Magnetism of ultrathin intergranular boundary regions in Nd–Fe–B permanent magnets

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Abstract

The magnetism of a thin grain-boundary (GB) phase that envelopes the Nd₂Fe₁₄B grains in optimally annealed Nd–Fe–B sintered magnets was investigated by electron holography. The phase shift measured from a thin-foil specimen containing a tilted amorphous GB phase (~3 nm in width) was –0.34 rad, which is substantially smaller than that expected for the nonferromagnetic GB phase of –1.2 rad. Simulations of the phase shift with various magnetization values suggest that the magnetic flux density of the GB phase is ~1.0 T. The observations imply significant exchange coupling between Nd₂Fe₁₄B grains, which can explain the avalanche propagation of magnetization reversal observed in sintered magnets.

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1. Introduction

Due to the large magnetocrystalline anisotropy ($K_u \approx 4.5 \text{ MJ m}^{-3}$) and saturation magnetization ($\mu_0 M_s = 1.6 \text{ T}$) of the Nd₂Fe₁₄B matrix phase, sintered Nd–Fe–B magnets can achieve the highest maximum energy product ($>400 \text{ kJ m}^{-3}$) of all permanent magnets [1–3]. Since the large maximum energy product leads to a remarkable degree of miniaturization of motors and actuators, these magnets can significantly contribute to power saving and/or green technologies. In fact, Nd–Fe–B

magnets have been applied in traction motors of hybrid electric vehicles, and as actuators of hard disk drives.

A drawback of Nd–Fe–B sintered magnets is their low coercivity. Although the coercivity of commercial sintered magnets is ~1.2 T at room temperature, this value is reduced significantly at elevated temperature. For example, the coercivity becomes only ~0.2 T at the operation temperature of the motors used in hybrid electric vehicles (~470 K). A way to solve this crucial problem is the partial substitution of Dy for Nd, i.e., the substitution of Dy for approximately one-third of Nd effectively enhances the anisotropy field of the Nd₂Fe₁₄B matrix phase [2,4,5], achieving the coercivity of ~3 T at room temperature. However, this substitution reduces the maximum energy product to 250 kJ m^{-3} because of the antiferromagnetic spin alignment between Dy and Fe [2]. The use of Dy, a heavy rare-earth element, raises an additional industrial concern

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because of the scarcity of natural resources [6]. These problems have motivated recent extensive studies on the coercivity mechanism in Nd–Fe–B-based magnets [2].

Nanostructure optimization is crucial for enhancing the coercivity of permanent magnets. In the case of Nd–Fe–B-based permanent magnets, researchers have sought an ideal configuration with ferromagnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains coated by a thin amorphous grain-boundary (GB) phase [7–13]. The GB phase, produced by an optimal post-sinter heat treatment, had been believed to suppress the intergranular exchange coupling that causes avalanche propagation of magnetization reversal. In previous studies, the GB phase was assumed to be nonferromagnetic and accordingly terminate the domain wall propagation. However, this narrow interface region has not allowed in-depth experimental examination of the magnetism. Recently, the three-dimensional (3-D) atom probe study by Sepehri-Amin et al. [14] reported an unexpectedly high concentration of Fe (>60%) within the thin GB phase. They also suggested that the thin GB phase was ferromagnetic, based on the magnetic measurements of a model thin film with the chemical composition close to that determined by the atom probe study. These results have stimulated researchers to directly measure the magnetism of the GB region in actual sintered magnets. However, revealing the magnetism in the extremely thin intergranular layer remains challenging.

In this study, we used electron holography that allowed pinpoint analysis of magnetism of the ultrathin GB region in commercial Nd–Fe–B sintered magnets. Because of the high-precision measurements for the phase shift of electrons, on the order of 0.1 rad or better [15–19], electron holography has been widely applied in the studies of magnetic nanostructures [20–26]. We used this method to determine the magnetic flux density in the thin GB region.

