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Effect of primary amines on magnetic properties of Fe-Ni films electroplated in a DES-based plating bath

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Fe-Ni alloy films were electroplated in DES-based plating baths with various primary amines, and we investigated the effect of the primary amines on the magnetic and the structural properties of the films. The primary amines of ammonium sulfamate, DL-α-alanine and L-glutamic acid reduced the coercivity and the surface roughness of the Fe-rich films (Fe > 70 at.%), and the reduction tendencies of the coercivity and the roughness show good agreement with the result of our previous study on another primary amine of glycine. From the results for the TEM observation, we found that the texture of the Fe-rich film is clearly different from that for the Fe-poor one (Fe < 30 at.%), and we concluded that the primary amines are effective additives for the Fe-rich films electroplated in the DES-based plating baths.
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I. INTRODUCTION

DESs (Deep Eutectic Solvents) have many industrial advantages such as wide electrochemical window,[1–3] very low vapor pressure and low cost, and the DESs are expected as novel solvents for electroplating of metal films. Some researchers have employed DESs as solvents for electroplating, and studies on magnetic films electroplated in DES-based plating baths have been increasing in recent years.[4–10]

Recently, we have reported that glycine is an interesting additive for Fe-Ni films electroplated in the DES-based baths since the coercivity of the films for the glycine-used bath decreases with increasing the Fe content from 20 to 75 at.%.[11] In typical Fe-Ni alloys, as the magnetocrystalline anisotropy and the magnetostriction constants become nearly zero at $Fe_{22}Ni_{78,}$ the variation of the coercivity for the glycine-used bath cannot be explained by the change in the magnetocrystalline anisotropy and the magnetostriction. Consequently, we concluded that this unexpected behavior of the coercivity against the change in the Fe content is attributed to the reductions in the surface roughness and the effective magnetocrystalline anisotropy due to the grain refinement effect in our previous study. When applying Fe-Ni films to magnetic devices, the result for the glycine-used bath is attractive since we can obtain the Fe-Ni films with high saturation magnetization and low coercivity simultaneously.

DESs are a mixture of a hydrogen bond acceptor and a hydrogen bond donor, and we considered that amine-based additives are effective as additives since the amino group is polar and readily forms hydrogen bonds. In fact, as the glycine is a primary amine, we focused on other primary amines. In the present study, we employed primary amines of ammonium sulfamate ($NH_4NH_2SO_3$), DL-α-alanine ($CH_3CH(NH_2)COOH$), and L-glutamic acid ($HOOCCH_2CH_2CH(NH_2)COOH$) as additives in the DES-based plating baths, and evaluated the effect on structural and magnetic properties of the electroplated Fe-Ni films.

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II. EXPERIMENTAL PROCEDURE

A. Electroplating of Fe-Ni films

The composition of the plating bath is summarized in Table I. We prepared a DES by stirring choline chloride (10 g) and ethylene glycol (10 g), and added Iron chloride (x (g)) and Nickel chloride ($15 - x$ (g)) into the DES. We also added primary amines of ammonium sulfamate, DL-α-alanine and L-glutamic acid as additives in the bath.

We carried out an electroplating method to obtain the Fe-Ni films. A Ni plate and a Cu one were used as an anode and a cathode, respectively, and the distance between the electrodes was fixed at 20 mm. We supplied a direct current (DC) to the plating bath using a computer-aided dc current source (Matsusada, P4K-80). The plating conditions are summarized in Table II. Consequently, we obtained 75-mm^2 Fe-Ni films on the cathode (the Cu plates).

B. Measurements

The thickness of the film was measured with a micrometer (Mitutoyo, CPM15-25MJ) at different nine points, we determined the thickness by averaging the measured values. Since the total supplied charge was fixed at 60 C, the thicknesses for all films were almost the same value (approx. 20 μm). The dc magnetic properties (f = 50 mHz) was evaluated using the B-H loops measured with a B-H curve tracer. The maximum applied field were 4 kA/m for the measurement of the loops, and we determined the coercivity from the measured loop. The surface roughness R_a were evaluated using a surface roughness tester (Mitutoyo, SURFTEST SV-400), and the composition was analyzed using an energy dispersive X-ray (EDX) spectroscopic system (Hitachi High-technologies S-3000). Thin Fe-Ni foils were prepared using an argon-ion beam milling for cross-section TEM (Transmission Electron Microscope) observations. The TEM (JEOL, JEM-2010) was operated at an acceleration voltage of 200 kV.

III. RESULT AND DISCUSSION

Figure 1 shows the coercivity H_c of the as-plated Fe-Ni films as a function of Fe content in the film. The results for 0 - 3 g of ammonium sulfamate are shown in Fig.1. The coercivity for the ammonium-sulfamate-used baths decreased in Fe-rich content area. As mentioned in INTRODUCTION, the coercivity for the glycine-used baths also decreased in the same Fe

TABLE I. Bath composition.

