Structure and chemical compositions of the grain boundary phase in Nd-Fe-B sintered magnets

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Abstract

We revisited the microstructure of a commercial Nd-Fe-B sintered magnet using scanning electron microscopy (SEM) and aberration corrected scanning transmission electron microscopy (STEM) in order to clarify the microstructure feature that is relevant to the coercivity. Two types of thin Nd-rich grain boundary (GB) phases were found: one is crystalline and the other is amorphous. The crystalline Nd-rich GB phase form at the flat surface of c-plane of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, which contains a higher amount of Nd compared to the amorphous GB phase that form on the grain boundaries nearly perpendicular to the c-planes. This indicates that the intergranular exchange coupling in sintered Nd-Fe-B magnets is anisotropic. Correlative SEM and STEM analysis of triple junction Nd-rich phases revealed five types of Nd-rich phases, *i.e.*, fcc-NdO, hcp- Nd_2O_3 , NdFe_4B_4 , metallic Nd-rich phases with the fcc structure and the $\text{Ia}\bar{3}$ structure. The metallic Nd-rich phases form at the sharp edges of Nd-rich oxide and boride grains, from which thin Nd-rich phases is infiltrated along grain boundaries to form the thin GB phase. Misaligned $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are often observed in direct contact with the Nd_2O_3 grains.

Keywords: Nd-Fe-B, sintered magnet, Nd-rich phase, grain boundary phase

1. Introduction

(Nd_{1-x}Dy_x)–Fe–B based sintered magnets are used for traction motors and generators of hybrid (electric) vehicles and wind turbines because of their excellent balance of remanence and coercivity. However, due to the limited natural resources and high cost of Dy, finding a way to enhance the coercivity of Nd-Fe-B sintered magnets without using Dy has received intense research interest recently [1–3]. The coercivity of the Nd-Fe-B magnet is influenced not only by the magnetocrystalline anisotropy energy of the Nd₂Fe₁₄B phase, but also by various microstructural features such as the grain size [4, 5], grain alignment [6–8], constitution of Nd-rich phases at triple junctions [9,10], and presence of thin Nd-rich grain boundary (GB) layers (phases) and their magnetism [3,11]. A variety of Nd-rich triple junction phases have been reported including dhcp-Nd, fcc-Nd(Fe), NaCl-type NdO, and hcp-Nd₂O₃ in Nd-Fe-B sintered magnets [12–21]; however, there are still inconsistencies in literature because the Nd-rich phases are easily oxidized during specimen preparation for scanning electron and transmission electron microscope observations. Model experiments and simulations discussed the effect of these Nd-rich phases on the coercivity in terms of the interfacial structure, chemical composition and strain field around Nd₂Fe₁₄B/Nd-rich interfaces [22–33]. However, the key microstructural features that govern the coercivity of sintered magnets is still elusive due to the lack of the complete identification of the types of the Nd-rich phases and their correlations with the formation of the GB phases. The complete distinction of the Nd-rich phases in sintered magnets in large area has been technically difficult due to their similar imaging contrasts in backscattered electron (BSE) images in scanning electron microscopy (SEM). Most of the phase identification works on the Nd-rich phases have been performed by selected area electron diffraction within the limited field of view in transmission electron microscopy (TEM), while micron-scale structure is more relevant to the magnetization reversal processes. Metallic Nd-

rich phases are rapidly oxidized in air, and some of previous TEM results appear to have identified the oxides that are formed after TEM specimens.

