Effects of Addition Agents on the Electrodeposition of Ni-Fe Alloys

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Kanji NAKAMURA* and Tadao HAYASHI**

Effects of addition agents on the eletrodeposition of Ni-Fe alloys from a sulfate-chloride bath have been studied. Saccharin, disodium naphthalene 1,5 disulphonate (DNS), thiourea, 2-butyne 1,4 diol, coumarin and L-arginine were used as an addition agent. The polarization curves, composition of Ni-Fe alloy deposits, internal stress and structure of Ni-Fe alloy deposits were measured as a function of the concentration of addition agents in the Ni-Fe plating bath at 50 °C. Saccharin, DNS, coumarin, 2-butyne 1,4 diol or L-arginine shifted the polarization curves towards more negative value in the electrodeposition. The Fe content of Ni-Fe alloy deposits increased with an addition of coumarin or 2-butyne 1,4 diol at a low current density. The internal stress of Ni-Fe alloy deposits decreased with an addition of saccharin, DNS, thiourea or L-arginine. The increase of the Fe content of Ni-Fe alloy deposits led to an increase of the internal stress. X-ray diffraction analysis revealed that the lattice spacing of Ni-Fe alloy deposits increased with an increase of the Fe content of the alloy deposits.

1. Introduction

The commercial use of decorative Ni-Fe alloy deposits occurred more than 10 years ago. A large number of physical and metallurgical properties of Ni-Fe alloys depend on the plating variables but interdependence was not yet well understood.

Henstock[1] reported that the Fe content of the Ni-Fe alloy deposits decreased with an increase of the film thickness. Shenoi et al.[2] reported that the internal stress of the Ni-Fe alloy deposits increased with an increase of the Fe content of the Ni-Fe alloy deposits but the leveling decreased in the same condition. Under the optimum plating conditions, the Ni-Fe alloy deposits have the low tensile stress, good brightness and superior ductility.

In the previous papers,[3,4] we have reported the effect of the plating variables on the ductility of Ni-Fe alloy deposits, and also the influence of saccharin on the electrodeposition of Ni-Fe alloy deposits.

In the present study, the effect of organic addition agents on the formation of Ni-Fe alloy deposits have been discussed in detail as a function of the plating variables, especially the nature of the organic additives and current density.

2. Experimental

2.1 Measurement of polarization curves

Bath composition and addition agents used in the present study were shown in Table 1. An electrochemical cell of the standard H type was used in this work. The cathode used for the measurement of polarization curves was a commercial

* Graduate Student, Department of Applied Chemistry, Division of Engineering, Graduate School.
** Department of Applied Chemistry, College of Engineering.

Table 1 Bath composition and addition agents

$NiSO_4 \cdot 6H_2O$	85 g/l
$NiCl_2 \cdot 6H_2O$	135 g/l
H_3BO_3	50 g/l
Citric acid	0.6 g/l
$FeSO_4 \cdot 7H_2O$	0–60 g/l

Addition agents; Saccharin, Disodium naphthalene 1,5 disulphonate, Thiourea, 2-Butyne 1, 4 diol, Coumarin, L-arginine

nickel rod (ϕ 5.0 m/m). The sulfur-activated nickel was used as an anode. The nickel rod and Luggin capillary were encapsulated in acrylic resin pipe with Araldite to keep a constant distance between the cathode and Luggin capillary. The cross section of the nickel rod and Luggin capillary was ground to 1500 grit finish and was degreased in alkaline cleaning solution before each measurement. The electrode assembly was inserted into the cell and pure nitrogen was passed through the solution before each measurement. The measurement of the polarization curves in Ni-Fe electrodeposition was carried out by the potential sweep method (20 mV/ min) at 50°C, pH 3.0. The concentration of each addition agent in the plating bath was 0.5–10 mM/l or 0.4–12 g/l.

