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Magnetic properties of Nd–Fe–B nanocomposite films prepared by a new method using pulsed laser deposition

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Abstract

Nanocomposite film-magnets with the thickness of several tens of microns were prepared by the pulsed laser deposition method with a rotating $Nd_{2.6}Fe_{14}B/Fe_3B$ composite target. As-deposited films were composed mainly of amorphous Nd–Fe–B and Fe–B phases and exhibited soft magnetic properties. Annealing crystallized the films into the composite state composed of $Nd_2Fe_{14}B$ and α-Fe/Fe_2B. Superior hard magnetic properties were developed, when the calculated thickness of the period of Nd–Fe–B/Fe–B layers is approximately 90 nm. Films annealed in situ by the Joule-heating were prevented from surface oxidation and their magnetic properties were improved compared with those of films annealed with an infrared furnace. The obtained coercivity, remanence and $(BH)_{max}$ were 323 kA/m, 1.05 T and 85.7 kJ/m^3, respectively. The above remanence and $(BH)_{max}$ values are higher than the corresponding values reported for the film-magnets prepared from a single $Nd_{2.6}Fe_{14}B$ target. Considering the strong spring-back phenomenon and the existence of soft phases in our films, a large remanence value and resultantly, a large $(BH)_{max}$ value of our films can be attributed to the remanence enhancement based on the effective intergrain interaction.

Keywords: Pulsed laser deposition; Nanocomposite magnet; Magnetic film; Nd–Fe–B; Multi-layers; Remanence enhancement

1. Introduction

Nanocomposite magnets are hopeful candidates for high-performance magnets in the next generation and are expected to exhibit superior magnetic properties by controlling their nanostructures [1,2]. One of the promising methods of controlling nanostructures is synthesis of an artificial layered structure, because the layered structure is expected to prevent the growth of grains and to achieve a fine nanostructure [3,4]. Therefore, superior magnetic properties would be obtained, when the thickness of a layer is comparable with the suitable grain size of a film-magnet. On the other hand, we need to prepare 10^3 to 10^4 layers in order to synthesize film-magnets applicable to electronic devices, such as a millimeter-size-motor. The pulsed laser deposition (PLD) with a composite target is suitable to prepare the layered structure for this purpose. In this contribution, we report magnetic properties of $Nd_2Fe_{14}B$-based nanocomposite film-magnets prepared by the PLD method using a composite target.

2. Experimental

Composite targets ($Nd_{2.6}Fe_{14}B/Fe_3B$) shown in Fig. l were prepared and were ablated by a YAG laser beam ($\lambda = 355$ nm) in a vacuum chamber. The ablated materials were deposited on a Ta substrate for 1 h, and we obtained composite films with the thickness of several tens of microns. During the deposition, a target was rotated with the speed of 3–13 rpm, suggesting that 360–1440 layers are prepared in 1 h. The repetition frequency of the laser was set to 30 Hz. The thickness of a layer was controlled by varying the laser power (3.8–4.2 W) and the distance between a target and a substrate (7–10 mm).

As as-deposited films exhibited soft magnetic properties, they were annealed in vacuum (approximately 10^{-5} Torr) with an infrared furnace or a Joule-heating system. Precipitated phases by annealing were studied by the X-ray

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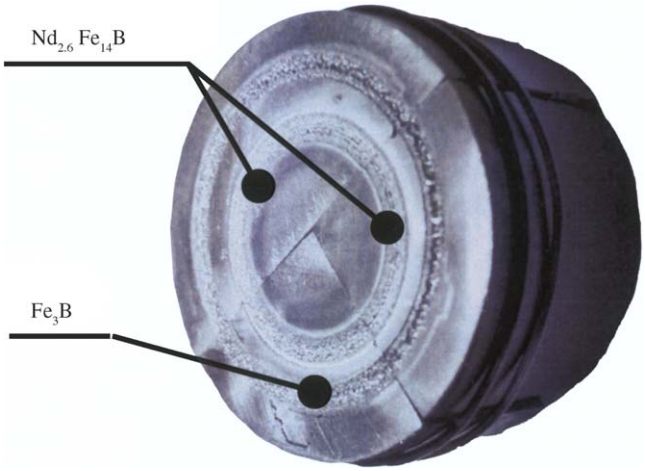

Fig. l. Photograph of a composite target used in this study. The target consists of $Nd_{2.6}Fe_{14}B$ and Fe_3B parts.

diffractometory and the thermomagnetic analysis. In-plane magnetic properties of the films were measured with a vibrating sample magnetometer after magnetization under a pulse field of 6.4 MA/m.

