickness, alloys were electroplated to various thickness (0.2–1.0 μm) at 0.5 A dm^{-2} and temperature 50° C with pH 4.8. Figure 3 shows the variation of % nickel content of the deposit with thickness of the deposit. The composition of the alloy was almost constant throughout its thickness.

3.2. *Cathodic current efficiency*

Cathodic current efficiency was calculated for each experiment. The value of the current efficiency during the deposition of the Fe–Ni alloys varied with the plating conditions. The value at various current densities in the presence of amines and also under stirred conditions at representative pH and temperature are given in Table 4. The values of current efficiency for different amines were in the order

$$\mathrm{EDA} > \mathrm{BA} \approx \mathrm{TEA} \approx \mathrm{DEA} > \mathrm{EA}$$

At a given current density and in the presence of known concentration of amine, the current efficiency was increased with increase of pH or temperature of the bath solution. The stirring of the medium decreased the efficiency considerably. For a given amine, the current efficiency increased with increase of current density up to a certain value (0.5 A dm^{-2}) and then decreased on further increase of current density.

3.3. *Deposition potential*

Plating potentials were recorded at different time intervals during the electroplating of Fe–Ni alloys both in the presence and absence of amines at 50° C and pH 4.8 with various current densities. In the absence of amines, at each current density, the plating potential increased slightly with time and then attained a steady value. Similar results were also obtained in the presence of various amines. However, the steady potentials varied significantly with current density. Figure 4 shows the variation of steady plating potentials with current density with and without 0.15 mol dm^{-3} amines at 50° C and pH 4.8. At each current density, the plating steady potential (V_0) in the absence of amine drifted in a less noble direction in the presence of amines. In the lower current density range, the steady plating potential in the presence of amines was in the order:

$$V_0 > V_{\mathrm{EDA}} > V_{\mathrm{EA}} > V_{\mathrm{TEA}} \approx V_{\mathrm{DEA}} \approx V_{\mathrm{BA}}$$

and this order changed to;

$$V_{\mathrm{EDA}} > V_0 > V_{\mathrm{EA}} > V_{\mathrm{TEA}} \approx V_{\mathrm{DEA}} \approx V_{\mathrm{BA}}$$

Table 3. Composition of alloy with stirring and without stirring at 50° C (bath composition and operating conditions as Table 1). Plating potentials are given in parenthesis (mV).

Condition	*Percentage Ni*				
	EA	*DEA*	*TEA*	*BA*	*EDA*
Without stirring	80 (−710)	74	73 (−740)	67	87 (−645)
With stirring	48 (−695)	50	49 (−690)	52	77 (−710)

Table 4. Cathodic current efficiency at 50° C and pH 4.8.

Current density (A dm^{-2})	*Cathodic current efficiency*				
	EA	*DEA*	*TEA*	*BA*	*EDA*
0.05	65	71	73	79	82
0.1	74	76	79	84	89
0.5	93 (78)	94 (80)	94 (76)	96 (81)	100 (88)
0.5*	78	75	76	74	81
1.0	78	83	85	88	93
1.0†	66	71	74	77	83
2.0	72	76	79	83	88

* Stirring, values at pH 3 are given in parenthesis.
† Values at 30° C.

when the current density was increased above 0.625 A dm^{-2}.

3.4. *Surface topography*

The surface of the Fe–Ni alloy was observed under a metallurgical microscope after each experiment. At each current density and in the presence of various amines, the deposit appeared bright and uniform when the nickel content of the deposit was at or above 75%. The grain size of the deposit increased gradually either with increase of temperature or thickness of the deposit. However, the increase of current density decreased the grain size of the deposit.