2. Methods

2.1. Specimen preparation and electron microscopy observations

For transmission electron microscopy (TEM) studies, a commercial sintered Nd–Fe–B magnet with a nominal composition of $\text{Nd}_{10.9}\text{Pr}_{3.1}\text{Fe}_{77.4}\text{Co}_{2.4}\text{B}_{6.0}\text{Ga}_{0.1}\text{Cu}_{0.1}$ (at.%) was shaped into thin foils using a focused ion beam (FIB) system (Helios Nanolab 650, FEI) with an acceleration voltage of 30 kV. To reduce surface damage, the foil was polished using a Ga ion beam with a low acceleration voltage (5 kV) at the final stage of specimen preparation. Cross-sectional TEM observations (of specimens prepared using FIB) were used to determine the specimen thickness t , which was found to be approximately 105 nm in the region of interest; i.e., the area indicated by the R–S line in Fig. 4a. Strictly speaking, the thickness only gradually changed over the region of interest (i.e., the thickness at point R was $t_1 = 101$ nm, and the thickness at point S was $t_2 = 109$ nm).

TEM observations, electron holography and Lorentz microscopy were conducted using a 300 kV electron

microscope (HF-3300S, Hitachi). When electron holography and Lorentz microscopy were conducted, the specimen was subjected to a negligible magnetic field (of the same order as the geomagnetic field) due to the shielding design of the microscope. Images were recorded using a charge-coupled device camera (USC 4000, Gatan). Scanning electron microscopy (SEM) images were acquired using the same equipment as that used in the FIB polishing. The secondary electrons were collected using the in-lens detector.

2.2. Determination of magnetic flux density by electron holography

Here, we briefly describe our method of determining the magnetic flux density due to the GB phase based on electron holography observations. Fig. 1a schematically shows the experimental setup of electron holography [15,16]. The electron wave that has traversed a thin-foil specimen is referred to as the “object wave”. The object wave is subjected to a phase shift ϕ due to the electromagnetic field of the specimen. Accordingly, measurement of ϕ determines the electromagnetic field of the specimen. In order to determine ϕ experimentally, we use an electron biprism that makes the object wave interfere with the reference wave (passing through the vacuum region), and acquire an electron hologram made of interference fringes. Phase information is stored in the hologram in the form of modulations in the interference fringes. The information on ϕ can be retrieved from the digitized electron hologram by using a Fourier transform. This process yields a plot/mapping of ϕ for the region of interest.

Fig. 1. Electron-beam diagrams showing the electron holography experiments: (a) conventional electron holography; (b) slit-illumination electron holography employed to determine magnetic flux density in the grain boundary (GB) region. See text for details.

In general, the phase shift ϕ is due to both the electric field and the magnetic field, as expressed by the first and second terms, respectively, in Eq. (1):

$$\phi = \sigma \int V_0 dz - \frac{e}{\hbar} \iint B_y dx dz \quad (1)$$

σ , V_0 , e , $\hbar$ and B_y represent the interaction constant, the electric potential, elementary charge, Planck's constant divided by 2π and the y component of the magnetic flux density, respectively. Refer to Fig. 1 for the x – y – z coordinate system. For metallic specimens wherein electrical charging induced by the electron exposure is negligible, V_0 represents the mean inner potential in the crystal (i.e., $V_0 = 0$ for the outside of the specimen, $V_0 \neq 0$ for the inside of the specimen). The integral in the second term is carried out over the area enclosed by the paths of electrons [15,16].

Let us consider the phase shift ϕ observed in the line connecting points R and S in Fig. 2a, which schematically shows a cross-section of the specimen. When the specimen thickness t is approximately constant, the phase shift due to the mean inner potential V_0 (i.e., contribution from the first term in Eq. (1)) can be negligibly small, compared to the phase shift due to the magnetic field of the Nd–Fe–B permanent magnet. (In Sections 3 and 4, we discuss the phase shift due to a gradual change in t over this area, as well as the effect of a change in V_0 in the GB region, in greater detail.) Thus, the observation of ϕ can be related to the in-plane magnetic flux density B_y :

$$\phi \approx -\frac{e}{\hbar} \iint B_y dx dz \quad (2)$$

As illustrated in Fig. 2a and b, the thin-foil specimen made of single-crystalline Nd₂Fe₁₄B shows a monotonic increase in ϕ along the R–S line. When a specimen contains a GB phase with reduced magnetic flux density, as shown in Fig. 2c, the slope of the aforementioned curve changes over the GB area (Fig. 2d). Accordingly, the magnetic flux density in the GB region can be determined from $\Delta\phi$, which represents the deviation of the observed phase shift (in the GB area) from the extrapolated curve assuming the absence of a GB phase (Fig. 2d). It should be noted that B_y within the GB region has two sources: (1) spontaneous magnetization of the GB phase, and (2) the stray magnetic field that exists in the GB region (e.g., the stray field from the neighboring Nd₂Fe₁₄B grains). The stray magnetic field (B_{ST}) can be calculated straightforwardly, both inside and outside the specimen, once the specimen shape, orientation of individual grains, and other such parameters are known; this is discussed in Section 3.

