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Electroplating of Fe–Ni alloys: effects of sulphamic acid and sulphosalicylic acid

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The electroplating of thin films of Fe–Ni alloys from acidic sulphate baths containing sulphamic acid and sulphosalicyclic acid has been studied under different plating conditions. The alloy composition varied with bath composition, current density and the concentrations of sulphosalicylic acid and sulphamic acid. Stirring of the bath solution enhanced the percentage of Fe in the alloy. The deposition potential became less noble with increase in the current density. Under some plating conditions, the plating system had a cathodic current efficiency greater than 90%. The coercivity values of the alloys were in the range 5–18 oersteds. From the X-ray analysis data fcc structure is assigned to the alloy films. Electroplating conditions have been optimized in order to obtain thin films of 20–80 Fe–Ni permalloy.

1. Introduction

Thin films of magnetic alloys find extensive applications in the microelectronic industries [1, 2]. Electroplating has the unique advantage of producing alloy films of varying magnetic properties by manipulating the plating conditions [3]. Recent developments on the electroplating and properties of binary magnetic alloys have been summarized [4].

In recent years there has been a trend towards bath solutions containing a lower concentration of electrolytes operating at low temperature. Sulphur-containing organic compounds have been used widely as additives or as complexing agents in order to produce electrodeposits with desired properties. Sulphamic acid (SA) [5] and sulphosalicylic acid (SSA) [6] have been used in the electroplating bath for Fe–Ni alloys. Thin films of 20–80 Fe–Ni magnetic alloy have been electroplated from an acidic sulphate bath containing amines [7], thioglycollic acid and mercaptoethanol [8].

A review of literature [4] reveals a lack of comprehensive work on the electroplating of thin films of Fe–Ni permalloy from sulphate baths containing organic sulphur compounds. The present communication deals with results pertaining to the effects of SA and SSA on the electroplating of thin films of Fe–Ni alloys from acid sulphate baths.

2. Experimental procedure

The solutions were prepared using distilled water and reagent grade chemicals. All experiments were carried out at 30° C and pH 4.8 to a constant thickness (0.4 μm) under unstirred conditions. The plating bath solution had the composition: $FeSO_4 + NiSO_4 = 0.1$ M, (50–90% Ni), boric acid 20 g l^{-1}, ascorbic acid 0.01 M, SA 0.3 M, SSA 0.24 M.

Experiments were performed in a three-compartment cell. Freshly prepared copper coated platinum foil (2 × 2 cm) and cylindrical platinum foil were used as cathode and auxiliary electrode respectively. Deposition potentials were recorded with reference to the saturated

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calomel electrode using a digital multimeter. A 90 V battery in series with a resistor was used as the source of direct current. The surface of the electroplated alloy was observed under a metallurgical microscope.

After each experiment the alloy was dissolved in dilute HNO_3 (1 : 4) and the composition of the alloy was obtained by atomic absorption spectrometry. The coercivity of each sample was measured. The samples were subjected to X-ray diffraction analysis and the structure and lattice parameters were elucidated.

3. Results

Fe–Ni alloys were electroplated at various current densities (0.1–1 A dm^{-2}) from acid sulphate baths with different amounts of nickel (50–90%) and in the presence of known concentrations of SSA and SA. Tables 1 and 2 give the alloy composition at various bath compositions at current densities 0.1, 0.5 and 1.0 A dm^{-2} in the presence of SA and SSA respectively. In the presence of SSA (0.24 M) at a current density of 1 A dm^{-2}, the amount of Ni in the alloy varied from 45 to 85% for a variation in the bath composition of 50 to 90% nickel. Similar results were also obtained in the presence of SA (0.3 M). In most cases the percentage of nickel in the alloy was slightly lower than the percentage of nickel in the bath solution.