2.2 Analysis of Ni-Fe alloy deposits

For the determination of alloy composition, Ni-Fe alloy deposits electroplated on platinum sheet (0.75×4.0 cm^2) were dissolved in a small amount of 10 vol. % HCl-H_2O_2 solution, and Ni and Fe were determined by chelatemetry.[5] The electricity used for the electrodeposition of Ni-Fe alloy films was 70 coulombs.

2.3 Measurement of internal stress in electrodeposition of Ni-Fe alloy deposits

The cathode used for the measurement of internal stress was a copper sheet (1.2×3.0 cm^2) which was annealed in vacuum at 400°C for 2 h. The back side of the copper sheet was sealed with Frontex resin on which the strain gauge was adhered. In the electrodeposition of Ni-Fe alloys at 3 Adm^{-2}, the generated strain on the electrode was measured by strain gauge. From the measured strain-thickness curves the strain value (dE/t_d) was determined. From the strain value (dE/t_d) the internal stress was calculated by the following equation,[6]

$$S = f(t_d) \times (dE/t_d) t_d$$
$$f(t_d) = 2 \times (E \times t((1 - u \times u_d) \times T_s - (1 - u^2) \times T_e) + E_d \times t_d (1 - u^2)$$
$$\times (T_s - T_e))/(u \times (1 - u_d) \times (1 - u^2) \times (t + t_d))$$
$$T_s = t/(6 \times (1 + t_d/t))$$
$$T_e = T_s \times (1 + ((1 + u_d) \times E \times t)/((1 + u) + E_d \times t/) - u \times t$$
$$\times (1 + t_d/t)/2)/(1 + u + (1 + u_d) \times E \times t/E_d/t_d)$$

where, S; internal stress, E, u, t; Young's modulus, Poisson's ratio, thickness of substrate, respectively. E_d, u_d, t_d; Young's modulus, Poisson's ratio, thickness of deposits, respectively

2.3 X-ray diffraction

The X-ray diffraction patterns of the Ni-Fe alloys, as-plated and annealed at 400°C for 1 h were taken with Fe K_α radiation. A manganese filter was used to absorb K_β radiation. Ni-Fe alloy deposits were electroplated with 40 μm thickness.

3. Results and Discussion

3.1 Polarization curves

Effect of saccharin on the polarization curves for the electrodeposition of Ni-Fe alloys is shown in Fig. 1. The polarization curves were shifted towards more negative value with increasing the concentration of saccharin. Polarization curves in the lower current density region were found to shift towards more negative value by 150 mV. These results indicated that saccharin was adsorbed strongly on the electrode surface and suppressed the deposition of Ni-Fe alloys in proportion to the saccharin concentration.
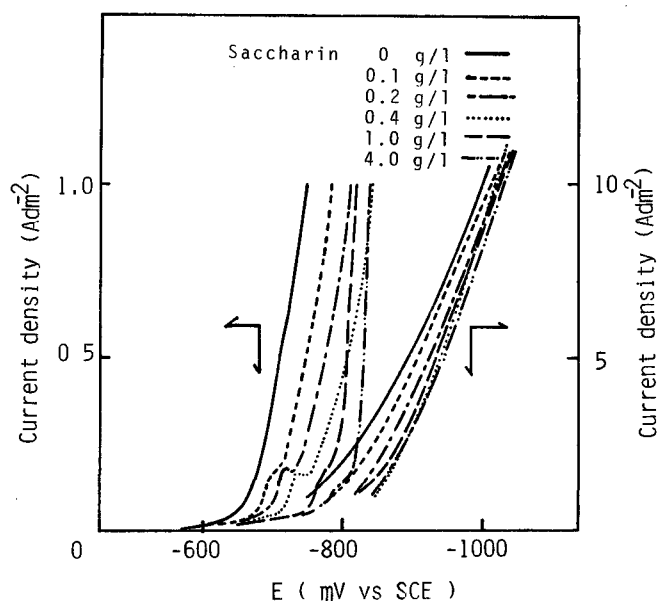

Fig. 1   Effect of saccharin on the cathodic polarization curve of Ni-Fe alloy deposition