To predict the value of $\Delta\phi$ for the thin foil specimen, we calculated the 3-D magnetic field using a commercial computer code ELF/MAGIC (ELF Co.) which employs the integral element method. The calculations were carried out assuming several values of B_{GB} , the magnetic flux density due to the spontaneous magnetization of the GB phase; i.e., $B_{GB} \neq 0$ for the ferromagnetic GB phase and $B_{GB} = 0$

for the nonferromagnetic GB phase. B_{GB} is referred to as “magnetic flux density due to the GB phase” in what follows, and this is different from B_{ST} . As we describe in greater detail in Section 4, B_{GB} was determined by the best fit of simulations of $\Delta\phi$ with observations. Note that for the simulations, we also considered the phase shift due to the mean inner potential, which originates from a gradual change in the specimen thickness, as described later in detail.

2.3. Accuracy in measuring the phase shift

As shown in the electron micrograph of the thin-foil specimen (Fig. 3a), the GB phase we focus on (indicated in yellow) was $\sim 1 \mu\text{m}$ away from the specimen edge. To acquire an electron hologram from this GB region, a wide area of the specimen (including both the specimen edge and the GB) must be exposed to the object electron wave, as illustrated in Fig. 1a. However, this type of illumination reduces the beam intensity, and accordingly deteriorates the signal-to-noise (S/N) ratio in the electron holograms. Since the measurement accuracy of electron holography is limited mainly by the S/N ratio of holograms [18], it was difficult to achieve satisfactory precision in measuring the phase shift from the Nd–Fe–B specimen with the conventional experiment of electron holography (Fig. 1a).

To solve this problem, we employed split-illumination electron holography [27]. As schematically shown in Fig. 1b, the object wave can be largely separated from the reference wave by the additional condenser biprism. This method allows the illumination for only a limited portion in the specimen including the GB with sufficient beam intensity. Because of the improvement of the S/N ratio in the holograms, the split-illumination electron holography achieved a satisfactory precision in measuring the phase shift of $\pm 0.08 \text{ rad}$ ($\approx 2\pi/79$) for the thin-foil specimen. As a result, the magnetic flux density in the GB region could be determined with an accuracy of $\pm 0.1 \text{ T}$, as described in Section 4. The precision of $\pm 0.08 \text{ rad}$ was determined by the maximum deviation in the observed phase shift (i.e., plot of ϕ measured for a line within the Nd₂Fe₁₄B grain) from curve fitting, following the method demonstrated in Ref. [19]. It appears from previous studies that the precision is related to several factors, such as quantum noise in the detector, surface roughness of the specimen, local excitation of Bragg reflections, structural imperfections in the specimen, etc. [15,16,18,19].

3. Results

3.1. Crystallographic microstructure in the thin-foil specimen

The thin-foil specimen of the Nd–Fe–B sintered magnet contained several crystallographic grains, labeled with symbols A–I, as shown in the transmission electron micrograph in Fig. 3a. Grains A–E were identified as the ferromagnetic Nd₂Fe₁₄B phase (i.e., the matrix phase of Nd–Fe–B magnets) by electron diffraction. In addition to energy

dispersive X-ray spectroscopy (EDS; see Table 1), SEM provided additional information for identifying the other crystallographic grains, F–I. Depending on the emission efficiency of secondary electrons, which were collected using the in-lens detector, each crystal phase can be imaged at a distinct level of brightness [28]. For example, the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix grains (A–E) have the same brightness, as shown in Fig. 3b. Following the study by Sasaki et al. [28], the NdFe_4B_4 phase should appear darker than the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix grains (A–E) due to the poor emission efficiency. Thus, grain H was identified as NdFe_4B_4 . Since the image intensities from grains F and G are higher than that for the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix, they are most likely NdO_x (x varies depending on the extent of oxidization), which is a major oxide inclusion in sintered magnets. Grain I, seen as the brightest area in the SEM image, should be α -Nd (metallic Nd) containing small amounts of Co and Cu. It appears that the α -Nd phase also exists in triple junctions and the boundary region of the NdFe_4B_4 grain H. These phase identification results are consistent with the EDS observations shown in Table 1. The crystal phases of NdFe_4B_4 , NdO_x and α -Nd are all nonferromagnetic at room temperature [14,29,30].