3. Results and discussion

As mentioned in Section 2, as-deposited films exhibited soft magnetic properties. Thermomagnetic properties of an as-deposited film are shown in Fig. 2. As seen in the figure, the as-deposited film is magnetically in multi-phase state, and the phase with the lowest Curie temperature seems to be amorphous Nd–Fe–B, considering its Curie temperature. The increase in magnetization starting at approximately 450 °C would correspond to the crystallization of the amorphous Fe–B phase, which has the Curie temperature higher than 450 °C. It should be noted that the amorphous $Fe_{75}B_{25}$ alloy was reported to be crystallized at 450 °C or a lower temperature and to have the Curie temperature higher than the crystallization temperature [5,6]. Therefore, as-deposited films are expected to be mainly composed of amorphous Nd–Fe–B and Fe–B phases, which is consistent with soft magnetic properties of the as-deposited films.

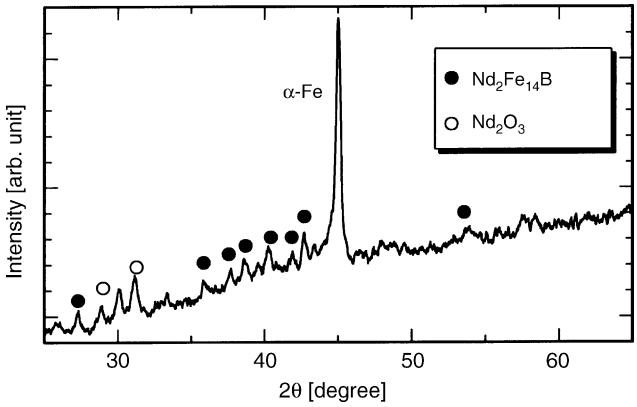

Fig. 3. X-ray diffraction pattern of a crystallized film by annealing with an infrared furnace.

Crystallization of as-deposited films due to an annealing at 700 °C with an infrared furnace developed hard magnetic properties. As seen in Fig. 3, precipitation of $Nd_2Fe_{14}B$ contributes to this hardening, although the diffraction peaks from Nd_2O_3, α-Fe and unidentified phases are also observed.

The obtained $(BH)_{max}$ values are shown in Fig. 4 as a function of the calculated thickness of the period of Nd–Fe–B/Fe–B layers, T_p. The thickness of the period T_p was determined by dividing the thickness of a prepared film by the total rotation numbers of the target. As seen in the figure, the largest $(BH)_{max}$ value was obtained, when T_p was approximately 90 nm, which corresponds to the rotational speed of 5–7 rpm in our experimental condition. Assuming that the thicknesses of Nd–Fe–B and Fe–B layers are propor-

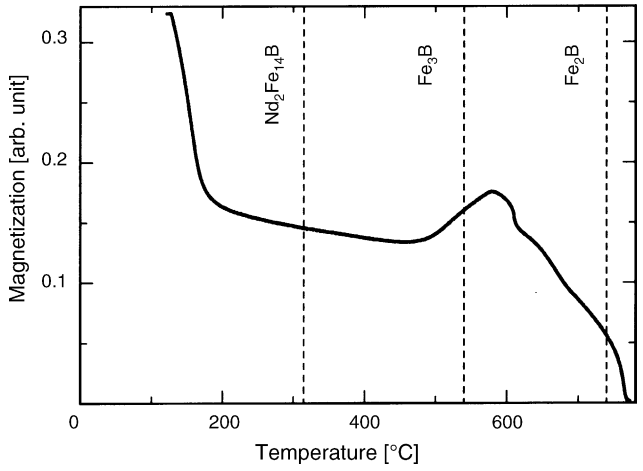

Fig. 2. Temperature dependence of magnetization of an as-deposited film. The Curie temperatures of $Nd_2Fe_{14}B$, Fe_3B and Fe_2B are shown by broken lines as a reference.