Effects of other addition agents on the polarization curves in the electrodeposition of Ni-Fe alloys are shown in Fig. 2. An increase of the DNS concentration hardly affected the polarization curves which were merely shifted towards more negative value by 50 mV. Addition of thiourea (0.5 mM/l), however, led to a positive shift of the polarization curves in 100 mV. Further addition of thiourea above 0.5 mM/l, shifted the polarization curves more negative value. With an addition of thiourea (10 mM/l), the polarization curve was found to shift more negative value by 100 mV compared to additive-free bath. An addition of coumarin
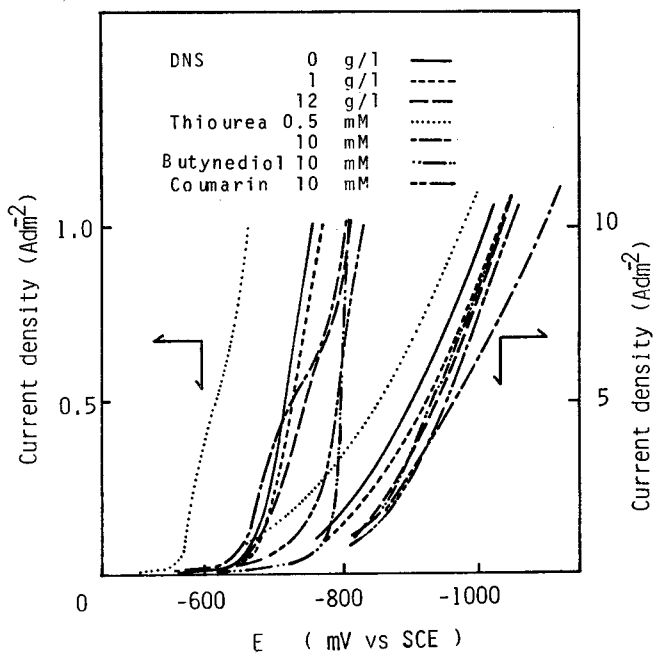
Fig. 2   Effects of various additives on the cathodic polarization
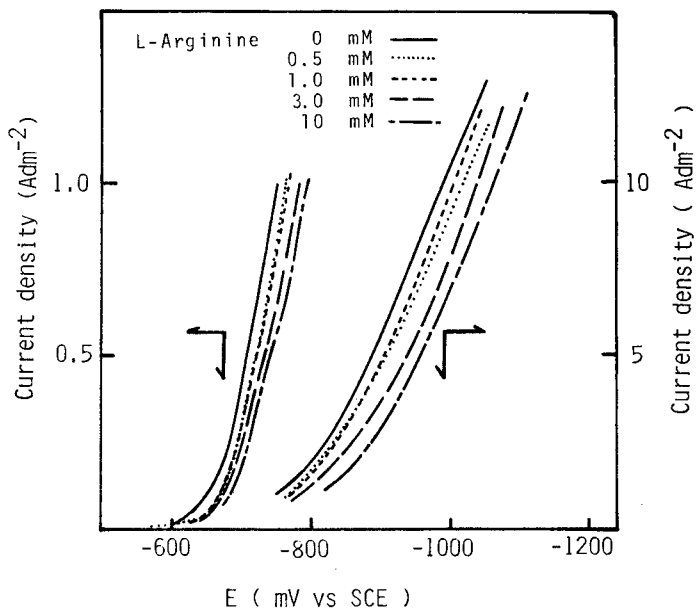curves of Ni-Fe alloy deposition

Fig. 3   Effects of L-arginine on the polarization curve of Ni-Fe alloy
deposition

or 2-butyne 1,4 diol, resulted in a negative shift of the polarization curves.

Effects of L-arginine on the polarizotion curve was shown in Fig. 3.   Addition of L-arginine led to the negative shift of the polarization curves of the electrodeposition of Ni-Fe alloys.   In general, the electrodeposition of Ni-Fe alloy deposits was suppressed by the increase of the concentration of addition agents studied except thiourea.

