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Improvement in current efficiency of electroplated Fe-Ni films prepared in citric-acid-based baths

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Fe-Ni films were electroplated in a citric-acid-based plating bath, focusing on the current efficiency of the plating process. We prepared the plating baths with various citric acid contents, and evaluated the magnetic properties of the films and the current efficiency. The film with Fe content of approximately 22 at. % was obtained by adjusting the iron sulfate content in the plating bath, and we found that the Fe-Ni films with low coercivity (<30 A/m) could be obtained in the baths with various citric acid contents. For the current efficiency, we found that the baths with low citric acid content are effective to obtain high efficiency. The bath with the citric acid content of 10 g/l showed high current efficiency (85%), and the high efficiency enables us to increase the plating rate. The maximum plating rate was 186 μm/h, and we obtained 1.3 times higher rate compared to that for our previous study. Therefore, we concluded that the bath with low citric acid content is a suitable plating bath to obtain thick Fe-Ni films in a short time.
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I. INTRODUCTION

Fe-Ni alloys have good soft magnetic properties,[1,2] and their films have been applied to various magnetic devices, such as inductors and sensors.[3–7] In particular, the thick films ($\approx$20 μm) with Fe content of approximately 22 at. % have been widely used as the core and the shield in the sensor components due to their good soft magnetic properties. Electroplating method is one of hopeful methods to obtain the thick films since the process has high economic advantages and a high plating rate, and there have been many reports on electroplated Fe-Ni films.[8–10]

When considering the mass production of the soft magnetic thick films for applications as described above, the current efficiency as well as the good soft magnetic properties is one of important factors since the high efficiency enables us to obtain the films in short plating time. Although many plated Fe-Ni films with good soft magnetic properties have been reported, the efficiency are relatively low (60–70%)[11,12] compared to that for plated Ni films (>95%).[13] Recently, we have reported the Fe-Ni films with good soft magnetic properties prepared in a citric-acid-based plating bath.[14–16] The efficiency for our process was also low (65%) and we need to improve the efficiency.

In present study, we focused on the citric acid content in the bath. The citric acid forms complex with nickel ions and affects the efficiency and the properties of the films.[13] In order to improve the efficiency of the electroplating process, we plated the Fe-Ni films in plating baths with various citric acid contents, and evaluated the effect of the citric acid content on the magnetic properties and the current efficiency.

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II. EXPERIMENTAL PROCEDURES

A. Preparation of electroplated Fe-Ni films

We carried out the electroplating to obtain the Fe-Ni films by using a direct current. The contents of electrolyte are shown in Table I. In order to investigate the effect of the citric acid content on the current efficiency of the electroplated Fe-Ni films, we varied the citric acid content in the bath. We also varied the iron sulfate content to control the composition of the Fe-Ni films. 500 μm-thick and 5 mm-wide Ni and Cu plates were used as the anode and the cathode electrodes, respectively. The distance between the electrodes was set at 25 mm, and Fe-Ni films were plated on the 75 mm^2-Cu plate. The current density and the plating time were controlled by a computer-aided dc current source. Conditions of the electroplating are shown in Table II.

B. Measurements

The thicknesses and the dc-hysteresis loops of the electroplated Fe-Ni films were measured with a micrometer (Mitutoyo CPM15-25 MJ) and a B-H tracer (Riken Denshi BHS-40) operated at a field sweep rate of 50 mHz. The maximum excitation field of approximately 4 kA/m was used for

TABLE I. Electrolytes in plating bath.

Components	Concentration
$NiSO_4 \cdot 6H_2O$ (nickle sulfate)	275 g/l
$FeSO_4 \cdot 7H_2O$ (iron sulfate)	15–65 g/l
NaCl (sodium chloride)	50 g/l
$C_6H_8O_7 \cdot H_2O$ (citric acid)	10–30 g/l
$C_7H_4NNaO_3 \cdot 2H_2O$ (saccharin)	5 g/l

TABLE II. Electroplating conditions.