To understand the magnetism of the GB phase between ferromagnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, we focused on the boundary between grain A and grain B; refer to the GB indicated in yellow in Fig. 3a. This GB was inclined from the foil plane. Since the TEM image is a projection, the trace of the GB is widened when the GB plane is tilted away from the direction of the incident electrons. The edge-on condition (Fig. 3c), in which the GB plane is almost parallel to the incident electrons, could be determined by tilting the specimen by $\theta_1 = 56.3^\circ$ around the y -axis, at which the trace of the GB phase was minimized. The x – y – z coordinate system was defined as shown in Fig. 3a. The y -axis was parallel to the portion of the GB indicated by the R–S line; refer to Fig. 4a. The z -axis was parallel to the direction of the incident electrons. Because of the aberration of the electron microscope and/or imperfect flatness of the GB plane, the interface between the matrix and GB phase is not very clear in Fig. 3c. Nevertheless, the observation

provides useful information on the width of the GB phase. The GB width determined by this method, ~ 3 nm, is consistent with the value reported in previous studies on sintered Nd–Fe–B magnets [10,31]. The TEM observations also determined the tilt angle of the GB with reference to the foil plane to be $\theta_2 = 33.7^\circ$. Electron diffraction measurements indicated the direction of the c -axis (i.e., easy magnetization axis) to be $[0.077, -0.961, -0.267]$ for grain A and $[0.103, -0.965, -0.242]$ for grain B. The deviation of these orientations was about 2.1° . (Because of the truncation, the magnitude of the vectors A and B is not exactly unity. We considered this point for the determination of the deviation angle.) Thus, the stray magnetic field in the GB region (at the point crossing the R–S line) was calculated to be about 0.02 T in the direction of the y -axis; i.e., the magnetic flux component that is responsible for the phase shift measured in the R–S line. It is to be noted that lattice fringes are unclear for grain A in the TEM image shown in Fig. 3c. This is due to the orientational deviation between the crystal grains A and B; i.e., although some reciprocal points $00l$ in grain B intersected with the Ewald sphere, the orientational deviation suppressed the intersection in the region of grain A. In addition, elastic distortion in the thin-foil specimen caused local misalignment of the lattice, which may be another source for missing lattice fringes in grain A in Fig. 3c.

3.2. Magnetic domain structure in the thin-foil specimen

Fig. 4a and b shows a TEM image (identical to Fig. 3a) and a Lorentz micrograph of the thin-foil specimen observed in a demagnetized state. The Lorentz micrograph shows magnetic domain walls, which are imaged as bright and dark lines [32], within the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains A–E. The magnetic contrast is absent within the other grains F–I, as they are nonferromagnetic phases. One of the magnetic domain walls was located in the GB between grain A and grain B. The rectangular area shown in Fig. 4a is enlarged in Fig. 4d, for which electron holography was used to generate a map of the phase shift, i.e., a reconstructed phase image shown in Fig. 4e. To suppress the undesired diffraction contrast, the specimen was inclined by ($\theta_1 =$) 16.9° around the y -axis, and by 6.8° around the x -axis, when the electron holograms were acquired; that is, the GB was tilted with respect to the direction of the incident electrons, as illustrated in Fig. 2c. Fig. 4e presents the phase shift in terms of $\cos\phi$. The spacing of the contour lines (i.e., the phase shift per unit length) provides information regarding the in-plane magnetic flux density [15]. However, in Fig. 4e, the spacing is anomalously large in the GB area because the magnetic signal from grain A is reduced by that from grain B (superimposed onto grain A over this area), which is magnetized antiparallel. The spin rotation that occurs within the magnetic domain wall hampers the analysis of magnetic flux density in this area [33]. To avoid this complexity, the domain wall was removed by applying a magnetic field in the direction indicated by the black arrow

Table 1

Fraction of metallic elements, with reference to Nd, in grains A, B, F, G, H and I. The Fe/Nd, Co/Nd and Cu/Nd ratios were determined by EDS observations, using the $L\alpha$ -line from Nd and the $K\alpha$ -lines from Fe, Co and Cu. Grain B (identified as $\text{Nd}_2\text{Fe}_{14}\text{B}$ by electron diffraction) was used as a standard sample to provide the composition ratios: i.e., the Fe/Nd ratio for grain B was calibrated to be 7.0, which corresponds to the nominal composition ratio between Fe and Nd in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

