

Coercivity enhancement of Dy-coated Nd-Fe-B flakes by crystallization

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The coercivity of isotropic Dy-coated Nd-Fe-B flakes was enhanced by crystallization and simultaneous diffusion of Dy from their surfaces. Amorphous Dy-coated Nd-Fe-B flakes were crystallized by heating them to 923 K over a 2 min period followed by rapid cooling. During crystallization, the Dy on the surface diffused into the flakes. This low-temperature rapid annealing produced flakes with fine grains and the Dy diffusion enhanced their coercivity. The coercivity after crystallization increased with increasing Dy layer thickness, although the remanence decreased when the layer thickness exceeded 3 μm . Thick coatings of over 6 μm resulted in the formation of DyFe_2 , which degraded the magnetic properties of the crystallized flakes. Flakes with a 3- μm -thick coating exhibited excellent magnetic properties after annealing: They had a coercivity of 1880 kA/m and a remanence of 78 emu/g. This coercivity is approximately 500 kA/m higher than that of uncoated flakes, whereas the remanence is comparable to that of uncoated flakes. © 2011 American Institute of Physics. [doi:10.1063/1.3549604]

I. INTRODUCTION

Although Nd-Fe-B-based magnets have the highest energy product at room temperature of all of the magnets, their coercivity H_c drops drastically above 100 °C because of their low Curie temperature and low anisotropy field.¹ This disadvantage can be overcome by partially substituting Nd in $\text{Nd}_2\text{Fe}_{14}\text{B}$ by a heavy rare-earth element such as Dy or Tb because both $\text{Dy}_2\text{Fe}_{14}\text{B}$ and $\text{Tb}_2\text{Fe}_{14}\text{B}$ have high anisotropy fields at high temperatures.²

However, substituting Nd with a heavy rare-earth element reduces the magnetization of magnets. Furthermore, because there are limited supplies of heavy rare-earth elements it is desirable to reduce their usage. One method of overcoming this problem is to diffuse a heavy rare-earth element only in the vicinity of grain surfaces. The coercivity of a sintered Nd-Fe-B-based magnet has been enhanced by diffusing a heavy rare-earth metal from its surface.^{3–6} Sintering has also been used to diffuse a heavy rare-earth element to $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain surfaces.^{7,8} In both of these methods, the heavy rare-earth element is diffused by annealing at high temperatures of over 1000 K. A low-temperature process is required for isotropic magnets that are fabricated by crystallizing an amorphous powder because high-temperature annealing causes $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains to grow, which degrades the magnetic properties of isotropic magnet powders.⁹

In this study, we developed a low-temperature method for diffusing Dy into isotropic Nd-Fe-B crystalline flakes, thereby enhancing their coercivity.

II. EXPERIMENTAL PROCEDURES

A 14- μm -thick Dy layer was deposited on one surface of amorphous $\text{Nd}_{2.36}\text{Fe}_{14}\text{B}_{1.05}$ flakes by pulsed laser deposition (PLD) in a vacuum. The Dy-coated flakes were then crystallized by heating them to 923 K followed by rapid cooling in an infrared furnace. Dy diffused into the flakes during crystallization. The heating rate was 462 K/min and the Dy layer thickness was 1 μm to 12 μm . Dy or Tb-coated amorphous $\text{Nd}_{2.4}\text{Fe}_{14}\text{B}$ films, approximately 16 μm thick, were also prepared for observations with transmission electron microscopy (TEM) to analyze the microstructure produced by PLD. Dy and Tb were then diffused by applying the same annealing conditions as those used for the flakes.

The magnetic properties of the samples were measured using a vibrating sample magnetometer after magnetization under a pulsed field of 6.4 MA/m. The sample microstructures were observed by TEM and their compositions were determined by energy-dispersive X-ray spectroscopy (EDS). The phases in the samples were analyzed by X-ray diffraction.

III. RESULTS AND DISCUSSION

Figure 1 shows hysteresis loops of uncoated $\text{Nd}_{2.36}\text{Fe}_{14}\text{B}_{1.05}$ flakes and $\text{Nd}_{2.36}\text{Fe}_{14}\text{B}_{1.05}$ flakes coated with 3- μm -thick and 12- μm -thick Dy layers after crystallization. It clearly reveals that the Dy coating layer increases the coercivity H_c . However, the 12- μm -thick coating reduced the remanence M_r , and its demagnetization curve has a step in the low-field region, which suggests the presence of magnetically soft phases. The flakes coated with a 6- μm -thick Dy layer also had two-step demagnetization curves. Figure 2 shows plots of the obtained H_c and M_r as a function of the Dy layer thickness. The coercivity increased with increasing

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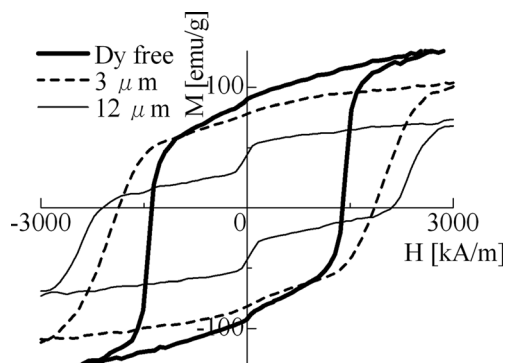


FIG. 1. M - H loops for uncoated Nd-Fe-B flakes and Nd-Fe-B flakes coated with 3- and 12- μ m-thick Dy layers after crystallization.

