

# Effect of Na ions in plating baths on coercivity of electroplated Fe-Pt film-magnets

T. Yanai<sup>1</sup>, J. Honda<sup>1</sup>, R. Hamamura<sup>1</sup>, H. Yamada<sup>2</sup>, N. Fujita<sup>2</sup>,  
K. Takashima<sup>1</sup>, M. Nakano<sup>1</sup>, H. Fukunaga<sup>1</sup>

<sup>1</sup>Nagasaki University, 1-14, Bunkyo-machi, Nagasaki, Nagasaki 852-8521, Japan

<sup>2</sup>National Institute of Technology, Nara College, 22 Yata-cho, Yamatokoriyama, Nara 639-1080, Japan

Fe<sub>50</sub>Pt<sub>50</sub> thick-films were electroplated on a Ta substrate using a direct current, and we evaluated the effect of Na ion concentration in plating baths on the magnetic properties of the annealed films. With increasing NaCl content from 2 to 30 g/L, the coercivity of the annealed Fe<sub>50</sub>Pt<sub>50</sub> films increased from 700 kA/m to approximately 900 kA/m. For obtaining further experimental evidence for the increase in the coercivity, we employed trisodium citrate instead of NaCl as an additive in the plating bath. Consequently, as the addition of the trisodium citrate as well as NaCl increased the coercivity, we concluded that a plating bath with high Na ion concentration is effective to obtain the Fe-Pt thick-films with high coercivity.

**Index Terms**— Fe-Pt, Electroplating, Na ion concentration, pH, Film magnet, Hard magnetic material.

## I. INTRODUCTION

L<sub>10</sub> TM-Pt (TM: Fe, Co) films are attractive film-magnets for medical devices since the films have good hard magnetic properties and high biological safety [1-3]. For applying film-magnets to small-sized medical devices, we need to prepare relatively thick films (> 10 μm) in a short time, and a fabrication process with high deposition rate is preferred. An electroplating is one of attractive methods to obtain magnetic thick films since the process has many industrial advantages, such as simplicity of the equipment and high deposition rate.

We recently reported Fe-Pt thick film-magnets (1-20 μm in thick) prepared in citric-acid-based plating baths, and confirmed that the coercivity of the Fe<sub>60</sub>Pt<sub>40</sub> film-magnet increases from 180 to 460 kA/m when the pH value increases from 2 to 4 [4]. It is well-known for typical electroplated films that pH values are one of important plating parameters to determine structural and magnetic properties, and some researchers have reported the pH-adjusted plating baths for electroplated Fe-Pt films [5-7]. As we used NaOH as a pH control agent in the previous study, the result for increase in the coercivity suggests two possibilities: (a) pH value of the bath and (b) Na ion concentration in the bath. Since high coercivity is one of important properties for thick film-magnets, it is effective for us to clarify reasons for the increase in the coercivity. Thus, we evaluated the effect of Na ion concentration in plating baths on the coercivity of the electroplated Fe-Pt film-magnets.

## II. EXPERIMENTAL PROCEDURES

### A. Electroplating of Fe-Pt films

We carried out an electroplating to obtain the Fe-Pt film-magnets by using a direct current. The contents of the electrolyte in the plating bath are shown in Table 1. In this study, we varied the content of NaCl or Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O to change the Na ion concentration in the bath.

Table 1. Components in the plating bath.

Components	Content (g/L)
FeSO <sub>4</sub> ·7H <sub>2</sub> O	5 - 10
Pt(NH <sub>3</sub> ) <sub>2</sub> (NO <sub>2</sub> ) <sub>2</sub>	10
Citric acid (C <sub>6</sub> H <sub>8</sub> O <sub>7</sub> ·H <sub>2</sub> O)	30
NH <sub>4</sub> Cl	25
Trisodium citrate (Na <sub>3</sub> C <sub>6</sub> H <sub>5</sub> O <sub>7</sub> ·2H <sub>2</sub> O)	0 - 150
Sodium chloride (NaCl)	0 - 150

The electroplating conditions are summarized in Table 2. A Pt mesh and a Ta plate were used as an anode and a cathode, respectively. The distance between the electrodes was 20 mm, and 75 mm<sup>2</sup> Fe-Pt films were plated on the Ta plate. The current density and the plating time were controlled by using a computer-aided dc-current source (MATSUSADA, P4K-80). The bath temperature was kept at 70°C during the plating.

