

Effect of an annealing on magnetic properties of Fe-Ni films electroplated in citric-acid-based plating baths

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We have already reported Fe-Ni films with good soft magnetic properties prepared by using an electroplating method. In the present study, we employed an annealing for further improvement in soft magnetic properties of the electroplated Fe-Ni films. The annealing reduces the coercivity of the films, and the reduction rate of the coercivity depended on the Cl^- ion concentration in the bath. The $\text{Fe}_{22}\text{Ni}_{78}$ films prepared in the plating bath with high Cl^- ion concentration showed large reduction rate of the coercivity, and we found that the annealing is more effective for high Cl^- ion concentration bath since much lower coercivity value can be obtained compared with that for low Cl^- ion concentration one. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.4991541>

I. INTRODUCTION

Fe-Ni films have been applied to magnetic cores of fluxgate sensors,^{1,2} and an electroplating method is one of effective methods to obtain soft magnetic films due to the high economic viability of the process. We reported Fe-Ni films with good soft magnetic properties prepared by an electroplating method,³ and many researchers also reported electroplated Fe-Ni soft magnetic films.⁴⁻⁸

In general, residual internal stress in soft magnetic materials degrades their soft magnetic properties, and the materials are typically annealed to release the stress and improve the magnetic properties. It is well-known that as-plated films also exist internal stress, and some additives in plating baths are employed to reduce the stress. Thus, it is expected that an annealing improves magnetic properties of the electroplated Fe-Ni films.

Recently, we have reported the effect of Cl^- ion concentration in plating baths, and confirm that moderate low Cl^- concentration is preferred for obtaining the $\text{Fe}_{22}\text{Ni}_{78}$ films with good soft magnetic properties.⁹ In electroplating of Ni film, Watts-type plating baths are widely used, and the baths contain a small amount of Cl^- ions to enhance Ni anode corrosion and prevent anode passivation. Moreover, it is well-understood that high Cl^- ion concentration in the Watts-type baths increases tensile stress in as-plated Ni films. Therefore, we considered that the Cl^- ion concentration affects degree of the improvement in soft magnetic properties by the annealing for stress relaxation. In the present study, we investigated an improvement in soft magnetic properties of the electroplated Fe-Ni films using an annealing, considering Cl^- ion concentration in plating baths.

II. EXPERIMENTAL PROCEDURE

A. Electroplating of Fe-Ni films

We electroplated Fe-Ni films on Cu substrates using a direct current. The components in plating baths are shown in Table I. To change the Cl^- ion concentration, we varied NaCl and FeCl_2

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TABLE I. Components in the plating bath.

Components	Content
NiSO ₄ · 6H ₂ O	275 g/L
FeSO ₄ · 7H ₂ O	30 - 50 g/L
FeCl ₂ · 4H ₂ O	<i>x</i> (g/L)
NaCl	10 - 100 g/L
C ₆ H ₈ O ₇ · H ₂ O (Citric acid)	10 g/L
C ₇ H ₄ NNaO ₃ · 2H ₂ O (Saccharin)	5 g/L

TABLE II. Electroplating conditions.

Conditions	Value
pH (Not-adjusted)	Approx. 2
Bath temperature	50°C
Current density	0.2 A/cm ²
Plating time	5 min
Anode	Ni plate
Cathode(Substrate)	Cu plate
Plated area	5 × 15 mm ²

concentrations in the plating baths. The plating conditions were determined based on our previous studies for Fe-Ni films,³ and summarised in Table II.

B. Annealing of Fe-Ni films

The films were annealed in a vacuum ($< 10^{-2}$ Pa). In this experiment, we varied the annealing temperature from 100 to 400°C. The temperature was ramped from room temperature to the annealing temperature for 5 min, and then kept at constant for 60 min.

