Effect of Carbon on the Coercivity and Microstructure in Fine-Grained Nd-Fe-B Sintered Magnet

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Abstract

We have investigated the effect of carbon on the coercivity and microstructure in fine-grained Nd-Fe-B sintered magnets fabricated by the press-less sintering method. The coercivity of the sample with the carbon content of 730 ppm (low-C) was 1.59 T while that of the sample with 1500 ppm (high-C) was 1.44 T in the as-sintered state. The low-C sample exhibited a larger coercivity increase by a post-sinter annealing, reaching the highest coercivity of 1.85 T while the high-C sample reached a lower coercivity of 1.54 T. Detailed microstructure investigations using scanning electron microscopy, scanning transmission electron microscopy and atom probe tomography revealed that the high carbon caused the formation of a Nd-carbide with a tetragonal structure and the reduction in the volume fraction of an α -Nd phase at triple junctions. This in turn decreased the Nd+Pr concentration in thin Nd-rich grain boundary phase, resulting in the lower coercivity.

Keywords: Nd-Fe-B, sintered magnet, coercivity, microstructure

1. Introduction

(Nd,Dy)–Fe–B based sintered magnets are currently used for traction motors and generators of (hybrid) electric vehicles because of their excellent combination of high maximum energy product, $(BH)_{\max}$, and coercivity, $\mu_0 H_c$. However, there is a strong demand to achieve the high coercivity without using Dy due to its scarce natural resources and high cost. Grain size refinement is an effective way to increase the coercivity [1-9] mainly because local stray fields can be reduced [10]. Apart from the grain size effect, impurities such as oxygen and carbon have been known to influence the coercivity [4, 11]. The adverse effect of the impurities is more pronounced for the grain size smaller than 3 μm , *i.e.*, coercivity deviates from the logarithmic grain size dependence of the coercivity for the grain size smaller than 3 μm [11]. This is because the oxygen that is contaminated during jet-milling and subsequent powder metallurgy process causes the oxidation of α -Nd phase, which hinders the formation of the continuous thin Nd-rich grain boundary phase [11]. By controlling the oxygen impurities using the pressless sintering (PLS) process, Une and Sagawa [12] reported that the logarithmic grain size dependence of sintered magnets can be extended to 1 μm grain size, in which they reported a coercivity of 2 T in Dy-free Nd-Fe-B sintered magnets.

Carbon is contaminated from the organic lubricant, which is added for better alignment of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains in the magnetic compaction, and the carbon impurity is known to be more sensitive to the coercivity compared to oxygen and nitrogen [13]; even the contamination of hundreds of ppm carbon causes significant decrease in the coercivity. Although the distribution of carbon and its effect on the hard magnetic properties had been a subject of previous studies [13-15], it still remains unclear how the carbon impurity affects the microstructure and the coercivity of sintered magnets. In this work, we have revisited the effect of carbon on the microstructure and coercivity of fine-grained sintered magnets fabricated by

the pressless sintering process [12] using scanning electron microscopy (SEM), aberration corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and three-dimensional atom probe (3DAP).

2. Experimental Procedure

Fine-grained sintered magnets with different carbon contents were prepared by the pressless sintering process [12]. Helium jet-milling technique was used to crash the strip cast flakes with the chemical composition of $\text{Fe}_{\text{bal.}}\text{Nd}_{26.4}\text{Pr}_{4.1}\text{B}_{1.0}\text{Cu}_{0.1}\text{Al}_{0.28}\text{Co}_{0.9}$ into the powders with a mean diameter of 1.3 μm . The powders were consolidated at 920 °C for 2 h after a magnetic compaction. In order to reduce the carbon content, the green compact was heat treated at 400 °C in a hydrogen atmosphere to decompose and remove the organic lubricant from the sample prior to the sintering. **Table 1** summarizes the chemical compositions and the density of the sintered samples. Hereafter, the samples containing 730 ppm and 1500 ppm carbon are denoted as low-C sample, and high-C sample, respectively. The as-sintered samples were then post-sinter annealed at 500°C for 1 h. The magnetic properties of the samples were measured by D.C. Recording Fluxmeter (TOEI INDUSTRY CO., LTD.).

