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We electroplated Fe-Co-Ni films in ammonium-chloride-based plating baths, and investigated the effect of the Co content on the magnetic properties and the structural ones of the as-plated films. The coercivity increased abruptly when the Co content become more than 60 at.%. As the rough surfaces were observed in the high Co content region, we considered that degradation of the surface is a factor of the abrupt increase in the coercivity. From the XRD analysis, we found that another factor of the abrupt increase is fcc-bcc phase transformation, and concluded that we need to keep the fcc structure to obtain Fe-Co-Ni films with low coercivity.
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I. INTRODUCTION

Fluxgate sensors are used in electric devices for detections of magnetic field and current values. Typical fluxgate sensors have a soft magnetic core, and magnetic materials with excellent soft magnetic properties, such as Fe-Ni alloys and Co-based amorphous ribbons, have been applied as the magnetic core materials.[1] Although the sensors with Fe-Ni alloys and Co-based amorphous ribbons have high sensitivity,[2,3] variation of sensitivity against temperature is relatively large (> 0.1%/K). As a large temperature dependence of sensitivity is attributed to low Curie temperature of the core material, soft magnetic materials which have higher Curie temperatures than those of Fe-Ni and Co-based amorphous alloys (200-550°C)[4,5] are required. It is well-known that Co has high Curie temperature and Co substitution for typical magnetic materials is one of effective methods to improve thermal stability of magnetic properties.[6]

An electroplating method is one of effective methods to obtain soft magnetic films due to the high economic viability of the process, and some researchers reported fluxgate sensors using electroplated soft magnetic alloys.[6–8] For electroplated Fe-Co-Ni films, magnetic and structural properties have been investigated,[9–13] and we considered that the films are attractive core materials for fluxgate sensors. In the present study, we plated Fe-Co-Ni films in ammonium-chloride-based baths,[13–15] and evaluated the magnetic properties of the films.

II. EXPERIMENTAL PROCEDURES

A. Electroplating

We carried out an electroplating to obtain Fe-Co-Ni films by using a direct current. The composition of the plating bath and the plating conditions are determined based on our previous study,[16] and summarized in Tables I and II, respectively.

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TABLE I. Plating bath conditions (Ammonium-chloride-based bath).

Components	Concentration
$NiSO_4 \cdot 6H_2O$ (Nickel sulfate)	275 - x g/L
$FeSO_4 \cdot 7H_2O$ (Iron sulfate)	30 - 170 g/L
$CoSO_4 \cdot 7H_2O$ (Cobalt sulfate)	x g/L
$C_7H_4NNaO_3 \cdot 2H_2O$ (Saccharin)	10 g/L
NH_4Cl (Ammonium chloride)	15 g/L
$C_{12}H_{25}OSO_3Na$ (Sodium lauryl sulfate)	3 g/L
$C_6H_8O_6$ (Ascorbic acid)	0.5 g/L

TABLE II. Plating conditions.

Conditions	Values
Bath temperature	50°C
Current density	200 mA/cm^2
Plating time	10 min
Anode (Ni)	5 mm × 15 mm
Substrate (Cu)	5 mm × 15 mm

B. Measurements

The thicknesses and the dc-hysteresis loops of the electroplated Fe-Co-Ni films were measured with a micrometer (Mitutoyo CPM15-25MJ) and a B-H tracer (Riken Denshi BHS-40) operated at a field sweep rate of 50 mHz, respectively. The maximum excitation field of approximately 4 kA/m was used for the B-H measurements and the coercivity was determined from the loop. The saturation magnetization was measured with a VSM (Vibrating Sample Magnetometer: Tamakawa). 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 grain size was calculated from the measured XRD patterns using the Scherrer's formula. The thickness and the composition of each 75 mm^2-films were determined by averaging the values obtained for approximately every 9 mm^2 (nine points). As we fixed the current density and the plating time, all films showed almost the same thickness (Approx. 20 µm). All measurements were carried out for the Fe-Co-Ni films in an as-plated state.

III. RESULTS AND DISCUSSION

Figure 1 shows the coercivity and the saturation magnetization of the as-plated Fe-Co-Ni films as a function of the Co content in the films. The Fe contents of the films were adjusted at approximately 22 at.% by varying the iron sulfate concentration in the bath. The saturation magnetization was linearly increased with increasing the Co content of films. Although the films with low Co content showed low coercivity, an abrupt increase in coercivity was observed when the Co content was higher than a threshold value (Approx. 60%).

To understand a factor of the abrupt increase in the coercivity, we evaluated the surface roughness of the films. Figure 2 shows the surface roughness of the as-plated Fe-Co-Ni films as a function of Co content in the films. The insets indicate photographs and SEM images for some Fe-Co-Ni films with different Co content. As shown in the SEM images, the surface states obviously changed depending on the Co content, and much rough surface was observed in higher Co content region. The R_a increased abruptly when the Co content becomes more than 40 at.%, and increase tendency of R_a shows good agreement with that for the coercivity shown in Fig. 1. Thus, we considered that the rough surface is a factor of the abrupt increase in the coercivity.

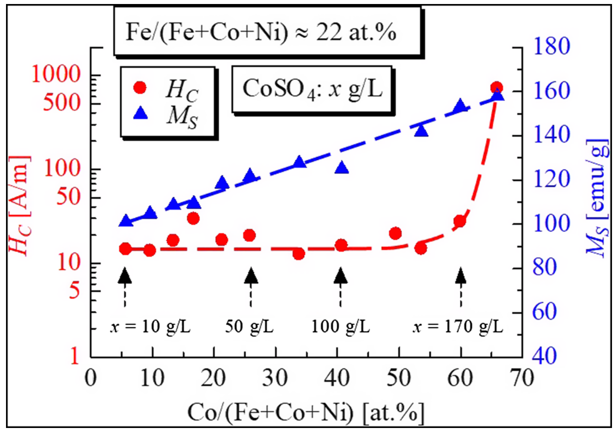

FIG. 1. The coercivity and the saturation magnetization of the as-plated Fe-Co-Ni films as a function of the Co content in the films.