Sepehri-Amin *et al.* reported that a thin Nd-rich GB phase forms by the infiltration of a liquid phase that form by the eutectic reaction between Nd/NdCu during a post-sinter annealing process [30]. The thin Nd-rich GB phase was reported to have an amorphous structure with the content of rare earth element (R) up to ~35 at.% from the high resolution transmission electron microscopy (HRTEM) and three dimensional atom probe (3DAP) analyses [30,34–37]. However, a more recent study using high angle annular dark field (HAADF) imaging using an aberration corrected STEM reported the presence of a crystalline Nd-rich GB phase in fine-grained Nd-Fe-B sintered magnets fabricated by the pressless-sintering process [10]. Since this study was carried out for the laboratory-made pressless-sintered magnets with unusually fine grain size, it still remains unclear whether or not such newly found crystalline GB phase is the special feature of the particular fine-grained magnet or a common feature in commercial Nd-Fe-B sintered magnet. This motivated us to revisit the microstructure of a Nd-Fe-B commercial sintered magnet.

The purpose of this work is to clearly establish the microstructure feature of a typical commercial sintered magnet with a high maximum energy product, $(BH)_{\max}$, of 400 kJ/m³ or 50 MGOe by identifying the triple junction Nd-rich phases using correlative SEM and TEM observaitons, and to confirm whether or not the anisotropic feature of the thin GB phase is a universal phenomenon in standard commercial sintered magnets.

2. Experimental

The sample used in this work was a 400 kJ/m³ grade commercial Nd-Fe-B sintered magnet. The chemical composition was Fe_{65.5}Nd_{29.9}Pr_{0.1}Dy_{0.5}Tb_{0.5}B_{1.1}Cu_{0.1}Al_{0.2}Ni_{0.4}Co_{1.6}O_{0.1} in wt.%

(Fe_{76.0}Nd_{13.5}Pr_{0.2}Dy_{0.2}Tb_{0.2}B_{6.6}Cu_{0.1}Al_{0.5}Ni_{0.4}Co_{1.8}O_{0.5} in at.%). The coercivity, $\mu_0 H_c$, maximum energy product, $(BH)_{max}$, and remanent magnetization, $\mu_0 M_r$, of the sample were 1.24 T, 411 kJ/m³, and 1.46 T, respectively. Scanning electron microscope (SEM) observation was performed using a field emission SEM, Carl Zeiss Cross Beam 1540 EsB, equipped with an in-lens type detector and energy dispersive spectroscopy (EDS) detector, Bruker XFlash 6 series. The SEM observation was performed for the surface milled by Ga-ion beam at an acceleration voltage of 30 kV. Crystallographic orientation was analyzed by scanning electron microscopy (SEM), FEI Helios Nanolab 650 dual beam FIB/SEM, equipped with Bruker electron backscatter diffraction (EBSD) system with the Esprit software platform. STEM observation was performed using a FEI Titan G² 80-200 TEM with a probe aberration corrector. Thin foils for STEM observation were prepared by the lift-out technique using FEI Helios Nanolab 650.

3. Results

Figure 1 shows backscattered electron (BSE) and in-lens secondary electron (IL-SE) SEM images and EDS elemental maps of Nd, Fe and O. Note that the specimen was prepared so that the easy axis is out of the plane. Nd-rich phases at grain boundary triple junctions are imaged with brighter contrasts with respect to the Nd₂Fe₁₄B matrix in the BSE SEM image except for the Nd-rich phase indicated as 5 in Fig. 1 (a). We recently reported that the combination of BSE and IL-SE images in SEM leads to an unambiguous identification of Nd-rich phases [10,38]. Based on these previous investigations, the Nd-rich phase 1 with the slightly brighter imaging contrast compared to the Nd₂Fe₁₄B matrix in the IL-SE SEM image in Fig. 1 (b) is identified as fcc-NdO. Nd-rich phase 2 exhibits darker contrast in the IL-SE image (Fig. 1 (a)) and a brighter contrast in the BSE image (Fig. 1 (b)) with respect to the Nd₂Fe₁₄B phase, and the EDS map in Fig. 1 (d) indicates that oxygen is enriched in the phase. Thus, the Nd-rich phase 2 is considered