	Fe/Nd ratio	Co/Nd ratio	Cu/Nd ratio
Grain A ($\text{Nd}_2\text{Fe}_{14}\text{B}$)	7.1	0.18	0.11
Grain B ($\text{Nd}_2\text{Fe}_{14}\text{B}$)	7.0	0.19	0.15
Grain F (NdO_x)	0.045	0.028	0.067
Grain G (NdO_x)	0.044	0.035	0.066
Grain H (NdFe_4B_4)	3.6	0.10	0.12
Grain I (Nd + Co, Cu)	0.074	0.24	0.21

Fig. 2. Methods of revealing the magnetic flux density in the GB phase. (a) Schematic cross-sectional view of a thin-foil specimen composed of only one $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain, A. (b) Phase shift of an electron wave (schematic representation) observed along the line connecting points R and S in (a). (c) Schematic cross-sectional view of a thin-foil specimen containing two $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, A and B, and a thin GB phase indicated by the red line. (d) Phase shift of an electron wave (schematic representation) observed along the line connecting points R and S in (c). When electron holograms were acquired, the specimen was inclined by ($\theta_1 =$) 16.9° around the y-axis, and by 6.8° around the x-axis, to suppress undesired diffraction contrast.

Fig. 3. Electron microscopy observations that reveal the crystallographic microstructure in the thin-foil Nd-Fe-B specimen. (a) TEM image from the thin-foil Nd-Fe-B specimen. (b) SEM image acquired using secondary electrons and an in-lens detector. The image intensity shows definite correlations with the individual phases, $\text{Nd}_2\text{Fe}_{14}\text{B}$, NdFe_4B_4 , NdO_x and $\alpha\text{-Nd}$ (metallic Nd). The image was obtained before completing the FIB polishing, and accordingly the specimen shape is slightly different from that shown in (a). (c) Schematic illustration showing the edge-on condition for observing the GB phase, in which the plane of the GB is parallel to the incident electrons (upper panel). TEM image revealing the thickness of the GB phase (lower panel).

in Fig. 4c. Fig. 4c and f shows the results in the remanent state, which demonstrates the elimination of the magnetic domain wall from the GB. We shall focus on this remanent state in subsequent discussion.

3.3. Phase shift observed in the GB region

The phase shift measured along the R–S line is plotted with light-blue dots in Fig. 5a. We consider each of three regions: (1) area A, including only grain A, (2) area GB, including the tilted GB sandwiched between grains A and B and (3) area B, including only grain B. To obtain phase information due to the GB phase, curve fitting was carried

out for area A. We used a quadratic function that was able to fit the observation: i.e., $\phi(x) = ax^2 + bx + c$, where the fitting parameters for the observation (Fig. 5a) were $a = 5.29 \times 10^{-5}$, $b = 2.00 \times 10^{-1}$, $c = 8.02 \times 10^{-2}$. The quadratic form is due to modulation of the reference electron wave by a stray magnetic field, along with a slight change in specimen thickness over this area. We describe the effects of the reference wave modulation and the gradual thickness change in the next section as well.

The results of fitting (representing the contribution from grain A) were extrapolated to the other areas, GB and B, as indicated by the red curve in Fig. 5a. The difference between the observations and the fitting is almost negligible

Fig. 4. Magnetic domain structures in a thin-foil specimen of the Nd–Fe–B sintered magnet. (a) TEM image showing crystallographic grains, A–I. (b) Lorentz micrograph for the demagnetized state, acquired in an over-focus condition. Bright and dark lines represent magnetic domain walls. Red arrows indicate the magnetization vectors (in-plane component of magnetization) of individual grains: red arrows in other panels (c, e, f) also indicate magnetization vectors. (c) Lorentz micrograph of the remanent state, acquired in an over-focus condition. The black arrow (H) shows the direction of the applied magnetic field, which was used to remove the magnetic domain wall from the GB between grains A and B. (d) Enlarged TEM image of the area indicated by the rectangle in (a). (e) Reconstructed phase image of the area shown in (d), observed in the demagnetized state. (f) Reconstructed phase image of the area shown in (d), observed in the remanent state.

