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The grain boundary diffusion (GBD) was applied to magnetically aligned Nd-Fe-B sintered magnets on their different surfaces. The demagnetization curves show better squareness for Dy diffusing from the pole surfaces than that from the side surfaces. Kerr magnetic domain patterns on magnet surfaces in aligned and unaligned magnets were observed together with in situ optical microscope images. It indicates that the anisotropy of the GBD effect is attributed to the anisotropic texture of the grain boundary Nd-rich phase in the magnet. © 2014 AIP Publishing LLC.

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Recently, grain boundary diffusion (GBD) process has been applied to different kinds of Nd-based permanent magnets and exhibited significant enhancement in intrinsic coercivity ($H_{cj}$) without obvious reduction in remanence ($B_r$).1–9 In the GBD process, Dy or Tb element in alloy powders, compound powders, or metallic vapor are supplied to the surface of the magnets and then diffuse into the magnets through the grain boundary phase during the heat treatment. With GBD treatment, the application of limited and expensive rare earth resources, such as Dy or Tb, can be optimized. The magnets with GBD treatment have been reported for motor applications where the high temperature environment asks for high $H_{cj}$.10 Many of previous research work about GBD process focused on microstructure of GBD treated magnets in efforts to reveal the mechanism of $H_{cj}$ enhancement.2,3,5,11,12 Some of the work studied the depth distribution of $H_{cj}$ and Dy/Tb diffused from the surface of the magnets.13,14 We found that as the channel for Dy/Tb diffusion, the Nd-rich grain boundary phase is critical for GBD treatment.15 However, the relationship of GBD effect and texture of boundary phase has not been clarified.

In this Letter, we report the investigation on the anisotropy of GBD process on different surfaces of the magnetically aligned Nd-Fe-B sintered magnet.

Sintered Nd-Fe-B magnet of SANMAG-N45H grade was sliced into cubes of $6.5 \mathrm{~mm} \times 6.5 \mathrm{~mm} \times 6.5 \mathrm{~mm}$, with one side parallel to the alignment direction. For investigating the anisotropy of the GBD process, four groups of samples were prepared by different types of treatment [Fig. 1].

(1) Sample A: the original magnet cubes.
(2) Sample B: on the original magnet cubes, Dy alloy powder was supplied to all six surfaces.
(3) Sample C//: Dy alloy powder was supplied only to the two opposite pole surfaces of which the normal lines are parallel to the magnetic alignment direction (also parallel to the c-axes of the matrix Nd$_2$Fe$_{14}$B grains).
(4) Sample C⊥: Dy alloy powder was supplied only to the two opposite side surfaces of which the normal lines are perpendicular to the magnetic alignment direction (also perpendicular to the c-axes of the matrix Nd$_2$Fe$_{14}$B grains).

Then groups of samples A, B, C∥, and C⊥ were heat treated at 750–1000°C in vacuum for 2 h, and then followed by annealing treatment at 490°C for 2.5 h.

Based on the nominal composition of SANMAG-N45SH grade magnet, sintered magnets of unaligned and 1.8 T transverse field aligned were also prepared. Original, pole surface GBD treated and side surface GBD treated cubes of $6.5 \mathrm{~mm} \times 6.5 \mathrm{~mm} \times 6.5 \mathrm{~mm}$ were prepared in the same way as samples A, C∥, and C⊥. Unaligned samples are referred as A0, C0∥, and C0⊥. And the samples aligned in transverse field of 1.8 T are referred as A1.8, C1.8∥, and C1.8⊥.

The $B$-$H$ curves of all samples were measured by a $B$-$H$ tracer (NIM-200C) at room temperature. The domain patterns of the thermally demagnetized samples were observed by a magneto-optical Kerr microscope (BH-786IP-PK). The in situ microstructure images on the etched surfaces were observed by a digital microscope (VHX-600E).

Fig. 2 shows the demagnetization curves of samples A, B, C∥, and C⊥. The corresponding data of magnetic properties are listed in Table I. Obviously, after GBD treatment the...
$H_{cij}$ of samples B, C$\parallel$, and C$\perp$ decreases compared to the original sintered magnet (sample A). As expected, the $H_{cij}$ enhancement ($\delta H_{cij} = H_{cij} - H_{cij}^{A}$) of sample B is the highest since all the six surfaces are covered by Dy alloy powder. Quantitatively, the squareness of demagnetization curves described by $H_{c/}/H_{c}$ are lower for samples B and C$\perp$ than those for samples A and C$\parallel$ as shown in Table I. Here, $H_{c}$ is defined as the demagnetizing field where the magnetization $4\pi M$ reduces to 90% of $4\pi M_{r}$ ($4\pi M_{r}$, residual magnetization). Although values of $\delta H_{cij}$ for samples C$\parallel$ and C$\perp$ are the same, their demagnetizing behaviors are quite different when the demagnetizing field closes to $H_{cij}$ (Fig. 2 inset (a)). In inset (b) of Fig. 2, the difference in magnetization between samples C$\parallel$ and C$\perp$, $\delta(4\pi M) = 4\pi M_{C/} - 4\pi M_{C\perp}$, is clear when the demagnetizing field increases from 18.64 to 19.79 kOe. The peak value is as large as 9.61 kGs at 19.52 kOe. The demagnetizing behavior of samples C$\parallel$ and C$\perp$ are almost the same when the demagnetizing field lower than 18.64 kOe. At this stage only a few magnetic moments are reversed. When the field further increases from 18.64 kOe, plenty of magnetic moments in sample C$\perp$ are continuously reversed, while the magnetic moments in sample C$\parallel$ remain unchanged until the demagnetizing field reaches 19.52 kOe. The different demagnetizing behavior between samples C$\parallel$ and C$\perp$ reflects the anisotropic behavior of GBD treatment on aligned magnet. Dy atoms distribute more homogeneously when Dy alloy powder is supplied on the pole surfaces. 

