Influence of misorientation angle between adjacent grains on magnetization reversal in Nd-Fe-B-based sintered magnet

T. Maki, R. Uchikoshi*, R. Ishii, M. Natsumeda, T. Nishiuchi, and M. Takezawa*
Magnetic Materials Research Laboratory, Magnetic Materials Company, Hitachi Metals, Ltd., 2-15-17 Egawa, Shimamoto-cho, Mishima-ku, Osaka 618-0013, Japan
*Department of Applied Science for Integrated System Engineering, Kyushu Institute of Technology, 1-1 Sensui-cho, Tobata-ku, Kitakyushu-shi, Fukuoka 804-8550, Japan

To clarify the difference between the degree of alignment dependence of coercivity and the angular dependence of coercivity, the crystal orientation distribution and demagnetization curve of Nd-Fe-B-based sintered magnets with different degrees of alignment were compared. It is suggested that the increase in coercivity due to a low degree of alignment cannot be explained only by the angular dependence of coercivity. A crystal orientation analysis and in situ observation of magnetic domains that were performed in the same area clarified that the ratio of the grain boundary where the magnetization reversal stopped became larger when the misorientation angle between adjacent grains became larger. This suggests that a grain boundary having a larger misorientation angle is one of the factors that suppresses magnetization reversal.

Key words: Nd-Fe-B magnet, coercivity, degree of alignment, Kerr microscope, magnetic domain

1. Introduction

Nd-Fe-B-based magnets used in motors for electric vehicles (EV) and hybrid electric vehicles (HEV) are required to have a high coercivity for maintaining thermal stability. Generally, heavy rare earth elements such as Dy and Tb are added to increase the magnetocrystalline anisotropy of the Nd$_2$Fe$_{14}$B compound to obtain a high coercivity. However, these elements are recognized as materials with a high supply risk, and there is a strong demand for Nd-Fe-B-based magnets to achieve a high coercivity with a lower amount of heavy rare earth elements.

The coercivity of the Nd-Fe-B-based magnet is greatly changed not only by the addition of heavy rare earth elements but also by the microstructure. It was pointed out that Nd-rich phases existing at the grain boundary play an important role in coercivity$^{[3,30]}$, and it was observed that a Nd-rich phase inhibited propagating magnetic domains$^{[4,5]}$. The coercivity of the Nd-Fe-B-based sintered magnet also strongly depends on the degree of alignment of the Nd$_2$Fe$_{14}$B phase, and it is experimentally known that the coercivity increases as the degree of alignment decreases$^{[6,7]}$. It was also reported that the coercivity increases when the angle $\theta$ between the easy magnetization direction of the Nd-Fe-B-based sintered magnet and the direction of the applied magnetic field becomes large, which is referred to as the angular dependence of coercivity$^{[8]}$. This dependency is explained by the magnetic domain wall motion model, which shows that the coercivity increases at a rate of $1/\cos \theta$. Attempts have been made to explain the dependence of the coercivity on the degree of alignment by combining the angular dependence and orientation distribution$^{[7]}$, but it is not fully understood. When the degree of alignment decreases, it is easy to expect that the distribution of the orientation angle $\theta$ between the applied magnetic field $H$ and the easy axis of magnetization of each Nd$_2$Fe$_{14}$B grain broadens as shown in Fig. 1. However, the distribution of the misorientation angle $\phi$ between the easy axis of magnetization of adjacent grains will change at the same time. There is a possibility that this change in the distribution of $\phi$ may be related to magnetic domain wall motion and coercivity, but no example has been reported experimentally.

