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ELECTROPLATING OF THIN FILMS OF MAGNETIC Fe-Ni ALLOYS

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ABSTRACT

Electroplating of thin films of Fe-Ni alloys from an acidic sulphate bath containing thioglycollic acid (TGA) and mercaptoethanol (MET) has been studied under different plating conditions. The composition of the alloy is altered with the plating variables. The cathodic current efficiency (CCE) is found to depend on current density, temperature and pH of the medium. The cathodic potential drifted towards less noble direction with increase of current density, temperature and concentration of the addition agent. TGA is a more effective addition agent than MET. The deposited alloy with higher nickel content is smooth and bright with small grain size and uniform solid solution. Electroplating conditions were optimised to get 20:80 Fe:Ni magnetic alloys with the required magnetic property.

INTRODUCTION

Electroplated Fe-Ni alloys find extensive applications in microelectronic [1] and metal finishing [2,3] industries. The Fe-Ni system shows a set of exceptional possibilities: no structural transformation above 30%, low anisotropy and low magnetostriction for special composition. Fe-Ni alloys with a wide range of specific desirable magnetic properties can be produced by adjusting plating variables [4] . In recent years there has been a greater emphasis on bath solutions containing lower concentrations of electrolytes with a low working temperature. Recently the electroplating of binary magnetic alloys has been reviewed [5] . Thin magnetic films of 20:80 Fe-Ni alloys have been electroplated from acid and alkaline complex baths by using pulse current [6] .

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direct current [7] and superimposing alternating current on direct current[8–10] . Sulphur compounds have been used as metal brightners [11] and to increase the anodic and cathodic efficiencies [12] . As part of a broad programme of work on electroplating of magnetic binary alloys, we report here electroplating of Fe–Ni alloys from an acidic sulphate bath containing addition agents such as thioglycolic acid (TGA) and mercaptoethanol (MET).

EXPERIMENTAL

The solutions were prepared by using distilled water and Reagent grade chemicals. Experiments were carried out at 30°C and pH 4.8 under unstirred conditions to a constant thickness. The molar ratio of Fe/Ni in the bath solution was 30/70. The bath solution had the composition: $NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M, ascorbic acid 0.006M, boric acid 20gm/L and addition agent 0.03M.

Freshly prepared copper-plated platinum foil (2 cm x 2 cm) and cylindrical platinum foil were used as cathode and auxiliary electrode, respectively. Deposition potentials were recorded with reference to the saturated Calomel electrode using a systronics digital multimeter (Model - 435). The surface morphology of the deposit was examined with a metallurgical microscope. The X–ray diffraction analysis of the alloy was carried out by the powder method. After each experiment, the alloy was stripped in HNO_3 solution (1:4) and composition of the alloy was obtained by atomic absorption spectrochemical analysis. The complex nature of the bath solution was examined by visible, UV and IR spectral analysis.

RESULTS

Effect of plating variables

Experiments were carried out to study the effect of plating variables such as current density (cd), pH, temperature, bath composition and stirring of the medium. In all these experiments, the pH was maintained constant using boric acid. Ascorbic acid was added to the bath solution to reduce Fe(III) to Fe(II), if any, and there by preventing the precipitation and subsequent incorporation of ferric hydroxide into the deposit.

The Fe–Ni alloy was electroplated to a constant thickness (0.4µm) at a constant cd of 0.5A dm^{-2} from the bath solutions containing various molar ratios of Fe/Ni (40/60 to 5/95) with a pH 4.8 and working temperature 30°C. The percentage values of Ni in the deposit at various bath compositions are given in Table 1.

Table I. Effect of Bath Composition on the Composition of Fe-Ni Alloys with and without Addition Agents.