Demagnetization curves of unaligned and aligned magnet cubes before and after GBD treatment are shown in Fig. 3. Though $H_{cij}$ values of magnets are different from those in Figure 2, the similar anisotropic characteristics can be recognized in aligned samples C$^{1,8}$ and C$^{1,8}$. However, the curves of unaligned magnet samples C$^{0}$ and C$^{0}$ completely overlap, indicating the isotropic behavior of GBD process. Therefore, the anisotropy of the GBD treatment only exists in aligned magnet.

Figs. 4(a) and 4(b) show the typical magnetic domain patterns on pole surface and side surface of an aligned magnet. The corresponding in situ microstructure images on etched surface are shown in Figs. 4(d) and 4(e). It can be seen from Fig. 4(a) that all domains are in maze structure on the pole surface. Correspondingly, etched Nd-rich grain boundaries clearly separate main phase grains from each other [Fig. 4(d)]. Very different from the pole surface, domains observed on side surface are in strip structure [Fig. 4(b)]. And there are very few etched edges can be recognized in microstructure image, which implies very few or very narrow Nd-rich

![FIG. 2. The demagnetization curves of samples A, B, C$\parallel$, and C$\perp$. The inset (a) shows the details of the demagnetization curves of samples C$\parallel$ and C$\perp$ close to $H_{cij}$. The inset (b) shows the magnetization difference $\delta(4\pi M)$ ($\delta(4\pi M) = 4\pi M_{C/} - 4\pi M_{C\perp}$).](image)

![FIG. 3. The demagnetization curves of unaligned and aligned magnets: original magnet samples A$^{0}$ and A$^{1,8}$, GBD treated samples C$^{0}$, C$^{0}$, C$^{1,8}$, and C$^{1,8}$.](image)

![FIG. 4. The magnetic domain Kerr images of (a) pole surface, (b) side surface of aligned magnet, and (c) surface of unaligned magnet, and their optical microscopy images of the same three areas after etching (d), (e), and (f).](image)

<table>
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<tr>
<th>TABLE I. The magnetic properties of samples A, B, C$\parallel$, and C$\perp$.</th>
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<td>Samples</td>
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boundary phase existing on side surface [Fig. 4(e)]. Figure 4 also shows domain pattern and in situ microstructure on any of the six surfaces of unaligned cubic magnet. The domain pattern indicates that grains are either in maze or in strip domain structure [Fig. 4(c)]. It is worth noting from the in situ microstructure image [Fig. 4(f)] that only part of the grains can be etched out. It is amazing that grains with maze domain in Fig. 4(c), such as grains marked “O,” “P,” and “Q,” are in one-to-one correspondence with the etched grains in Fig. 4(f). Therefore, the boundary of maze domain grains are always easy to be etched out no matter the magnet is aligned or not. In other words, if looking at a single grain in sintered magnet, the Nd-rich boundary phase tends to distribute on the surface around its c-axis. It can be deduced that, for sintered Nd-Fe-B magnets, the distribution of Nd-rich phase in the grain boundaries is strongly related to the c-axes distribution. It was reported that the thermal expansion (contraction) of Nd$_2$Fe$_{14}$B along c-axis is about 3 times larger than that along a-axis in the temperature range of 300 K to 900 K.19 Therefore, the anisotropic expansion (contraction) of Nd$_2$Fe$_{14}$B grains along and perpendicular to the alignment direction during sintering in an aligned magnet may cause the anisotropic distribution of Nd-rich grain boundary phase. When single crystalline particles are arranged in line parallel to their c-axes during magnetic alignment and sintered into aligned magnet, the Nd-rich phase will be squeezed out to form cylinder along c-axes to wrap main phase grains. As we presented in our previous work that the grain boundary phase is a diffusion channel for Dy/Tb,15 it is expected that there are better diffusion effects through the wider channel parallel to the magnetic alignment direction (c-axes) in aligned magnets.

In aligned Nd-Fe-B sintered magnet, the demagnetization curves show better squareness for Dy diffusion from side surfaces than that from side surfaces, which is considered as the anisotropy of GBD effect. The domain patterns together with in situ microstructure images of etched samples indicate that the Nd-rich phase tends to distribute along c-axis. As the diffusion channel of GBD treatment, the anisotropic texture of Nd-rich phase results in the anisotropy of the GBD effect.

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