to be an oxide with a different structure and composition from the fcc-NdO phase. The structure of this phase will be described later based on selected area electron diffraction. Nd-rich phases 3 and 4 are metallic phase since oxygen enrichment was not detected from EDS elemental map (Fig. 1 (d)). Nd-rich phase 3 can be identified as α -Nd since it exhibits the brightest contrast in the IL-SE image (Fig. 1 (b)) like the α -Nd phase reported previously [38]. Nd-rich phase 4 may be identified as the one with the $Ia\bar{3}$ structure, which is dimly imaged in the IL-SE image (Fig. 1 (b)), having a brighter contrast compared to the α -Nd phase in the BSE image. Nd-rich phase 5 can be identified as NdFe_4B_4 [38]. The inset image to Fig. 1 (a) also shows that thin Nd-rich layer is formed at the $\text{NdFe}_4\text{B}_4/\text{Nd}_2\text{Fe}_{14}\text{B}$ interfaces.

Figure 2 (a) and (b) show BSE and IL-SE images including two different oxide Nd-rich phases 1 and 2. Although both oxides are observed with the same bright contrast in the BSE image in Fig. 2 (a), they show completely different contrast in the IL-SE image in Fig. 2 (b). The selected area electron diffraction (SAED) patterns obtained from the Nd-rich phase 1 can be indexed as fcc-NdO ($\text{Fm}\bar{3}m$, NaCl type, $a = 0.52 \text{ nm}$ [12,13,16–18,20]). The oxide phase 2 can be identified as hcp- Nd_2O_3 phase ($\text{P}\bar{3}m1$, La_2O_3 type, $a=0.383\text{nm}$, $c=0.600$ [15,18,20]) from the SAD patterns shown in Fig. 2 (e) and (f).

Figure 3 (a) shows IL-SE image including Nd-rich phase 3 in Fig. 1. Fig. 3 (b) and (c) rule out the possibility of the dhcp structure in contrast to the previous report [39]. Rather, it can be identified as a fcc phase. Figure 3 (d) shows IL-SE image including Nd-rich phase 4. The SAED patterns in Fig. 3 (e) and (f) of Nd-rich phase 4 are consistent with the $Ia\bar{3}$ structure (Mn_2O_3 type, $a=1.108 \text{ nm}$ [12,20,23]). The EDS spectra, Fig. 3 (g), obtained from the fcc Nd-rich phase (Nd-rich phase 3) indicates that Cu and Co are enriched in the Nd-rich phase 3, $\sim\text{Nd}_{73}\text{Fe}_3\text{Co}_{13}\text{Cu}_{11}$. On the other hand, not much Cu and Co were detected from the $Ia\bar{3}$ phase (Nd-rich phase 4), $\sim\text{Nd}_{92.6}\text{Fe}_{2.5}\text{Co}_{0.7}\text{Cu}_{4.2}$. Therefore, we can conclude that there are two types

of metallic Nd-rich phases, one is Co and Cu enriched fcc-Nd and the other is $\text{Ia}\bar{3}$ phase with a small amount of Cu. These metallic Nd-rich phases fill the sharp edges of the triple junctions surrounding NdO or Nd_2O_3 grain.

EBSD analysis was performed for the same region in Fig. 1. Note that metallic Nd-rich phases were not indexed. This is because Kikuchi patterns were not clearly visible due to the oxidation of the metallic Nd-rich phases during specimen handling. The inverse pole figure (IPF) map and the (001) pole figure (PF) analyzed from the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (Fig. 4 (a)) show the [001] directions of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are strongly textured. Figure 4 (b) is a phase map showing the distribution of Nd_2O_3 and NdO phases as well as the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. The location of the Nd_2O_3 and NdO phases identified from the phase map is consistent with that identified from the image contrasts in Fig. 1 (a) and (b). Figure 4 (c) shows IPF maps showing the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains with their [001] axis tilted larger than 20° . Hereafter, these grains are defined as misaligned grains. Fig. 4 (d) shows these misaligned grains are in contact with some of the Nd_2O_3 grains. This suggests that the presence of Nd_2O_3 particles in the jet-milled powders might have hindered crystal rotation during the magnetic field alignment.