for the region close to grain A, as shown in Fig. 5b, which is an enlargement of the lower-left rectangle in Fig. 5a. In contrast, the results definitely deviate in the region close to grain B in Fig. 5c, which is an enlargement of the upper-right rectangle in Fig. 5a. For convenience, the deviation ($\Delta\phi$) was plotted as a function of position along line R–S (Fig. 5d). The value of $\Delta\phi$ continued to decrease over the GB area, reaching a minimum of -0.34 rad at the border of this area. $\Delta\phi$ slightly increased over area B because of misalignment of the c -axis from that of area A. Curve fitting for area B did not allow an accurate measurement of $\Delta\phi$; e.g., it gave a slightly negative fitting parameter of a . This is likely due to several reasons including an artificial phase shift in area B, induced by a local diffraction effect (which could not be removed completely by tilting the specimen), structural imperfections and surface roughness. Nevertheless, the fitting for area A is useful for extracting the deviation $\Delta\phi$, which depends on B_{GB} , from the original plot of the phase shift.

Note that the magnitude of $\Delta\phi$ observed at the border of the GB area increases with a reduction of B_{GB} (magnetic flux density due to the GB phase). When B_{GB} is equal to the

magnetic flux density in the Nd₂Fe₁₄B matrix, it is difficult to discriminate the GB phase from the matrix region using electron holography observations: i.e., $\Delta\phi \approx 0$ for the plot of Fig. 2d. In contrast, when the GB phase is nonferromagnetic, this layer does not contribute to the magnetic phase shift: accordingly, the phase shift ϕ observed by electron holography is reduced in the GB area, as illustrated in Fig. 2d. As a result, the magnitude of $\Delta\phi$ (i.e., deviation from the plot assuming the whole volume in the Nd₂Fe₁₄B phase) is maximized for the nonferromagnetic GB phase. Using the geometric and magnetic parameters that were described earlier (i.e., specimen thickness, GB width, tilting angles θ_1 and θ_2 , directions of the c -axis, saturation flux density of Nd₂Fe₁₄B (1.6 T), stray magnetic field in the GB region), Eq. (2) predicts an approximate value of $\Delta\phi \approx -1.2$ rad for the nonferromagnetic GB phase. For the ferromagnetic GB phase, the absolute value of $\Delta\phi$ should be smaller than the value expected for the nonferromagnetic GB phase. Even if the uncertainty of the phase measurement (± 0.08 rad) is taken into account, the absolute value of the observation ($\Delta\phi = -0.34$ rad) is definitely smaller than that expected for the nonferromagnetic GB phase.

Fig. 5. Experimental results of the phase shift due to the ultrathin GB phase. (a) Phase shift observed along the R–S line shown in Fig. 4. Labels A and B indicate the regions of grains A and B (i.e., areas A and B), respectively. In the middle (area GB), a thin GB phase (tilted away from the incident electrons) is sandwiched between portions of grains A and B; refer to Fig. 2c. The light blue dots show the observed phase shift. The red line represents a curve fitting result for area A, although it is plotted for the extended regions including GB and B. (b) Enlarged portion of the plot, for the area indicated by the lower-left rectangle in (a). (c) Enlarged portion of the plot, for the area indicated by the upper-right rectangle in (a). (d) Difference between the observations and the fitting curve, which determined the phase shift due to the GB phase to be -0.34 rad at the border of area GB.

Thus, the electron holography study indicates ferromagnetism in the GB phase.

4. Discussion

4.1. Determination of magnetic flux density due to GB phase

To determine the magnetic flux density due to the GB phase, B_{GB} , the observation of $\Delta\phi$ was compared with simulations that were carried out for various values of B_{GB} . For the structure model used in the simulation (Fig. 6a), the size, shape, and magnetization vectors of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (A–E) were fitted with the microscopic observations. The nonferromagnetic grains (F–I; Fig. 3a) were treated as vacuum regions. For the ferromagnetic GB phase, which must be exchange coupled with neighboring $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, the direction of the magnetization vector was assumed to be the average of the directional cosines of grains A and B; i.e., $[0.090, -0.963, -0.254]$. The simulation predicted a 3-D magnetic field, both inside and outside of the specimen. As mentioned earlier, the electron holography observations in Figs. 4 and 5 are related to the y -component of the magnetic flux density, B_y . For example, Fig. 6c displays B_y (assuming $B_{GB} = 1.0$ T) calculated for the cubic region, which is identical to that enclosed by the orange lines in Fig. 6a. The direction and magnitude of B_y (only plotted for the range -80 mT $< B_y < 80$ mT)

are represented using colors, based on the color bar. Although a weak stray magnetic field is present in this cubic region, portions showing a small magnitude of B_y (e.g., -30 mT $< B_y < 30$ mT) were made almost transparent. Portions with $B_y < -80$ mT (i.e., the specimen region, showing $B_y \approx -1.5$ T) are indicated by the same color as that of -80 mT. The inset shows B_y for the y – z plane cross section (including the p–q line in Fig. 6a), along with the white arrows indicating the directions of the magnetic flux (y – z component).