The nickel content of the deposit increased with increase in the current density in the presence of SA and SSA. Electroplating from a bath solution containing 90% Ni and 0.24 M SSA showed an initial increase in the nickel content in the deposit with increase in the current density, followed by a constant composition after a certain current density. Electroplating from a bath solution containing 0.3 M SA and $\leqslant$80% nickel showed an initial decrease and then an increase in the nickel content of the alloy with increase in the current density. This trend was predominent when the nickel content in the bath solution was at or above 70%. The electroplating from a bath solution containing 90% nickel and 0.3 M SA resulted in an enhancement of the amount of nickel in the deposit with increase in the current density.

To study the effect of pH on alloy composition, Fe–Ni alloys were electroplated from a bath solution of different pH values (3–6) with a fixed ratio of iron to nickel at constant temperature and in the presence of known concentrations of SA and SSA. The percentage of nickel in the deposit decreased with increase in pH of the bath solution (Table 3).

Electroplating experiments were carried out at different temperatures (30–50° C) keeping the other plating conditions constant. In the presence of SSA (0.24 M), there was no significant change in the alloy composition with increase in temperature. The percentage of nickel in the deposit increased from 48 to 61% when the temperature was raised from 30 to 50° C in a bath solution containing 0.3 M SA. The variation of alloy composition with temperature in the presence of SA and SSA is shown in Table 3.

Experiments were performed at different concentrations of SA and SSA at representative plating conditions. There was a slight decrease in the nickel content of the alloy with increase in the concentration of either SA or SSA. Fe–Ni

Table 1. Dependence of alloy composition on bath composition and current density*

Bath composition (% Ni)	% Ni in the alloy			
	0.1 (A dm^{-2})	0.5 (A dm^{-2})	0.5 (A dm^{-2})†	1.0 (A dm^{-2})
50	51 (−840)	30 (−950)	39 (−1020)	39 (−1020)
70	65 (−820)	48 (−910)	52 (−990)	62 (−1010)
80	67 (−810)	64 (−925)	66 (−970)	76 (−1015)
90	77 (−820)	81 (−930)	78 (−1000)	92 (−1025)

* $NiSO_4 + FeSO_4 = 0.1$ M, boric acid 20 g l^{-1}, ascorbic acid 0.01 M, SA 0.3 M, pH 4.8, T 30° C, thickness 0.4 μm.
† Absence of SA.
Plating potentials are given in parenthesis (mV).

Table 2. Dependence of alloy composition on bath composition and current density*

Bath composition (% Ni)	% Ni in the alloy			
	0.1 ($A\,dm^{-2}$)	0.5 ($A\,dm^{-2}$)	0.5 ($A\,dm^{-2}$)†	1.0 ($A\,dm^{-2}$)
50	29 (−920)	28 (−1010)	39 (−1020)	45 (−1125)
70	41 (−910)	46 (−980)	52 (−990)	57 (−1080)
80	61 (−870)	59 (−950)	66 (−970)	74 (−1080)
90	63 (−880)	82 (−1010)	78 (−1000)	83 (−1110)

* $NiSO_4 + FeSO_4 = 0.1$ M, boric acid 20 g l^{-1}, ascorbic acid 0.01 M, SA 0.24 M, pH 4.8, T 30° C, thickness 0.4 μm.
† Absence of SSA.
Plating potentials are given in parenthesis (mV).

alloys were electroplated to different thickness values (0.2–1 μm) from a bath solution containing a fixed ratio of iron to nickel and constant concentrations of SA and SSA. The percentage of nickel in the alloy decreased and attained a constant value with increase in thickness in the presence of 0.3 M SA. The extent of decrease in the nickel content with increase in thickness was lower in the presence of SSA than with SA. The variation of alloy composition across the thickness is shown in Fig. 1.

Some experiments were carried out under stirred conditions in order to obtain information concerning the part played by diffusion in the electrolyte on the alloy composition. The values of alloy composition obtained both under stirred and unstirred conditions are given in Table 4. Stirring of the bath solution decreased the nickel content of the alloy, the effect being considerable with SSA.