Figure 5 (a) shows a IL-SE image with the easy axis out of plane. Nd_2O_3 , fcc-Nd and $\text{Ia}\bar{3}$ phases are present in triple junctions. The corresponding Lorentz TEM image (Fig. 5 (b)) taken in the zero magnetic field (demagnetized state) shows that most of the grains exhibit the maze-like domain structure to minimize the magnetostatic energy. However, the grains, which is in contact with the Nd_2O_3 phase shows stripe-shaped domain structure because of the large misalignment of the [001] axis as indicated by arrows. After applying magnetic field until the domains were swept away (Fig. 5 (c)), the applied magnetic field was decreased; then, demagnetization occurs from the misaligned grain (Fig. 5 (d) and (e)) followed by the occurrence of the demagnetization in other grains (Fig. 5 (f) and (g)). This indicates that the

demagnetization in this thin foil specimen is initiated from the misaligned grain.

Figure 6 shows HAADF-STEM images of various $\text{Nd}_2\text{Fe}_{14}\text{B}$ /Nd-rich phase interfaces with EDS elemental maps. The concentration profiles across the interfaces were calculated from the elemental maps excluding boron. The Nd-rich phase in Fig. 6 (a) can be identified as fcc-Nd phase since it has the chemical composition similar to that of Nd-rich phase 3 in Fig. 3, $\text{Nd}_{77.1}\text{Fe}_{3.7}\text{Co}_{11.4}\text{Cu}_{7.8}$. The fcc-Nd and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain are in direct contact with each other. The concentration profiles across the $\text{Nd}_2\text{Fe}_{14}\text{B}$ /fcc-Nd interface, Fig. 6 (b), shows the strong enrichment of Cu at the interface, $\sim 30\text{at.\%Cu}$. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ /NdO (Fig. 6 (c)) and $\text{Nd}_2\text{Fe}_{14}\text{B}$ /Nd₂O₃ interfaces (Fig. 6 (e)) also show the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain is in direct contact with these oxides. However, unlike the $\text{Nd}_2\text{Fe}_{14}\text{B}$ /fcc-Nd interface, no segregation of Cu is observed at the interfaces with oxides. Sepehri-Amin et al. reported weak segregation of Cu at the interfaces with oxides [30], which may be below the detection limit of the EDS analyses. A thin Nd-rich phase is clearly observed at the $\text{Nd}_2\text{Fe}_{14}\text{B}$ /NdFe₄B₄ interface (Fig. 6 (g)), which is a mixture of amorphous and crystalline phases. The compositional profile shows that the Nd-concentration at the thin Nd-rich boundary phase is $\sim 85.1 \pm 1.0 \text{ at.\%}$, and Cu is segregated at the interfaces between the Nd-rich boundary phase and NdFe₄B₄ and NdFe₄B₄ grains.

Figure 7 shows IL-SE images with the easy axis (a) in the plane and (b) out of the plane, respectively. Thin Nd-rich GB phase is uniformly formed along the grain boundaries. Metallic Nd-rich phases fill sharp corner edges at triple junctions surrounding Nd-rich oxides and boride as indicated by arrows. This means that the metallic Nd-rich phases are present at both ends of the thin GB phases, and these metallic Nd phase serves as Nd pool for the formation of the thin GB phase during post-sinter annealing as proposed by Sepehri-Amin et al. [30].

Figure 8 (a) shows a HAADF-STEM image taken from a sample with the easy axis out of the plane. When one of neighboring $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains is looked down from the [001] zone axis

of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain “A”, the other $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain “B” is slightly tilted from the [001] zone axis as shown in the SAD patterns in Fig. 8 (b) and (c). This means that the thin Nd-rich GB phase is nearly normal to the (001) plane of the grain “A”. The thin Nd-rich GB phase has the width of 1.8 ± 0.2 nm with the amorphous structure. The amorphous structure is also obvious from the HAADF-STEM image and halo nano-beam diffraction pattern in Fig. 8 (d). The concentration profiles across this particular GB phase (Fig. 8 (e)) shows the Nd concentration of 29.1 ± 2.1 at.%, which is consistent with the previous report determined by 3DAP [30]. Note that the oxygen signal is ignored in the analysis since they are considered to come from the surface of the TEM specimen and the previous atom probe work reported the absence of oxygen in the thin Nd-rich GB phase [30].