3.2   Composition of Ni-Fe alloy

Effects of current density on the Fe content of Ni-Fe alloys electrodeposited from the Ni-Fe plating bath with additives such as saccharin, DNS, thiourea, coudemarin, 2-butyne 1,4 diol and L-arginine were shown in Fig. 4 (a), (b), (c).   By an addition of saccharin or DNS in the Ni-Fe plating bath, the Fe content was found to be hardly affected compared with the pure bath.   The Fe content of the Ni-Fe alloys was found to give a maximum value at a current density of 1 Adm^{-2} and to decrease with increasing the current density.   An addition of thiourea led to a decrease of the Fe content of Ni-Fe alloys.   At the current densities of 0.5–1.0 Adm^{-2}, the Fe content of Ni-Fe alloys was found to be zero with a concentration of 1.0–3.0 mM/l thiourea.   These results indicated that the addition of thiourea depolarizes nickel deposition.   These phenomena are well accord with the positive shift of the polarization curves of the Ni-Fe alloy deposition in the concentration
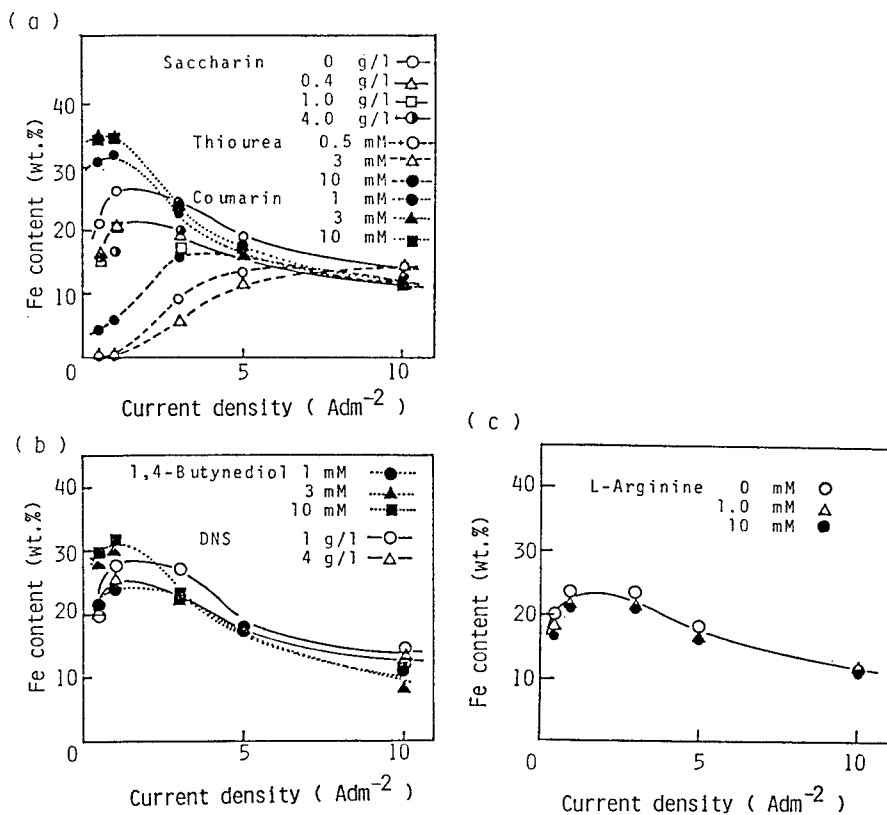

Fig. 4   Effects of additives on Fe content of Ni-Fe alloy deposits

of 0.5–3.0 mM/l.   With an addition of 10 mM/l thiourea, the Fe content increased appreciably but no maximum value was obtained contrary to the other addition agents.   These results imply that the Fe deposition was hindered at lower current densities in the electrodeposition of Ni-Fe alloys.   The Fe content of Ni-Fe alloys was found to increase with an addition of coumarin or 2-butyne 1,4 diol.   These results seemed to correspond to the nagative shift of the polarization curves in the lower current density ranges.

