Electroplated Fe-Co films prepared in citric-acid-based plating baths with saccharin and sodium lauryl sulfate

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ABSTRACT

We electroplated Fe-Co films in a citric-acid-based plating bath with saccharin and sodium lauryl sulfate and evaluated the magnetic properties of the films. The Fe content in the film can be readily controlled by the change in the ratio of the Fe reagent and the Co one, and the Fe content could be obtained from 10 to 90 at.% in our experimental conditions. The change in the saturation magnetization over the Fe content of the film almost agreed with the expected change from the Slater-Pauling curve. The coercivity decreased with increasing the Fe content. From the structural analysis, we found that the grain size reduced with increasing the Fe content, and the grain refinement effect works effectively to reduce the coercivity.

I. INTRODUCTION

Soft magnetic materials with high saturation magnetization are hopeful for industrial applications, and Fe-Co alloys are well-known as high saturation magnetization materials. Taking into the high saturation magnetization, some Fe-Co films with good soft magnetic properties have been reported[1–6] and are typically fabricated by sputtering, vapor deposition, and electroplating.

Electroplating is one of the attractive methods to obtain thick-films due to the high deposition rate and high economic viability, and we have reported the fabrication process of Fe-Ni thick-films (>1 μm) using electroplating with high deposition rate (>100 μm/h). In our previous studies on the electroplated Fe-Ni films, citric acid was a good complex agent to stabilize plating baths and to obtain good soft magnetic properties.[7–9] From these hopeful results, we also employed a citric-acid-based plating bath to fabricate Fe-Co films with good magnetic properties.[10] More recently, we introduced a deep eutectic solvent (DES) as a solvent for electroplating of Fe-Co films to obtain high current efficiency of the plating process.[11]

Although the above-mentioned Fe-Co films have high saturation magnetization, the coercivity is typically higher than that of Fe-Ni ones. In soft magnetic materials, one of the popular ways to reduce the coercivity is a reduction in grain size.[12] In fact, we confirmed that Fe-Ni films electroplated in the citric-acid-based plating baths have small grains (<50 nm), and the fine structure effectively works to realize good soft magnetic properties.[13–15] For improvement in the magnetic properties of Fe-Co films, we focused on the grain size. In the present study, we employed a citric-acid-based plating bath with additives of saccharin and sodium lauryl sulfate and evaluated the magnetic and structural properties of the films.

II. EXPERIMENTAL PROCEDURES

A. Electroplating

We electroplated Fe-Co films on Cu substrates using a direct current. The composition of the plating bath and the plating conditions are shown in Tables I and II, respectively. In our previous study of the citric-acid-based bath,[10] a large amount of citric acid (>100 g/L) was added into the plating baths. We recently confirmed that the current efficiency of the process for the Fe-Ni films decreased with increasing the citric acid,[9] indicating that a large amount of the

TABLE I. Plating bath conditions.

Components	Concentration
$FeSO_4 \cdot 7H_2O$ (Iron sulfate)	x = 25 - 225 g/L
$CoSO_4 \cdot 7H_2O$ (Cobalt sulfate)	250 - x [g/L]
$C_6H_8O_7 \cdot H_2O$ (Citric acid)	1 - 20 g/L
NaCl (Sodium chloride)	10 g/L
$C_7H_4NNaO_3S$ (Saccharin)	5 g/L
$C_{12}H_{25}OSO_3Na$ (Sodium lauryl sulfate)	1 g/L

TABLE II. Plating conditions.

Conditions	Values
Bath temperature	50°C
Current density	100, 200 mA/cm^2
Plating area	5 mm × 25 mm
Plating time	3 - 6 min

citric acid is not suitable to obtain thick films. Therefore, a small amount of citric acid (<20 g/L) was employed in this experiment. To reduce the grain size and improve surface roughness, we added two additives of the saccharin and the sodium lauryl sulfate into plating baths.

B. Measurements

The thicknesses of the Fe-Co films were measured at different 30 points with a micrometer (Mitutoyo CPM15-25MJ), and we determined the thickness by averaging the measured values. The saturation magnetization and the coercivity were measured with a VSM (Vibrating Sample Magnetometer: Tamagawa). The compositions and the crystal structures of the films were analyzed by EDX (Energy Dispersive X-ray spectroscopy: Hitachi High-technologies S-3000) and XRD (X-Ray Diffraction: Rigaku Miniflex 600-DX), respectively. The microstructure of the film was evaluated with a transmission electron microscope (TEM) system (JEOL JEM-2010).