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 2 kV. 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 a dual beam FIB/SEM, FEI Helios Nanolab 650. 3D atom probe (3DAP) analyses were performed using a locally built laser assisted wide angle tomographic atom probe (LAWATAP) with a ultraviolet

femtosecond laser of the wavelength of 343 nm. Needle like specimen including the region of interest was lift out using FEI Helios Nanolab 650, and placed on a sharpened W wire, and fabricated into the needle shape using annular Ga ion beam using Carl Zeiss CrossBeam 1540 EsB.

3. Results

Figure 1 shows the second quadrant of the magnetization curves of the low-C and high-C samples in as-sintered and post-sinter annealed conditions. **Table 1** summarizes the magnetic properties of the samples. While all the samples show the same remanent magnetization ($\mu_0 M_r$) of 1.44 T, the coercivity of the as-sintered low-C sample (1.59 T) is higher than that of the as-sintered high-C sample (1.44 T). After the post-sinter annealing, the coercivity increased to 1.85 and 1.54 T for the low-C and high-C samples. The increase of the coercivity by the post-sinter annealing is larger in the low-C sample compared to the high-C sample, indicating the carbon impurity substantially affect coercivities in both as-sintered and optimally heat treated samples.

Figure 2 shows a backscattered electron (BSE) SEM image, in-lens secondary electron (IL-SE) SEM image, EDS elemental maps of Nd, Fe, and those for O and C obtained from an as-sintered high-C sample. Nd-rich phases are imaged with brighter contrasts with respect to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix in both BSE (Fig. 2 (a)) and IL-SE images (Fig. 2 (b)). Among phase identification studies on the Nd-rich phase located at the grain boundary triple junction [7, 8, 16-18], Sasaki et al reported that the combination of the BSE and IL-SE images in SEM led to an unambiguous identification of the Nd-rich phase. Since the samples used in this work are fine-grained magnet with similar chemical composition fabricated by the press-less sintering process as well as the one reported by Sasaki et al. [18], the phase constitution of the present

samples should be same as the one reported in the past [18]. Therefore, the Nd-rich phase can be identified based on the imaging contrast in the BSE and IL-SE SEM images and EDS elemental maps. The Nd-rich phase grains indicated by arrows 1 are identified as the α -Nd phase based on the EDS map. As we reported previously [18], the α -Nd phase exhibits the brightest contrast in the IL-SE image, in which oxygen and carbon are not enriched as shown in the EDS elemental map in **Fig. 2 (e)**. The Nd-rich phase indicated by arrow 2 is the one with the $Ia\bar{3}$ structure, which is dimly imaged in the IL-SE SEM image having a brighter contrast compared to the α -Nd phase in the BSE SEM image. The Nd-rich phase indicated by arrow 3 is enriched in oxygen as shown in the oxygen elemental map in **Fig. 2 (e)** and the EDS spectrum, **Fig. 2 (f)**; hence, it is identified as fcc-NdO_x [18]. From the imaging contrasts in the BSE and IL-SE images, the Nd-rich phase 4 was identified as the NdFe₄B₄ phase [18]. The Nd-rich phase indicated as 5 has an irregular shape compared to the other Nd-rich phases, which is darkly imaged compared to the NdO_x phase in the BSE image, **Fig. 2 (a)**, while it shows a similar imaging contrast to the NdO_x phase in the IL-SE image, **Fig. 2 (b)**. Note that carbon is enriched in this phase as shown in the EDS elemental map, **Fig. 2 (e)**, and the EDS spectrum, **Fig. 2 (f)**. Since **Fig. 2 (e) and (f)** also show the presence of Fe in the carbon enriched Nd-rich phase, we conclude that the carbon enriched phase is a compound mainly consisting of Nd, Fe and C, probably a neodymium carbide (hereafter denoted as Nd-carbide).