L-arginine[7] was reported to act as a stress reducer in the electrodeposition of Fe, therefore, it was expected that the Fe content of Ni-Fe alloys might be influenced by an addition of L-arginine.   Contrary to the expectation, the Fe content of Ni-Fe alloys was found to be hardly affected by an addition of L-arginine and the Fe content was approximately equal to that obtained from the saccharin containing bath.

3.3   Measurement of internal stress of the Ni-Fe alloy deposits

Effects of addition agents on the internal stress of the Ni-Fe alloy deposits was shown in Fig. 5.   The Ni-Fe alloy deposits were prepared at a cathode current density of 3.0 Adm^{-2}.   The Fe content of the Ni-Fe alloys shown in Fig. 5 was approximately 20–28%.   Thickness of the Ni-Fe alloy deposits in this test was 20 μm.   It was found that the internal stress generated in the electrodeposition of Ni-Fe alloys was highly tensile in all specimens.   The internal stress was found
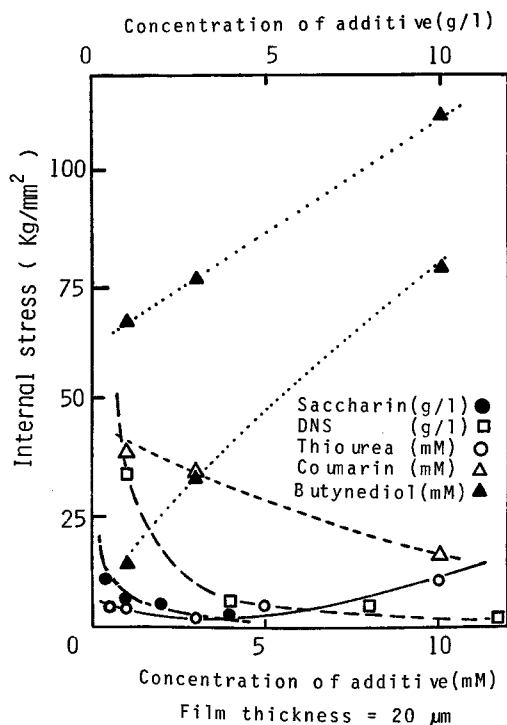

Fig. 5   Effects of additives on internal stress of Ni-Fe alloy deposits

to decrease with an addition of coumarin, thiourea, DNS or saccharin. The effect of saccharin on the internal stress of the Ni-Fe alloy deposits was remarkable. Up to 0.4 g/l, saccharin hardly affected the internal stress of the deposits, but beyond 0.4 g/l the internal stress decreased abruptly with increasing the addition of saccharin. DNS also reduced the internal stress of Ni-Fe alloy deposits, but not to the same extent as saccharin. With an addition of DNS more than 4.0 g/l, the internal stress of the Ni-Fe alloy deposits was found to decrease just like the case of saccharin. Coumarin had the slight tendency to reduce the internal stress. It was reported[7] that thiourea was effective in reducing the internal stress of Fe electrodeposits, therefore, it was expected that thiourea might be effec tive to reduce the internal stress of the Ni-Fe electrodeposits. With an addition of thiourea up to 3 mM/l, the internal stress of the Ni-Fe deposits was found to decrease, and these results seemed to be attributable to a decrease of the Fe content of the Ni-Fe alloy deposits. The internal stress of the Ni-Fe deposits, therefore, increased with an increase of the Fe content resulted from the increase of thiourea. It seemed that thiourea is not effective in reducing the internal stress. With an addition of 2-butyne 1,4 diol, the internal stress of Ni-Fe deposits increased with an increase of the additive concentration. These results are well accord with an increase of the internal stress of the Ni electrodeposits with an addition of 2-butyne 1,4 diol.