III. RESULTS AND DISCUSSION

Figure 1 shows the Fe content and the coercivity Hc of the Fe-Co films as a function of the citric acid concentration. In this experiment, the $FeSO_4$ concentration was fixed at 175 g/L (x = 175 in Table I), and the result for the citric acid concentration of 0 g/L was removed since the surface was obviously rough. As shown in Fig. 1, the Fe content was almost the same value (approximately 70 at.%), indicating that the Fe content does not depend on the citric acid concentration. The coercivity decreased with increasing the citric acid concentration from 1 to 10 g/L, followed by an increase in the higher acid concentrations. The coercivity at 10 g/L was approximately 500 A/m, and this value is lower than that for Refs. 1–3.

To clarify the reason for the change in the coercivity, we carried out an XRD analysis. Figure 2 shows the grain size as a function of

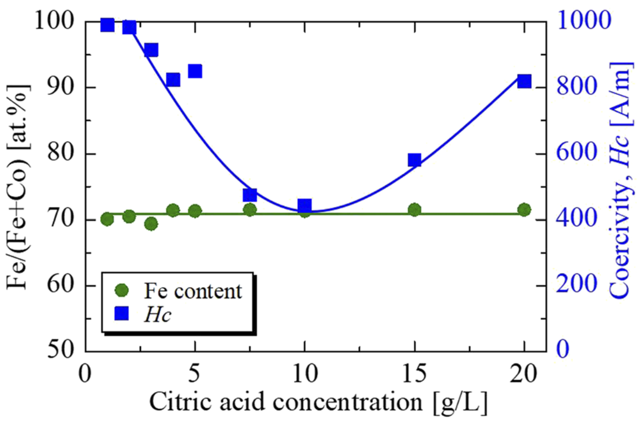

FIG. 1. The Fe content and the coercivity as a function of the citric acid concentration in plating baths. The $FeSO_4$ concentration was fixed at 175 g/L.

the citric acid concentration. The grain size was calculated from the measured XRD patterns using the Scherrer's formula. As shown in Fig. 2, the grain size varied depending on the citric acid concentration, and small grain was obtained around 10 g/L. For soft magnetic nanocrystalline materials, it is well-known that the reduction in the grain size is effective in improving the soft magnetic properties.[12] To confirm the effect of the grain size on the coercivity, the coercivity results in Fig. 1 are replotted in Fig. 3 as a function of the grain size. As shown in Fig. 3, we confirmed the good correlation between the grain size and the coercivity, and this result implies that the reduction in the grain size works effectively to reduce the coercivity in our experimental conditions. We, therefore, considered that the low coercivity around 10 g/L in Fig. 1 was attributed to the small grain size.

To investigate the effect of the composition on the magnetic and structural properties, we varied the Fe content in the film by the

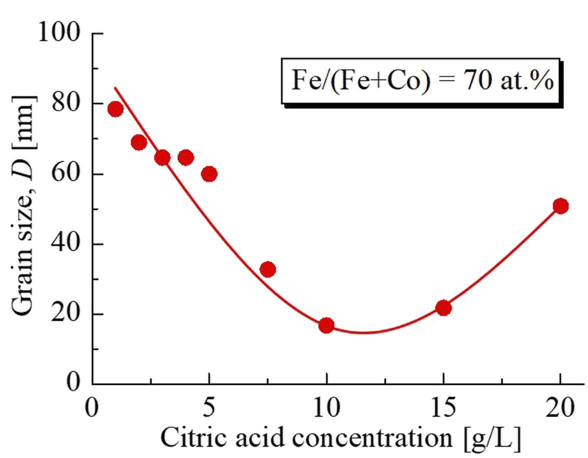

FIG. 2. The grain size as a function of the citric acid concentration in plating baths.

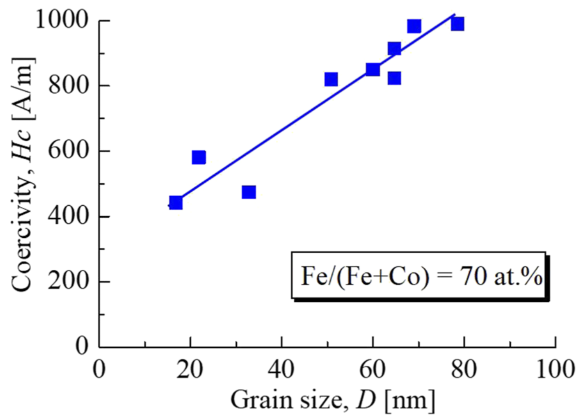

FIG. 3. The coercivity as a function of the grain size of the $Fe_{70}Co_{30}$ films.

change in the ratio of the iron sulfate and the cobalt one in the plating bath. Figure 4 shows the coercivity *Hc* and the saturation magnetization *Ms* as a function of the Fe content in the Fe-Co films. The change in *Ms* over the Fe content almost agreed with the expected change from the Slater-Pauling curve and that for the DES-based plating bath.[11] The maximum *Ms* was 228 emu/g around $Fe_{65}Co_{35}$, and this value was higher than that of the Fe-Co nanopowder.[16] In contrast, we obtained the low value of coercivity for the Fe-rich films (Fe > 56 at.%). These results indicate that we can obtain the Fe-Co films with high *Ms* and low *Hc* by adjusting Fe content around 70 at.%. To confirm the reasons for the low coercivity, we carried out the structural analyses.