Bath composition* (% Ni)	% Ni in the deposit		
	None	TGA	MET
60	49	83.8	64.0
70	52	90.9(88.6)	75.8(62.5)
80	61	95	83
90	75	97.2	94.0
95	82	98.5	97.0

* Boric acid 20gm/l, ascorbic acid 0.006M, TGA or MET 0.03M, pH 4.8, Temp. 30°C, cd0.5A dm^{-2}, thickness 0.4 μm.

The values of the percentage of Ni in the deposit under stirred conditions are given in parenthesis.

In the absence of addition agents, the percentage of Fe in the deposit was more than in the bath solution. However, the situation was quite different in the presence of addition agents. Each bath solution containing an addition agent with a higher percentage of Fe was found to give the alloy containing a lower percentage of Fe. Under identical plating conditions and concentration of addition agent, the extent of the increase of Ni in the deposit was more with TGA than with MET.

Experiments were also carried out at different cd values (0.1 - 2A.dm^{-2}) using a bath solution containing a constant molar ratio of Fe/Ni (30/70) and 0.03M addition agent at 30°C. The percentage of Ni in the deposit, electroplated from the bath solution containing TGA or MET, decreased gradually and then attained a constant value with increase of cd (Fig.1). In the presence of MET, the compositions of the alloy varied significantly with cd. However, the effect of cd on the percentage of Ni in the deposit was not much in the presence of TGA.

pH and temperature are considered to be the important plating variables during plating of metals and alloys. Hence, to find the influence of pH and temperature on the composition of the Fe-Ni alloy, the alloy was electroplated at different pH values (2-6) and temperatures (30-50°C). The percentage of Ni in the deposit decreased with increase of pH of the bath solution containing a known

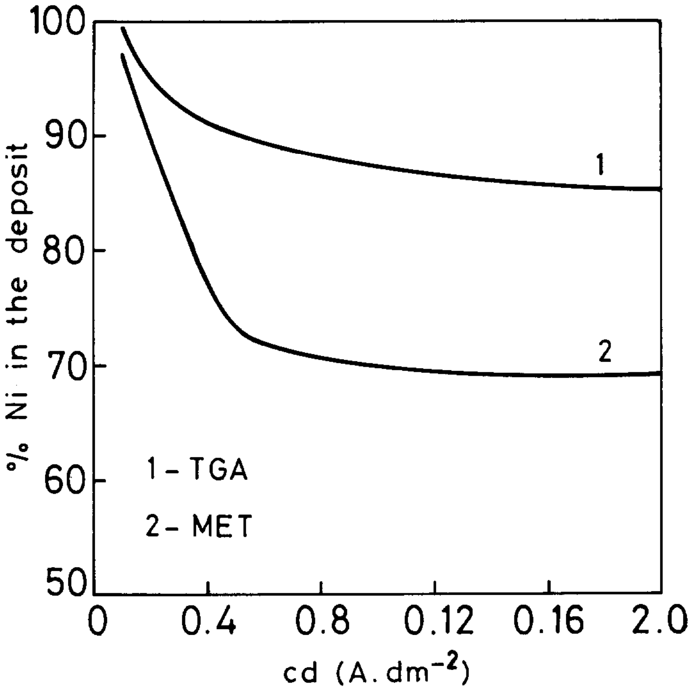

Fig.1. Effect of current density on percentage of Ni in the deposit at 30°C and pH 4.8, thickness 0.4 µm, $NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M, ascorbic acid 0.006M, boric acid 20g/l, TGA or MET 0.03M.

concentration (0.03M) of MET (Table 2). An increase in temperature enhanced the percentage of Ni in the deposit (Table 2). Similar effects of temperature and pH on the composition of the alloy were observed in the presence of TGA.

Table 2. Dependence of the Composition of the Alloy on Temperature and pH.

Addition agent	pH*				Temperature^{+}		
	% Ni in the deposit						
	2.0	3.0	4.8	6.0	30°C	40°C	50°C
TGA	96.7	93.7	90.9	82.1	90.9	91.0	92.7
MET	99.0	92.5	75.8	60.0	75.8	86.0	98.7

* Temperature 30°C, $^{+}$ pH 4.8. Bath composition: $NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M, ascorbic acid 0.006M, TGA or MET 0.03M, thickness 0.4µm, cd0.5A dm^{-2}.