To understand directly the relationship between the microstructure and magnetic domain structure in the Nd-Fe-B-based magnet, various methods for evaluating the magnetic domain structure on the surface of the magnet are studied, such as the magneto/optical Kerr microscope$^{[9,10]}$, Lorentz transmission electron microscope (Lorentz-TEM)$^{[11,12]}$, electronic holography$^{[13]}$, magnetic force microscope

Fig. 1 Schematic images of orientation angle $\theta$ between easy axis of magnetization of each grain and applied magnetic field $H$ and misorientation angle $\phi$ between easy axis of adjacent grains.
(MFM)\cite{12,13}, and spin-polarized scanning electron microscope (spin-SEM)\cite{14,15}. Among them, the magneto-optical Kerr microscope can perform in-situ observation in a high magnetic field, so it is an effective method for directly observing the magnetization behavior of the Nd-Fe-B magnet\cite{16}. Takezawa et al. reported the in-situ magnetic domain observation of a Nd-Fe-B-based sintered magnet in a magnetic field. Several grains were simultaneously reversed along the direction of the easy axis of magnetization, and when the applied magnetic field increased, the magnetization reversal propagated\cite{17,18}. It is important to observe a wide area to understand the propagation of magnetization reversal across multiple grain groups, and the magneto-optical Kerr microscope is also suitable in this respect.

In this study, first, to clarify the difference between the degree of alignment dependence of coercivity and the angular dependence of coercivity, we investigated the $\theta$ distribution and $\phi$ distribution of Nd-Fe-B-based sintered magnets with different degrees of alignment. The coercivity was measured by changing the angle between the magnetic field and sample. Subsequently, the magnetization process was analyzed by using recoil curves\cite{20}. Next, to experimentally evaluate the relationship between the difference in the misorientation angle between adjacent grains and the magnetic domain structure in the Nd-Fe-B-based sintered magnet, a scanning electron microscope with an electron backscatter diffraction (SEM/EBSD) analysis and the in-situ magnetic domain observation in the magnetic field by using a magneto-optical Kerr microscope were conducted in the same observed area.

2. Experimental method

Highly aligned (HA) and moderately aligned (MA) sintered magnets that had a composition of $30.2\text{Nd-67.6Fe-1.0B-0.9Co-0.1Al-0.1Cu-0.1Ga}$ (mass\%) were prepared by using an ordinary process except for pressing, which applied a different magnitude of magnetic field. The remanence $B_r$ and the coercivity $H_c$ of the HA and MA magnets were $B_r = 1.44$ T, $H_c = 1038$ kA/m, $B_r = 1.33$ T, and $H_c = 1126$ kA/m, respectively. The distribution of the degree of grain alignment was analyzed by observing the polished surface plane that was parallel to the easy magnetization direction of the magnet with SEM/EBSD. The sintered magnets were shaped into spheres for magnetic measurement. After magnetization with a pulse magnetic field of 5.6 MA/m, the demagnetization curves were measured in the range of 1.6 to $-1.6$ MA/m with a vibrating sample magnetometer (VSM). In the case of changing the angle of the applied magnetic field with respect to the easy magnetization direction of the sample, the electromagnet of the VSM was rotated at a 1° pitch with respect to the sample. Each demagnetization curve was corrected by setting the demagnetizing factor $N$ of the sphere to $N = 0.33$. The recoil curve measurement was repeated by increasing the demagnetization field by 40 kA/m in the second and third quadrants of the demagnetization curve and returning to 0 kA/m, as described in the previous paper\cite{20}.

