Microstructure and temperature dependent of coercivity of hot-deformed Nd-Fe-B magnets diffusion processed with Pr-Cu alloy

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The coercivity of hot-deformed Nd-Fe-B magnet was substantially enhanced from 1.0 T to 2.6 T by the grain boundary diffusion process using Pr-Cu alloy. However, the temperature dependence of coercivity is larger compared to the sample diffusion processed with Nd-Cu. Microstructure studies showed a good isolation of platelet shaped Nd₂Fe₁₄B grains by Pr-rich intergranular phase, which explains pronounced coercivity at room temperature. **Small portions of Nd₂Fe₁₄B become** (Nd,Pr)₂Fe₁₄B phase, which has a higher anisotropy field compared to that of the Nd₂Fe₁₄B **phase** at room temperature, while it becomes lower than that of the Nd₂Fe₁₄B phase above ~110°C. Co is depleted from the **(Nd,Pr)₂Fe₁₄B phase**, which is considered to cause a slight decrease in Curie temperature. Micromagnetic simulations with the magnetically isolated grains **including (Nd,Pr)₂Fe₁₄B regions** showed that the degradation of thermal stability of coercivity in the Pr-Cu diffusion processed sample is due to the large temperature dependence of anisotropy field in the **(Nd,Pr)₂Fe₁₄B regions**.

Key words: Nd-Fe-B hot-deformed magnets, coercivity, microstructure, magnetic anisotropy field.

1. Introduction

Anisotropic hot-deformed Nd-Fe-B magnets, prepared by hot-compaction and hot-deformation of rapidly solidified ribbons, are composed of (001)-textured platelet shaped $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains with ~ 250 nm in width and ~ 100 nm in height [1,2]. These platelet-like grains are surrounded by thin Nd-rich intergranular phase [3]. In spite of their fine grain size, comparable to the single magnetic domain particles, the coercivity of the hot-deformed magnets is much lower than that expected from the empirical grain size dependence of coercivity for sintered magnets [4]. A great advantage of the hot-deformed magnets is its improved temperature coefficient of coercivity ($\beta \sim -0.45$ to -0.5 %/ $^{\circ}\text{C}$) compare to that of Nd-Fe-B sintered magnets ($\beta \sim -0.60$ %/ $^{\circ}\text{C}$) [5]. This is considered to be due to the smaller local demagnetization field for finer grains [6,7]. Hence, hot-deformed Nd-Fe-B magnets recently regained interest as excellent alternative to Dy-containing Nd-Fe-B sintered magnets [4]. However, despite their nearly single domain grain size, the maximum coercivity of Dy-free hot-deformed Nd-Fe-B magnets is only around 1.8 T at room temperature [3]. Detailed microstructure characterizations using 3D atom probe tomography have shown that the concentration of ferromagnetic elements, Fe and Co, in the Nd-rich intergranular phase was as high as 50 at.% [3]. This suggests that the intergranular phase in the hot-deformed Nd-Fe-B magnets is ferromagnetic and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are exchange coupled, as was reported for Nd-Fe-B sintered magnets [8-10]. Hence, the magnetic isolation of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains with a non-ferromagnetic intergranular phase is expected to enhance the coercivity of hot-deformed magnets further.

One way to modify the chemical composition and the structure of the grain boundary phase in the ultra-fine grain sized Nd-Fe-B magnets is to infiltrate low melting point eutectic alloys through grain boundaries (eutectic grain boundary diffusion process). Sepehri-Amin et al.

[11] and Mishima et al. [12] independently demonstrated that the diffusion of low melting point Nd-Cu eutectic alloy into the hydrogen disproportionation desorption recombination (HDDR) processed Nd-Fe-B powders through grain boundaries increases the coercivity substantially. This method was found to be effective to enhance the coercivity of anisotropic hot-deformed Nd-Fe-B magnets too [13-15]; the surface of a bulk hot-deformed Nd-Fe-B magnets was coated with Nd₇₀Cu₃₀ powders followed by heat treatment at around 600°C [13]. Then, the eutectic Nd₇₀Cu₃₀ alloy melts and diffuses into the magnet through the grain boundaries, which reduces intergranular exchange coupling, thereby enhancing the coercivity.