Table 2. Electroplating conditions.

Conditions	Value
Bath temperature	70°C
Current density	1 A/cm <sup>2</sup>
Plating time	5 - 20 min

### B. Annealing of Fe-Pt films

As-plated Fe-Pt films showed a disordered A1 (fcc) structure and low coercivity. To transform the disordered A1 (fcc) structure to the ordered L1<sub>0</sub> (fct) one, we annealed the as-plated films at 700°C. The temperature was ramped from room temperature to 700°C at the constant heating rate of 100°C/min, and then kept at constant for 60 min.

Table 3. Annealing conditions.

Conditions	Value
Heating rate	100°C/min
Annealing temperature	700°C
Annealing time	60 min
Atmosphere	Vacuum (< 4×10 <sup>-3</sup> Pa)

### C. Measurements

The thicknesses of the 75 mm<sup>2</sup> Fe-Pt films were measured at different 9 points with a micrometer (Mitutoyo, CPM15-25MJ), and we determined the thickness by averaging the measured values. The thickness of the films was within 3 - 20 μm in this experiment. The compositions of the films were measured with a SEM-EDX (Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy) system (Hitachi High-technologies, S-3000). The crystal structures were evaluated by an XRD (X-ray diffraction) analysis (Rigaku, MiniFlex600), and the hysteresis loops of the annealed films were measured with a vibrating sample magnetometer. The maximum applied field was approximately 2 MA/m for the measurements of the loop, and we obtained the coercivity of the annealed films from the measured loops.

## III. RESULTS AND DISCUSSION

Figure 1 shows hysteresis loops of the annealed Fe-Pt films prepared from plating baths with various NaCl contents (2, 8, and 30 g/L). The composition of the films was adjusted at Fe<sub>50</sub>Pt<sub>50</sub> by the change in the FeSO<sub>4</sub> content in the plating bath. As shown in Fig.1, the coercivity increases with increasing the NaCl content in spite of the same composition of Fe<sub>50</sub>Pt<sub>50</sub>. Generally, large coercivity for Fe-Pt-system bulk magnets is attributed to the presence of finely dispersed mixture of the ordered and the disordered Fe-Pt crystalline phases and domain wall pinning at twins and anti-phase boundaries [8-12]. On the other hands, for nanocrystalline Fe-Pt and Co-Pt materials, increases in the volume fractions of the ordered phases are more important than the above-mentioned structural factors to obtain large coercivity since the coercivity is typically directly related to the ordered volume fraction [2, 13-15]. Therefore, we carried out an XRD analysis to confirm the development state of the L1<sub>0</sub> ordering for the annealed films. Figure 2 shows the XRD patterns of the annealed Fe<sub>50</sub>Pt<sub>50</sub> films for NaCl = 2, 8, and 30 g/L. We also show the XRD pattern for the as-plated Fe<sub>50</sub>Pt<sub>50</sub> film (NaCl = 30 g/L) in Fig.2. As shown in Fig.2, the as-plated film has only the fcc Fe-Pt crystalline phase, and all the annealed films have only the fct one. As all the annealed films show almost the same diffraction patterns, we confirmed that our annealing conditions are enough to develop the L1<sub>0</sub> ordering in the NaCl-content range from 2 to 30 g/L.

To evaluate the effect of the NaCl content on the structure of the annealed films, we focused on the peak splitting ( $\Delta 2\theta$ ) between (200) and (002) peaks in Fig.2. Figure 3 shows the peak splitting for the annealed Fe<sub>50</sub>Pt<sub>50</sub> films as a function of the NaCl content in the plating bath. As shown in Fig.3,  $\Delta 2\theta$  increased with increasing the NaCl content. This result implies that we can obtain highly ordered films using the baths with high NaCl content. Since the ordering degree is one of important factors to obtain high coercivity for the Fe-Pt film-magnets, we consider that the difference of the ordering degree affected the difference of the coercivity in Fig.1.