Once B_y is calculated, Eq. (1) predicts the phase shift observed along the R–S line. For calculation of the phase shift ϕ , we considered the modulation of the reference wave due to the stray magnetic field that exists outside the specimen, based on the method proposed by Matteucci et al. [34]. In addition, we incorporated the phase shift due to the mean inner potential caused by a gradual change in the specimen thickness along the R–S line; i.e., 7.1×10^{-3} rad nm^{-1} ($t_1 = 101$ nm, and $t_2 = 109$ nm; Fig. 6b). With respect to the stray magnetic field that exists above ($z > 0$) and below ($z < 0$) the thin-foil specimen, the simulation indicated that B_y became negligibly small in both regions, $z > 10$ μm and $z < -10$ μm . We accordingly calculated the integral of the second term in Eq. (1) over the range -30 $\mu\text{m} \leq z \leq +30$ μm . The simulation provided plots of $\Delta\phi$ that could be observed in the R–S line. Calculations of $\Delta\phi$ for several values of B_{GB} are presented in

Fig. 6. Simulations of the 3-D magnetic field using the model specimen. (a) Structural model used in the simulation, representing the ferromagnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains A–E. (b) Schematic illustration showing the magnetization vectors (indicated by red arrows) in the region containing the line R–S. t_1 and t_2 represent the specimen thickness at points R and S, respectively. (c) Calculations of B_y , displayed for the cubic region of $4\text{ }\mu\text{m} \times 4\text{ }\mu\text{m} \times 4\text{ }\mu\text{m}$ dimensions. This cubic region is identical to that enclosed by the orange lines in (a).

Fig. 7a. Importantly, the calculations reproduce all of the trends observed in the experiments; i.e., the decrease in $\Delta\phi$ over the GB area, the minimum appearing at the GB border, and the gradual increase in $\Delta\phi$ in area B. Fig. 7b shows the relationship between B_{GB} and $\Delta\phi$ calculated at the GB border. The value of B_{GB} that explains the observation ($\Delta\phi = -0.34\text{ rad}$) is 1.1 T. More strictly, we should consider the difference in the mean inner potential (ΔV_0) between the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and the GB phase (e.g., $\text{Nd}_{33}\text{Fe}_{63}\text{B}_3\text{Cu}_1$) [14]. Assuming the same volume density for these metallic phases, the non-binding approximation using atomic scattering factors [16] predicts $\Delta V_0 \approx 3\text{ V}$. For the thin GB phase observed in this study, ΔV_0 causes only a small phase shift of 0.09 rad, which may lead to overestimation of B_{GB} by 0.1 T. We accordingly evaluated B_{GB} at 1.0 T, with an uncertainty of $\pm 0.1\text{ T}$ originating from the accuracy of the phase shift analysis. Recent studies using X-ray magnetic circular dichroism [35] and spin-polarized SEM [36] have also indicated ferromagnetism in the GB phase, although these methods could not determine the magnetic flux density in this intergranular region.

4.2. Ferromagnetic GB phase and coercivity

Within the framework of the Stoner–Wohlfarth theory that describes coherent spin rotation in isolated nano-particles, the theoretical upper limit of coercivity corresponds to the value of the magnetic anisotropy field, i.e., $\sim 7\text{ T}$ in $\text{Nd}_2\text{Fe}_{14}\text{B}$ [2]. However, the coercivity in commercial Nd–Fe–B magnets is typically less than 20% of this limit. This low coercivity is due to several factors originating from the microstructure of bulk magnets, including avalanche

Fig. 7. Determination of magnetic flux density due to the GB phase. (a) Comparison of observations and calculations (simulations), specifically $\Delta\phi$; i.e., difference between the observed phase shift and the fitting curves for area A. The calculations of $\Delta\phi$ were obtained for several values of B_{GB} of 1.2 T, 1.1 T, 1.0 T, 0.9 T, 0.5 T, and 0 T. (b) Relationship between $\Delta\phi$ and magnetic flux density due to the GB phase, B_{GB} .