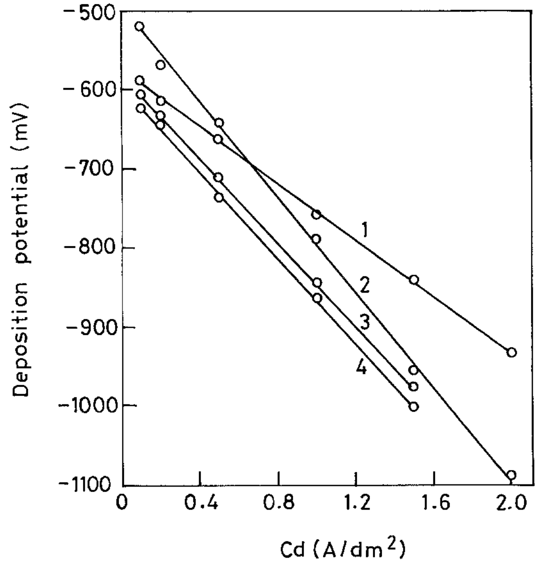

Fig. 4. Deposition potential as a function of current density at 50° C and pH 4.8. 1, EDA; 2, no amine; 3, EA and 4, TEA. Bath: 0.06 mol dm^{-3} $NiSO_4$, 0.015 mol dm^{-3} $FeSO_4$, 0.005 mol dm^{-3} ascorbic acid, 20 g dm^{-3} boric acid and 1 g dm^{-3} saccharin.

4. Discussion

Electroplating of Fe–Ni alloys exhibits the phenomenon of anomalous co-deposition [13]. The less noble metal Fe deposits in preference to the more noble metal Ni. Usually the plating of Fe–Ni alloys proceeds with simultaneous Ni^{2+} ion discharge under activation control and Fe^{2+} and H^+ ions discharge under mass transport control. The H_2 evolution during alloy plating brings about a rise in local pH around the electrode and this increases the formation of ferrous or ferric hydroxide which retards the discharge of Ni^{2+} ions. Some addition agents are used to minimize the precipitation of these hydroxides [14]. Buffers are used in the bath solution to avoid a pH rise [15, 16]. However, the use of buffer does not eliminate completely anomalous co-deposition [6].

During plating of alloys from complex baths, the composition of the alloy depends on the stability of the complex or relative stability of the complexes which is a function of many plating variables. Amines form complexes with metal ions [17]. The nitrogen atom of amines possesses a pair of electrons which coordinate with a proton or any Lewis acid. The co-ordination capacity of nitrogen decreases from primary amine to secondary amine to tertiary amine.

In order to understand the complex nature of the bath solutions, complexes were isolated from the typical bath solutions. Spectral data of the complexes revealed the preferential complexing of Ni^{2+} ions with amines [18, 19]. It is known that in some cases the complexing agent is incorporated into the deposit and affects the magnetic properties of the deposit [7]. To ensure this possibility some plated alloys were dissolved in dilute HNO_3 and the solutions were subjected to spectral analysis. These results indicated the absence of amines in the alloys.

Electroplating of Fe–Ni alloys from the bath solution under investigation in the absence of amines shows the characteristics of anomalous co-deposition (Table 1), the extent of which is decreased considerably in the presence of amines by preferential complexation with Ni^{2+} ions. This is supported by the spectral data and also by the enhancement of percentage Ni in the deposit with increase of amine concentration (Fig. 2).

Since the phenomenon of anomalous co-deposition is unusual, it is not surprising that the relation between alloy composition and current density is also unusual. The type of variation of the composition of Fe–Ni alloy with the current density mostly depends on the range of current density employed and the nature of the plating bath. Deposition of the alloy at moderate current densities results in an impoverishment, of mainly Fe^{2+} ion, of the cathode diffusion layer, and causes the deposition to come under diffusion control. This is the reason that most of the curves in Fig. 1 show a slight decrease in Fe content of the alloy with current density [20].

The effect of temperature on the composition of the alloy during anomalous co-deposition (Table 2) could be explained by considering two opposing influences – polarization and diffusion, the relative effects of which is related to the nature of the plating system and the bath. On raising the temperature, there may be a reduction in the large polarization required for Ni^{2+} reduction which subsequently enhances the rate of deposition of this metal. Temperature may also affect the composition of the alloy indirectly through its effect on the cathode current efficiency. It is known that an increase in temperature increases the cathode current efficiency of preferentially complexing metal ions [21]. Hence an increase of temperature increases the amount of Ni in the deposit.

In the literature, there are no specific effects of pH on the alloy plating system. Amines being nitrogen bases undergo protonation in aqueous acidic solution, the rate of which decreases with increase of pH. The capacity of amines to form complexes increases with increase of pH. Hence one could expect the increase of both complexing of amines and rate of deposition of Ni^{2+} ions with increase of pH. This is in accordance with the observed results (Table 2) and also noticed previously in a similar system [22].

