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ABSTRACT

We prepared $L1_0$ ordered $Fe_{50}Pt_{50}$ thick-films on Cu substrates using the electroplating method and evaluated their high-temperature properties in the temperature range of 25-200°C. The Hc and the $(BH)_{max}$ at 150°C for the $Fe_{50}Pt_{50}$ films annealed by ordinary annealing method (700°C, 60 min) were 500 kA/m and 50 kJ/m^3, respectively, and the thermal coefficient of Hc was -0.3%/°C. To improve the high-temperature properties, we employed a flash annealing method using an infrared furnace (8 kW). The flash annealing method improved the high-temperature properties (Hc = 700 kA/m, $(BH)_{max}$ = 70 kJ/m^3 at 150°C) and the thermal coefficient (-0.21%/°C). The thermal stability of the films is comparable to those for Sm-Co-system magnets and better than for Nd-Fe-B-system ones. We, therefore, found the $L1_0$ ordered $Fe_{50}Pt_{50}$ films prepared by the electroplating and the flash annealing are one of the hopeful small magnets in the wide temperature range.

I. INTRODUCTION

In recent years, Nd-Fe-B and Nd-Fe-B bonded magnets with high $(BH)_{max}$ and Sm-Co ones with good high-temperature properties were reported for applications in micro-electro-mechanical systems (MEMS) devices. For MEMS applications, small-size magnets and film-shaped ones are required, and Nd-Fe-B thick-films and Sm-Co ones are often deposited by vapor deposition and sputtering methods.[1,2] Although these methods are used to prepare film-magnets with good hard-magnetic properties, their deposition rates are typically low. Electroplating methods are one of the commercially used processes to fabricate films, and they have high economic viability and high deposition rates. It, however, is difficult to prepare rare earth film-magnets such as Nd-Fe-B and Sm-Co alloys since the rare earth elements cannot be obtained from aqueous solutions due to their very low reduction potentials.

$L1_0$ ordered transition-metal (TM; Fe and Co)-Pt alloys are one of the well-known hard-magnetic materials. Although the saturation magnetic polarization of the TM-Pt alloys is smaller than that of Nd-Fe-B alloys, they can be obtained by electroplating methods and are hopeful materials as isotropic permanent magnets due to a remanence enhancement effect.[3] Taking advantage of high remanence and high coercivity of the TM-Pt alloys, some researchers have reported TM-Pt thick-films as small magnets for MEMS applications.[4,5] We also reported the Fe-Pt thick-films (> 10 μm) on Ta substrates with large coercivity prepared by an electroplating method.[6] To use the films as small magnets, not only hard magnetic properties but also surface conditions is important. Recently, we investigated the improvement in the surface conditions of the films and clarified that Cu plates are effective to obtain the smooth surface.[7] Although we evaluated the magnetic properties at room temperature in our previous studies, the properties under high temperatures are also important to apply the films to devices. In the present study, we, therefore, investigated high-temperature properties of the Fe-Pt thick-films on the Cu substrate prepared by the electroplating method.

II. EXPERIMENTAL PROCEDURES

A. Electroplating

We carried out electroplating to obtain Fe-Pt thick films (5 - 10 μm) using a direct current. The electrolyte of the plating bath contained the following: 10 g/L of $Pt(NO_2)_2(NH_3)_2$, 5-10 g/L of $FeSO_4 \cdot H_2O$, 25 g/L of $H_6N_2O_3S$, 30 g/L of $C_6H_8O_7 \cdot H_2O$ (Citric acid). A 5 mm-wide Pt mesh and a 500 μm-thick Cu plate were used as the anode and the cathode, respectively. 75 mm^2 (5 mm × 15 mm) and 25 mm^2 (5 mm × 5 mm) Fe-Pt films were electroplated on the Cu plate. The current density of 1 A/cm^2 and the plating from 10 to 60 min were controlled by using a computer-aided DC current source (MATSUSADA, P4K-80). The bath temperature was kept at 70°C during the plating.

B. Annealing

As-plated Fe-Pt films have an fcc structure (A1 disordered phase) and show low coercivity. To transform the fcc structure to the fct one ($L1_0$ ordered phase), we annealed as-plated Fe-Pt films using two types of the annealing, "ordinary annealing" and "flash annealing."

1. Ordinary annealing

We annealed the Fe-Pt films in a vacuum (< 10^{-2} Pa) using an electric furnace (FULL-TECH, FT-01 VAC-30). The annealing temperature was ramped up to 700°C for 7 min and then held for 60 min. In the experiment related to Fig. 3, we varied the holding time from 0 to 170 min.

2. Flash annealing

We annealed the Fe-Pt films with short annealing time and high heating rate using an infrared furnace with the rated output of 8 kW, (ULVAC-RIKO, RHL-E410P) in a vacuum (< 10^{-3} Pa). The output of the furnace was set at 100%, and the annealing period was varied from 3 to 10 s.