Figure 3 shows the bright field TEM image and energy filtered images for Nd, Fe and C of a post-sinter annealed high-C sample. These images clearly show the presence of the Nd-carbide with an irregular shape. The bright field TEM image in **Fig. 3 (a)** shows that the carbide is monocrystalline like oxide grains [16, 18]. The selected area diffraction (SAD) pattern obtained from the carbon-rich phase is consistent with the tetragonal structure with the lattice parameters of $a=1.01$ nm and $c=1.449$ nm as reported by Pan et al [14].

Figure 4 shows the IL-SE SEM images obtained from the as-sintered low-C and high-C samples. To measure the areal fraction of the Nd-rich phases, a particular type of Nd-rich phase was manually filled with a white color using an image editor, and the areal fraction was determined using Gatan Digital Micrograph. The areal fractions of the Nd-rich phases in the low-C and high-C samples were similar, 8.1 and 6.6 %, respectively. As shown in the insets to **Fig. 4 (a) and (d)**, the number density of the Nd-rich phase at triple junctions appears to be higher in the low-C sample compared to that in the high-C sample. This is also evident from the histograms, **Fig. 4 (b) and (e)**, showing the number density of the Nd-rich phases as a function of their sizes. Note that the particle size was calculated from an area assuming the circular shape of the Nd-rich phase. The total number density of the Nd-rich phases in the low-C sample is $2.7 \times 10^{12} \text{ m}^{-2}$, which is higher than that in the high-C sample, $8.6 \times 10^{11} \text{ m}^{-2}$. The fractions of the constituent Nd-rich phases are also different in the low-C and high-C samples. **Figure 4 (c) and (f)** shows the areal fraction of the constituent Nd-rich phases in the low-C and high-C samples analyzed from the IL-SE and BSE images. In the low-C sample, about 50% of the Nd-rich phases is either α -Nd or $\text{La}\bar{3}$ (metallic Nd-rich phases). Note that the $\text{La}\bar{3}$ phase is classified as the metallic phase since only a small amount of oxygen was detected from this particular phase [18]. The fraction of the metallic Nd phases in the high-C sample is only 37.3%, which is lower than that in the low-C sample while there are no significant differences in the phase fractions of the oxides and borides in these two samples. Note that the phase fraction of the carbide phase is higher in the high-C sample, i.e., the fractions of the carbide are 7.8 and 20.8 % for the low-C and high-C samples, respectively.

Figure 5 (a) and (c) are the IL-SE SEM images obtained from the post-sinter annealed low-C and high-C samples, respectively. The areal fraction of the Nd-rich phase is 8.6 and 6.1 % for the low-C and high-C samples, which are similar to those in the as-sintered high-C and low-

C samples, 8.1 and 6.6%. The total number density of the Nd-rich phase in the low-C sample, $4.8 \times 10^{11} \text{ m}^{-2}$, is higher than that in the high-C sample, $2.6 \times 10^{11} \text{ m}^{-2}$, indicating that the fine α -Nd phase is more densely dispersed in the low-C sample compared in the high-C sample. The fractions of the constituent phases do not change before and after the post-sintered annealing in both the low-C and high-C samples. **Figure 5 (b) and (d)** show the fraction of each constituent Nd-rich phase in the low-C and high-C samples after the post-sintered annealing. The fractions of the constituent Nd-rich phases are similar to those in the as-sintered samples.

Figure 6 shows the BSE SEM images of the (a) as-sintered and (b) post-sinter annealed low-C samples, and (c) as-sintered and (d) post-sinter annealed high-C samples. Note that the imaging contrast is enhanced so that the thin Nd-rich grain boundary phase is clearly observed. The darkly imaged region corresponds to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, and the brightly imaged region is the Nd-rich phases. Bright contrast also appears along the grain boundaries for both high-C and low-C samples, indicating the formation of the Nd-rich thin grain boundary phases as reported previously [6-9, 19]. The Nd-rich grain boundary phases are uniformly formed in both the as-sintered and post-sinter annealed samples regardless of the carbon content. This means that there is no distinct differences in the Nd-rich grain boundary phase observed by SEM. These images also indicate that no distinct grain growth occurred during the post-sinter annealing at 500°C , *i.e.*, the grain sizes were 1.2 ± 0.9 and $1.4 \pm 1.4 \text{ }\mu\text{m}$ for the low-C samples in the as-sintered and post-sinter annealed conditions, and 1.3 ± 0.9 and $1.3 \pm 1.0 \text{ }\mu\text{m}$ for the high-C samples in the as-sintered and post-sinter annealed conditions, respectively.