Dy layer thickness, and it reached 1880 kA/m at a thickness of 3 μ m. A remarkable reduction in M_r was observed when the Dy layer thickness exceeded 3 μ m: M_r of the flakes coated with a 3- μ m-thick Dy layer was nearly the same as that of the uncoated flakes.

Figure 3 shows X-ray diffraction patterns for uncoated Nd-Fe-B flakes and Nd-Fe-B flakes coated with a 12- μ m-thick Dy layer. The diffraction patterns of the Dy-coated flakes were obtained from the coated surfaces. The diffraction pattern of the as-quenched flakes indicates that they are amorphous. Peaks from Dy and R_2O_3 (R =Dy or Nd) were observed after deposition of Dy, which suggests that a Dy layer was formed on the surfaces. A peak from $DyFe_2$ appeared after crystallization. The thermomagnetic analysis results shown in Fig. 4 also confirm the presence of $DyFe_2$. As $DyFe_2$ has a cubic structure¹⁰ with a magnetic anisotropy constant of 2.1×10^6 J/m³, this phase is considered to be responsible for the two-step demagnetization curve of this sample.

To confirm the diffusion of Dy, cross sections of flakes were observed by scanning electron microscopy (SEM) and the depth profile of the Dy content was analyzed by EDS. Figure 5 shows the Dy, Nd, and Fe contents (the B content was omitted from this analysis) in a crystallized flake as a function of depth from the surface. The Dy layer is approximately 2.5 μ m thick, as indicated by the profile. Dy diffused

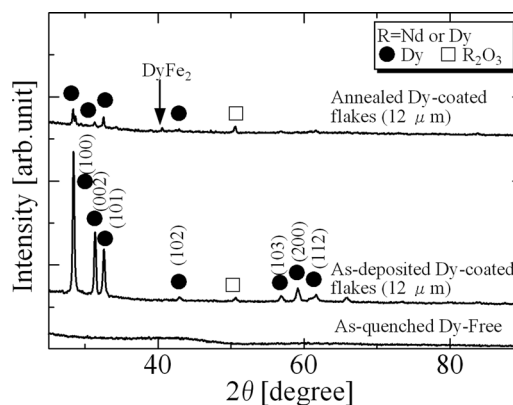


FIG. 3. X-ray diffraction patterns of uncoated Nd-Fe-B flakes and Nd-Fe-B flakes coated with a 12- μ m-thick Dy layer. The patterns of the coated flakes were obtained from the Dy-coated surfaces.

up to 6.5 μ m into the flake despite a very short annealing time.

Further analysis was performed for 16- μ m-thick $Nd_{2.4}Fe_{14}B$ films coated with a Dy or Tb layer. After crystallization at 923 K, both the Dy and Tb layers increased H_c ; H_c of the $Nd_{2.4}Fe_{14}B$ film with a 2- μ m-thick Tb layer exceeded 2000 kA/m. Figure 6 shows typical TEM images of this film. The sample was composed of fine grains and the map of the Tb-M line indicates that Tb is concentrated in the vicinity of grain boundaries, which agrees with previous observations of sintered magnets.³⁻⁶ Detailed results for the TEM observations have been published elsewhere.¹¹ As Tb and Dy have similar diffusion behaviors,⁵ the Dy in the present Dy-coated flakes is expected to be concentrated in the vicinity of grain boundaries after crystallization. Therefore, the observed H_c enhancement of these flakes is attributed to the diffusion of Dy through the grain boundaries.

IV. CONCLUSIONS

Amorphous Nd-Fe-B flakes coated with a Dy layer were crystallized. Their coercivity H_c was enhanced by diffusion of Dy from their surfaces during crystallization. SEM and

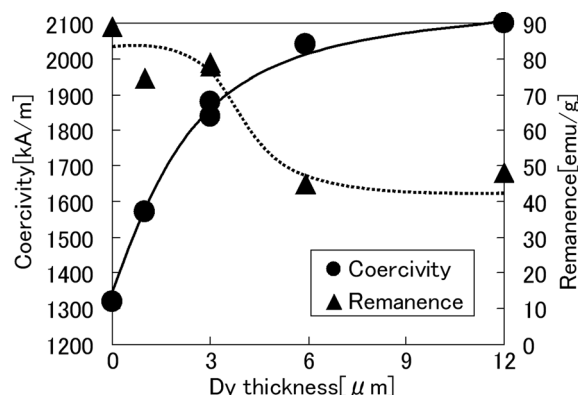


FIG. 2. Coercivity and remanence of Dy-coated flakes as a function of Dy layer thickness.