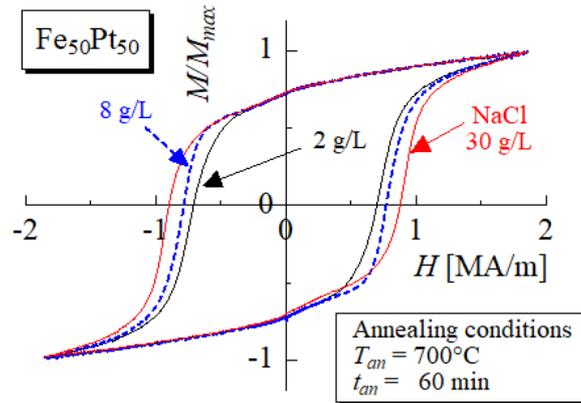


Fig.1 Hysteresis loops of the annealed  $Fe_{50}Pt_{50}$  films prepared at NaCl = 2, 8, and 30 g/L.

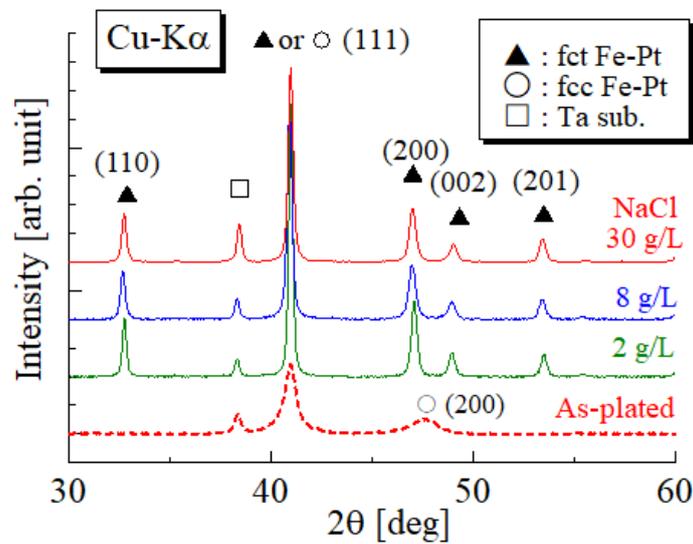


Fig.2 XRD patterns of the as-plated  $Fe_{50}Pt_{50}$  film for NaCl = 30 g/L and the annealed ones for NaCl = 2, 8, and 30 g/L.

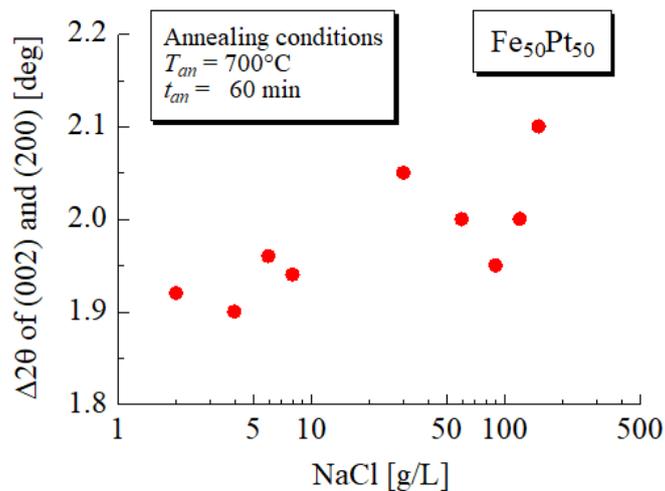


Fig.3 Diffraction peak splitting between (002) and (200) for the annealed  $Fe_{50}Pt_{50}$  films as a function of the NaCl content in the plating bath

As the development of the  $L1_0$  ordering was confirmed by the annealing in Fig.2, we decided to evaluate the effect of the NaCl content on the coercivity systematically. Figure 4 shows (a) the coercivity and (b) the grain size of the annealed  $Fe_{50}Pt_{50}$  films as a function of the NaCl content in the plating bath. The grain size of the as-plated  $Fe_{50}Pt_{50}$  films is also shown in Fig.4 (b). As shown in Fig.4 (a), the coercivity increases with increasing the NaCl content, and this result implies that NaCl ( $Na^+$  ions or  $Cl^-$  ions) affects the coercivity of the annealed films. As mentioned in “INTRODUCTION”, we have already confirmed that the addition of NaOH increases the coercivity [4]. From the results for the previous study and Fig.4 (a), we considered that the Na ion concentration is an important factor to obtain high coercivity for the electroplated Fe-Pt film-magnets because the  $Cl^-$  ions in the plating bath don't increase by the addition of NaOH.