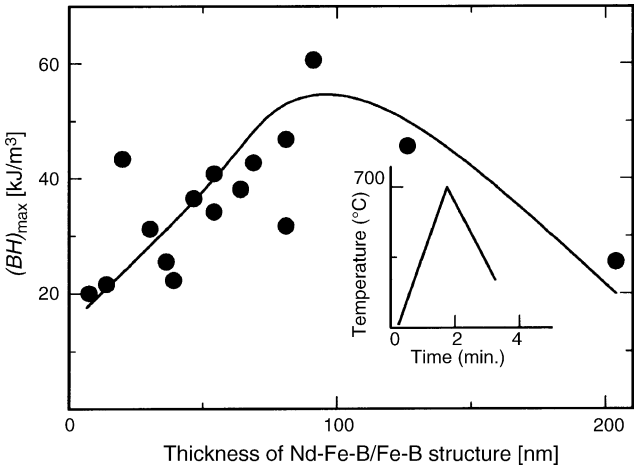

Fig. 4. $(BH)_{max}$ of films annealed with an infrared furnace as a function of thickness of period of Nd–Fe–B/Fe–B layers. The inset indicates the change of temperature during annealing schematically.

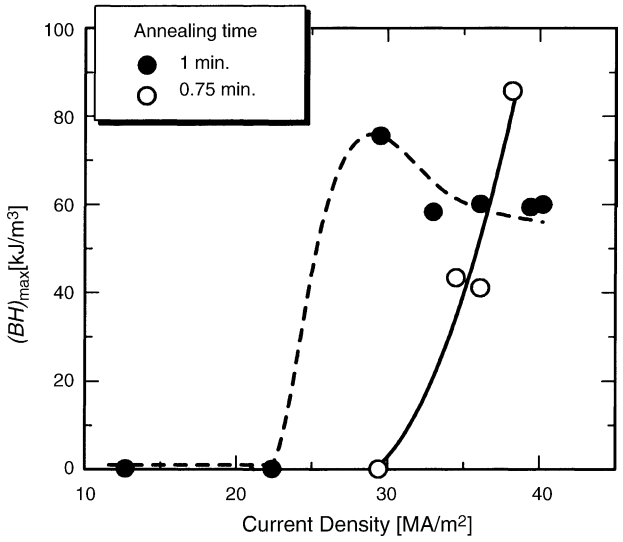

Fig. 5. $(BH)_{max}$ of films annealed in situ in the vacuum chamber by Joule-heating as a function of current density. The films were heated by passing current through a Ta substrate and a film, and the current density was determined by dividing the current value by the total cross-sectional area of the substrate and the film.

tional roughly to the areas of $Nd_{2.6}Fe_{14}B$ and Fe_3B targets, the thickness of a magnetically soft Fe–B layer is calculated to be about 20 nm for $T_p = 90$ nm. This value is consistent with the result of the micromagnetic calculation [2].

The large (1 1 0) diffraction peak from α-Fe observed in Fig. 2 can be partially attributed to surface oxidation of the annealed film, because we can also observe the strong peaks from Nd_2O_3. In order to suppress the surface oxidation, we annealed as-deposited films in situ in the vacuum chamber by passing current through a Ta substrate and a film. For this experiment, T_p was controlled between 50 and 90 nm by using the rotational speed of 7 rpm. Fig. 5 shows the obtained $(BH)_{max}$ as a function of the current density. The current density was determined by dividing the current value by the total cross-sectional area of the substrate and the film. As seen in the figure, hard magnetic properties were developed abruptly, when the current density exceeded a critical value. The temperature of a sample was not determined because of the short durations of the annealing. The largest value obtained was improved by 25 kJ/m^3 compared with that obtained with an infrared furnace.