Under a set of plating conditions such as: bath composition (Fe/Ni - 30/70), cd (0.5A dm^{-2}), pH (4.8) and temperature (30°C), alloys were electroplated in the presence of various concentrations (0-0.15M) of TGA and MET. Fig.2 illustrates the dependence of percentage of Ni in the deposit on the concentration of addition agent. The amount of Ni in the deposit increased slightly and attained a limiting value with an increase in MET concentration. However, in the presence of TGA the percentage of Ni decreased continuously with an increase in concentration of TGA.

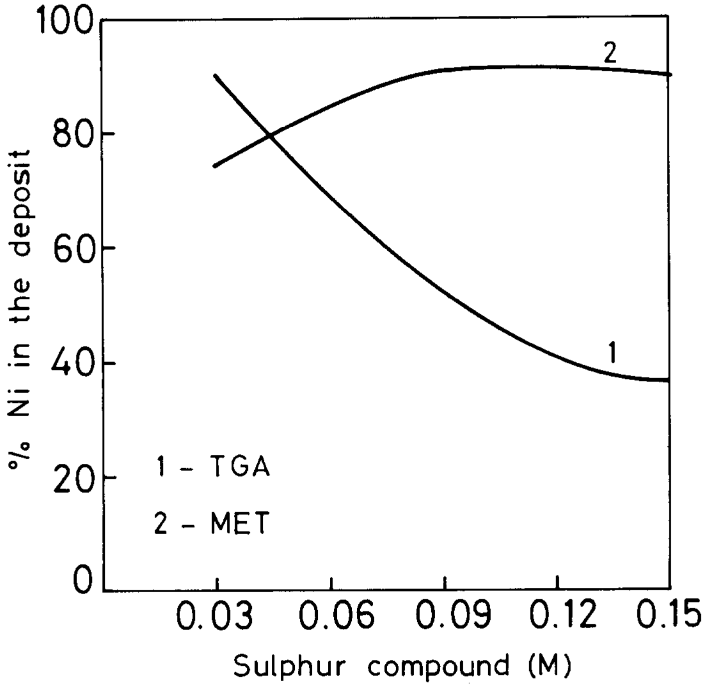

Fig.2. Dependence of percentage of Ni in the deposit on addition agent concentration at 30°C and pH 4.8, thickness 0.4µm. $NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M, ascorbic acid 0.006M, boric acid 20g/l, cd 0.5A dm^{-2}.

To investigate the effect of thickness on the composition of the alloy, experiments were performed to various values of thickness (0.1 - 0.5µm) at constant cd (0.5 A dm^{-2}), temperature (30°C), and pH (4.8). Fig. 3 shows the variation of the percentage of Ni with the thickness of the deposit. The composition of the alloy deposited from a bath solution containing TGA was constant throughout its thickness. In the presence of MET the percentage of Ni in the