The sintered magnets used for magnetic domain observations had two compositions (30.2-xNd-xDy-67.6Fe-1.0B-0.9Co-0.1Al-0.1Cu-0.1Ga (x = 0, 5.0) with different Dy content, and the MA magnets were used. The magnetic property of a Dy doped (x = 5.0) magnet was $B_r = 1.24$ T and $H_c = 1958$ kA/m. Each sample was cut into $3 \times 3 \times 3$ mm, and the plane that was polished was parallel to the easy magnetization direction for an observation surface. First, SEM/EBSD analyses were performed at the center of the polished plane, and the magnetic domain was then observed with the magneto-optical Kerr microscope. An SiO film was deposited on the surface of each sample by vacuum evaporation for antireflection\cite{17}. Each sample was magnetized in the orientation direction with a pulsed magnetic field of 4.0 MA/m and then set in the magneto-optical Kerr microscope. A DC magnetic field was applied to the samples in the range of 1.6 to $-1.6$ MA/m. Magnetization reversal was detected from the change in contrast in an observation image, and the reversed area was extracted by image processing\cite{18}. To obtain the effective magnetic field in the observation area, the demagnetizing field at the center of the plane that is parallel to the easy magnetization direction of the cubic Nd-Fe-B magnet was calculated by using a three-dimensional finite element method (3D-FEM). The effective magnetic field $H_{eff}$ was obtained from the relationship of $H_{eff} = H_a - H_b$, where $H_a$ and $H_b$ are the external magnetic field and the demagnetizing field from a sample, respectively. For example, in the case of $x = 0$, $H_{eff} = -250$ kA/m when $H_a = 0$ kA/m.

3. Results and discussion

3.1 Distribution of $\theta$ and $\phi$

Figure 2 shows inverse pole figure maps of the MA and HA magnets with the horizontal direction as an orientation direction. Compared with the HA magnet, the MA magnet had a large dispersion of crystal orientation. The orientation angle $\theta$ between the direction of the applied magnetic field $H$ and the direction of the easy axis of magnetization in each grain was calculated from the direction cosine of the RD direction and <001> direction of each grain. The misorientation angle $\phi$ between the easy axis of adjacent grains that was defined regardless of the relative position of adjacent grains was calculated from the direction cosine of <001> directions of adjacent grains. Figures 3(a)-(d) show the distribution of $\theta$ and $\phi$ in each sample. Compared with the HA magnet, both of the distributions of $\theta$ and $\phi$ in the MA magnet were broad, and the frequencies on the higher angle were large. It was found that not only the orientation angles
but also the misorientation angles between adjacent grains had a wide distribution when the degree of alignment decreased.

3.2 Relationships between distribution of $\theta$, $\phi$, and coercivity

Figure 4 shows demagnetization curves of the HA magnet, MA magnet, and HA magnets that were inclined at 23° and 48° with respect to the direction of the applied magnetic field. When the HA magnet was tilted at an angle of 23°, the coercivity was clearly lower than that of the MA magnet, whereas the squareness $J_r/J_s$ of each sample was almost the same. When trying to obtain the same coercivity as the MA magnet, the HA magnet must be tilted up to 48° with respect to the applied magnetic field. Figure 3(e) shows the distribution of $\theta'$ which was obtained by calculating the angle $\theta'$ between the direction of the easy axis of magnetization in each grain and the direction that was intentionally deviated 23° from the RD direction. The distribution of $\theta'$ was similar to the distribution of $\theta$ of the MA magnet. Therefore, the MA magnet and HA magnet tilted at 23° had approximately the same orientation distribution as the direction of the applied field, which was consistent with the fact that $J_r/J_s$ was the same in the demagnetization curve. These results suggest that the large increase in coercivity due to the low degree of alignment cannot be explained only by the angular dependence of coercivity.

Figure 5(a) shows whole recoil curves of the MA magnet and HA magnet.
magnet and HA magnet tilted at 23°, and Fig. 5(b) shows recoil curves of both samples that returned to near the origin. The curvature of the recoil curve of the MA magnet was smaller than that of the tilted HA magnet. In the previous paper[20], it was pointed out that the recoil curve of a Nd·Fe·B sintered magnet that has an average grain size of several μm contains domain wall motion in its magnetization process. The small curvature of the recoil curve suggests that the magnetic domain wall motion in the MA magnet was small. As shown in Fig. 3(d), the MA magnet had a large distribution of θ, which may be related to the

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Fig. 4 Demagnetization curves measured for HA magnet, MA magnet, and HA magnet inclined at 23° and 48° with respect to magnetic field direction (spherical sample, demagnetizing factor N= 0.33). 