Conditions	Values
Bath temperature	50 °C
Current density	200 mA/cm^2
Plating time	2–10 min

the B-H measurements, and the coercivity was determined from the loop. The compositions and the crystal structures of the films were analyzed by means of SEM-EDX (Hitachi High-technologies S-3000) and XRD (Rigaku Rint 2000), respectively. Both the thicknesses and the compositions of the films were measured at different nine points and determined by averaging the measured values. The current efficiency was calculated from the actual weight of electroplated Fe-Ni films and the theoretical weight obtained by Faraday's law. All measurements were carried out for the Fe-Ni films in an as-plated state.

III. RESULTS AND DISCUSSION

Figure 1 shows the Fe content of the films as a function of the iron sulfate content in the plating baths. The results for the baths with the citric acid content of 10, 20, and 30 g/l are shown in Fig. 1. The Fe contents all increased proportionally with increasing the iron sulfate, indicating that the composition of the Fe-Ni films can be readily controlled by adjusting the iron sulfate content. Figure 2 shows (a) the coercivity and (b) the current efficiency of the as-plated films. It is well-known that the magnetic properties of the Fe-Ni alloys are affected by the alloy's composition. We, therefore, described the results in Fig. 2 as a function of the Fe content of the films. The coercivity shows a dramatic decrease with increasing the Fe content from 0 to 20 at. % followed by a moderate increase in the higher Fe contents. We obtained the Fe-Ni films with low coercivity (<30 A/m) around the Fe content of approximately 22 at. %. The current efficiency values were almost constant, indicating that the efficiency was not affected by the film composition.

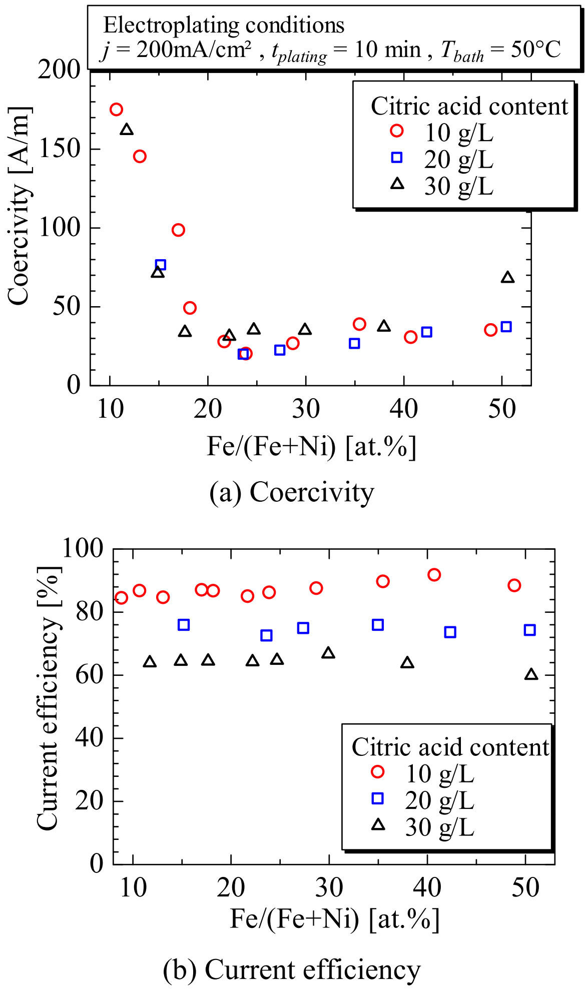

FIG. 2. (a) Coercivity and (b) current efficiency of the films as a function of the Fe content of the films. The results for the baths with the citric acid contents of 10, 20, and 30 g/l were shown in the figure.