In Fig. 1, the Fe-Co-Ni films with low Co content show relatively low coercivity even though the intrinsic magnetocrystalline anisotropy and magnetostriction of the films are expected to be high.[17] In order to understand this behavior, we investigated the crystal structure of the films. Figure 3 shows the grain size of the as-plated Fe-Co-Ni films as a function of the Co content in the films. The insets indicate the XRD patterns for some Fe-Co-Ni films with high Co content (> 50 at.%). As shown in Fig. 3, the grain size decreases with increasing the Co content of the films. As it is well-known that coercivity of nanocrystalline materials scales with the 6th power of the grain size,[18] we considered that the grain refinement effectively works to keep low coercivity. From the XRD patterns in Fig. 3, a change in crystal structure was observed for the films with high Co content. Thus, we considered that the phase transition from fcc structure to bcc one is another factor for the abrupt increase in coercivity.

From the results for Figs. 1–3, we considered that the phase transition is a more dominant factor to determine the coercivity compared with the surface roughness since the Co content for the phase transition (approx. 60 at.%) is almost the same as that for the abrupt increase in coercivity. To discuss the correlation between the phase transition and the abrupt increase in coercivity, we electroplated Fe-Co-Ni films in a wide composition range. Figure 4 shows a ternary diagram for the coercivity of the Fe-Co-Ni films. The blue band indicates the fcc-bcc phase boundary for the Fe-Co-Ni films, and the boundary was obtained from our experimental result for the XRD analysis. Some researchers reported the fcc-bcc phase transition for electroplated Fe-Co-Ni films, and our result for the phase

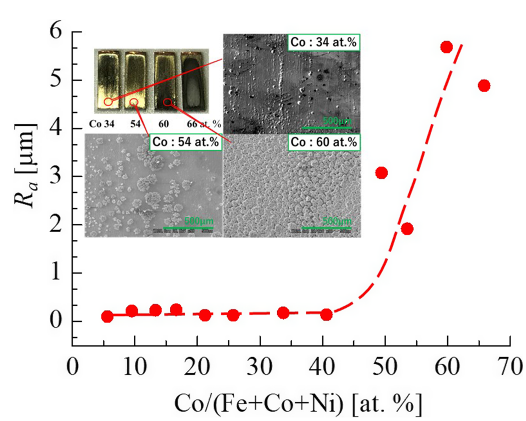

FIG. 2. The surface roughness of the as-plated Fe-Co-Ni films as a function of the Co content in the film. The insets indicate photographs and SEM images for some Fe-Co-Ni films.

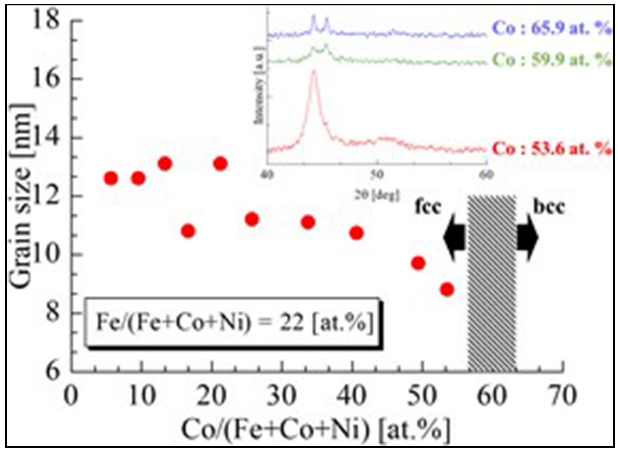

FIG. 3. The grain size of the as-plated Fe-Co-Ni films as a function of amount of the Co content in the films. The insets indicate XRD patterns for the Fe-Co-Ni films with high Co content.

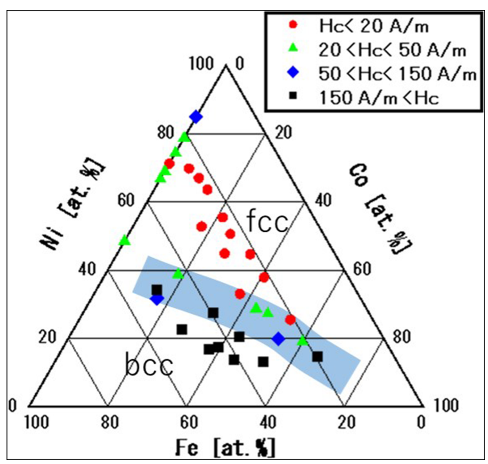

FIG. 4. Ternary diagram for the coercivity of the Fe-Co-Ni films.

transition almost agrees with the previous reports.[11–13] The coercivity increased around the blue band, indicating that we need to pay attention to keep fcc structure for obtaining low coercivity when increasing the saturation magnetization and the Curie temperature of the films by the increase in the Co content.

IV. CONCLUSION

We have investigated the structural and the magnetic properties of the Fe-Co-Ni films prepared from an ammonium-chloride-based plating bath. The obtained results are summarized as follows:

(1) The R_a increased abruptly when the Co content becomes more than 40 at.%, and increase tendency of R_a shows good agreement with that for coercivity.
(2) The grain size decreased with increasing Co content of the films. The grain refinement effectively works to keep low coercivity.
(3) The Fe-Co-Ni films obtained in this study showed low coercivity (< 20 A/m), high saturation magnetization (> 140 emu/g) and high Curie temperature (Approx. 800°C).

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