C. Measurements

The dc-hysteresis loops of the sheet-shaped Fe-Ni films (15 mm in length, 5 mm in width, and approx. 15 μm in thick) were measured with 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 the B-H measurements, and the coercivity values were obtained for the measured loops. The compositions and crystal structures of the films were analyzed with an energy dispersive X-ray spectrometry (Hitachi High-technologies S-3000) and X-ray diffraction patterns (Miniflex 600-DX), respectively. The thicknesses of the as-plated Fe-Ni films were measured with a micrometer (Mitutoyo, CPM15-25MJ). As we fixed the current density and the plating time, all films showed almost the same thickness (approx. 15 μm).

III. RESULTS AND DISCUSSION

To determine an annealing temperature, we annealed an electroplated Fe₂₂Ni₇₈ film, and evaluated the coercivity value of the annealed one. Figure 1 shows coercivity of the annealed Fe₂₂Ni₇₈ film as a function of annealing temperature. The coercivity for the as-plated films (before annealing) is also shown as a dashed line. As shown in Fig.1, the coercivity slightly decreases with increasing the annealing temperature from 100 to 300°C, and then dramatically increased.

From the result for Fig.1, we determined the annealing temperature as 300°C.

Figure 2 shows the coercivity of the as-plated Fe-Ni films and the annealed ones as a function of NaCl concentration in the bath. In this experiment, we fixed FeSO₄·7H₂O concentration at 50 g/L. As shown in Fig.2, the coercivity for the as-plated Fe-Ni film increases with increasing the NaCl concentration whereas that for the annealed one decreases.

Figure 3 shows reduction ratio of the coercivity, $\Delta H_c/H_c$, and Fe content of the Fe-Ni films as a function of NaCl concentration in the bath. We calculated $\Delta H_c/H_c$ using the result for Fig.2 and the

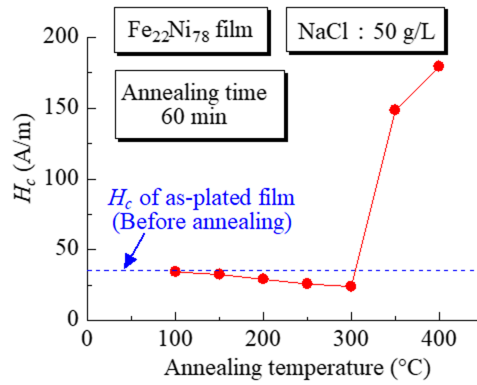


FIG. 1. Coercivity of the annealed Fe₂₂Ni₇₈ film as a function of annealing temperature. The dashed line is the coercivity value of the as-plated film.

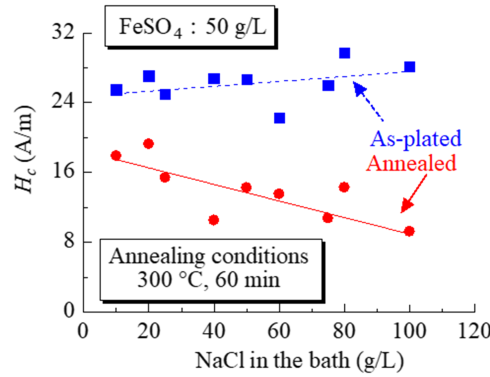


FIG. 2. Coercivity of the as-plated Fe-Ni films and the annealed ones as a function of NaCl concentration in the bath.

following equation:

$$\frac{\Delta H_c}{H_c} = \frac{H_{c, \text{annealed}} - H_{c, \text{as-plated}}}{H_{c, \text{as-plated}}} \tag{1}$$

With increasing the NaCl concentration, $\Delta H_c/H_c$ linearly decreases and the Fe content slightly decrease. This result implies that degree of $\Delta H_c/H_c$ is affected by the changes in (a) the Fe content of the film, (b) Na⁺ concentration, and (c) Cl⁻ one in the bath.