Figure 9 (a) is a HAADF-STEM image showing a thin Nd-rich grain boundary phase, which is parallel to the (001) plane of one the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. Unlike many previous reports on the amorphous structure of thin Nd-rich GB phases [30,34–37], this GB phase shows a distinct crystalline feature. The EDS line profile analyzed from the mapped area in Fig. 9 (a) shows that the Nd concentration is 59.6 ± 1.7 at.%. The thin Nd-rich GB phase tilted about 7° from the (001) plane, Fig. 9 (b), also shows crystalline feature and high Nd content of 64.7 ± 1.4 at.%. However, the thin Nd-rich GB phase, which is tilted about 45° from the (001) plane shows amorphous structure (Fig. 9 (c)). The EDS line profile shows the lower Nd concentration of 38.2 ± 1.4 at.% compared to the crystalline GB phase in Fig. 9 (a) and (b). When the angle between the GB phase and (001) plane is 70° , the GB phase shows an amorphous structure with the Nd concentration of 44.4 ± 4.3 at.% as well as the one tilted 45° from the (001) plane, Fig. 9 (d) and (d).

Figure 10 (a) shows IL-SE image with the easy axis in the foil plane. Figure 10 (b) shows the change of the magnetic domain structure as external magnetic field is increased. In the

thermally demagnetized state, a domain wall is split into two as magnetic domains cannot exist within the nonmagnetic Nd-rich phase as indicated by black arrows. By applying a magnetic field, these domain walls move to the left to merge into one domain wall due to the dipolar interaction. In another region shown in Fig. 10 (c), stripe-shaped domain walls can be seen within a grain, in which the dark and bright contrasts of the domain walls are attributed to the opposite in-plane magnetization directions in neighboring domains. Domain walls indicated by white arrows start to move so they come close to each other, and disappear by applying the magnetic field. On the other hand, the one indicated by the black arrow moves towards the GB, and is pinned at the grain boundary. These domain wall displacements in the two regions indicate that the grain boundaries parallel to the c-plane of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain does not cause any pinning force for the domain wall displacements, while the grain boundaries perpendicular to the c-planes act as pinning sites for the domain wall displacements.

4. Discussion

In this work, we have thoroughly characterized the microstructure of a standard Nd-Fe-B sintered magnet. Figure 11 schematically illustrates the microstructure of the Nd-Fe-B sintered magnet observed in this work. As Nd-rich triple junction phases, fcc-NdO, hcp- Nd_2O_3 , fcc-Nd, $\text{La}\bar{3}$, and NdFe_4B_4 phases are present at GB triple junctions. At interfaces between these Nd-rich phases and $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase keeps perfect crystallinity with the segregation of Cu. The absence of lattice distortion in the HAADF-STEM image in Fig. 4 indicates that there is no significant strain near the interface. Murakami et al. reported that the largest strain was observed at the interface between the metallic Nd and $\text{Nd}_2\text{Fe}_{14}\text{B}$, which is only $\sim 1\%$ [39]. Although the metallic Nd-rich phase was reported to have the dhcp structure in previous reports [13,17,20,23], the metallic Nd-rich phase observed in this work had either fcc