Figure 7 shows HAADF-STEM images and EDS line profiles taken across grain boundaries typically observed in the as-sintered low-C sample, the post-sinter annealed low-C sample, and the post-sinter annealed high-C sample, respectively. All images contain a thin Nd-

rich grain boundary layer of about ~ 2 nm in thickness. The EDS line profiles in **Fig. 7 (b), (d) and (f)** show the enrichment of Nd and Pr as reported in the fine-grained magnet fabricated by the pressless process [12, 19]. While the concentration of Nd+Pr is ~ 40 at.% for the as-sintered low-C sample, the post-sinter annealing increased the Nd+Pr concentration to ~ 50 at.%. On the other hand, the thin Nd-rich grain boundary phase in the post-sinter annealed high-C sample has the Nd+Pr concentration of ~ 40 at.%, which is as high as that of as-sintered low-C sample.

The enrichment of Nd in the grain boundary phase is also obvious from the 3D atom maps. **Figure 8** shows 3D atom maps including a thin Nd-rich grain boundary phase taken from the post-sinter annealed (a) low-C and (c) high-C samples. **Fig. 8 (b) and (d)** are concentration profiles analyzed from the selected volumes in **Fig. 8 (a) and (c)**. The Nd + Pr concentration in the thin Nd-rich grain boundary phase in the low-C sample is about 55.3 ± 4.9 at.%, which is higher than that in the high-C sample, $41 \pm 4.8\%$. The composition of the grain boundary phase was calculated to be Fe-50.9Nd-4.4Pr-5.7B-2.8Cu-1.8Co-0.92Al (at.%) for the low-C sample, and Fe-37.0Nd-4.4Pr-5.8B-1.5Cu-3.7Co-1.0Al for the high-C sample. In addition to Nd+Pr, Cu is also enriched in the grain boundary phase as reported previously [20]. Note that no C was detected from the grain boundary phase. The 3DAP data taken from the high-C sample showed the concentration of C in the Nd₂Fe₁₄B phase was only 0.07 at.% (130 ppm), which means the carbon was not dissolved into the matrix, but was mainly consumed to form the Nd-carbide.

Figure 9 shows the HAADF-STEM images of showing typically observed features in Nd-rich grain boundary phases in the post-sinter annealed low-C and high-C samples. **Figure 9 (a)** shows a thin Nd-rich grain boundary phase. The grain boundary is misaligned from the (001) plane of the Nd₂Fe₁₄B grain by 58° . The Nd-rich grain boundary phase shows an amorphous structure as is widely accepted as the general structural feature of the grain boundary phase [8, 9, 18, 21]. The grain boundary consists of ledges with irregular height and spacing.

On the other hand, the one tilted by 30° from the (001) plane forms ledges with the step height consistent with the unit cell of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ crystal, 1.2205 nm, and (001) plane appears on the surface of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain, **Fig. 9 (b)**. Interestingly, the thin Nd-rich grain boundary phase tilted by 30° from the (001) plane of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain shows the crystalline nature. The thin Nd-rich grain boundary phase parallel to the (001) plane also shows the crystalline nature, **Fig. 9 (c)**. On the other hand, the thin Nd-rich grain boundary phase in the post-sinter annealed high-C sample shows the amorphous structure regardless of the orientation of the grains as shown in **Fig. 9 (d) and (e)**. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain boundary in contact with a thin amorphous Nd-rich grain boundary phase, **Fig. 9 (d)**, shows constant ledge height and terrace spacing. On the other hand, some grain boundary phases in the high-C sample showed the crystalline nature as shown in **Fig. 9 (f)**.