Effects of the Fe content on the internal stress of the Ni-Fe deposits were shown in Fig. 6. The internal stress of the Ni-Fe alloy deposits obtained from the Ni-Fe plating bath with saccharin was found to increase linearly with an increase of the Fe content of Ni-Fe alloy deposits. In the case of Ni-Fe alloy deposits containing 10% Fe, the internal stress of the deposits was found to change
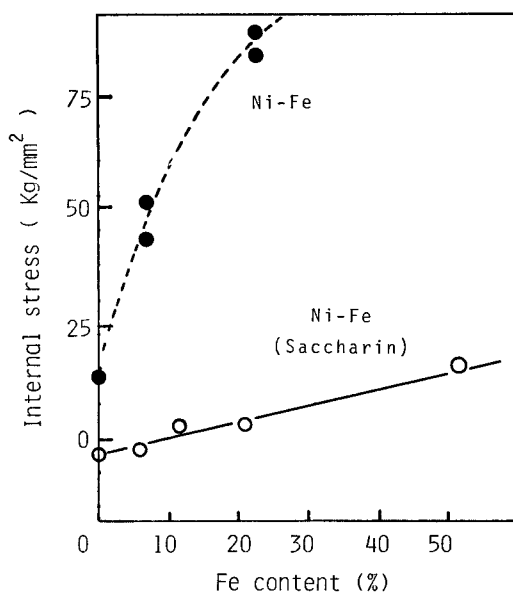

Fig. 6 Effects of Fe contents of Ni-Fe alloy deposits on internal stress of Ni-Fe alloy deposits

from compressive to tensile. The internal stress of the Ni-Fe alloy deposits ob-
tained from the plating bath without any additive increased rapidly with an increase
of the Fe content of Ni-Fe alloys.

    Effects of L-arginine on the internal stress of Ni-Fe alloy deposits were shown
in Fig. 7. The internal stress of the Ni-Fe deposits decreased with an addition
of L-arginine. Especially, the internal stress of the Ni-Fe alloy deposits did not
increase with increasing the Fe content of Ni-Fe alloys. Occasionally, many cracks
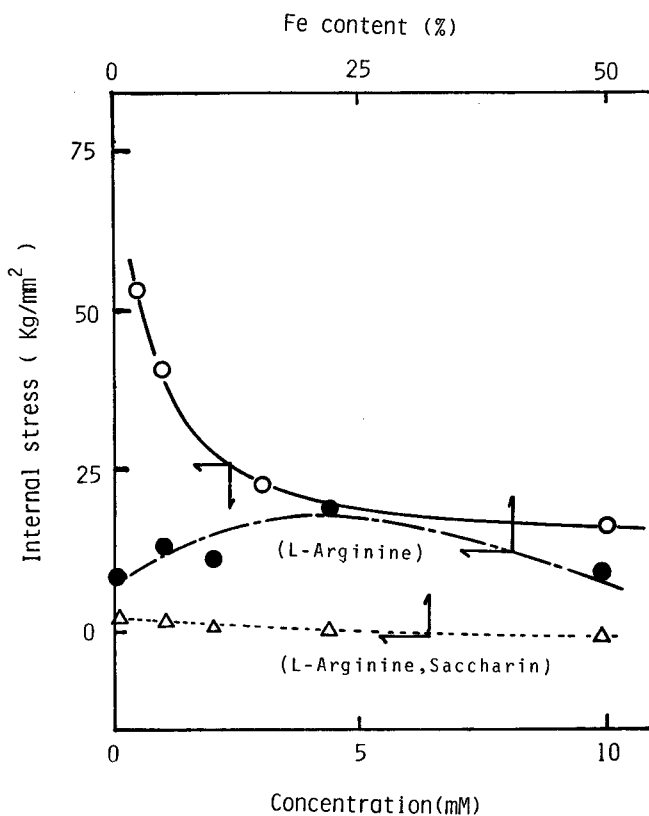
Fig. 7   Effects of L-arginine and Fe content of Ni-Fe alloy deposits
          on internal stress of Ni-Fe alloy deposits

were generated in the Ni-Fe alloy deposits, therefore, the internal stress seemed
to be released by the crack formation. At 50% Fe content of Ni-Fe alloys, the
internal stress became smaller comparing with that in 22 % Fe content alloy de-
posits. These results imply that L-arginine is not effective in reducing the internal
stress in the Ni deposition, but effective in Fe deposition. With an addition of
both saccharin (4 g/l) and L-arginine (10 mM/l), the internal stress of the Ni-Fe
alloy deposits was found to decrease with increasing the Fe content of Ni-Fe alloys.
The internal stress was found to change from tensile to compressive. It was found
that addition of both saccharin and L-arginine resulted in crack-free and dull
deposits.