Figure 5 shows the grain size as a function of the Fe content of the films. The grain size decreased with increasing Fe content of the films. From Figs. 1 and 4, we found that the grain size affects the coercivity, and the citric acid concentration and the Fe content change the grain size.

To obtain direct evidence of the fine structure, a TEM observation was carried out, and the result is shown in Figure 6. Large grains were not observed in the bright-field image, and we confirmed that the fine structure effectively works to reduce the coercivity.

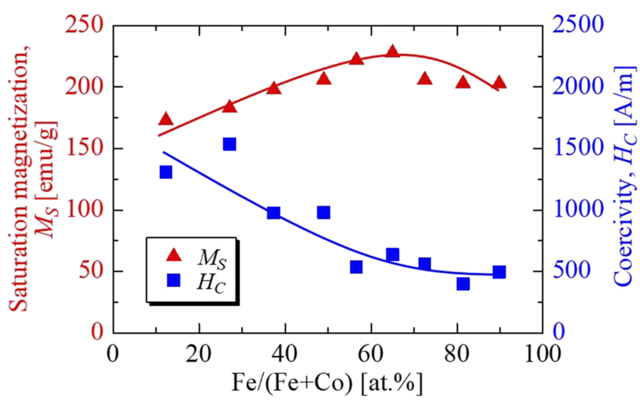

FIG. 4. The coercivity and the saturation magnetization as a function of the Fe content of the Fe-Co films.

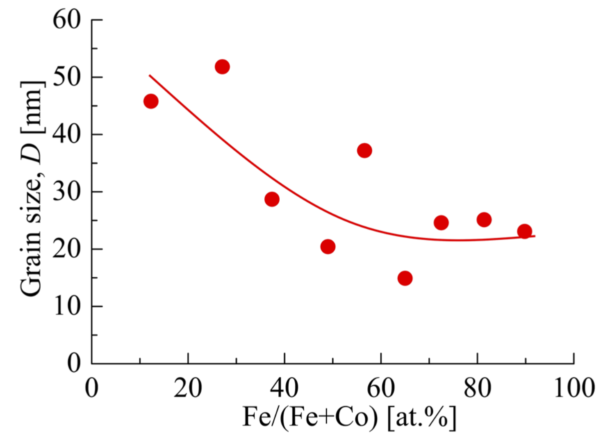

FIG. 5. The grain size as a function of the Fe content of the Fe-Co films.

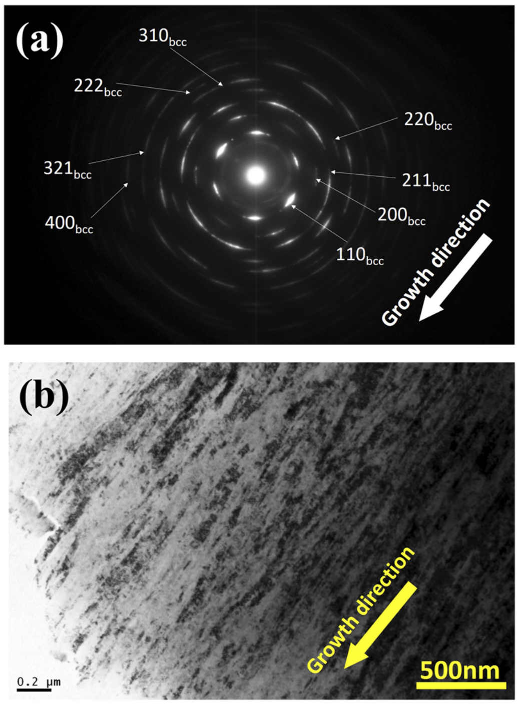

FIG. 6. TEM images of the cross-section of the $Fe_{70}Co_{30}$ film: (a) diffraction pattern and (b) bright-field image.

From these results, we concluded that the citric-acid-based bath with saccharin and sodium lauryl sulfate is attractive for obtaining Fe-Co films with high *Ms* and low *Hc*.