4. Discussion

This work has investigated the effect of carbon on the coercivity and microstructure in fine-grained Nd-Fe-B sintered magnets fabricated by the press-less sintering method [12]. While the samples showed the same remanent magnetization of 1.44 T regardless of the carbon content, the carbon affected the coercivity substantially. The coercivity of the as-sintered sample decreased from 1.59 to 1.44 T with the increase in carbon content from 730 to 1500 ppm, **Fig. 1 and Table 2**. The coercivity increment, $\mu_0\Delta H_c$, by the post-sinter annealing is larger in the low-C sample, 0.26 T, than that of the high-C sample, 0.10 T, giving rise to the coercivity of 1.85 and 1.54 T in the low-C and high-C samples after post-sinter annealing. **Figure 10** summarizes the relationship between the coercivity and the grain size in various sintered magnets [2, 4, 5, 11, 12, 19]. The coercivity of the as-sintered samples was much lower than the values expected from the reported coercivity-grain size relationship. Although the post-

sinter annealing increased the coercivity, the resultant coercivity of the high-C sample is still lower than the value expected from the extrapolation of the coercivity-grain size relationship. Only the post-sinter annealed low-C sample exhibited the coercivity equivalent to the extrapolated value. Therefore, we can conclude that the control of the carbon content is critically important to achieve high-coercivity in Nd-Fe-B magnets.

3D atom probe analyses showed that the carbon was not segregated in the thin Nd-rich grain boundary phase as shown in **Fig. 7 and 8**. The 3DAP analysis of the matrix has also shown that the dissolution of carbon in the Nd₂Fe₁₄B phase was only 0.07 at.% (130 ppm), which is much lower than the nominal concentration of carbon, 1500 ppm. Nd-carbide grains were observed at grain boundary triple junctions, and its volume fraction increased with the carbon content as shown in **Fig. 4 and 5**. Electron diffraction analysis has shown that the carbide phase has the tetragonal structure with lattice parameters of $a = 1.014$ and $c = 1.449$ nm, **Fig. 3 (d)** [14]. Pan et al reported that the tetragonal Nd-carbide phase and Fe were formed by the following reaction during annealing the mixture of the Nd₂Fe₁₄B powders with 1.2wt.% of carbon powders at 900 °C, which is close to the sintering temperature of the present samples, 920°C [14];

where A is the carbon enriched phase with the tetragonal structure. They explained that the A-phase formed as a consequence of the reaction between the carbon and Nd₂Fe₁₄B phase without considering the presence of the Nd-rich phase. However, the Fe particles were not observed in the EDS elemental map in **Fig. 1 (b)**, ruling out the possibility of this reaction. Instead, the volume fraction of the α -Nd phase decreased with increasing the Nd-carbide, **Fig. 4 (c) and (f)**. Therefore, we conclude that α -Nd phase was consumed to form the Nd-carbide.

In both low-C and high-C samples, the post-sintered annealing did not affect the volume fraction and phase constitution of the Nd-rich phases, **Fig. 3 (c) and (f)**, and **Fig. 4 (b) and (d)**. The amount of α -Nd has a close correlation with the coercivity since α -Nd phase at triple junctions serves as Nd pool for the formation of the thin grain boundary phase during post-sinter annealing [20]. The increase in the carbon content caused the increase in the volume fraction of the Nd-carbide at the expense of the α -Nd phase, **Fig. 3 and 4**. Therefore, the coercivity decrease due to the carbon contamination can be explained by the characteristics of the thin grain boundary phase, *i.e.*, the increased carbon concentration causes the decrease of the Nd+Pr concentration in the grain boundary phase, resulting in a stronger intergranular exchange coupling [22]. Since the Nd+Pr concentration of the thin Nd-rich grain boundary phase is almost the same between the as-sintered low-C sample and post-sinter annealed high-C sample, **Fig. 7 (a) and (b)**, their similar coercivity can be also understood.