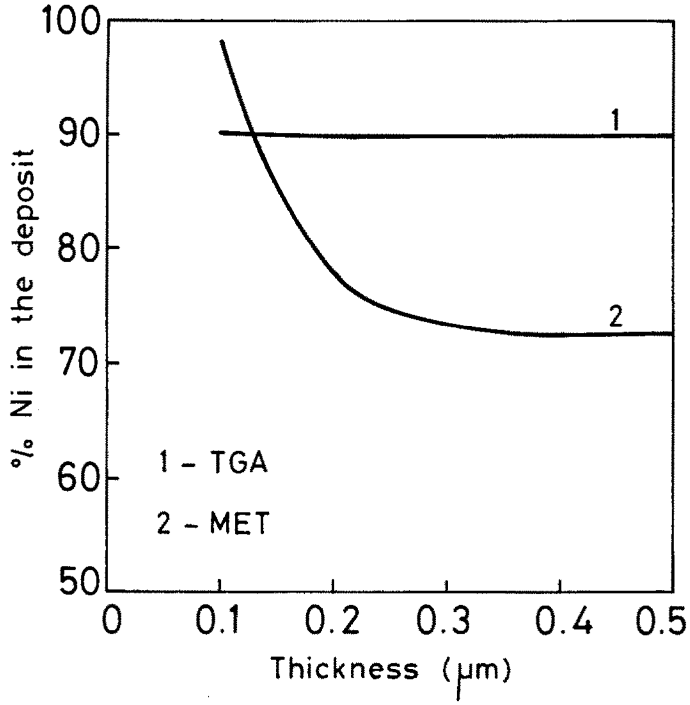

Fig.3. Variation of percentage of Ni in the deposit with thickness at 30°C and pH 4.8, $NiSO_4$ 0.0525M, $FeSO_4$ 0.0275M, ascorbic acid 0.006M, boric acid 20g/l, cd 0.5A dm^{-2}.

deposit decreased initially and attained a limiting value with an increase of thickness.

In order to know the part played by diffusion during electroplating of Fe-Ni alloys, some experiments were carried out under stirred conditions. At a given cd, temperature, bath composition and concentration of addition agent, agitation of the solution did not affect the composition of the alloy much (Table 1). Agitation of the medium decreased the percentage of Ni slightly, both in the presence of TGA and MET.

Deposition potential

Deposition potentials were recorded at different time intervals during deposition of Fe-Ni alloys under various plating variables. The deposition potential in the absence and presence of addition agents slightly decreased with time and attained a steady value. The steady deposition potential was a function of the Fe/Ni ratio in the bath solution, temperature, pH, cd and the nature and concentration of the addition agent. Fig. 4 illustrates the

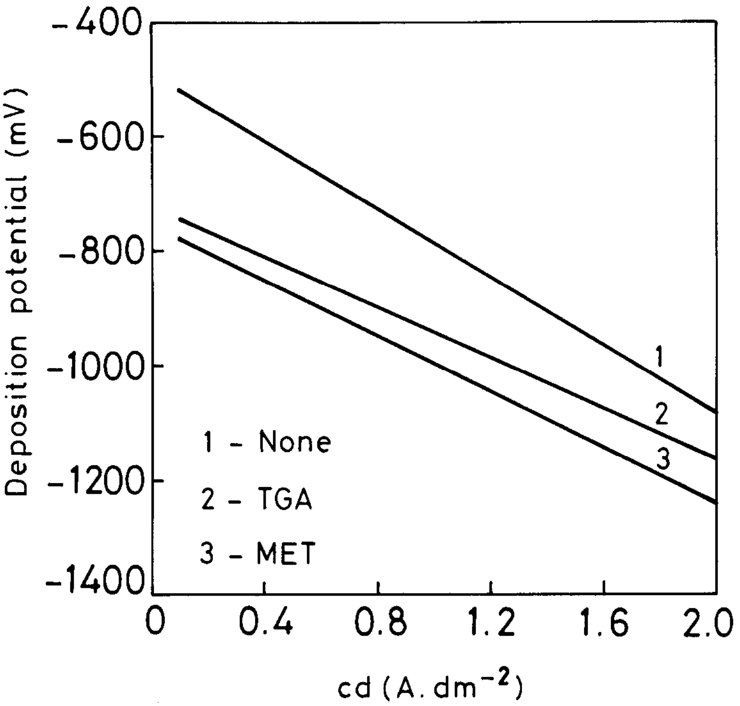

Fig. 4. Deposition potential as a function of current density at 30°C pH 4.8, thickness 0.4 um. $NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M, ascorbic acid 0.006M, boric acid 20g/l, TGA MET 0.03M.

variation of steady deposition potential with cd with and without 0.03M addition agent at 30°C and pH 4.8. At each cd, the steady deposition potential in the absence of addition agent (V_o) drifted towards a less noble direction in the presence of addition agents. Under identical plating conditions, the steady deposition potentials are in the order $V_o > V_{TGA} > V_{MET}$.