Fig. 5 (a) Recoil curves of MA magnet and HA magnet measured by tilting 23° with respect to magnetic field direction and (b) comparison of two recoil curves returning to near origin position.

Fig. 6 Reversed region in each effective magnetic field H_{eff} extracted from Kerr microscope image in demagnetization process of (a) Dy undoped (x = 0) and (b) Dy doped (x = 5.0) MA magnets.

Fig. 7 Changes in ratio of unreversed area with regards to H_{eff} in demagnetization process of each of four observed fields for x = 0 and x = 5.0 samples extracted from Kerr microscope image.
suppression of the domain wall motion.

3.3 Relationship between propagation of magnetization reversal and misorientation angle $\phi$

Figure 6 shows magnetically inverted areas in each magnetic field $H_{dt}$ extracted from the magnetic domain observation results for the demagnetization process of the Dy undoped ($x = 0$) and Dy doped ($x = 5.0$) MA magnets. These samples had almost the same distribution of $\theta$ and $\phi$. Grain boundaries in the sample are indicated by white dotted lines to facilitate recognition. The unversed areas were considered to be undetected areas because of a significantly weak change in contrast and were excluded from the evaluation. Several grains were reversed simultaneously along the magnetic easy axis direction, which is similar to the case of highly aligned Nd-Fe-B sintered magnets. To estimate the repeatability of the demagnetization process in the same $H_{dt}$, we prepared four samples for both $x = 0$ and $x = 5.0$ under the same condition and observed these samples at the center of each polished plane with the same method discussed above. Figure 7 shows changes in the ratio of the unversed area with respect to $H_{dt}$ in the demagnetization process of each of the four observed fields with $x = 0$ and $x = 5.0$. In the surface layer for $x = 5.0$, which had a large amount of Dy, the magnetization reversal propagated at a higher magnetic field. It is thought that the magnetization propagation on the surface depended on the magnitude of magnetcocrystalline anisotropy of the (Nd,Dy)$_2$Fe$_{14}$B phase, even though the coercivity of the polished surface layer was lower than the interior of the magnet due to the deterioration and lack of a Nd-rich grain boundary phase. When a group of grains was reversed in a certain applied magnetic field, positions where the magnetization reversal stopped often existed along the grain boundary. To clarify how the misorientation angle $\phi$ between two grains on both sides of the grain boundary affects the magnetization reversal, the grain boundaries were divided into two groups: GBa and GBb. GBa is a grain boundary where the magnetization reversal stopped, which is indicated by the borders of the different colored regions in Fig. 6. GBb is a grain boundary where the magnetization reversal did not stop that is located inside the colored region. In this study, the relationship between GBa and $H_{dt}$, as well as GBb and $H_{dt}$, was not considered. The grain boundaries that were clearly separated by a large Nd-rich phase were excluded from the evaluation. Figure 8(a) shows the result of dividing about 900 grain boundaries into GBa and GBb for the $x = 0$ samples and the ratio of GBa and GBb in each angular range of $\phi$. It was found that the ratio of GBa became larger when $\phi$ became larger. This tendency was similar when about 1000 grain boundaries were analyzed in the samples with $x = 5.0$, as shown in Fig. 8(b). These results experimentally suggest that a grain boundary with a larger misorientation angle of adjacent grains $\phi$ has the ability to suppress magnetization reversal. It is also considered that the influence of the misorientation angle on suppressing magnetization reversal does not differ much even when the saturation magnetization and magnetocrystalline anisotropy of the main phase are different.