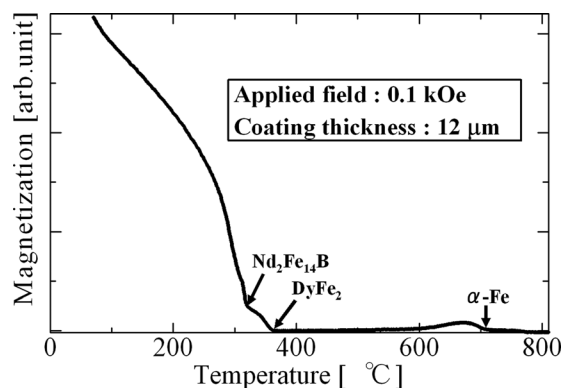


FIG. 4. Thermomagnetic properties of Dy-coated flakes after crystallization. The arrows indicate the Curie temperatures of $Nd_2Fe_{14}B$, $DyFe_2$, and α -Fe.

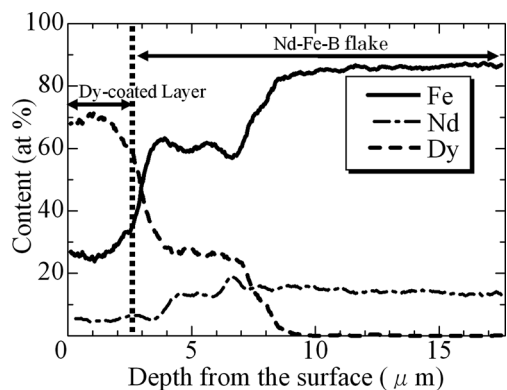


FIG. 5. Depth profile of Dy, Nd, and Fe contents in a flake after crystallization. The Dy layer is approximately 2.5 μm thick.

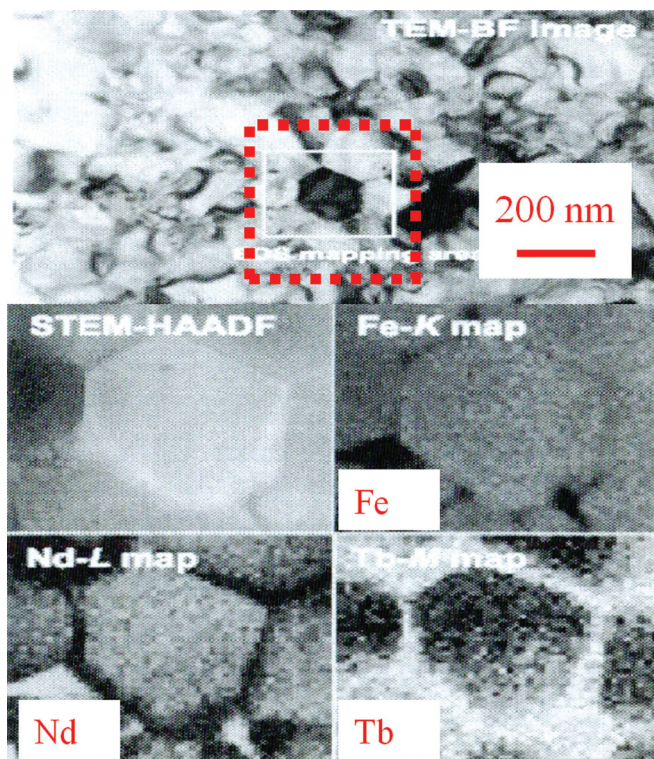


FIG. 6. (Color online) Typical TEM images of Tb-coated $\text{Nd}_{2.4}\text{Fe}_{14}\text{B}$ film after crystallization. The lower part shows images obtained using Fe-K, Nd-L, and Tb-M lines. Detailed results of TEM observations have been published elsewhere (Ref. 11).

EDS analyses confirmed that Dy diffuses into the flakes. This investigation used a much lower annealing temperature (932 K) and a much shorter annealing time (0 min) than those employed for diffusing Dy in sintered magnets. This enabled us to obtain isotropic Nd-Fe-B-based flakes consisting of fine grains with a high H_c .

The coercivity after crystallization increased with increasing Dy layer thickness, although M_r decreased when the coating thickness exceeded 3 μm . Coatings that were more than 6 μm thick resulted in the formation of DyFe_2 , which deteriorated the magnetic properties of the crystallized flakes. Flakes coated with a 3- μm -thick layer exhibited excellent magnetic properties ($H_c = 1880$ kA/m and $M_r = 78$ emu/g). This H_c value is approximately 500 kA/m higher than that of the uncoated flakes, whereas M_r is comparable to that of the uncoated flakes.

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