To investigate the effect of the Na concentration on structural properties of the films, we estimated the grain sizes using Scherrer's equation (Fig. 4 (b)). As shown in Fig. 4 (b), the grain size of the as-plated films does not depend on the NaCl content, and shows almost constant value of approximately 15 nm. In contrast, that of the annealed film decreases with increasing the NaCl content, indicating that the NaCl prevents from the grain growth by the annealing. In Fe-Pt-system alloy films, a grain size of crystalline magnetic phase is a factor to determine their magnetic properties [15-18]. We, therefore, considered that the grain size of the annealed films is a factor to determine the coercivity. To confirm the relation between the coercivity and the grain size, we re-plotted the coercivity as a function of the grain size of the annealed films using the results for Fig. 4 (a) and (b). The re-plotted result is shown in Fig.5. As the coercivity slightly decreases with increasing the grain size, we considered that the suppression of the grain growth during the annealing is one of factors for high coercivity in high Na ion concentration.

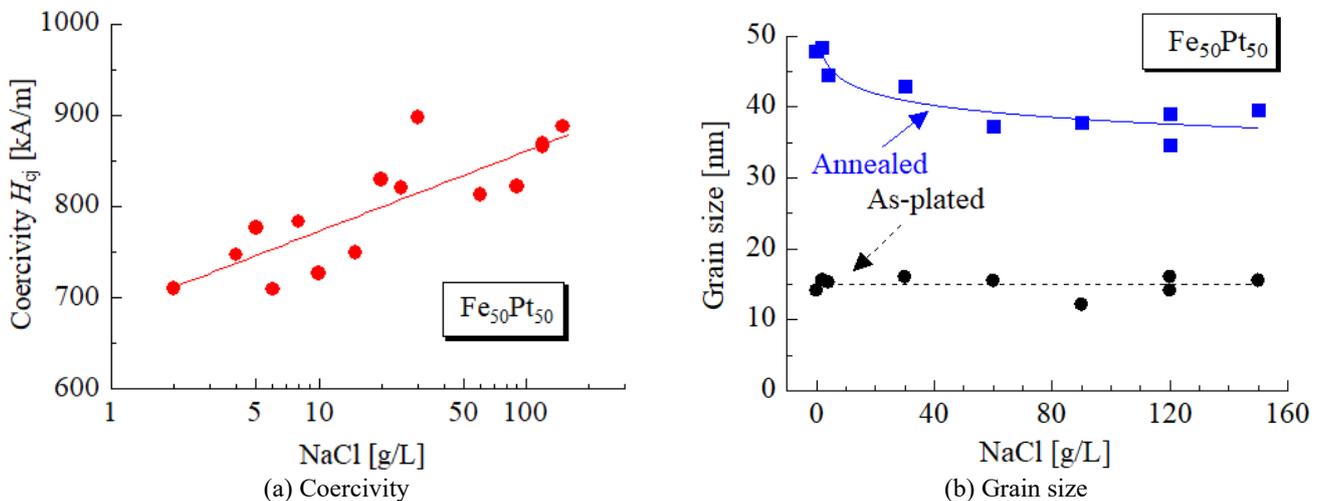


Fig.4 Coercivity and grain size of the annealed  $Fe_{50}Pt_{50}$  films as a function of NaCl content in the plating bath. The grain size of the as-plated  $Fe_{50}Pt_{50}$  films is also shown in Fig.4 (b).

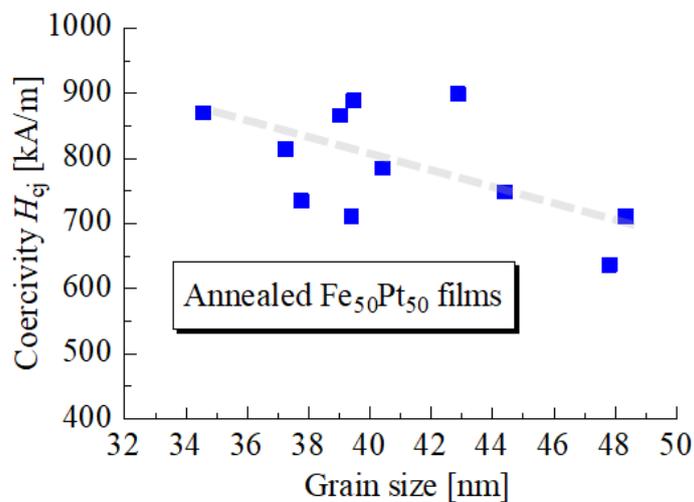


Fig.5 Coercivity of the annealed  $Fe_{50}Pt_{50}$  films as a function of the grain size.