Components	Weight (g)
Choline chloride	10
Ethylene glycol	10
$FeCl_2 \cdot 4H_2O$	x
$NiCl_2 \cdot 6H_2O$	15 - x
Ammonium sulfamate	0 - 5
DL-α-alanine	0 - 2.5
L-glutamic acid	0 - 2.5

TABLE II. Electroplating conditions.

Conditions	Values
Bath temperature	100°C
Current density	66.7 mA/cm^2
Plating area	75 mm^2 (15 mm × 5 mm)
Plating time	20 min
Total charge	60 C

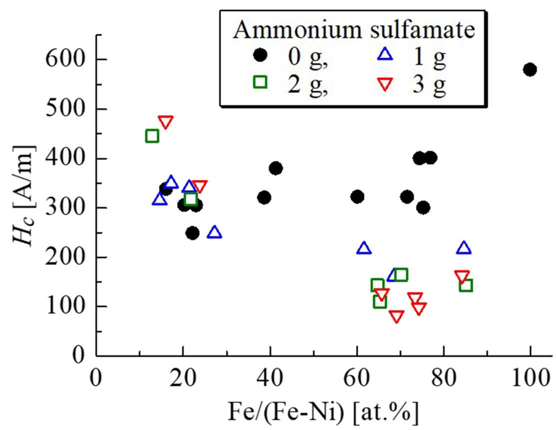


FIG. 1. Coercivity of the as-plated Fe-Ni films as a function of Fe content in the films. The concentration of the ammonium sulfamate was varied from 0 to 3 g.

content area,[11] and this result implies that primary amines work effectively to reduce the coercivity for the Fe-rich films (≈ 75 at.%).

To confirm the reduction in the coercivity for the Fe-rich films by the addition of the primary amine, we employed other primary amines of DL-α-alanine and L-glutamic acid. Figure 2 shows coercivity of the as-plated Fe-Ni films electroplated in the DES-based baths with various primary ammines as a function of Fe content in the films. The coercivity for all the primary-amine-used baths decreased in Fe-rich content area, and we found that the primary ammines are effective additives for electroplating of Fe-Ni films with high Fe contents.

To investigate the effect of primary amine concentration on the magnetic properties of the films, the amount of the amines was changed from 0 to 5 g. Figure 3-(a) shows the coercivity of the as-plated Fe-rich Fe-Ni films as a function of the amount of primary ammines. The composition of the films was adjusted to the Fe content (= 70-75 at.%) by the change in the amount of the Fe reagent (x in Table I). As shown in Figure 3-(a), the coercivity of the Fe-rich films decreased with increasing the primary amines. In typical soft magnetic films, the coercivity is affected by surface roughness since a domain wall pinning is induced by the surface roughness. Therefore, we evaluated surface roughness R_a of the Fe-rich films, and investigated the relationship between the coercivity and the R_a. The relationship is shown Figure 3-(b). As shown in Figure 3-(b), we observed good correlation between the surface roughness and the coercivity. Therefore, we considered that a factor of the decrease in the coercivity by the addition of the primary amines in the Fe-rich films is attributed to the reduction in the surface roughness.

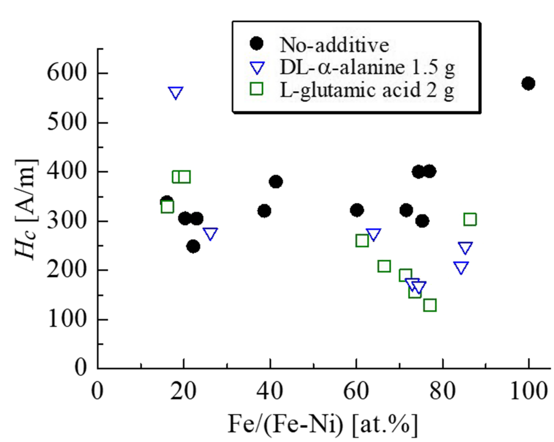


FIG. 2. Coercivity of the as-plated Fe-Ni films as a function of Fe content in the films electroplated in the DES-based baths with various primary ammines.