Cathodic current efficiency

The values of cathodic current efficiency (CCE) were calculated under different plating conditions. CCE was found to depend on bath solution, pH, temperature and the concentration of addition agent. The values of CCE at representative plating variables are given in Table 3. At a given cd and concentration of addition agent, the percentage CCE increased with an increase in pH or temperature; agitation of the medium decreased the percentage CCE considerably.

Table 3. Cathodic Current Efficiency

Current density (A dm^{-2})	Cathodic current efficiency (%)	
	TGA	MET
1.0	98.5	65.0
5.0	97.2(64.5)	77.8(67.6)
5.0*	81.0	62.9
5.0^{+}	100.0	90.1
5.0‡	54.8	64.9

Bath composition and operating conditions as in Table 2.

* Stirring, $^{+}$ at 50°C, ‡ TGA or MET 0.15M. Values at pH 3 are given in parenthesis.

A decrease in the percentage CCE was noticed either with an increase in cd or with an increase in concentration of addition agent (at constant cd). Under identical experimental conditions, the percentage CCE in the presence of TGA was slightly greater than in the presence of MET.

Surface morphology

After each experiment, the surface morphology of the Fe-Ni alloy was examined under a metallurgical microscope. The Fe-Ni alloy deposited from the bath solution free from addition agent was dull and had a rough structure. In the presence of an addition agent, under a certain range of pH and temperature, the alloy deposit appeared bright, fine grained and uniform when the Ni content of the deposit was above 70% (Fig. 5A). The grain size of the deposit increased gradually with an increase in temperature or thickness of the deposit or a decrease in cd. The alloys with a high percentage of Fe appeared spongy and dull. After heat treatment of the alloy deposits in a vaccum electric furnace at 500°C for two hours, the deposits from the addition agent free bath did not change appreciably, but grain growth was observed (Fig.5B) in the deposit from the bath solution containing an addition agent.

DISCUSSION

Electroplating of Fe-Ni alloys from simple salt baths exhibits [13] anomalous co-deposition, Fe, being the less noble metal, deposits in preference to the more noble metal Ni. H_2 evolution during plating brings about a rise in local pH around the cathode which favours the formation, precipitation and deposition of

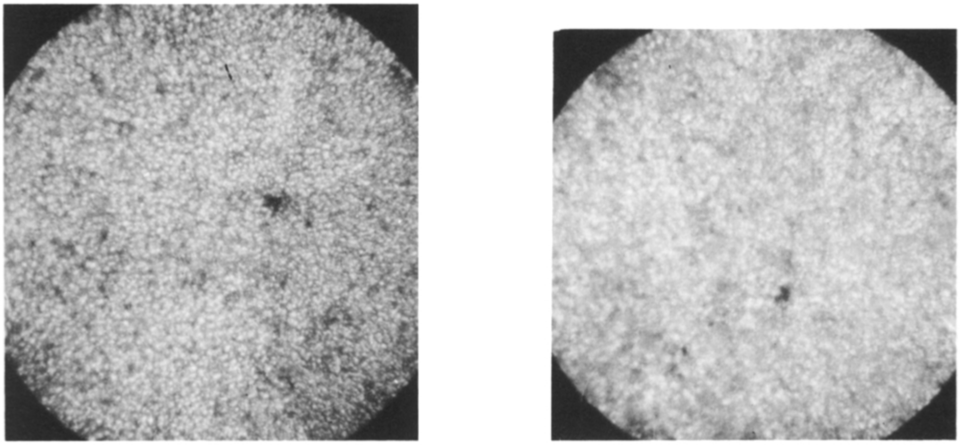

Fig.5. A. Photomicrograph of Fe-Ni alloy (x600) deposits from the bath solution: $NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M, ascorbic acid 0.006M, boric acid 20g/l, TGA 0.03M, cd 0. 5A dm^{-2}, temp. 30°C, thickness 0.4µm, pH 4.8. B. Heat treatment (500°C, 2 h).

