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 Nd2Fe14B 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-NdO2, NdFe2B, metallic Nd-rich phases with the fcc structure and the In3 structure. The metallic Nd-rich phases form at the sharp edges of Nd-rich oxide and boride grains, from which thin Nd-rich phases are infiltrated along grain boundaries to form the thin GB phase. Misaligned Nd2Fe14B grains are often observed in direct contact with the Nd2O3 grains.

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1. Introduction

(Nd1−xDy)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-NdO3 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

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(HRTEM) and three dimensional atom probe (3DAP) analyses. 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. 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, \( (BH)_{\text{max}} \), of 400 kJ/m\(^3\) or 50 MGOe by identifying the triple junction Nd-rich phases using correlative SEM and TEM observations, 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/m\(^3\) grade commercial Nd-Fe-B sintered magnet. The chemical composition was Fe\(_{65.5}\)Nd\(_{29.9}\)Pr\(_{0.1}\)Dy\(_{0.5}\)Tb\(_{1.1}\)Cu\(_{0.2}\)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\(_{0.5}\)Ni\(_{0.4}\)Co\(_{1.8}\)O\(_{0.5}\) in at.%). The coercivity, \( H_c \), maximum energy product, \( (BH)_{\text{max}} \), and remanent magnetization, \( M_r \), of the sample were 1.24 T, 411 kJ/m\(^3\), 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. The sample for the EBSD analysis was prepared by Ar-ion milling (Hitachi IM4000 ion milling system). 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

Fig. 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 Nd\(_2\)Fe\(_{14}\)B 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. Based on these previous investigations, the Nd-rich phase 1 with the slightly brighter imaging contrast compared to the Nd\(_2\)Fe\(_{14}\)B matrix in the BSE 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(b)) and a brighter contrast in the BSE image (Fig. 1(a)) with respect to the Nd\(_2\)Fe\(_{14}\)B 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 \( \alpha \)-Nd since it exhibits the brightest contrast in the IL-SE image (Fig. 1(d)) like the \( \alpha \)-Nd phase reported previously. Nd-rich phase 4 may be identified as the one with the Ia\(_3\) structure, which is dimly imaged in the IL-SE image (Fig. 1(b)), having a brighter contrast compared to the \( \alpha \)-Nd phase in the BSE image. Nd-rich phase 5 can be identified as Nd\(_{2}\)Fe\(_4\)B\(_4\) [38]. The inset image to Fig. 1(a) also shows that thin Nd-rich layer is formed at the Nd\(_{2}\)Fe\(_4\)B\(_4\)/Nd\(_2\)Fe\(_{14}\)B interfaces.

Fig. 2(a) and (b) show BSE and IL-SE images including two