To remove the effect of the change in the Fe content, we controlled the Fe content at approximately 22 at.%, by the change in the FeSO₄·7H₂O concentration and re-evaluated the effect of the NaCl concentration on $\Delta H_c/H_c$. Figure 4 shows $\Delta H_c/H_c$ of the Fe₂₂Ni₇₈ films as a function of NaCl

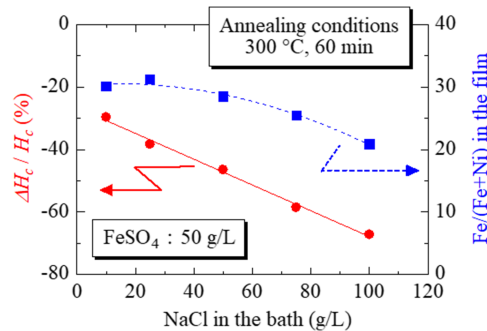


FIG. 3. $\Delta H_c/H_c$ and Fe content of the Fe-Ni films as a function of NaCl concentration in the bath.

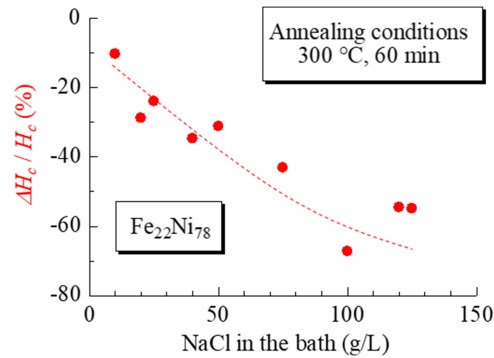


FIG. 4. $\Delta H_c/H_c$ of the $\text{Fe}_{22}\text{Ni}_{78}$ films as a function of NaCl concentration in the bath.

concentration in the bath. Since the $\Delta H_c/H_c$ clearly decreases with increasing the NaCl concentration, we found that the Na^+ and/or Cl^- concentrations affect degree of $\Delta H_c/H_c$.

As mentioned in Introduction, we have already confirmed Cl^- ion concentration affects coercivity of the as-plated Fe-Ni films. Therefore, we focused on Cl^- ion concentration in our plating bath, and varied the Cl^- ion concentration by a replacement of FeSO_4 with FeCl_2 . Figure 5 shows the coercivity of the as-plated $\text{Fe}_{22}\text{Ni}_{78}$ films and the annealed ones as a function of FeCl_2 concentration. For the as-plated films, the coercivity increases with increasing the FeCl_2 concentration. This result implies that lower Cl^- ion concentration is preferable to obtain low coercivity for as-plated $\text{Fe}_{22}\text{Ni}_{78}$ films, and agrees with our previously-reported result.⁹ The annealing reduces the coercivity of the films, and slight decrease in coercivity was observed with increasing the FeCl_2 concentration. From the result for Fig.5, we found that the ΔH_c for the bath with high Cl^- concentration is much larger than that for low Cl^- one. Consequently, the $\text{Fe}_{22}\text{Ni}_{78}$ films prepared in the plating bath with high Cl^- concentration show large reduction rate of the coercivity.

To further understand the effect of the Cl^- ion concentration, we calculated the grain size from the measured XRD patterns using the Scherrer's formula. Figure 6 shows grain size of the as-plated films and the annealed ones as a function FeCl_2 concentration in the bath. As the grain growth by the annealing was inhibited for high Cl^- concentration bath compared with that for low Cl^- concentration one, we considered that much smaller grain size of the annealed film is a factor to obtain low coercivity, indicating that the grain refinement reduces the effective magnetic crystalline anisotropy of fcc Fe-Ni nanocrystalline phase.^{10,11}

From the above-mentioned results, we found that the Cl^- concentration in the bath affects the grain size and the coercivity of the as-plated Fe-Ni films and the annealed ones. In our experimental conditions, a plating bath with low Cl^- concentration is preferable for the as-plated films, and that with high Cl^- one is suitable for the annealed ones.