Agitation of the bath solution increases the concentration of the metal ions which are preferentially depositing in the cathodic diffusion layer. A significant increase of the amount of Fe in the deposit by agitation of the bath solution (Table 3) clearly indicates that the plating system is of the diffusion controlled anomalous type, similar to that generally observed for the deposition of Co–Ni alloys [23].

The current density potential curves for the mutual co-deposition of Fe group metals have some points of interest, but do not contribute very much to an understanding of the cause of anomalous co-deposition. The trend in variation of plating potential with current density depends on many factors [24, 25]. The shift of the plating potential in the less noble direction due to the presence of amines probably indicates the complexing of amines with one of the metals ions in the bath solution [26].

Table 5. Magnetic properties of 80:20 Ni–Fe alloys under different plating conditions.

*Bath solution**	*Magnetic properties*	
	Hk (oe)	*He* (oe)
$NiSO_4$ (0.06 mol dm^{-3}) $FeSO_4$ (0.015 mol dm^{-3}) EA (0.15 mol dm^{-3})	4.0 (4.2†)	1.8 (5.1†)
$NiSO_4$ (0.0675 mol dm^{-3}) $FeSO_4$ (0.0075 mol dm^{-3}) TEA (0.15 mol dm^{-3})	3.8 (3.9‡)	2.1 (2.2‡)
$NiSO_4$ (0.0525 mol dm^{-3}) $FeSO_4$ (0.0225 mol dm^{-3}) EDA (0.15 mol dm^{-3})	4.2 (10.2§)	1.9 (7.8§)

* At 50° C and pH 4.8, current density, 0.5 A dm^{-2}, thickness, 0.4 μm; boric acid 20 g dm^{-3}, saccharin 1 g dm^{-3}, ascorbic acid 0.005 mol dm^{-3}.
† At 0.1 μm.
‡ 0.3 mol dm^{-3} TEA.
§ pH 6.0.

Table 6. Optimum experimental conditions to electroplate 80:20 Ni–Fe alloy

Amines	*Bath solution**		*pH*	*Temperature*
EA	0.06 mol dm^{-3} 0.015 mol dm^{-3} 0.15 mol dm^{-3}	$NiSO_4$ $FeSO_4$ Amine	4.8	50° C
DEA	0.06 mol dm^{-3} 0.015 mol dm^{-3} 0.15 mol dm^{-3}	$NiSO_4$ $FeSO_4$ Amine	6.0 4.8	50° C 60° C
TEA and BA	0.0675 mol dm^{-3} 0.0075 mol dm^{-3} 0.15 mol dm^{-3}	$NiSO_4$ $FeSO_4$ Amine	4.8	50° C
	0.0545 mol dm^{-3} 0.0225 mol dm^{-3} 0.15 mol dm^{-3}	$NiSO_4$ $FeSO_4$ Amine	4.8	50° C
EDA	0.06 mol dm^{-3} 0.015 mol dm^{-3} 0.15 mol dm^{-3}	$NiSO_4$ $FeSO_4$ Amine	4.8	40° C
	0.06 mol dm^{-3} 0.15 mol dm^{-3} 0.04 mol dm^{-3}	$NiSO_4$ $FeSO_4$ Amine	4.8	50° C

* Boric acid, 20 g dm^{-3}; saccharin, 1 g dm^{-3}; ascorbic acid, 0.005 mol dm^{-3}; current density, 0.5 A dm^{-2}.

The decrease of current efficiency at higher current densities and at lower pH (Table 4) may be due to the increase of rate of evolution of hydrogen during alloy plating. The constancy of the percentage of Ni in the deposit with variation in the thickness (Fig. 3) is suggestive of a steady rate of deposition of Fe and Ni from the bath solution. The magnetic properties (Hk and He) of a few typical Fe–Ni alloys were measured and these properties (Table 5) were found to depend similarly on pH, temperature, current density, Fe^{2+} ions content in the bath, amine concentrations and thickness of the deposit as noticed earlier with a similar system [7]. From the present results obtained, one could optimize the experimental conditions (Table 6) to get thin films of 20:80 Fe–Ni magnetic alloys.

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