Under most plating conditions, the deposition potential drifted towards less noble values and attained a steady value with time. At different bath compositions both in the presence of SA and SSA, the deposition potential shifted towards less noble values with an increase in current density (Tables 1 and 2). At a given current density and bath composition, the steady deposition potential shifted towards more noble values on increasing the concentration of SA or SSA or the temperature of bath solution. The deposition potential in the presence of both SA and SSA became less noble with stirring of the bath solution (Table 4) or with increase in the pH of the bath solution.

The cathodic current efficiency was calculated for electroplating of Fe–Ni alloy under each set

Table 3. Effects of temperature and pH on alloy composition

Sulphur compound	% Ni in the alloy					
	pH*			Temperature† (° C)		
	3.0	4.8	6.0	30	40	50
SSA	59.9	46.0	44.6	46.0	47.0	47.5
SA	67.3	48.0	48.5	48.0	48.0	61.0

* Temperature 30° C.
† pH = 4.8.
Bath: $NiSO_4$ 0.07 M, $FeSO_4$ 0.03 M, boric acid 20 g l^{-1}, ascorbic acid 0.01 M, SSA 0.24 M, SA 0.3 M, current density 0.5 A dm^{-2}, thickness 0.4 μm.

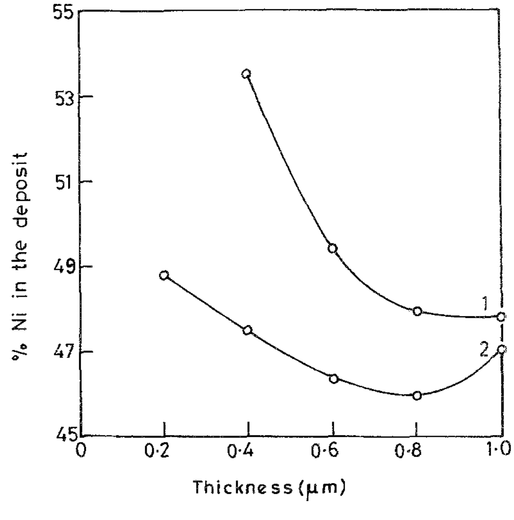

Fig. 1. Amount (%) of Ni in the deposit as a function of film thickness at 30° C. Bath: $NiSO_4$ 0.07 M, $FeSO_4$ 0.03 M, boric acid 20 g l^{-1}, ascorbic acid 0.01 M, pH 4.8, current density 0.5 A dm^{-2}. (1) 0.3 M SA; (2) 0.2 M SSA.

Table 4. Composition of the alloy with and without stirring at 30° C

Condition	*% Ni in the alloy*	
	SSA	*SA*
Without stirring	46.0 (−990)	48.0 (−930)
With stirring	29.9 (−1040)	37.1 (−970)

Bath: $NiSO_4$ 0.07 M, $FeSO_4$ 0.03 M, boric acid 20 g l^{-1}, ascorbic acid 0.01 M, SSA 0.24 M, SA 0.3 M, current density 0.5 A dm^{-2}, pH = 4.8.
Plating potentials are given in parenthesis (mV).

of experimental conditions. The values of cathodic current efficiency at representative plating conditions are given in Table 5. The cathodic current efficiency (percentage) decreased with decrease in current density and with stirring. In the presence of SSA, the elevation of pH of the bath solution resulted in an increase of cathodic current efficiency. However, the reverse trend in the effect of pH on cathodic current efficiency was noticed in the presence of SA.