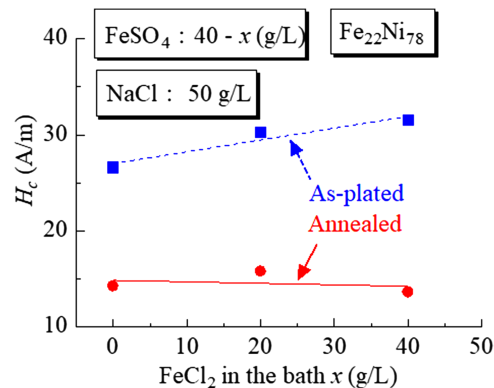


FIG. 5. Coercivity of the as-plated $\text{Fe}_{22}\text{Ni}_{78}$ films and the annealed ones as a function of FeCl_2 concentration in the bath.

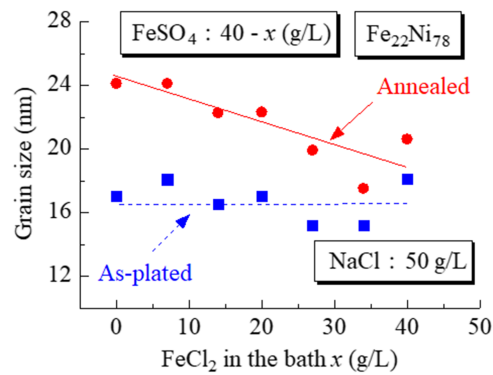


FIG. 6. Grain size of the as-plated $\text{Fe}_{22}\text{Ni}_{78}$ films and the annealed ones as a function of FeCl_2 concentration in the bath.

IV. CONCLUSION

In conclusion, we investigated an improvement in soft magnetic properties of the electroplated Fe-Ni films using the annealing. The obtained results are summarized as follows;

- (1) The coercivity of the $\text{Fe}_{22}\text{Ni}_{78}$ film prepared in the bath with low Cl^- ion concentration shows much smaller value compared with that for high Cl^- ion one.
- (2) The annealing reduced the coercivity, and the reduction rate of coercivity for the bath with high Cl^- ion concentration showed high value.
- (3) The Cl^- ion concentration affects the grain size and the soft magnetic properties of the as-plated Fe-Ni films and the annealed ones.

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- ¹ H.-S. Park, J.-S. Hwang, W.-Y. Choi, D.-S. Shima, K.-W. Na, and S.-O. Choi, *Sens. Act. A: Phys.* **114**, 224 (2004).
- ² T. M. Liakopoulos and C. H. Ahn, *Sens. Act. A: Phys.* **77**, 66 (1999).
- ³ T. Shimokawa, T. Yanai, K. Takahashi, M. Nakano, K. Suzuki, and H. Fukunaga, *IEEE Trans. Magn.* **48**, 2907 (2012).
- ⁴ M. Theis, S. Ediger, M. T. Schmitt, J.-E. Hoffmann, and M. Saumer, *Phys. Status Solidi A* **210**, 853 (2013).
- ⁵ Y. Kamo and T. Miyamoto, *IEEE Trans. Magn. Jpn.* **1**, 502 (1985).
- ⁶ D. Flynn and M. P. Y. Desmulliez, *IEEE Trans. Magn.* **46**, 979 (2010).
- ⁷ J. M. Quemper, S. Nicolas, J. P. Gilles, J. P. Grandchamp, A. Bosseboeuf, T. Bourouina, and E. Dufour-Gergam, *Sens. Act. A: Phys.* **74**, 1 (1999).
- ⁸ E. R. Spada, L. S. de Oliveira, A. S. da Rocha, A. A. Pasa, G. Zangari, and M. L. Sartorelli, *J. Magn. Magn. Mater.* **272–276**, e891 (2004).
- ⁹ T. Yanai, K. Koda, K. Eguchi, K. Takashima, T. Morimura, M. Nakano, and H. Fukunaga, "Effect of ammonium chloride in plating baths on soft magnetic properties of electroplated Fe-Ni films," *IEEE Trans. Magn.* (to be published).
- ¹⁰ G. Herzer, *IEEE Trans. Magn.* **26**, 1397 (1990).
- ¹¹ K. Suzuki, A. Makino, N. Kataoka, A. Inoue, and T. Masumoto, *Materials Transactions JIM* **32**, 93 (1991).