3.4 X-ray diffraction patterns of the Ni-Fe alloy deposits

Effects of addition agents on the orientation of Ni-Fe alloy deposits were shown in Table 2. The orientation index was evaluated by the Willison's method. The pure nickel deposit exhibited the preferred orientation of Ni (311). These result seemed to be attributable to the presence of chloride ion in the plating bath. With respect to the preferred orientation of Ni deposits, sulphamate and sulphosalicylate[8] exhibited a quite distinctive (100) orientation as characteristic of "free growth" of Ni layer. It was reported[9] that chloride exhibited the preferred orientation of Ni (311) owing to the strong adsorption of chloride ion. On the other hand, saccharin gave rise to the preferred orientation of Ni (100).[10] In the present study, saccharin does not seem to give the preferred orientation of Ni (200), and to merely diminish the orientation of Ni (220). Concerning the Ni-Fe alloy deposits, an

Table 2 Orientation indexes of deposits

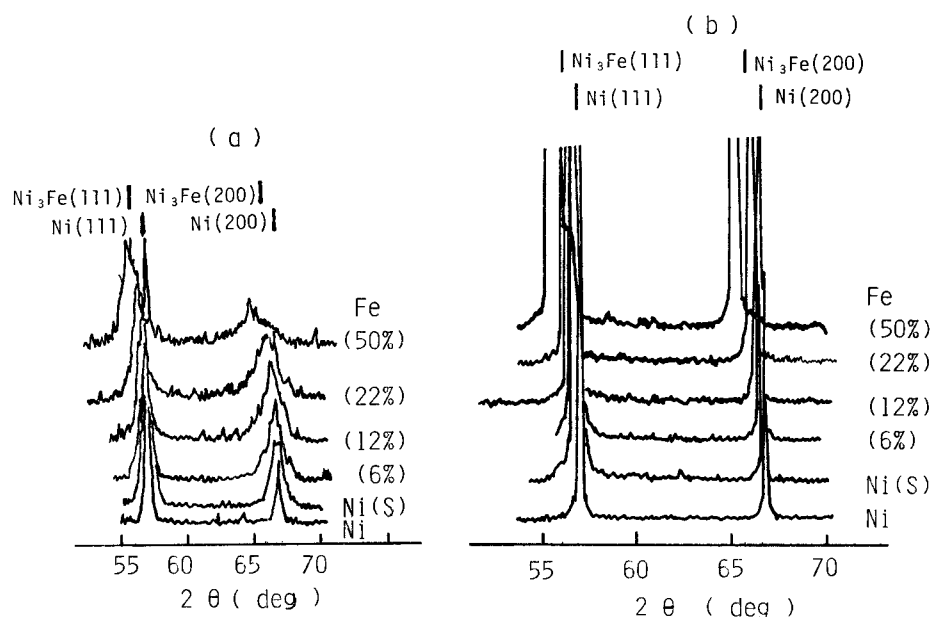| Deposits	Addition agent	Orientation indexes			
		(111)	(200)	(220)	(311)
Ni-Fe	None	1.18	0.83	1.40	0.47
Ni-Fe	Saccharin	0.95	2.87	0	0.22
Ni-Fe	DNS	1.23	1.63	0	0.46
Ni-Fe	Thiourea	1.0	2.59	0	0.29
Ni-Fe	Coumarin	1.36	0.57	0.81	0.51
Ni-Fe	2-Butyne 1, 4 diol	1.39	0.63	0.51	0.56
Ni	None	1.05	0.65	0.60	1.90
Ni	Saccharin	1.25	0.74	0	1.34