X-ray diffraction patterns of a few electroplated Fe–Ni alloys were taken and lattice parameters for each alloy were calculated. The X-ray data revealed the true solid solution nature of the alloys with fcc structure (Table 6). Some favourable experimental conditions to obtain Fe–Ni alloys of composition 78–80% Ni are tabulated in Table 7. Coercivity is one of the important magnetic properties in the application of ferromagnetic materials. The desirable magnetic properties of films for memory units are low coercive force and a square hysteresis loop. A low coercive force indicates that a metal is easily magnetized and demagnetized. The coercivity, in oersteds, of the alloys electroplated under different plating conditions are given in Table 8.

Table 5. Cathodic current efficiency at 30° C and pH 4.8

Current density ($A\,dm^{-2}$)	*Cathodic current efficiency (%)*	
	SSA	*SA*
0.5	66.9	67.4
0.1	33.6	45.4
0.5*	63.5	65.7
0.5†	69.5	63.4
1.5	88.2	99.2
0.5‡	70.6	64.5

* With stirring.
† pH = 6.
‡ Temperature 50° C.

Table 6. X-ray data of Fe–Ni alloy*

θ	(hkl)	a (Å)
21.75	(1 1 1)	3.608
25.10	(2 0 0)	3.639
37.05	(2 2 0)	3.596

* Cu$K\alpha$ radiation.
Bath: $NiSO_4$ 0.08 M, $FeSO_4$ 0.02 M, boric acid 20 g l^{-1}, ascorbic acid 0.01 M, SA 0.3 M, pH 4.8, T = 50° C, thickness 0.4 μm, current density 0.5 A dm^{-2}.

4. Discussion

The electroplating of Fe–Ni alloys from the bath solutions under investigation, in the absence and presence of sulphur compounds, exhibits the phenomenon of anomalous codeposition [9]. Iron, being the less noble metal, deposits in preference to the more noble metal nickel. Usually the plating of Fe–Ni alloys proceeds with simultaneous discharge of nickel ions under activation control and iron and hydrogen ion discharge under diffusion control. The anomalous codeposition results due to the

Table 7. Favourable experimental conditions for electroplating 20 : 80 Fe–Ni alloys

*Bath solution**	*Current density ($A\,dm^{-2}$)*	*Temperature (° C)*
0.084 M $NiSO_4$ 0.016 M $FeSO_4$ 0.3 M SA	1.0	30
0.09 M $NiSO_4$ 0.01 M $FeSO_4$ 0.3 M SA	0.4	30
0.088 M $NiSO_4$ 0.012 M $FeSO_4$ 0.24 M SSA	1.0	30
0.09 M $NiSO_4$ 0.01 M $FeSO_4$ 0.24 M SSA	0.5	30

* Boric acid 20 g l^{-1}, ascorbic acid 0.01 M, pH 4.8.

Table 8. Coercivity of Fe – Ni alloys

Current density $(A\,dm^{-2})$	*Covercivity (oersteds)*	
	SSA	*SA*
1.5	15	16
1.5*	11	17.6
0.5	9	17.0
0.5†	–	6.5
0.5‡	–	5.9

* SA or SSA 0.6 M.
† Temperature 30° C.
‡ Thickness 1 μm.
Bath: $NiSO_4$ 0.08 M, $FeSO_4$ 0.02 M, boric acid 20 g l^{-1}, ascorbic acid 0.01 M, SA 0.3 M, SSA 0.3 M, T = 50° C, pH 4.8, thickness 0.4 μm.