The grain boundary phase observed in the post-sinter annealed low-C sample has Nd+Pr concentration over ~50 at.%. This is much higher than the Nd+Pr concentration of the thin Nd-rich grain boundaries in other sintered magnets, ~30 at.% [8, 9, 19]. Under the presence of such thin Nd-rich grain boundary phase, the Nd₂Fe₁₄B grains are expected to be more weakly exchange coupled. The Nd₂Fe₁₄B grains are expected to be magnetically decoupled if the Nd-concentration in the grain boundary phase increases above 70at.% [23]. If that is the case, the magnetic reversal on the surface of each Nd₂Fe₁₄B grains may need to be considered. As shown in **Fig. 9**, some of the thin Nd-rich grain boundary phase in the post-sinter annealed low-C sample was crystalline. The presence of the crystalline grain boundary phase has been reported in the some sintered Nd-Fe-B magnets [7, 24] and the Nd-Fe-B magnet subjected to hydrogen-disproportion-desorption-recombination (HDDR) process [25]. Since the grain boundary phase observed in the low-C sample had a higher Nd+Pr concentration up to 56 at.% compared to the

ones observed in the High-C sample, ~45at.%, and other sintered magnets ~ 30 at.% [8, 9, 19], high Nd+Pr content might be one reason for the formation of the crystalline grain boundary phase. The chemical composition of the crystalline grain boundary phase is about Fe:Nd:Cu=48:48:4, and there is neither known ternary compound close to this composition nor Nd-Fe binary compounds with similar stoichiometry to the crystalline grain boundary phase [26]; so the phase is considered to be metastable. In addition, the surface plane of the Nd₂Fe₁₄B grain might be also related to the formation of crystalline grain boundary phase. Figure 9 shows that the crystalline grain boundary phase is formed when the (001) plane appears on the surface in one of the neighboring Nd₂Fe₁₄B grains. However, since the other neighboring grain is slightly off-axis, the (001) plane is not resolved, the misorientation angle of the two grains is not clear. Further work on the correlation between the structure of the grain boundary phase and grain misorientations will shed light on the condition for the formation of the crystalline grain boundary phase.

4. Conclusions

We have investigated the effect of carbon on the coercivity and microstructure in pressless sintered fine-grained Nd-Fe-B magnets. The carbon content strongly affects the coercivity and the coercivity increment by the post-sintered annealing. The low carbon sample, which contains 730 ppm of carbon, exhibited the coercivity of 1.59 and 1.85 T in the as-sintered and post-sinter annealed conditions, respectively, while the high carbon sample containing 1500 ppm of carbon exhibited much lower coercivities of 1.44 and 1.54 T in the as-sintered and post-sinter annealed conditions, respectively. This can be explained by the change in the chemical composition of the thin Nd-rich grain boundary phase. The impurity carbon causes the formation of a Nd-carbide with a tetragonal structure. This causes an increase in the volume

fraction of the Nd-carbide at the expense of the α -Nd phase. This results in the sparse dispersion of the α -Nd phases, decreasing the Nd concentration in the thin grain boundary phase. The STEM-EDS and 3DAP analyses have shown that the thin Nd-rich grain boundary phase in the low carbon sample has the higher Nd+Pr concentration compared to that in the high carbon sample. This is considered to affect the pinning force of the domain wall and the coercivity.

Acknowledgement

This work was supported by JST, CREST.