$Fe(OH)_2$ or $Fe(OH)_3$ and retards the rate of discharge of Ni(II) ions. Some addition agents [14] and suitable buffers [15] are used to avoid the precipitation of these hydroxides and a pH rise in the electroplating baths.

The present electroplating system in the absence of addition agents show the characteristics of anomalous co-deposition (Table 1) which is decreased considerably by the presence of addition agents. The study of the effect of addition agent on alloy plating is very complex. The varied nature of the effects of addition agents makes it improbable that they can all be explained by one single action. From the typical bath solutions, complexes were isolated and were subjected to Uv, visible and IR spectral analysis. The mercaptide ion exhibited an intense band in the uv region which shifted to the larger wave length on complexation. The IR spectra of both Fe and Ni complexes showed the absence of SH stretching frequency and shifting of the C=O stretching frequency. Even the visible absorption spectra (Fig.6) showed the complexation of both Fe (II) and Ni(II) ions with TGA and MET. Some of these spectral data are in accordance with the earlier spectral reports [16-18] on the complexes of Fe and Ni with TGA and MET.

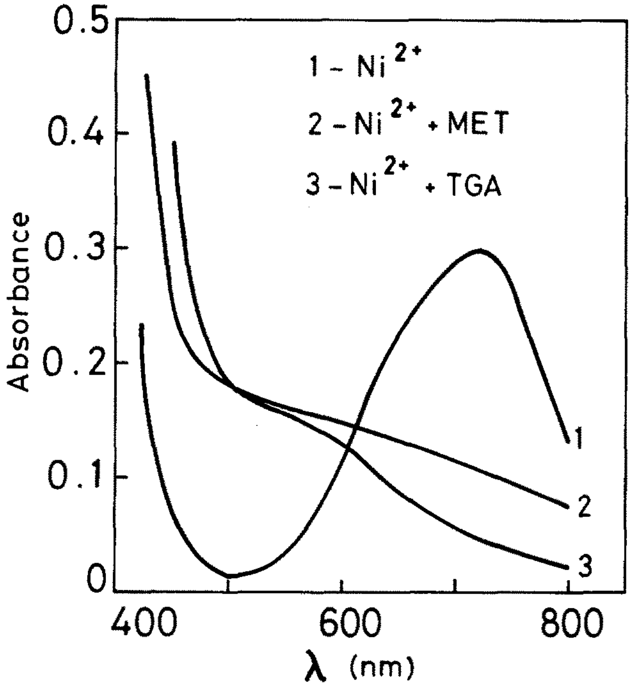

Fig. 6. Absorption spectra of Ni-TGA system and Ni-MET system (pH 4.8). (1) $NiSO_4$ 0.15M, boric acid 20g/l, ascorbic acid 0.006M. (2) $NiSO_4$ 0.0525M, MET 0.03M, boric acid 20g/l, ascorbic acid 0.006M. (3) $NiSO_4$ 0.0065M, TGA 0.03M, boric acid 20g/L, ascorbic acid 0.006M.

It is known that compounds containing as SH group lower the cathodic polarization and stimulate electrochemical discharge reactions by preventing hydrogen ion (or atom) adsorption [19,20]. Experimental results in the presence of an addition agent shows: (i) lowering of plating potential at a given cd, and (ii) enhancement of the percentage of Ni in the deposit. This confirms the preferential adsorption and discharge of Ni complexes on the cathode [21]. This brings about the concentration polarization (considerable decrease of concentration of Ni(II) ions and increase of concentration of complexing agent at the cathode diffusion layer), which depends on the pH of the medium, the nature and concentration of the complexing agent, the stability of the complex and the cd. During co-deposition of two metals, it is unlikely that each metal would experience the same extent of concentration polarization.

