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Improvement in surface conditions of electroplated Fe-Pt thick-film magnets

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Fe-Pt thick-films were electroplated on Ta, Ti, Co, Ni, and Cu plates (substrates) using a direct current, and the surface morphology, the magnetic properties, and the crystal structure of the films were evaluated. The films plated on the Co, Ni, and Cu substrates showed much smooth surface compared with those for the Ta and Ti ones, and we confirmed that the Cu plate was the most attractive substrate due to very small cracks after an annealing for $L1_0$ ordering. High coercivity (>800 kA/m) for the Cu substrate is almost the same as that for our previous study in which we employed the Ta substrate, and we found that the Cu plate is a hopeful substrate to improve the surface conditions of electroplated Fe-Pt thick-film magnets. © 2018 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/10.1063/1.5007196>

I. INTRODUCTION

$L1_0$ ordered Fe-Pt thick films (>1 μm) are hopeful candidates of small-sized magnets for medical applications since the films have good hard magnetic properties and high biological safety.^{1,2} When the Fe-Pt films are used as the small-sized magnets, a fabrication process with high deposition rate is required. An electroplating method is one of hopeful processes to obtain thick films since deposition rates for chemical processes are generally higher than those for dry ones such as sputtering and vapor deposition methods. Some researchers have reported Co-Pt thick-film magnets (2 – 25 μm) using electroplating methods,^{3,4} and we have also reported some Fe-Pt thick-film magnets (>10 μm) on a Ta substrate with high coercivity (>700 kA/m).^{5,6} Although the Fe-Pt thick films in our previous studies showed high coercivity, many cracks were observed on the surface of the annealed films. As electroplated Co-Pt thick films reported by Oniku *et al.*⁷ also have many cracks, a reduction in the cracks is an important study for (Fe, Co)-Pt thick-film magnets. Since large cracks of the Fe-Pt films were often observed after the annealing,^{5,8} we considered that difference in thermal expansion between Fe-Pt and Ta (substrate) is a factor of the cracks. In the present study, we, therefore, focused on coefficients of thermal expansion (CTE) of substrate materials, and evaluated the surface conditions and the magnetic properties of the Fe-Pt films electroplated on various metal substrates.

II. EXPERIMENTAL PROCEDURES

A. Electroplating of Fe-Pt films

We carried out an electroplating using a direct current to obtain Fe-Pt thick-films. The contents of the electrolyte in the plating bath contained the following: 10 g/L of $\text{Pt}(\text{NO}_2)_2(\text{NH}_3)_2$, 2-30 g/L

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TABLE I. Coefficient of thermal expansion.⁹⁻¹³

| Material | CTE ($\times 10^{-6}/\text{K}$) |
|----------|-----------------------------------|
| Ta | 6.3 |
| Ti | 8.8 |
| Co | 12.5 |
| Ni | 13.4 |
| Cu | 16.6 |

of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 25 g/L of NH_4Cl , 30 g/L of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (Citric acid). The pH in the bath was not adjusted. The anode was a Pt mesh, and Ta, Ti, Co, Ni, and Cu plates were used as the cathode. The CTE of the metals used for the cathode are summarized in Table I.⁹⁻¹³

The distance between the electrodes was 20 mm, and Fe-Pt films were electroplated on the metal plates (substrates). The current density of 1 A/cm² 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. Consequently, we obtained 75-mm² Fe-Pt films (Plating area: 5 mm \times 15 mm).

B. Annealing of Fe-Pt films

To transform a disordered A1 (fcc) structure of Fe-Pt crystalline phase in the as-plated film to an ordered L1₀ (fct) one, we annealed the as-plated films at 700°C using an electric furnace (FULL-TECH, FT-01 VAC-30). The temperature was ramped from room temperature to the annealing temperature at the constant heating rate of 100°C/min, and then kept at constant for 60 min under a vacuum ($<4.0 \times 10^{-3}$ Pa).

C. Measurements

The thicknesses and the compositions of the as-plated films were measured at nine points (approximately every 9 mm²) with a micrometer (Mitutoyo CPM15-25MJ) and a SEM-EDX (scanning electron microscope-energy dispersive X-ray spectroscopy) system (Hitachi High-technologies S-3000), respectively. We determined the thickness and the composition of the film by averaging the obtained nine values. To discuss the surface conditions of the films quantitatively, the surface roughness R_a was evaluated using a surface roughness tester (Mitutoyo, SURFTEST SV-400). The hysteresis loops of the annealed Fe-Pt films were measured with a VSM (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 loop. The XRD (X-ray diffraction) patterns of the annealed films were evaluated by an X-ray diffractometer with Cu-K α radiation (Rigaku, Miniflex600-DX).

III. RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the Fe-Pt thick films ($>10 \mu\text{m}$) plated on the Ta, Ti, Co, Ni, and Cu substrates before and after the annealing. As shown in Fig. 1, the annealing tends to increase and develop the cracks, and we found that the annealed films on the Ta and Ti substrates have large cracks. In contrast, we did not observe large cracks of the films for the Co, Ni, and Cu substrates, and confirmed that the substrate material affects the surface condition.

As mentioned in INTRODUCTION, we considered that the difference in the thermal expansion between Fe-Pt films and substrate material affects the surface conditions. To discuss the relationship between the surface conditions of the films and the CTE of the substrate quantitatively, we evaluated the surface roughness of the films before and after the annealing. Figure 2 shows (a) the surface roughness R_a of the as-plated films and the annealed ones and (b) the increased ratio of R_a by the annealing as a function of CTE of the substrate. We prepared several films for each substrate, and averaged R_a values are shown in Fig. 2. As shown in Fig. 2, the films plated on the Ta substrate and

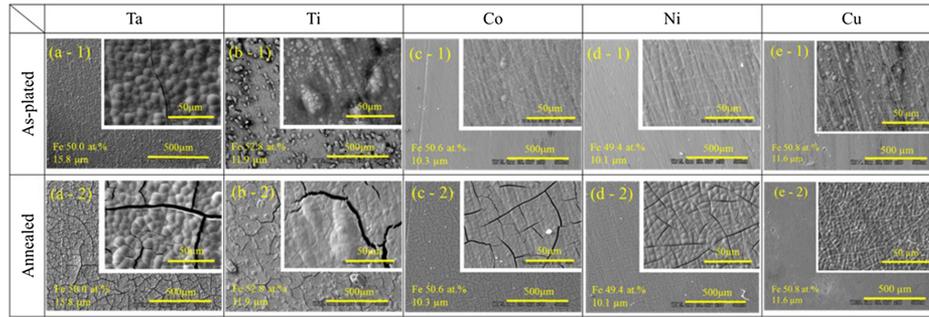


FIG. 1. SEM images of the Fe-Pt thick-film plated on the (a) Ta, (b) Ti, (c) Co, (d) Ni, and (e) Cu substrates before (a-1, b-1, c-1, d-1, and e-1) and after the annealing (a-2, b-2, c-2, d-2, and e-2).

the Ti ones have large variations in R_a , the tendency of the roughness was clearly divided into two types based on the CTE of the Fe-Pt alloy.¹⁴ This result implies that a substrate with slight higher CTE value compared with the value for the Fe-Pt alloy is preferable, and we found that the Cu plate is a hopeful substrate to fabricate the Fe-Pt thick-film magnets with good surface conditions from Figs. 1–2.

Focusing on the SEM images of the as-plated films for the Co, Ni, and Cu substrates in Fig. 1 again, we can find many white lines on the surface, indicating that the films already have many sources of the crack before the annealing. Oniku *et al.* electroplated Co-Pt films and reported that the hydrogen generated by the decompose of water, which is the solvent for their plating bath, leads to microcracking of the Co-Pt layer.⁷ In plating baths and plating conditions for our studies, a large amount of hydrogen generates due to low current efficiency (<10 %) of the plating process. We, therefore, consider that an improvement in the current efficiency is one of important factors to reduce the microcracking before the annealing.

Figure 3 shows coercivity of the annealed Fe-Pt thick films for the Ta substrates and the Cu ones as a function of the Fe content in the films. The maximum value of the coercivity was approximately 900 kA/m for both substrates. It is well-known that the $L1_0$ Fe-Pt crystalline phase shows high magnetocrystalline anisotropy around 50 at.%-Fe. Although the films for the Cu substrate also showed relatively high coercivity of approximately 500 kA/m at 50 at.%-Fe, the maximum value was obtained around 45 at.%-Fe. To understand this behavior, we decided to evaluate the structural properties of the annealed films using an X-ray diffraction.