or $Ia\bar{3}$ structure (Fig. 3). In the fcc-Nd phase, larger amounts of Cu and Co are contained compared to the Nd-rich phase with the $Ia\bar{3}$ structure. Since Nd does not have any solubility with Cu, this apparent Cu concentration must be due to the dispersion of NdCu precipitates in the fcc-Nd [30,38]. Mo et al reported that the structure of the Nd-rich phase transforms from dhcp to fcc structure when the oxygen content increases beyond the solubility in Nd ($>11\text{at.}\%$) [20]. Although substantial amount of oxygen was detected in the Nd-rich phases 3 and 4 by STEM-EDS (Fig. 3) [20], oxygen was not detected in these metallic Nd-rich phases using the EDS mapping obtained from the SEM sample that was prepared in-situ by Ga ion beam (Fig. 1) and 3D atom probe analysis [30]. This clearly means that the oxygen detected from the TEM specimen is an artifact from the oxide layer formed on the surface of thin foil specimens. Therefore, we conclude that Cu and Co dissolution may cause the stabilization of fcc structure as well as O, or there might be other reasons that determine the structure of the metallic Nd-rich phases. Further work will shed light on to the clarification of the origin of the structure of the metallic Nd-rich phase.

Previous TEM and 3DAP studies reported that the thin Nd-rich GB phase has an amorphous structure with the rare earth element (R) content up to $\sim 35\text{ at.}\%$ [30,34–37]. Since all thin Nd-rich GB phase is connected with the metallic Nd-rich phase at GB triple junction (Fig. 6), the GB phase is expected to have the same structure and chemical composition. However, this work has shown that the structure and chemical composition of the Nd-rich GB phase are different depending on the orientation with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. Although the structure of the crystalline GB phase and the orientation relationship between the GB phase and the neighboring $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain still remain unclear, the thin Nd-rich GB phase parallel to the (001) plane is crystalline whereas the thin Nd-rich GB phases tilted by $> 45^\circ$ from the (001) plane has an amorphous structure, Fig. 9. The Nd content in the crystalline GB phase is much higher than the thin Nd-

rich GB phase with the amorphous structure. The crystalline Nd-rich GB phase has Nd content up to ~60 at.%, which is much higher than those in the amorphous Nd-rich GB phase. The Nd content in the thin Nd-rich GB phase analyzed by STEM-EDS might be underestimated due to the convolution effect of characteristic x-ray since the Fe content in the neighboring Nd₂Fe₁₄B grains is much higher (~82.3at.%) than that in the thin Nd-rich GB phase. Sepehri-Amin et al. reported that the Nd+Pr concentration in the amorphous GB phase is ~33 at.% [30], and Sasaki et al., reported that the Nd+Pr concentration in crystalline GB phase in pressless sintered magnet is ~55at.% [10]. These reports indicate that the difference in the Nd concentration between the crystalline and amorphous GB phases in the present sample is in good agreement with the previous atom probe results. Although further 3DAP experiment is needed to precisely analyze the chemical compositions of the GB phases, the result by EDS analyses at least shows that the difference in the Nd content between the amorphous and crystalline GB phase is significant.

The formation of crystalline thin Nd-rich GB phase was reported in the fine grain sized Nd-Fe-B sintered magnets fabricated by the pressless sintering process [10] and in the hydrogenation disproportionation desorption recombination (HDDR) processed powder [29,40]. Since the sample observed in this work is an anisotropic magnet, the easy axes of the individual grains are similarly aligned, which means the misorientation angle between the neighboring Nd₂Fe₁₄B grains is small. As shown in Fig. 9, amorphous GB phase was formed between the Nd₂Fe₁₄B grains with their planes parallel to the c-axes while the crystalline GB phase is formed with their planes normal to the c-axes. Therefore, we can conclude that the crystallinity of the GB phase depends on the surface of the Nd₂Fe₁₄B grain rather than the misorientation angle between the Nd₂Fe₁₄B grains; the crystalline GB phase can be formed when the (001) plane surface appears at least one of the Nd₂Fe₁₄B grain.