Fig. 8 Effects of Fe content on the X-ray diffraction profiles of Ni-Fe alloy deposits, as-deposited (a) and annealed at 400°C for 1h (b)

addition of sulfur compound such as saccharin, DNS and thiourea gave rise to the preferred orientation of Ni-Fe (200) and to diminish the orientation of Ni-Fe (220). The presence of saccharin and Fe^{2+} ion in the Ni-Fe plating bath exhibited the preferred orientation of Ni-Fe (200).

Effects of the Fe content on the diffraction profiles of Ni-Fe alloy deposits obtained from the Ni-Fe plating bath with saccharin (4 g/l) were shown in Fig. 8 (a) and (b). The lattice spacing and crystallite size calculated from X-ray diffraction data are summarised in Table 3. With an increase of the Fe content of Ni-Fe alloy deposits, the diffraction line shifted towards more lower angle and the diffraction line was broadened remarkably. The lattice spacing of Ni-Fe alloy deposits was found to increase with an increase of the Fe content of Ni-Fe alloy deposits. The increase of the half width of the diffraction line seemed to be attributable to a decrease of crystallite size. On annealing the Ni-Fe alloy deposits at 400°C for 1 h, the diffraction line was found to become more sharp, but the diffraction angle seemed to be unchanged. Under these conditions, the crystallite size of Ni-Fe alloy deposits seemed to increase, but the lattice spacing of Ni-Fe alloy deposits was unchanged.

Table 3   Crystallite size and lattice spacing of deposits

Deposits	Crystallite size (Å) (as-deposited)	(annealed)	Lattice spacing(Å) (Ni (111)) (as-deposited)	(annealed)
Ni (S)	227	947	2.033	2.035
Ni-Fe (6%)	189	568	2.037	2.038
Ni-Fe (12%)	162	568	2.040	2.042
Ni-Fe (22%)	138	513	2.050	2.051
Ni-Fe (50%)	125	513	2.063	2.073

Crytallite size was calculated by Scherrer's equation.

4.   Conclusion

Polarization curves in the electrodeposition of Ni-Fe alloys were shifted towards more negative value with increasing the concentration of saccharin, 2-butyne 1,4 diol, coumarin or L-arginine in Ni-Fe alloy plating bath. An increase of the DNS concentration slightly affected the polarization curves which were merely shifted towards more negative value by 50 mV. An addition of thiourea (0.5 mM/l) led to the positive shift of the polarization curves in 100 mV. Further addition of thiourea above 0.5 mM/l, shifted the polarization curves more negative value.

With an addition of saccharin, DNS or L-arginine in the Ni-Fe plating bath, the Fe content was found to be hardly affected by the additives compared with the pure bath. An addition of thiourea resulted in a decrease of the Fe content of Ni-Fe alloys. On the other hand, the Fe content of Ni-Fe alloys was found to increase with an addition of coumarin or 2-butyne 1,4 diol. The internal stress of Ni-Fe alloy deposits decreased with an addition of coumarin, thiourea, DNS, saccharin or L-arginine.

The internal stress of Ni-Fe alloy deposits increased with an addition of 2-

butyne 1,4 diol.   The internal stress of Ni-Fe alloy deposits obtained from the Ni-Fe plating bath with saccharin was found to increase linearly with an increase of the Fe content of Ni-Fe alloy deposits.   An addition of both saccharin (4 g/l) and L-arginine (10 mM/l) resulted in the decrease of the internal stress of the Ni-Fe alloy deposits with increasing the Fe content of Ni-Fe alloys.

X-ray diffraction analysis revealed that the lattice spacing of Ni-Fe alloy deposits increased with an increase of the Fe content of the deposits.   Sulfur compound such as saccharin, DNS and thiourea gave rise to the preferred orientation of Ni-Fe (200).

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