IV. CONCLUSION

In conclusion, we investigated the electroplated Fe-Co thick-films prepared in the citric-acid-based plating bath with saccharin and sodium lauryl sulfate. The obtained results are summarized as follows;

(1). The increase in the citric acid concentration reduced the grain size, and we obtained low coercivity of approximately 500 A/m around 10 g/L in our experimental conditions.
(2). When the citric acid concentration was kept at constant, the grain size was affected by the Fe content in the films. The grain size decreased with increasing the Fe content.
(3). The saturation magnetization over the Fe content was varied based on the expected change from the Slater-Pauling curve.
(4). We obtained the Fe-Co films with high saturation magnetization (>200 emu/g) and low coercivity (<500 A/m) around the Fe content of 70 at.%. These superior soft magnetic properties were attributed to the very fine crystal structure.

REFERENCES

[1] T. Chotibhawaris, T. Luangvaranunt, P. Jantaratana, and Y. Boonyongmaneerat, "Effects of thermal annealing on microstructure and magnetic properties of electrodeposited Co-Fe alloys," Intermetallics **93**, 323 (2018).
[2] Y. Zhang and D. G. Ivey, "Electrodeposition of nanocrystalline CoFe soft magnetic thin films from citrate-stabilized baths," Materials Chemistry and Physics **204**, 171 (2018).
[3] T. Osaka, T. Yokoshima, D. Shiga, K. Imai, and K. Takashima, "A high moment CoFe soft magnetic thin film prepared by electrodeposition," Electrochemical and Solid-State Letters **6**, C53 (2003).
[4] S. Han, I. Kim, J. Kim, K. H. Kim, and M. Yamaguchi, "Soft magnetic properties and high-frequency characteristics of Fe (Co)-based nanocrystalline films," Journal of Magnetism and Magnetic Materials **272-276**(Part 2), 1490 (2004).
[5] A. Chansena and S. Sutthiruangwong, "Corrosion behavior of electrodeposited Co-Fe alloys in aerated solutions," Journal of Magnetism and Magnetic Materials **429**, 251 (2017).
[6] N. V. Myung, D.-Y. Park, D. E. Urgiles, and T. George, "Electroformed iron and FeCo alloy," Electrochimica Acta **49**, 4397 (2004).
[7] T. Shimokawa, T. Yanai, K. Takahashi, M. Nakano, K. Suzuki, and H. Fukunaga, "Soft magnetic properties of electrodeposited Fe-Ni films prepared in citric acid based bath," IEEE Transactions on Magnetics **48**, 2907 (2012).
[8] T. Shimokawa, T. Yanai, K. Takahashi, M. Nakano, K. Suzuki, and H. Fukunaga, "Electrodeposited Fe-Ni films prepared from a tartaric-acid-based bath," Journal of the Korean Physical Society **62**, 1963 (2013).
[9] Y. Watanabe, T. Yanai, M. Otsubo, A. Takahashi, T. Ohgai, M. Nakano, K. Suzuki, and H. Fukunaga, "Improvement in current efficiency of electroplated Fe-Ni films prepared in citric-acid-based baths," Journal of Applied Physics **117**, 17A326 (2015).
[10] T. Yanai, H. Uto, T. Shimokawa, M. Nakano, and H. Fukunaga, "Electrodeposited Fe-Co films prepared from a citric-acid-based plating bath," Journal of the Korean Physical Society **62**, 1966 (2013).
[11] T. Yanai, K. Shiraishi, Y. Watanabe, T. Ohgai, M. Nakano, K. Suzuki, and H. Fukunaga, "Magnetic Fe-Co films electroplated in a deep-eutectic-solvent-based plating bath," Journal of Applied Physics **117**, 17A925 (2015).
[12] G. Herzer, "Grain size dependence of coercivity and permeability in nanocrystalline ferromagnets," IEEE Transactions on Magnetics **26**, 1397 (1990).
[13] T. Yanai, K. Koda, K. Eguchi, T. Morimura, K. Takashima, M. Nakano, and H. Fukunaga, "Effect of an annealing on magnetic properties of Fe-Ni films electroplated in citric-acid-based plating baths," AIP Advances **8**, 056239 (2018).
[14] T. Yanai, K. Azuma, K. Eguchi, Y. Watanabe, T. Ohgai, M. Nakano, and H. Fukunaga, "Effects of annealing and pulse plating on soft magnetic properties of electroplated Fe-Ni films," AIP Advances **6**, 055923 (2016).
[15] T. Yanai, T. Shimokawa, Y. Watanabe, T. Ohgai, M. Nakano, K. Suzuki, and H. Fukunaga, "Effect of current density on magnetic properties of electrodeposited Fe-Ni films prepared in a citric-acid-based-bath," Journal of Applied Physics **115**, 17A325 (2014).
[16] B. Lee, Y. J. Lee, K. H. Min, D. Kim, and Y. D. Kim, "Synthesis of nano-sized Fe–Co alloy powders by chemical solution mixing of metal salts and hydrogen reduction (CSM-HR)," Materials Letters **59**, 3156 (2005).