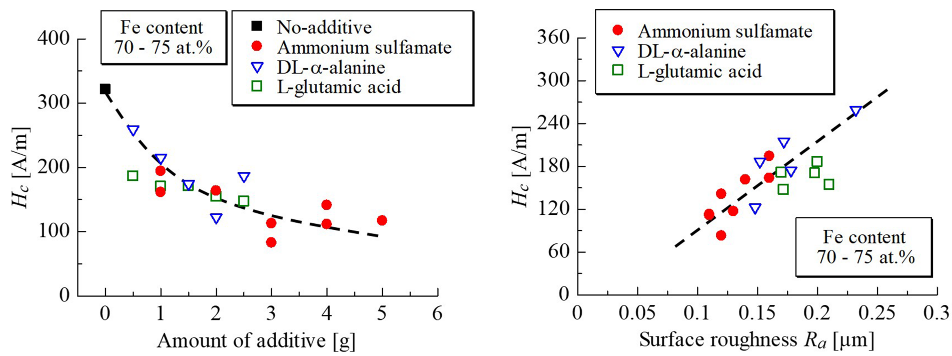
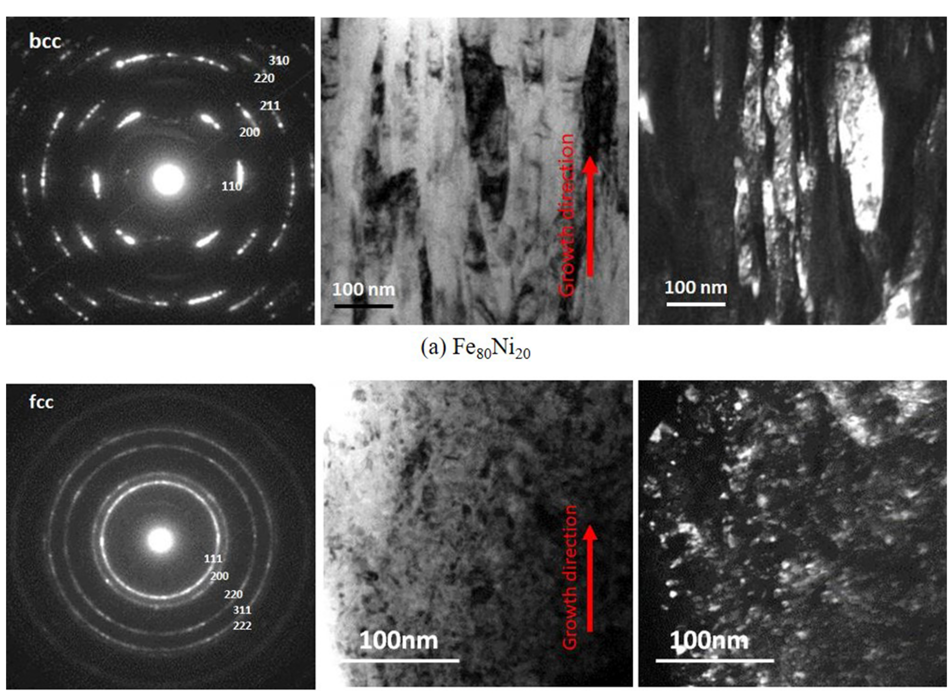


FIG. 3. Relationship among the coercivity, the surface roughness R_a and amount of the primary amines.

To discuss the micro structure of the films, we carried out a TEM observation. Figure 4 shows an electron diffraction pattern, and bright and dark-field TEM images of an Fe-rich film ($\approx Fe_{80}Ni_{20}$) and an Fe-poor one ($\approx Fe_{20}Ni_{80}$) electroplated in the DES-based baths with 3 g of ammonium sulfamate. From the diffraction rings, the Fe-rich film and the Fe-poor one have the bcc structure and the fcc one, respectively, which is consistent with the previous reported XRD results for the no-additive bath.[12] The bright and dark-field TEM images suggest the columnar texture for Fe-rich film and the random one for the Fe-poor film. Gu *et al.* and Yang *et al.* reported that Ni deposits electrodeposited from a DES-based bath have a fine crystal structure,[13,14] and the result for the Fe-poor film in this study were consistent with that for the Ni deposits. As the texture of the Fe-rich film is clearly different from that for the Fe-poor one, we considered that the change in the micro structure is another factor to reduce the coercivity in the Fe-rich film.



(b) $Fe_{20}Ni_{80}$

FIG. 4. Electron diffraction pattern, and bright and dark-field TEM images of (a) an Fe-rich film and (b) an Fe-poor one electroplated in the DES-based baths with 3 g of ammonium sulfamate.

From these results, we found that the primary amines were hopeful additives for Fe-rich films prepared in the DES-based plating baths since the coercivity and the surface roughness were reduced. As shown in INTRODUCTION, the variation of the coercivity against the change in the Fe content for the primary-amine-used baths cannot be explained by the change in the magnetocrystalline anisotropy and the magnetostriction of the films. Our result suggests that the change in the texture is one of factors to explain the unexpected variation of the coercivity against the change in the Fe content.

IV. CONCLUSIONS

We electroplated Fe-Ni films in DES-based bath with primary amines (ammonium sulfamate, DL-α-alanine and L-glutamic acid), and investigated the effect of the primary amines on structural and magnetic properties of the Fe-Ni films. The obtained results are summarized as follows:

(1) All the primary amines reduced the coercivity and the surface roughness of the Fe-Ni films with high Fe content ($\approx$ 75 at.%).
(2) Good correlation between the coercivity and the surface roughness for the Fe-rich films (70-75 at.%Fe) was observed.
(3) The Fe-rich film has the columnar texture, and the micro structure was clearly different from the Fe-poor film.

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