To obtain further experimental evidence for the increase in the coercivity in high Na ion concentration, we employed trisodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) as an additive instead of NaCl. Figure 5 shows (a) the coercivity of the annealed  $\text{Fe}_{50}\text{Pt}_{50}$  films and (b) the pH of the plating bath as a function of the Na ion concentration in the plating baths. The result for NaCl (Fig.4 (a)) is also shown in Fig.6 (a). As shown in Fig.6 (a), we found that not only the NaCl but also the trisodium citrate increases the coercivity. As mentioned in “INTRODUCTION”, pH values of plating baths affect qualities and properties of electroplated films. Thus, we evaluated the pH values of the NaCl-used bath and the trisodium-citrate-used one (Fig.6 (b)). In high Na ion concentration region, the pH value for the trisodium-citrate-used bath is much higher than that for the NaCl-used one. The results for Fig. 6 (a) and (b) implies that the dominant factor for the increase in the coercivity is not the pH value of the bath but the Na ion concentration.

From the above-mentioned results, we found that the Na ion concentration in the plating bath affects the coercivity of the Fe-Pt film-magnets, and that high Na ion concentration is effective to obtain high coercivity.

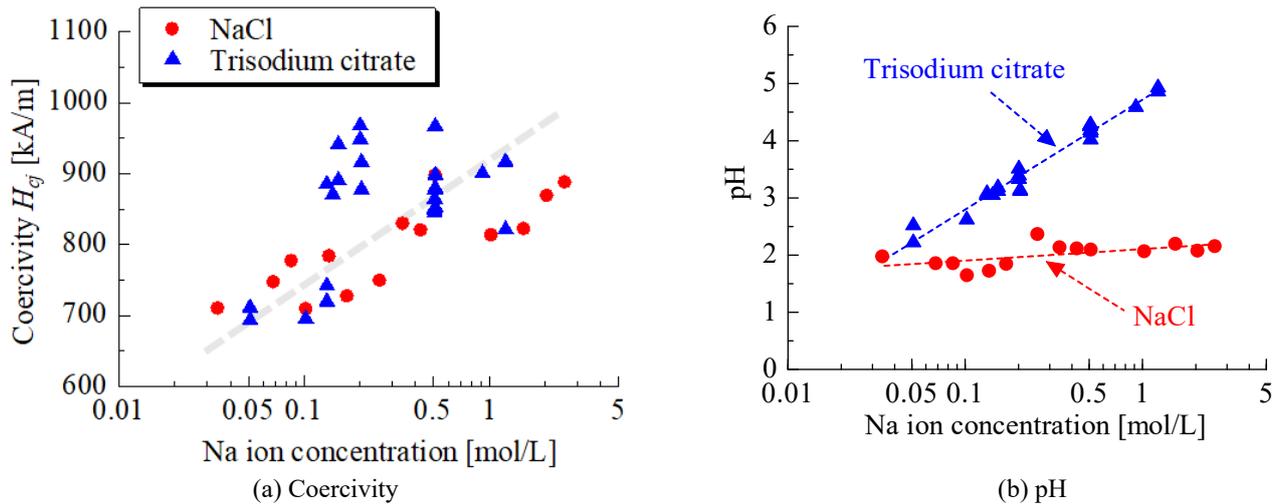


Fig.6 Coercivity of the annealed  $\text{Fe}_{50}\text{Pt}_{50}$  films and pH values of the NaCl-used bath and the trisodium-citrate-used one as a function of the Na ion concentration in the plating baths.

#### IV. CONCLUSION

We investigated the magnetic and the structural properties of the electroplated Fe-Pt thick-films, focusing on the Na ion concentration in the plating bath. The obtained results are summarized as follows;

- (1) The  $\text{Fe}_{50}\text{Pt}_{50}$  films prepared from plating baths with high Na ion concentration tend to show high coercivity.
- (2) The grain size of the annealed  $\text{Fe}_{50}\text{Pt}_{50}$  films decreases with increasing the Na ion concentration in the plating baths, suggesting that the Na ion prevents from the grain growth during the annealing for the ordering of Fe-Pt crystalline phase.

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