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Tables

Table 1: Chemical composition of the samples

	Chemical Composition									Density		
	wt. %								ppm			g/cm^3
	Nd	Pr	Dy	B	Cu	Al	Co	Fe	O	N	C	
Low-C	26.4	4.14	0.01	0.97	0.1	0.28	0.9	bal.	1500	580	730	7.53
High-C									1600	580	1500	7.51

Table 2: Magnetic properties of the samples

		Remanent Magnetization	Coercivity	Maximum Energy Product
		$\mu_0 M$ (T)	$\mu_0 H_C$ (T)	$(BH)_{\max}$ (MGOe)
Low-C	As-Sintered	1.44	1.59	51.18
	Annealed	1.44	1.85	51.04
High-C	As-Sintered	1.44	1.44	51.37
	Annealed	1.44	1.54	51.53

Figure Captions

Figure 1: Second quadrant of magnetization curves for the samples

Figure 2: (a) Backscattered electron (BSE) and (b) In-Lens secondary electron (IL-SE) SEM images obtained from the as-sintered high-C sample. (c), (d) and (e) are the EDS elemental maps of Nd and Fe, and Oxygen and Carbon. (f) shows the EDS spectra obtained from the matrix and Nd-rich phases enriched in oxygen and carbon matrix.

Figure 3: (a) bright field TEM image obtained from the post-sinter annealed high-C sample. (b), (c) and (d) are the energy filter elemental maps of Nd, Fe and C, respectively. (e) is the selected area diffraction (SAD) pattern obtained from a Nd-rich phase enriched in carbon.

Figure 4: (a) IL-SE SEM image obtained from the as-sintered low-C sample. Inset figure is the magnified image showing the distribution of fine α -Nd phase. (b) is the histogram showing the size distribution of the Nd-rich phase analyzed from the as-sintered low-C sample. (c) is the circular graph showing the fraction of the constituent Nd-rich phase analyzed from the as-sintered low-C sample. (d) is IL-SE SEM image obtained from the as-sintered high-C sample with the high magnification image in the inset. (e) is the histogram showing the size distribution of the Nd-rich phase analyzed from the as-sintered high-C sample. (f) is the circular graph showing the fraction of the constituent Nd-rich phase analyzed from the as-sintered high-C sample. Note that the fraction of the constituent Nd-rich phase is analyzed from the imaging contrast of the IL-SE and BSE SEM images.

Figure 5: (a) IL-SE SEM image obtained from the post-sinter annealed low-C sample. (b) is the circular graph showing the fraction of the constituent Nd-rich phase. (c) is IL-SE SEM image obtained from the post-sinter annealed high-C sample. (d) is the circular graph showing

the fraction of the constituent Nd-rich phase. Note that the fraction of the constituent Nd-rich phase is analyzed from the imaging contrast of the IL-SE and BSE SEM images.

Figure 6: BSE SEM images with enhanced contrast showing the formation of Nd-rich grain boundary phases in (a) as-sintered and (b) post-sinter annealed low-C samples, and (c) as-sintered and (d) post-sinter annealed high-C samples.

Figure 7: (a) High angle annular dark field-scanning TEM (HAADF-STEM) images obtained from the as-sintered low-C sample, and (b) EDS compositional profile obtained from a region including the thin grain boundary phase. (c) and (d), and (e) and (f) are the ones taken from the post-sinter annealed low-C sample, and post-sinter annealed high-C sample, respectively.

Figure 8: (a) 3D atom map obtained from the post-sinter annealed low-C sample. (b) is the 1D compositional profile obtained from a volume (shown in blue in (a)) including thin Nd-rich grain boundary phase. (c) 3D atom map obtained from the post-sinter annealed high-C sample. (d) is the 1D compositional profile obtained from a volume (shown in blue in (a)) including thin Nd-rich grain boundary phase.

Figure 9: HAADF-STEM images including thin Nd-rich grain boundary phase obtained from the post-sinter annealed low-C and high-C samples. (a), (b) and (c) are the ones in which the thin Nd-rich grain boundary phase is aligned 58, 30° and parallel to the (001) plane of the Nd₂Fe₁₄B phase in the low-C sample. (d), (e) and (f) are the ones in which the thin Nd-rich grain boundary phase is aligned 30° and parallel to the (001) plane of the Nd₂Fe₁₄B phase in the high-C sample.

Figure 10: Variation in coercivity as a function of grain size for various Nd-Fe-B sintered magnets [2, 4, 5, 11, 12, 19].

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10