In order to discuss the effect of the citric acid content on the current efficiency, we re-arranged the results in Fig. 2(b). Figure 3 shows the current efficiency as a function of the citric acid content in the baths. The thickness of the films was

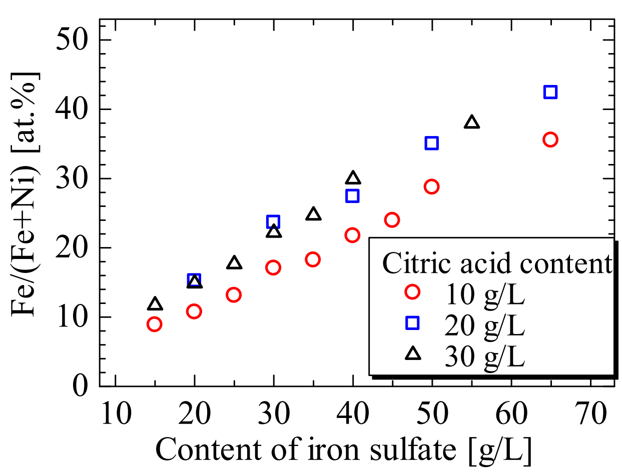

FIG. 1. Fe content of the films as a function of the iron sulfate content in the plating baths. The results for the baths with the citric acid contents of 10, 20, and 30 g/l were shown in the figures.

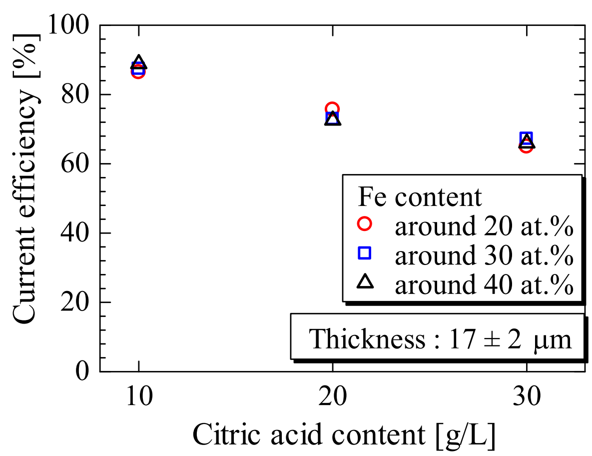

FIG. 3. Current efficiency as a function of the citric acid content in the plating baths. The thickness of the films was adjusted at 17 ± 2 μm by varying the plating time. The Fe contents of the films were controlled at approximately 20, 30, and 40 at. % by varying the iron sulfate content in the bath.

adjusted at $17 \pm 2\,\mu$m by varying the plating time. The Fe contents of the films were controlled at approximately 20, 30, and 40 at. % by varying the iron sulfate content in the bath. It is clear that not the Fe content but the citric acid content affects the current efficiency. The current efficiency was decreased by increasing the citric acid content, and the high current efficiency was obtained from the bath with low citric acid content. The efficiency of 85% for the $Fe_{20}Ni_{80}$ film is 1.3 times as high as 65% for our previous-reported films.[15] Quemper *et al.* and Spada *et al.* have been reported that the current efficiency of the films with Fe content of approximately 20 at. % prepared in boric-acid-based baths were 56% and 72%, respectively.[11,12] The efficiency of our electroplating process shows higher value compared to both groups. As described in Sec. I, the citric acid forms the complex with the nickel ion, and changes the deposition potential of the nickel. The result that the bath with high citric acid content showed low efficiency implies that the deposition potentials of nickel and/or iron ions were decreased.

From above-mentioned results, we found that the reduction in the citric acid content is effective to improve in the current efficiency.

In Fig. 2(a), despite the fact that the intrinsic magnetocrystalline anisotropy and the magnetostriction constants of the films are expected to become large, the films with high Fe content (>30 at. %) showed relatively low coercivity. This result implies that the grain size is sufficiently small enough to reduce the effective magnetocrystalline anisotropy. In order to confirm the structure of the films, we carried out the XRD analysis. Figure 4 shows the XRD patterns of the Fe-Ni films. Although the Fe content affected the diffraction patterns, the citric acid content did not affect the patterns. When the Fe content is high, the diffraction angle was shifted to the lower angle side, and broadening of the peaks was observed. The shift of the diffraction angle reflects the change of the lattice parameter of the Fe-Ni crystalline phase, and the broadening indicates the reduction in the grain size. Since the effective magnetocrystalline anisotropy could be reduced by grain refinement, the relatively low coercivity values of the films with high Fe content (>30 at. %) are attributable to the grain refinement effect. These results are