propagation of magnetization reversal due to the intergranular exchange coupling [37,38], structural imperfections that reduce the local magnetocrystalline anisotropy [39] and the demagnetization field from neighboring grains [40]. One efficient method of suppressing these undesired sources of magnetization reversal is to control the crystallographic microstructure of the sintered magnets [4,7–13]. In particular, the structure and chemistry of the GB phase appear to be the most influential for coercivity. Since $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are in physical contact with each other in the as-sintered condition [10], the magnets have low coercivity due to intergranular exchange coupling. Subsequent heat treatment produces an amorphous, thin GB phase (~ 3 nm in width), which was believed to decouple intergranular exchange of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. Since the ferromagnetic exchange length of $\text{Nd}_2\text{Fe}_{14}\text{B}$ is only ~ 1.3 nm [37], this scenario is most plausible if the GB phase is non-ferromagnetic. However, despite the optimal heat treatment for the individual $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains to be enveloped by the GB phase, the coercivity of Nd–Fe–B sintered magnets is less than 2 T at room temperature without using Dy. Our electron holography study confirmed that the GB phase in the sintered magnets is ferromagnetic, in agreement with the indirect measurement using the model intergranular phase reported by Sepehri-Amin et al. [14]. In addition, the magnetic flux density was determined to be ~ 1.0 T, above 60% of the flux density of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. This result implies that the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains remain exchange-coupled even after the optimal-sinter annealing. The ferromagnetism in the GB phase is attributed to an unexpectedly high concentration of magnetic elements [14]. This suggests that increasing the nonferromagnetic elements (i.e., diluting the ferromagnetism) in the GB phase is a key for further improvements in coercivity of the Nd–Fe–B magnets.

In this study, we have investigated only one thin amorphous GB phase (~ 3 nm width). This type of thin amorphous phase is commonly observed in the grain boundaries of optimally heat-treated sintered magnets. In addition to such a thin amorphous GB phase, there are several phases in sintered magnets. For example, a thicker GB phase, which was observed near the triple junction, shows a crystalline structure with a different chemical composition [8,10]. According to Refs. [10,14], a multi-scale characterization of a large field of view is required for a complete understanding of the magnetism of the secondary phases produced inside sintered magnets. However, these earlier investigations also indicate that the GB phase that usually influences the intergranular exchange coupling is the thin amorphous GB phase with a width of 2–3 nm. In this study, we selected such a thin amorphous GB phase for the electron holography analysis; thus, we believe that the results are representative of the most commonly observed thin GB phases. Of course, the possibility of scattering in the chemical composition or the magnetic flux density of individual grain boundaries must be considered. However, it is noted that the thin GB is produced by liquid infiltration due to the eutectic reaction of NdCu/Nd, as reported in Ref. [14]. The result

indicates that the chemical composition of the GB phase is determined by the phase equilibrium at the optimal heat treatment temperature. Thus, a large scattering in the chemical compositions is unlikely. For a future study, the electron holography technique can be extended to precise investigations of the scattering of magnetic flux density values in individual boundaries. Another challenge is to determine the magnetic flux density as a function of position in a continuous GB phase (e.g., measuring B_{GB} as a function of distance from the triple junction) when the width of GB changes. It is also interesting to simultaneously measure the magnetism and chemical composition from a specific GB region. These observations will provide useful information on GB engineering in Nd–Fe–B sintered magnets to enhance coercivity.

5. Summary

Electron holography studies revealed a phase shift of $\Delta\phi = -0.34$ rad (± 0.08 rad) due to a thin amorphous GB phase (~ 3 nm in width) sandwiched by $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains. This value of phase shift is substantially smaller than that expected for the nonferromagnetic GB phase, $\Delta\phi = -1.2$ rad, calculated using the geometric/magnetic parameters determined for the thin-foil TEM specimen. The result indicates that the GB phase is ferromagnetic. The best fit of simulations of $\Delta\phi$ with the observation evaluates the magnetic flux density of the GB phase to be ~ 1.0 T. This value is $\sim 60\%$ of the saturation magnetic flux density of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. The observation implies significant intergranular exchange coupling between $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains in commercial sintered magnets subjected to the optimal heat treatment.

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