The Lorentz TEM observations have shown that the GB phases parallel to the easy axis

work as pinning sites against the domain wall motion while it is not the case for the ones normal to the c-axis due to the dipole interaction. Since the sample for the Lorentz TEM observation is thin foil, in which demagnetizing field is totally different from that in bulk sample, the Lorentz TEM observation may not fully demonstrate the magnetization/demagnetization behaviors that occur in bulk samples. However, it is still possible to see the interaction between domain walls and grain boundary phases, and preferential magnetic reversal from magnetically weak grains. Therefore, the Lorentz TEM observation in this work at least shows that the GB parallel to the easy axis is critical for the coercivity rather than the GB phase normal to the easy axis. Liu et al. reported the pinning force against the domain wall motion is correlated with the Nd content in the GB phase in the hot-deformed magnets [36]. They also showed that domain walls are pinned at the grain boundaries parallel to the c-axis. They also reported that the Nd concentration in the intergranular phase is anisotropic, i.e. the Nd concentration in the intergranular phase parallel to the c-axis is smaller than that perpendicular to the c-axis. The present HAADF-STEM/EDS analyses of the standard commercial sintered magnet has also shown that the GB phase normal to the easy axis has low Nd concentration of ~30 at.% compared to the c-plane GB phase (Fig. 9). Therefore, the increase in the Nd content in the GB phase parallel to the c-axis would be critical for enhancing the coercivity of sintered magnet. In fact, using large scale micromagnetic simulations, Fujisaki et al. has shown that the reduction of the magnetization in the GB phase parallel to the c-axis will induce large coercivity enhancement regardless of the magnetization in the GB phase perpendicular to the c-axis [41].

The misaligned Nd₂Fe₁₄B grains are also considered to cause coercivity degradation since the nucleation field of the reversal domain is considered to decrease at misaligned grains [9]. This is also obvious from the Lorentz TEM observation showing preferential magnetic reversal at misaligned Nd₂Fe₁₄B grain (Fig. 5). As shown in Fig. 4, many misaligned Nd₂Fe₁₄B grains

are in contact with the Nd_2O_3 grains. The Nd_2O_3 grains are randomly oriented according to synchrotron radiation and EBSD studies as reported by Woodcock et al. [21,42]. In this work, no clear orientation relationship was found between the misaligned $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains and the Nd_2O_3 grains. Although further study is needed to clarify of the formation mechanism of the misaligned grains, the coercivity might be expected to increase by removing the Nd_2O_3 phase prior to the magnetic field alignment.

5. Summary

We revisited the microstructure of a standard Nd-Fe-B sintered magnet for better and detailed illustration of the microstructure relevant to the coercivity. Correlative SEM/TEM analysis revealed the presence of five different Nd-rich phases at grain boundary triple junctions, *i.e.*, fcc-NdO and hcp- Nd_2O_3 phases as oxides, fcc-Nd and $\text{Ia}\bar{3}$ type phases as metallic phases, and a NdFe_4B_4 phase. The dhcp-Nd phase that was reported as a constituent phase in sintered magnets was not confirmed in the sample. IL-SE image showed metallic Nd-rich phases such as Cu-enriched Nd with the fcc structure and a Cu-lean Nd with the $\text{Ia}\bar{3}$ structure are present at the corner of the oxides and borides. At small triple points, only metallic Nd-rich phases were confirmed. By this way, all thin Nd-rich grain boundary phases are terminated at metallic Nd-rich phases. EBSD and correlative IL-SE/TEM analyses suggested mis-aligned $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are mainly in adjacent to Nd_2O_3 grains, and the magnetization switching starts from these mis-aligned grains. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase keeps good crystallinity at the interfaces with the fcc and $\text{Ia}\bar{3}$ Nd-rich phases with strong segregation of Cu. HAADF-STEM observations have established that there are two types of thin grain boundary layers (phases) in the standard Nd-Fe-B sintered magnet; one is the crystalline GB phase parallel to the (001) plane of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains with a Nd content higher than 60at.% and the other is the amorphous GB phase

with a lower concentration of Nd (~35at.%), which is probably ferromagnetic as reported previously. This suggests that the inter-grain exchange coupling in Nd-Fe-B sintered magnets is anisotropic, i.e. lower exchange coupling along the c-axis. For obtaining a higher coercivity in sintered magnets, making the GB phase parallel to the c-axis would be critical.