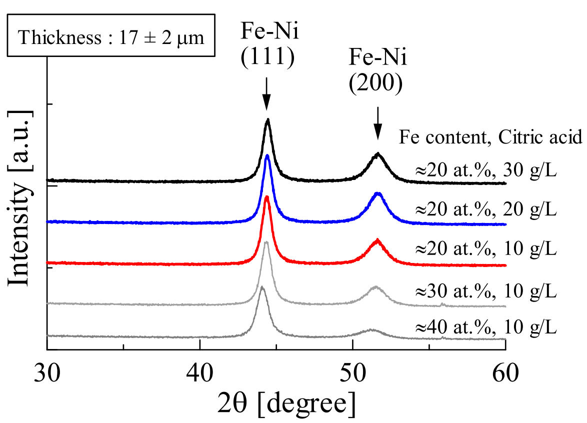

FIG. 4. XRD patterns of the Fe-Ni films prepared with various citric acid contents in the bath and Fe contents of the films. The thickness of the films was adjusted at $17 \pm 2\,\mu$m.

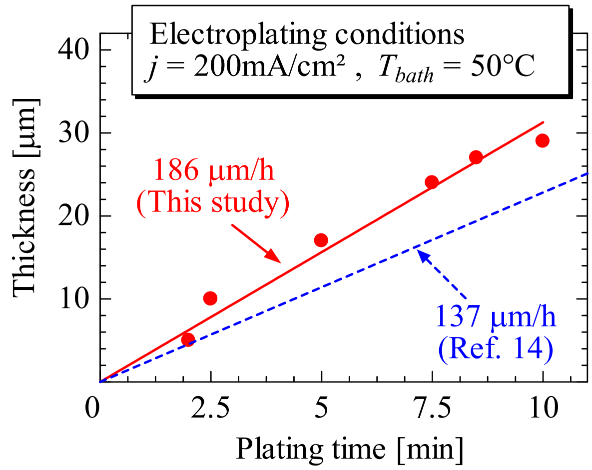

FIG. 5. Thickness of the $Fe_{22}Ni_{78}$ films as a function of the plating time. The result for our previous study of Ref. 14 is also shown in the figure.

consistent with the previously-reported ones by Theis *et al.* and Cheung *et al.*[8,17]

As a high current efficiency is expected to enhance the plating rate, we estimated the plating rate for our process. Figure 5 shows the thickness as a function of the plating time. In order to obtain the Fe-Ni thick film with low coercivity and high current efficiency, the contents of the iron sulfate and the citric acid were selected at 40 g/l and 10 g/l, respectively, based on Figs. 1 and 3. The result for our previous study under the same electroplating conditions[14] is also shown in Fig. 5. As shown in Fig. 5, the slope of the liner fitting line for present study is larger than that for our previous one (137 μm/h). The plating rate estimated from the slope is 186 μm/h and we confirmed the enhancement in the plating rate by the improved efficiency.

From above-mentioned results, we concluded that a plating bath with low citric acid content is suitable to obtain the Fe-Ni thick films with good soft magnetic properties since high current efficiency can be obtained.

IV. CONCLUSIONS

In present study, we have investigated the effect of the citric acid content on the magnetic properties and the efficiency of the electroplated Fe-Ni films prepared in citric-acid-based baths. The obtained results are summarized as follows:

(1) The Fe-Ni films with low coercivity were obtained from the baths with various contents of the citric acid by optimizing the iron sulfate contents.
(2) The plating bath with low citric acid content is one of effective plating baths to obtain the Fe-Ni films with good soft magnetic properties ($H_c < 30$ A/m) and high current efficiency (85%).
(3) The relatively low coercivity values in the films with high Fe content are attributable to the grain refinement effect.
(4) The plating rate of our process is 186 μm/h and this rate is 1.3 times higher than that for our previous study. The enhanced plating rate shows good agreement with the improved current efficiency.

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