Journal of Alloys and Compounds 752 (2018) 133–136

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

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

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ARTICLE INFO

Article history:
Received 1 August 2017
Received in revised form
28 March 2018
Accepted 9 April 2018
Available online 11 April 2018

Keywords:
Fe-Pt
Electroplating
Na ion concentration
pH
Film magnet
Hard magnetic material

ABSTRACT

$Fe_{50}Pt_{50}$ 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 $Fe_{50}Pt_{50}$ 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.

1. Introduction

$L1_0$ 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 $Fe_{60}Pt_{40}$ 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.

2. Experimental procedures

2.1. 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 $Na_3C_6H_5O_7 \cdot 2H_2O$ to change the Na ion concentration in the bath.

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^2 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

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https://doi.org/10.1016/j.jallcom.2018.04.126
0925-8388/

Table 1
Components in the plating bath.

Components	Content (g/L)
$FeSO_4 \cdot 7H_2O$	5–10
Pt $(NH_3)_2(NO_2)_2$	10
Citric acid ($C_6H_8O_7 \cdot H_2O$)	30
NH_4Cl	25
Trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$)	0–150
Sodium chloride (NaCl)	0–150

Table 2
Electroplating conditions.

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

kept at 70 °C during the plating.

2.2. 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 $L1_0$ (fct) one, we annealed the as-plated films at 700 °C. The annealing conditions are summarized in Table 3. 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.

2.3. Measurements

The thicknesses of the 75 mm^2 Fe-Pt films were measured at different 9 points with a micrometer (Mitutoyo, CPM15-25 MJ), 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.

3. Results and discussion

Fig. 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 $Fe_{50}Pt_{50}$ by the change in the $FeSO_4$ 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 $Fe_{50}Pt_{50}$. 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

Table 3
Annealing conditions.

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

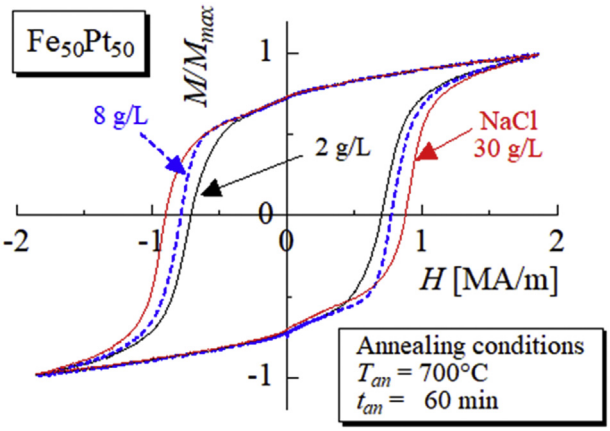

Fig. 1. Hysteresis loops of the annealed $Fe_{50}Pt_{50}$ films prepared at NaCl = 2, 8, and 30 g/L.

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 $L1_0$ ordering for the annealed films. Fig. 2 shows the XRD patterns of the annealed $Fe_{50}Pt_{50}$ films for NaCl = 2, 8, and 30 g/L. We also show the XRD pattern for the as-plated $Fe_{50}Pt_{50}$ 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 $L1_0$ 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 (Δ2θ) between (200) and (002) peaks in Fig. 2. Fig. 3 shows the peak splitting for the annealed $Fe_{50}Pt_{50}$ films as a function of the NaCl content in the plating bath. As shown in Fig. 3, Δ2θ 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

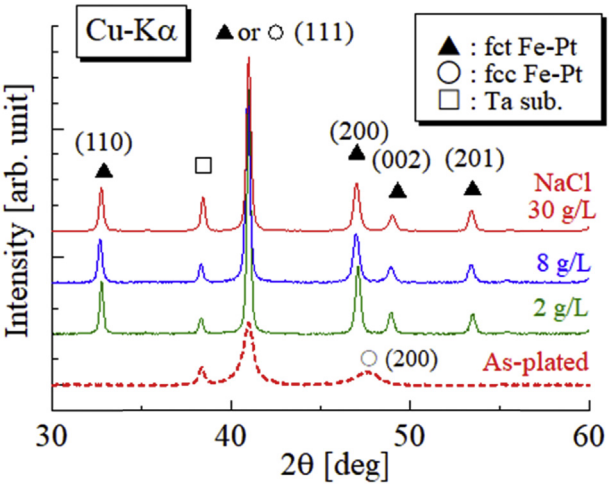

Fig. 2. XRD patterns of the as-plated $Fe_{50}Pt_{50}$ film for NaCl = 30 g/L and the annealed ones for NaCl = 2, 8, and 30 g/L.