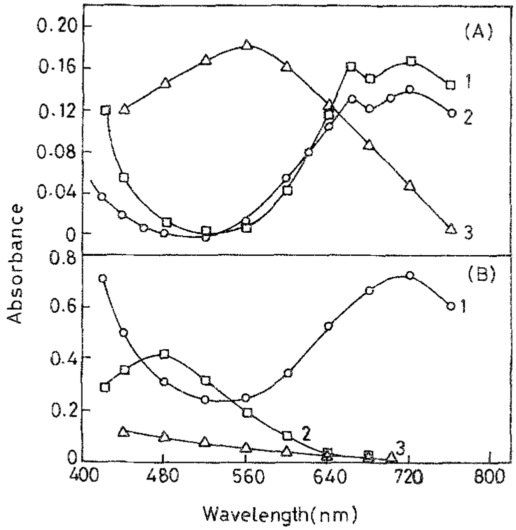

Fig. 2. Absorption spectra. Boric acid 20 g l^{-1}, ascorbic acid 0.01 M. (A)1. Ni^{2+} 0.1 M, SA 0.3 M; 2. Ni^{2+} 0.08 M, Fe^{2+} 0.02 M, SA 0.3 M; 3. Fe^{2+} 0.1 M, SA 0.3 M (B)1. Ni^{2+} 0.1 M, SSA 0.3 M; 2. Fe^{2+} 0.0016 M, SSA 0.005 M; 3. SSA 0.3 M.

rise of surface pH and subsequent hydrolysis of salt, and the precipitation of iron hydroxides at the cathode which finally reduces and discharges nickel ions [10]. There are many approaches to minimizing this type of codeposition of which the use of complexing agents is the most important [11, 12].

Despite extensive use of sulphur compounds in plating technology, little is known about their function because of the complexity of the process. The representative bath solutions are subjected to UV, visible and IR spectral analysis. Iron ions showed an intensive absorption band in the presence of SA and SSA only in the UV region. The IR spectra of nickel sulphamate indicate the shifting of the NH band. This showed the coordination of the amino group although a possible complexation may arise due to hydrogen bonding. The proton of the sulphamic group dissociates at pH 1 and forms 1 : 1 complexes [13] at pH 4.8.

Some of the observed spectral data (Fig. 2) indicate the complexation of both iron and nickel ions with SA and SSA, in accordance with the earlier reports [14]. During alloy plating from complex baths, the alloy composition depends on the stability of the complex or the relative stability of the complexes which are functions of many plating variables. It is known that, in many cases, the sulphur compounds stimulate the electrochemical discharge reaction by preventing hydrogen ion (atom) adsorption [15]. The experimental data confirmed the discharge of both nickel and iron complexes at the cathode. This brings about the concentration polarization. During codeposition of two metals from a complex bath, it is unlikely that each metal would experience the same extent of concentration polarization.

The trend in the variation of alloy composition with current density depends mainly on the range of current density used, the type of bath solution (complex or simple) and the nature of the discharge step (activation or diffusion controlled) at the cathode. Deposition of Fe–Ni alloys at moderate current densities results in an impoverishment of, mainly, Fe^{2+} ions in the cathode diffusion layer, and causes the deposition to come under diffusion control. This is the probable reason for the decrease in iron content of the alloy with increase in current density (Tables 1 and 2). This is also further supported by the results under stirred conditions which confirm earlier findings [16, 17].

The effect of temperature on the alloy composition can be explained by taking into account the relative influences of polarization and diffusion. On raising the temperature, there may be reduction in the polarization during nickel discharge which subsequently enhances the rate of deposition of nickel. Lowering of pH may activate the nickel complex suitably to discharge at a faster rate at the cathode which finally enhances the nickel content in the alloy.

The dependence of alloy composition across the film thickness is usually related to the concentration–time profile of metallic ions across the cathode diffusion layer. In the presence of SA or SSA, attainment of constant composition of the alloy after a certain thickness is due to the longer time required for the initial decrease and attainment of steady nickel ion concentration in the cathode diffusion layer. The trend in the variation of plating potential with current density depends on many factors [18]. The shift of the plating potential in the less noble direction with increase in current density in the presence of SA and SSA indicates the relative ease of complexation and discharge of metallic ions at the cathode [19].

The electroplating of Fe–Ni alloy shows increased polarization on agitation of the bath solution. Agitation of an alloy plating bath directly affects the composition of the alloy by reducing the thickness of the cathode diffusion layer and the composition of the deposit varies due to the concentration changes at the cathode solution interface.

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