Figure 4 shows the XRD patterns of the annealed Fe-Pt thick films plated on the Cu and Ta substrates. As shown in Fig. 4, clear difference in the XRD pattern was not confirmed between the films of $Fe_{46}Pt_{54}$ for the Cu substrate and $Fe_{51}Pt_{49}$ for the Ta one in which we obtained the maximum

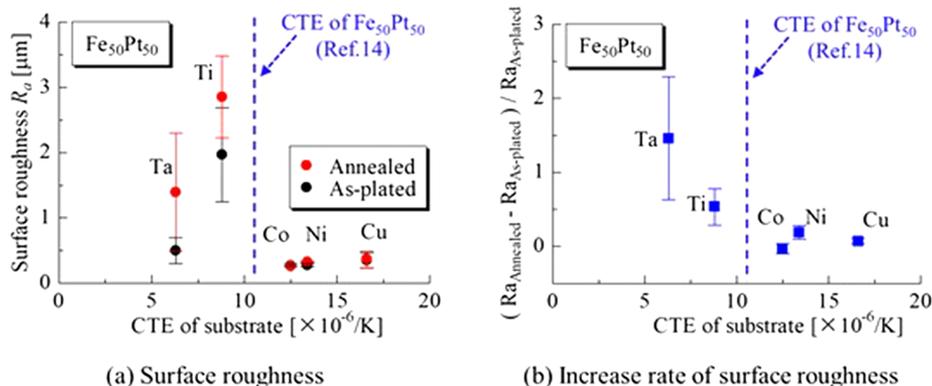


FIG. 2. (a) Surface roughness R_a of the as-plated Fe-Pt thick films and the annealed ones and (b) increased ratio of R_a by the annealing as a function of CTE of the substrate.

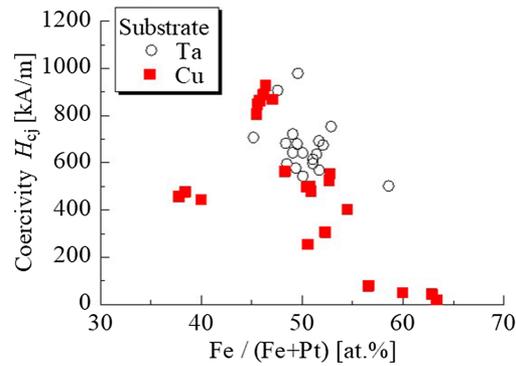


FIG. 3. Coercivity of the annealed Fe-Pt thick films for the Ta substrates and the Cu ones as a function of the Fe content in the films.

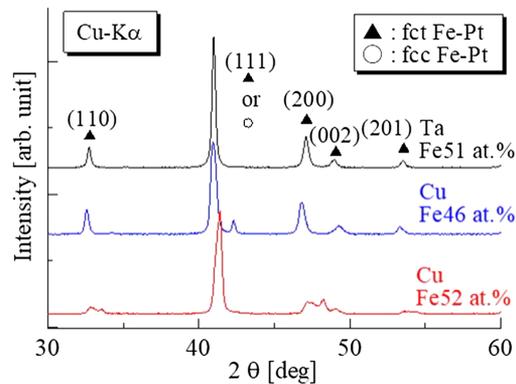


FIG. 4. XRD patterns of the annealed Fe-Pt films electroplated on the Ta substrate and the Cu one.

coercivity value for each substrate. In contrast, the XRD pattern for the $\text{Fe}_{52}\text{Pt}_{48}$ film on the Cu substrate was slight different from those for other films, and the splitting of (200) for the fcc phase into (200) and (002) for the fct one was under developing. This result implies that the $L1_0$ ordering of the $\text{Fe}_{52}\text{Pt}_{48}$ film was not fully developed. Maeda *et al.* reported that Cu element affects the ordering temperature of Fe-Pt alloys.¹⁵ Our result also suggests that the Cu substrate affects the ordering process.

From the above results, we confirmed that the Cu substrate dramatically reduces the cracks in the electroplated Fe-Pt thick-film magnets compared with the Ta substrate. Consequently, we realized significant improvement in the surface condition of the $L1_0$ ordered Fe-Pt thick films keeping their high coercivity.

IV. CONCLUSION

In conclusion, we investigated the surface conditions and the magnetic properties of the electroplated Fe-Pt thick-film magnets. The obtained results are summarized as follows:

- (1) The substrate materials clearly affected the surface conditions of the as-plated Fe-Pt thick films, and Co, Ni, and Cu substrates were preferable to obtain the smooth surface.
- (2) The annealed films on the Cu substrate showed very smooth surface.
- (3) A substrate with slight higher CTE value compared with the value for the Fe-Pt alloy was preferable to suppress large cracks on the surface.
- (4) The Cu substrate reduced the cracks and significantly improved the surface condition of the electroplated Fe-Pt thick-film magnets.

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