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Figure captions

Figure 1: (a) Backscattered electron (BSE) and (b) In-Lens secondary electron (IL-SE) SEM images of the anisotropic sintered magnet. (c) and (d) are EDS elemental maps of Nd and Fe, and O. The inset to (a) is the magnified image surrounded by a solid line.

Figure 2: (a) BSE and IL-SE SEM images including the Nd-rich phase “1” and “2”. (c) and (d) are selected area electron diffraction (SAED) patterns obtained from the Nd-rich phase “1” and (e) and (f) are those taken from the Nd-rich phase “2”.

Figure 3: (a) IL-SE SEM image including a Nd-rich phase “3”. (b) and (c) are microbeam diffraction pattern obtained from the Nd-rich Phase “3”. (d) IL-SE SEM image including a Nd-rich phase “4”. (e) and (f) are selected area electron diffraction (SAED) pattern obtained from the Nd-rich Phase “3”. (g) is EDS spectra obtained from the Nd-rich phases “3” and “4”.

Figure 4: (a) Inverse pole figure (IPF) map and pole figure (PF) of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains observed from the [001] axis out of plane. (b) Phase map of $\text{Nd}_2\text{Fe}_{14}\text{B}$, Nd_2O_3 and NdO_x grains. (c) is the IPF map indicating misaligned grains in (a), and (d) is the phase map showing the misaligned $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains and Nd_2O_3 phase.

Figure 5: (a) IL-SE image and Lorentz TEM image under (b) 0 T and (c) 4.2 T. Arrows in (b) indicate the misaligned $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. Lorentz TEM image upon demagnetization from 4.2 T to (d) 3.8 T, (e) 2.1 T, (f) 1.7 T and (g) 0 T. Note that arrow in (d) shows the magnetic domains.

Figure 6: HAADF-STEM image and concentration depth profiles obtained from the inset EDS mapping for (a) fcc-Nd/ $\text{Nd}_2\text{Fe}_{14}\text{B}$, (b) NdO_x / $\text{Nd}_2\text{Fe}_{14}\text{B}$, (c) Nd_2O_3 / $\text{Nd}_2\text{Fe}_{14}\text{B}$, and (d) NdFe_4B_4 $\text{Nd}_2\text{Fe}_{14}\text{B}$ interfaces. Note that oxygen is excluded from the compositional analyses since certain amount of oxygen is also detected from $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase as an artifact.

Figure 7: (a) Backscattered electron SEM image taken from the [001] axis in-plane and (b) In-Lens secondary electron SEM images taken from the [001] axis out of plane.

Figure 8: (a) High angle annular dark field-scanning TEM (HAADF-STEM) images observed from the [001] axis out of plane. (b) and (c) are SAD patterns obtained from Nd₂Fe₁₄B grain “A” and “B”. (d) is the nanobeam diffraction pattern obtained from the thin Nd-rich grain boundary (GB) phase. (e) is compositional profile analyzed from a region in (a)

Figure 9: HAADF-STEM images and EDS concentration profiles taken from the insets area containing a thin Nd-rich GB phase (a) parallel to (001) plane, (b) 7° tilted from the (001) plane, (c) 45° tilted from the (001) plane (d) 70° tilted from the (001) plane of a Nd₂Fe₁₄B grain.

Figure 10: (a) IL-SE SEM image with the easy axis in plane, and corresponding Lorentz TEM images in Fresnel mode taken from the region surrounded by solid lines on the (a) left and (b) right. In (b) and (c), the applied magnetic field is described in each figure.

Figure 11: Schematic illustration of the microstructure of Nd-Fe-B sintered magnet

Fig. 1

Fig. 2

Fig. 3

Fig. 4

fig. 5

Fig. 6

fig. 7

Fig. 8

Fig. 9

Fig. 10

fig. 11

Graphical Advance