Fig. 6 shows the hysteresis loop for the film annealed for 0.75 min under the current density of 38 MA/m^2. The remanence M_r, coercivity H_c and $(BH)_{max}$ are 1.05 T, 323 kA/m and 85.7 kJ/m^3, respectively. The obtained M_r and $(BH)_{max}$ values are larger than the corresponding values for isotropic Nd–Fe–B film-magnets prepared from a single $Nd_{2.6}Fe_{14}B$ target by the PLD method [7].

The X-ray diffraction pattern of a film annealed in situ is shown in Fig. 7. The observed pattern agreed qualitatively with that shown in Fig. 3 for the film annealed with an infrared furnace. However, it is clearly seen that the intensity of the

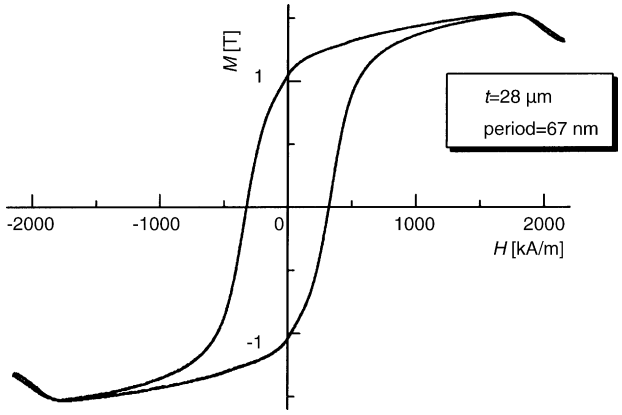

Fig. 6. Hysteresis loop for the film annealed in situ by Joule-heating. The current density and the duration are 38 MA/m^3 and 0.75 min, respectively.

(1 1 0) diffraction peak from α-Fe is decreased significantly, compared with that annealed with an infrared furnace. On the other hand, some unknown peaks are seen around 30°, which may indicate that the Joule-heated sample includes minor phases excluded in the samples crystallized with an infrared furnace. Thus, in addition to the suppression of the surface oxidation, difference in minor phases and a nanostructure may affect the observed improvement in magnetic properties.

Thermomagnetic properties of the above-mentioned films are shown in Fig. 8. The decrease in magnetization around 300 °C corresponds to the Curie temperature of $Nd_2Fe_{14}B$. Beyond 300 °C, the magnetization is constant, and then, increases again at approximately 580 °C. The increase in magnetization at 580 °C would correspond to the crystallization of the residual amorphous phase. Finally, the magnetization vanishes at 760 °C, which corresponds to the Curie temperature of α-Fe. As mentioned previously, the as-deposited films are mainly composed of amorphous Nd–Fe–B and Fe–B phases. Crystallization of the amorphous Fe–B phase is expected to precipitate α-Fe, Fe_3B, Fe_2B, Fe_3B_{26} and/or FeB, whose Curie temperature is 760, 510 [1], 742 [8], 425 [1] and 309–325 °C [9], respectively. Considering the thermomag-

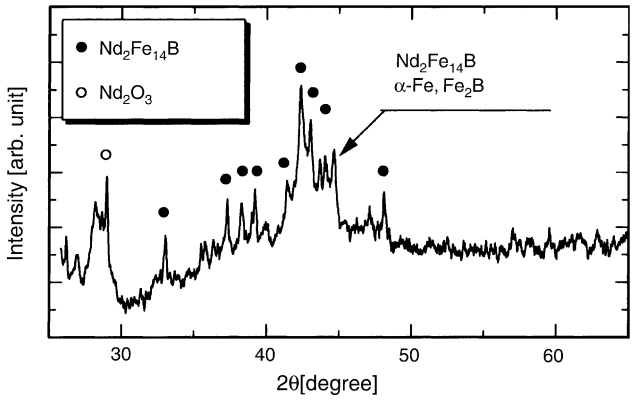

Fig. 7. X-ray diffraction pattern of the film annealed in situ by Joule-heating. The current density and the duration are 38 MA/m^3 and 0.75 min, respectively.