C. Measurements

The thickness of the as-plated Fe-Pt film was measured at different 25 points using a micrometer (Mitutoyo, CPM15-25MJ), and the measured values were averaged to determine the thickness. The compositions of the as-plated Fe-Pt films and the hysteresis loops of the annealed Fe-Pt ones were measured with a scanning electron microscope-energy dispersive X-ray spectrometry (SEM-EDX) system and a vibrating sample magnetometer (VSM), respectively. To evaluate the degree of the Cu diffusion, we also measured the Cu content in the annealed films with the SEM-EDX system. For the measurement of the Cu content, we focused and scanned the beam of electrons on the film surface, and the Cu content was determined by the intensity of the characteristic X-rays radiated from the surface. The microstructure of the annealed Fe-Pt film was evaluated with a transmission electron microscope (TEM) system (JEOL JEM-2010). Fe-Pt thin foils for cross-sectional TEM observations were prepared by using argon-ion beam milling.

III. RESULTS AND DISCUSSION

Figure 1 shows the coercivity Hc and $(BH)_{max}$ of annealed Fe-Pt thick-film on Cu substrate as a function of the measurement temperature. The $(BH)_{max}$ value at room temperature was approximately 70 kJ/m^3, and this value is almost the same as the reported ones for the electroplated Fe-Pt films (70 kJ/m^3,[8] 53 kJ/m^3[9]). The coercivity at 150°C and the thermal coefficient of Hc (25-200°C) were approximately 500 kA/m and -0.3%/°C, respectively. These values were lower than those for typical rare earth magnets of Sm-Co and Nd-Fe-B,[10,11] and this result suggests that we need to improve the hard-magnetic properties.

Although the Cu plate is an attractive substrate to obtain the Fe-Pt thick-films with smooth surfaces,[7] it is expected that the high-temperature annealing for the ordering enhances a Cu diffusion from the substrate. For Fe-Pt thin-films (< 1 μm), some researchers pointed out that the Cu diffusion degraded hard magnetic properties.[12–19] To investigate the Cu diffusion, we evaluated the microstructure of the annealed Fe-Pt films. The result of the TEM observation shows in Fig. 2. From Debye-Scherrer rings and the bright images, we confirmed that the film has a randomly oriented fct Fe-Pt crystalline phase and very small grains (< 100 nm). Table I shows the local composition of the film at A, B, C, and D in Fig. 2. The film has two phases with different Fe composition ($Fe_{80}(PtCu)_{20}$ phase and $Fe_{40}Pt_{40}Cu_{20}$ one), and this result suggests that the coercivity is attributed to (1) the magnetic phase with low coercivity (80 at.%-Fe phase) and/or (2) the $L1_0$ Fe-Pt phase (40 at.%-Fe one) with the reduced crystalline anisotropy by the Cu diffusion. Jading from the phase diagram of Fe-Pt-Cu alloy, 80 at.%-Fe-Pt-Cu alloys form fcc or bcc structure. In Fig. 2 (a), since only the fct structure was observed (no-observation of fcc or bcc structure), we consider that the effect of the 80 at.%-Fe-Pt-Cu phase on the coercivity is small. On the other hand, as the amount of Cu in the $L1_0$ Fe-Pt phase strongly affects magnetic properties such as the decreases in the crystalline anisotropy constant and the Curie temperature,[18] we need to reduce the Cu-diffusion for obtaining Fe-Pt thick-film magnets with good hard magnetic properties.

Figure 3 shows the coercivity and the Cu composition of the annealed $Fe_{50}Pt_{50}$ film as a function of annealing time. As we

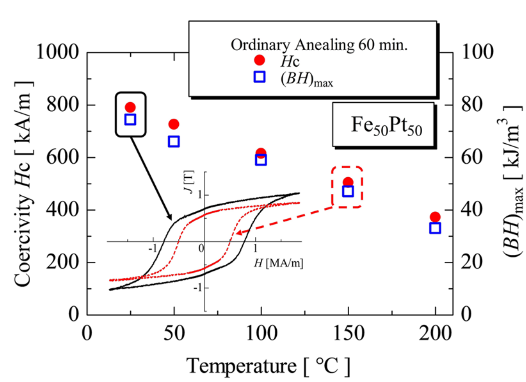

FIG. 1. The coercivity Hc and the $(BH)_{max}$ of the annealed Fe-Pt thick-film as a function of the measurement temperature. The inset indicates the hysteresis loops at room temperature and 150°C.