4. Conclusion

To clarify the difference between the degree of alignment dependence of coercivity and angular dependence of coercivity, the crystal orientation...
distribution and demagnetization curve of Nd-Fe-B based sintered magnets with different degrees of alignment were compared. It was shown that an increase in coercivity due to a low degree of alignment cannot be explained only by the angular dependence of coercivity and that domain wall movement is small in a magnet that has a low degree of alignment. A crystal orientation analysis and in-situ magneto-optical Kerr microscope observation performed in the same area clarified that the ratio of the grain boundary where the magnetization reversal stopped became larger when the misorientation angle between adjacent grains became larger. This suggests that a grain boundary having a larger misorientation angle is one of the factors that suppresses magnetization reversal. From the above results, it can be said that the increase in coercivity by the decrease in the degree of alignment is caused by the suppression of magnetization reversal at the grain boundary due to the increase in the misorientation angle between adjacent grains. The reason that the misorientation angle suppresses magnetization reversal is considered to be the reduction in magnetic interaction between grains or a change in the microstructural relationship between the main phase and grain boundary phase. Further understanding of the grain boundary structure and magnetization process is necessary in the future.

References

1. K. Hiraga, M. Hirabayashi, M. Sagawa, and Y. Matsumura: Jpn. J. Appl. Phys., 24, L30 (1985).
2. R. K. Mishra, J. K. Chen, and G. Thomas: J. Appl. Phys., 59, 2244 (1986).
3. F. Vial, F. Joly, E. Nevalainen, M. Sagawa, K. Hiraga, and K. T. Park: J. Magn. Magn. Mater., 242-245, 1329 (2002).
4. Y. Shinba, T. J. Konno, K. Ishikawa, and K. Hiraga: J. Appl. Phys., 97, 053504 (2005).
5. H. Sepehr-Amin, T. Ohkubo, T. Shima, and K. Hono: Acta. Mater., 60, 819 (2012).
6. A. Handstein, K. -H. Muller, D. Eckert, and P. Northagel: J. Magn. Magn. Mater., 101, 382 (1991).
7. Y. Matsumura, J. Hoshijima, and R. Ishii: J. Magn. Magn. Mater., 336, 88 (2013).
8. D. Givord, P. Tenaud, and T. Viadieu: J. Magn. Magn. Mater., 72, 247 (1988).
9. D. Li and K. J. Strnat: J. Appl. Phys., 57, 4143 (1985).
10. A. Fukuno and R. C. O’Handley: J. Appl. Phys., 66, 4959 (1989).
11. Y. -G. Park and D. Shindo: J. Magn. Magn. Mater., 238, 68 (2002).
12. T. Yamaoka, H. Tsujikawa, R. Hirose, A. Ito, H. Kawamura, and T. Sakon: J. Magn. Soc. Jpn., 35, 60 (2011) [in Japanese].
13. J. Thielisch, T.G. Woodcock, L. Schultz, and O. Gutfleisch: J. Appl. Phys., 111, 103901 (2012).
14. T. Kohashi, K. Motai, T. Nishiuchi, T. Maki, and S. Hirosawa: J. Magn. Soc. Jpn., 33, 874 (2009).
15. H. Suzuki, Y. Satsu, T. Kohashi, K. Motai, and M. Komuro: J. Appl. Phys., 109, 07A746 (2011).
16. M. Takezawa, T. Shimada, S. Kono, S. Mimura, Y. Morimoto, T. Hidaka, and J. Yamasaki: J. Appl. Phys., 101, 09K106 (2007).
17. M. Takezawa, Y. Kimura, Y. Morimoto, and J. Yamasaki: IEEE Trans. Magn., 49, 3262 (2013).
18. M. Takezawa, H. Oginoto, Y. Kimura and Y. Morimoto: J. Appl. Phys., 116, 17A733 (2014).
19. K. Toyoki, Y. Kotani, Y. Senba, D. Billington, H. Okazaki, A. Yasui, W. Ueno, H. Ohashi, Y. Shiratsuchi, S. Hirosawa, K. Hono, and T. Nakamura: Proc. 24th Int. Workshop on Rare Earth and Future Permanent Magnets and their Applications, Darmstadt, 2016, 129 (2016).
20. T. Maki and S. Hirosawa: J. Appl. Phys., 103, 043904 (2008).

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