The trend in variation of composition of Fe-Ni alloy with cd mostly depends on the range of cd used, thetype of bath solution (complexing or not) andthe nature of the discharge step (activation or diffusion controlled) at the cathode. An increase in cd suppressed the Ni content in the deposit (Fig.1), because Ni deposition is under diffusion control. At higher values of cd, the Fe content in the alloy deposit remained constant because of the co-deposition of an isoluble iron compound. Some of these results are in accordance with the general rule [22] in alloy plating that an increase in cd tends to increase the proportion of the less noble metal in the alloy deposition.

The dependence of the composition of the alloy with thickness is usually related to the concentration - time profile of metallic ions across the cathodic diffusion layer. In the presence of TGA, constant composition of the alloy across thickness (Fig.3) is due to the rapid decrease and attainment of a steady Ni(II) ion concentration at the cathode diffusion layer. However, a similar situation occurs in the presence of MET only after a short time lag. A slight increase of the amount of Fe in the deposit by agitation of the bath solution (Table 1) indicates that the plating system is of the diffusion-controlled anomalous type.

The effect of temperature on the composition of the alloy (Table 2) could be explained by taking into account the influence of polarization and diffusion. On raising the temperature, there may be a reduction in the polarization during Ni discharge which subsequently enhances the rate of deposition of Ni. It is known that an increase in temperature increases the cathode current efficiency of a preferentially depositing metal complex [23] . Hence, an increase in temperature increases the amount of Ni in the deposit. The complexing agent in an electroplating bath always favours the deposition of a metal by forming a cathodically active complex with the metal ions. The lowering of pH may activate the Ni complex suitably to discharge at a faster rate at the cathode which finally enhances the Ni content in the deposit (Table 2). The decrease in current efficiency at higher cd values and at lower pH values or with stirring of the medium (Table 3) may be due to the increase of rate of evolution of H_2 during alloy plating.

The measured values of coercivity of a few typical Fe-Ni alloys (Table 4) were found to vary with pH, temperature, cd, bath composition, concentration of the addition agent and thickness of the

Table 4. Magnetic Properties of 20:80 Fe-Ni Alloys

Bath solution* with plating conditions	Coercivity	
	Unheated	Heated
1. $NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M TGA 0.03M, pH 6, cd 0.5A dm^{-2} temp. 30°C, thickness 0.4μm.	8.4	2.1(2.2+)(0.8#)(4.9§)
2. $NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M, TGA 0.04M, pH 4.8, cd 0.5A dm^{-2}, temp. 30°C, thickness 0.4μm.	13.0	1.9
3 $NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M MET 0.03M, pH 4.8, cd 0.35 A dm^{-2}, temp. 30°C, thickness 0.4 μm.	9.5	2.4(0.4+)(5.8#)(0.6§)

* Ascorbic acid 0.006M, boric acid 20g/l,

\+ At 0.1 μm, # pH 4.8 (with MET pH 6), § TGA or MET 0.06M.

deposit. On the basis of the present work one could optimise the experimental conditions (Table 5) to get thin films of 20:80 Fe-Ni magnetic alloys.

Table 5. Optimum Experimental Conditions to Electroplate 80 : 20 Ni-Fe Alloys at 30°C to a Thickness of 0.4 μm.

Addition agent	Bath Solution*	pH	cd($A.dm^{-2}$)
TGA	$NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M TGA 0.04M	4.8	0.5
	$NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M, TGA 0.03M	6.0	0.5
MET	$NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M, MET 0.03M	4.8	0.35
	$NiSO_4$ 0.0525M, $FeSO_4$ 0.0225M MET 0.05M	4.8	0.5

* boric acid 20g/l, ascorbic acid 0.006M.

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