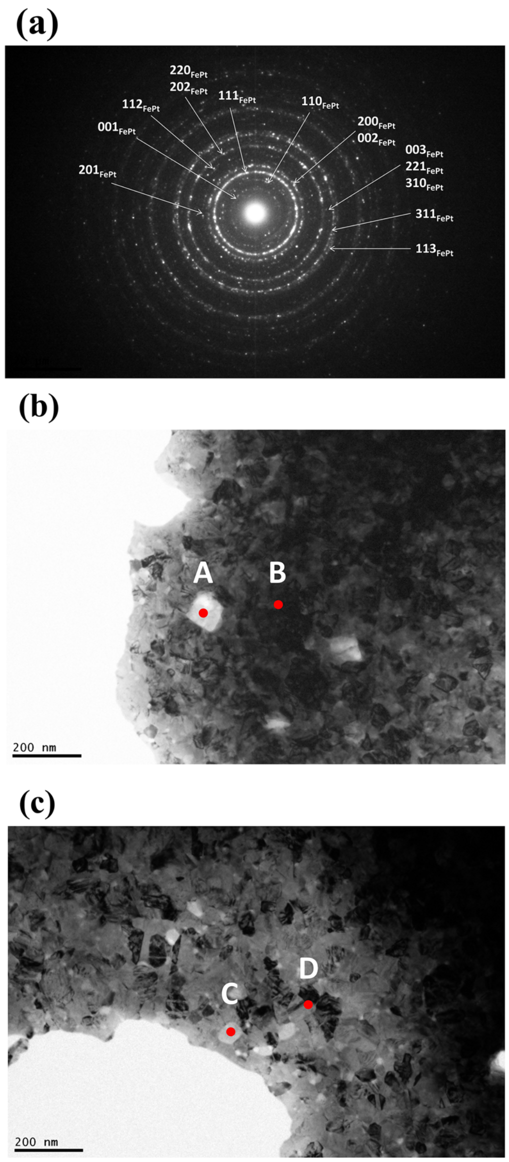

FIG. 2. TEM images of (a) electron diffraction pattern of the annealed Fe-Pt film. Bright field images of the film (b) near and (c) far from the Cu substrate were also shown.

annealed the same film repeatedly, the annealing time in Fig. 3 indicates integrated annealing time. With increasing the annealing time, the Cu composition increased from 3 to 23 at.% and the coercivity decreased from 900 to 600 kA/m. This result implies that the

TABLE I. Local composition of the Fe-Pt film.

	A	B	C	D
Fe (at.%)	79.3 ± 1.6	42.8 ± 0.4	86.2 ± 1.8	38.2 ± 0.7
Pt (at.%)	6.9 ± 1.5	38.1 ± 0.5	4.0 ± 1.5	42.6 ± 0.8
Cu (at.%)	13.8 ± 1.2	19.1 ± 0.38	9.8 ± 1.3	19.2 ± 0.6

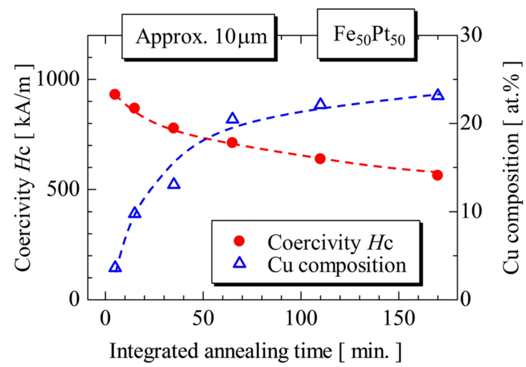

FIG. 3. The coercivity and the Cu composition of the annealed $Fe_{50}Pt_{50}$ film as a function of the integrated annealing time. The same films annealed repeatedly.

Cu diffusion degraded the hard-magnetic properties and that short annealing time is preferable.

For improvement in the high-temperature properties, it is well-known that the increase in the coercivity is effective. The result for Fig. 3 suggests that short-time annealing is attractive to increase the coercivity. To investigate the improvement in the hard-magnetic properties by the further reduction in the annealing time, we employed the flash annealing method using the infrared furnace, expecting a higher heating rate than the electric furnace.

Figure 4 shows the coercivity of the flash-annealed Fe-Pt films as a function of the annealing period. For comparison of the loop shape, we also show the hysteresis loops of the films (10 μm in thick) prepared by the ordinary annealing method and the flash annealing one as an inset. The high coercivity (≒ 900 kA/m) could be obtained around 7 seconds, and we confirmed that the flash annealing improves not only the coercivity but also the remanence and the squareness compared with the ordinary one. The evaluated Cu compositions of the flash-annealed Fe-Pt films were approximately

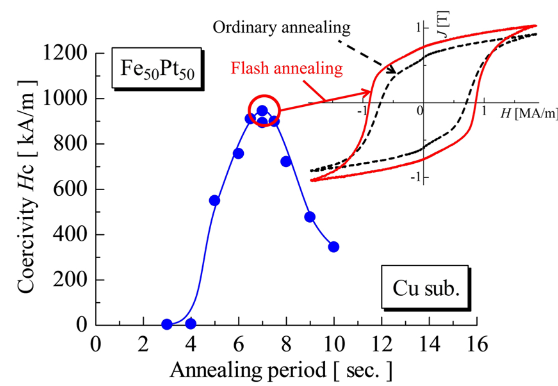

FIG. 4. The coercivity of the flash-annealed Fe-Pt films as a function of the annealing period. The inset indicates the hysteresis loops of the annealed 10 μm-thick films by the ordinary annealing method (black broken line) and the flash annealing one (red solid line).