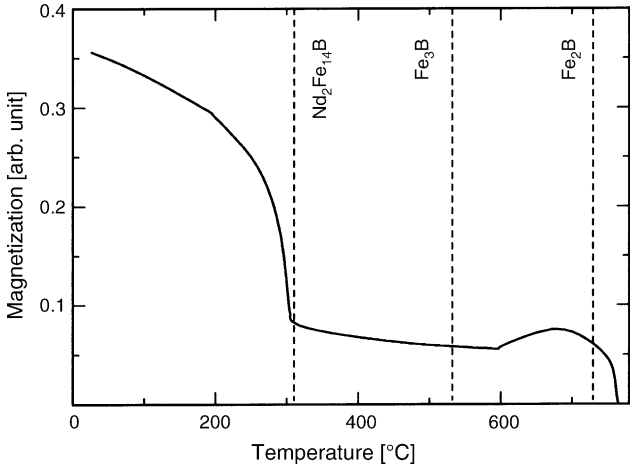

Fig. 8. Temperature dependence of magnetization of a film annealed by Joule-heating.

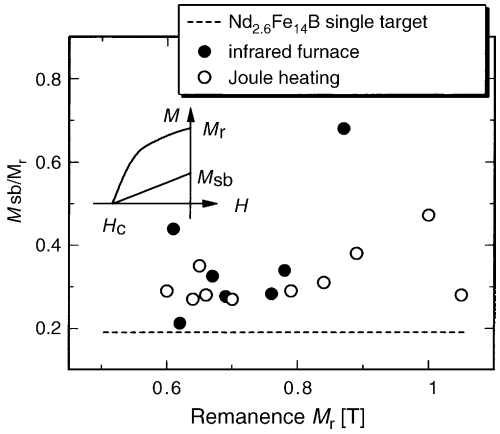

Fig. 9. Spring-back ratio M_{sb}/M_r as a function of remanence. The inset defines the spring-back ratio M_{sb}/M_r. The broken line indicates the result for a Nd–Fe–B film-magnet prepared from a single $Nd_{2.6}Fe_{14}B$ target by the PLD method.

netic properties shown in Fig. 8, the precipitated phases are α-Fe and/or Fe_2B rather than Fe_3B. This result is consistent with the X-ray diffraction pattern shown in Fig. 7.

Fig. 9 shows the spring-back ratio, M_{sb}/M_r, which is defined in the inset as a function of remanence. In the figure, the broken line indicates M_{sb}/M_r of a Nd–Fe–B film-magnet prepared from a $Nd_{2.6}Fe_{14}B$ target by the PLD method [7]. It is seen that an increase in remanence has a tendency of increasing M_{sb}/M_r. In addition, M_{sb}/M_r of our films are larger than that prepared from a single target. These results suggest that the existence of soft magnetic phases makes our film-magnets so-called "exchange-coupled spring-magnets", and that it contributes to the remanence enhancement observed for our film-magnets.

4. Conclusions

Nanocomposite film-magnets with the thickness of several tens of microns were prepared by the pulsed laser deposition method with a rotating $Nd_{2.6}Fe_{14}B/Fe_3B$ composite target, and their magnetic properties were studied. Main results are summarized as follows:

(1) As-deposited films were composed mainly of amorphous Nd–Fe–B and Fe–B phases and exhibited soft magnetic properties.
(2) Annealing crystallized the films into the composite state composed of $Nd_2Fe_{14}B$ and α-Fe/Fe_2B. Superior hard magnetic properties were developed, when the calculated thickness of the period of Nd–Fe–B/Fe–B layers is approximately 90 nm. The obtained coercivity, remanence and $(BH)_{max}$ were 1.05 T, 323 kA/m and 85.7 kJ/m^3, respectively. The above remanence and $(BH)_{max}$ values are higher than the corresponding values reported for the film-magnets prepared from a single $Nd_{2.6}Fe_{14}B$ target.
(3) Considering the strong spring-back phenomenon and the existence of soft magnetic phases in our films, a large remanence value and resultantly, a large $(BH)_{max}$ value of our films can be attributed to the remanence enhancement based on the intergrain interaction.

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