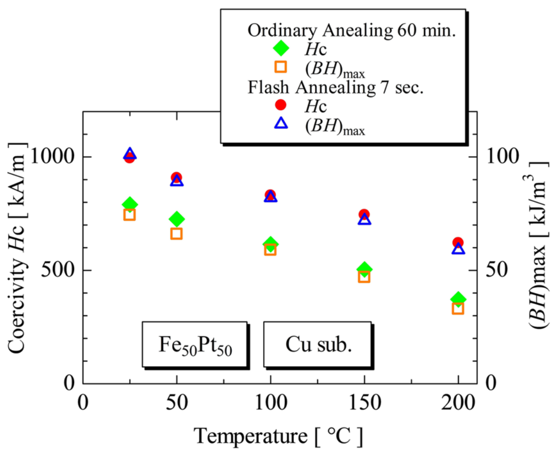

FIG. 5. The coercivity *Hc* and the $(BH)_{max}$ of the annealed Fe-Pt thick-film as a function of the measurement temperature.

1 at.% for 7 sec and 2 at.% for 10 sec, indicating that the flash annealing method was effective in suppressing the Cu diffusion.

The coercivity of approximately 900 kA/m is much higher than those for the sputtered Fe-Pt thick films (446 kA/m[20] and 580 kA/m[21]) and for the electroplated one (700 kA/m[6]). Although the remanence is slightly smaller than 0.9 T[20] and 0.8 T,[21] the obtained highest $(BH)_{max}$ value (100 kJ/m^3) was comparable to the values for the sputtered and arc-melted Fe-Pt thick-films.[22,23] Moreover, the annealing period of 7 sec to obtain high coercivity is much shorter than those of the previous reports (10 sec[24] and 300 sec[25]). We confirmed the flash annealing method enables us to prepare Fe-Pt films with high hard-magnetic properties.

Since the magnetic properties of $Fe_{50}Pt_{50}$ thick-films were improved by the flash annealing, we investigated the high-temperature properties again. Figure 5 shows the coercivity *Hc* and the $(BH)_{max}$ of the annealed Fe-Pt thick-film as a function of the measurement temperature. The coercivity and the $(BH)_{max}$ at 150°C were 700 kA/m and 70 kJ/m^3, respectively. These values were higher than those of the ordinary annealed films (Fig. 1). The thermal coefficient of *Hc* was also improved from -0.3%/°C to -0.21%/°C. The reported coefficients for the $Nd_{27}Dy_4Fe_{bal}Co_2Ga_{0.5}B_1$ magnet (20-150°C),[26] the Sm_1Co_7 one (RT-150°C),[27] and $Sm_1(Co_{bal}Fe_{0.07}Cu_{0.088}Zr_{0.025})_{7.5}$ one (25-500°C),[28] were -0.53%/°C, -0.16%/°C, and -0.14%/°C, respectively. We confirmed the thermal stability of the electroplated Fe-Pt film-magnets is comparable to those for Sm-Co-system magnets and better than for Nd-Fe-B-system ones.

From these results, we concluded that the $L1_0$ Fe-Pt films prepared by the electroplating and the flash annealing are one of the hopeful small magnets in the wide temperature range.

IV. CONCLUSION

We investigated the high-temperature properties of the $L1_0$ ordered Fe-Pt thick-film magnets. The obtained results are summarized as follows.

(1) The coercivity at 150°C and the thermal coefficient of *Hc* (25-200°C) for the film prepared by the ordinary annealing were approximately 500 kA/m and -0.3%/°C, respectively.
(2) Long annealing time enhanced the Cu diffusion into the $Fe_{50}Pt_{50}$ films, and the coercivity dramatically decreased when the Cu content was more than 20 at.%.
(3) The flash annealing method effectively worked to reduce the Cu diffusion. As a result, not only the coercivity but also $(BH)_{max}$ were improved.
(4) The coercivity and the $(BH)_{max}$ at 150°C for the flash-annealed film were 700 kA/m and 70 kJ/m^3, respectively. The thermal coefficient of *Hc* (25-200°C) was improved from -0.3%/°C to -0.21%/°C. These values were comparable to those for Sm-Co-system magnets and better than for Nd-Fe-B-system ones.

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