Various RE-TM (RE : rare earth, TM: transition metals) eutectic alloys have been used as diffusion sources for enhancing the coercivity. Although the upper limit of coercivity by the Nd-Cu diffusion process was around 2.3 T [13], the hot-deformed magnets diffusion processed with Pr-Cu alloy powders showed a very large coercivity enhancement to 2.6 T [14]. However, the temperature coefficient of coercivity (β) for the Pr-Cu diffusion processed hot-deformed magnets was found to be larger than that of the Nd-Cu diffusion processed magnet [14]. In this work, we studied microstructure of Pr-Cu diffusion processed hot-deformed magnets to clarify the underlying physics for the large temperature dependence of the coercivity of Pr-Cu diffusion processed Nd-Fe-B magnets.

2. Experimental procedure

Hot-deformed Nd-Fe-B magnets with the nominal composition of Nd_{13.2}Fe₇₆Co_{5.6}B_{4.7}Ga_{0.5} (at. %) and size of 4×4×2 mm³ were covered with Pr₉₀Cu₁₀ flakes with different mass fractions of 4, 10, and 20 wt. %, followed by heat treatment at 580°C for 180 min in vacuum. The preparation process of the hot-deformed sample was explained in our previous report [13]. The hypereutectic composition of Pr₉₀Cu₁₀ was selected in this work because it

induced the highest coercivity increment after the diffusion-process. The heat treatment at 580°C led to melting of $\text{Pr}_{90}\text{Cu}_{10}$ and infiltration into the hot-deformed magnets through the grain boundaries. The magnetic properties of the hot-deformed and diffusion-processed magnets were measured using a superconducting quantum interface device vibrating sample magnetometer (SQUID-VSM). Transmission electron microscopy (TEM) was performed using a Titan G2 80-200 TEM with a probe aberration corrector. Energy dispersive X-ray spectroscopy (EDS) was collected using a Super-X EDX detector. Three dimensional atom probe (3DAP) analysis was carried out using a locally built laser assisted 3DAP. The specimens for the 3DAP analyses were prepared by focused ion beam (Hitachi FB-2100) and a CrossBeam 1540EsB with the lift out method.

To simulate the magnetization reversals in the hot-deformed magnets, finite element micromagnetic simulations were performed using a model similar to experimentally observed microstructures. Modelled structure with platelet shaped $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains with the total model size of $100 \times 100 \times 100 \text{ nm}^3$ was constructed. In one model, some sections of the surface area of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains were modeled to be $(\text{Nd},\text{Pr})_2\text{Fe}_{14}\text{B}$ phase. In order to simulate the temperature dependence of coercivity, values of saturation magnetization ($\mu_0 M_s$), magnetocrystalline anisotropy (K_1), and the exchange stiffness (A) of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phase shown in Table 1 were used [16,17]. We assumed that the saturation magnetization and the anisotropy field change linearly from $\text{Nd}_2\text{Fe}_{14}\text{B}$ to $\text{Pr}_2\text{Fe}_{14}\text{B}$ phase depending on the amount of the substitution of Pr for Nd. The exchange stiffness of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phases were assumed to decrease with the same rate as the saturation magnetization at elevated temperatures. Tetrahedron meshes with a size of 2.0 nm were applied on the model, and the Landau-Lifshitz-Gilbert (LLG) equation at each node was solved by the FEMME software [18].

3. Results

3.1. Magnetic properties

Figure 1 shows coercivity ($\mu_0 H_c$), remanent magnetization ($\mu_0 M_r$), and maximum energy product $(BH)_{\max}$ of the Pr-Cu diffusion-processed samples with different amounts of Pr-Cu powders covered on the hot-deformed Nd-Fe-B magnet (0, 4, 10, and 20 wt.%). The initial sample showed $\mu_0 M_r = 1.51$ T, $\mu_0 H_c = 1.0$ T, and $(BH)_{\max} = 442$ kJ/m³. By the diffusion of 4, 10, and 20 wt. % Pr₉₀Cu₁₀ into the hot-deformed magnet, the coercivity was enhanced to 1.8, 2.3, and 2.6 T, respectively. The remanent magnetization and maximum energy product were decreased substantially to 1.18 T and 270 kJ/m³ for the sample diffusion processed with 20 wt.% Pr-Cu sample. Hereafter, we report the results of the as hot-deformed sample and diffusion processed sample with 20 wt.% Pr-Cu, only.

Figure 2 shows coercivity versus temperature for the as hot-deformed magnet, Nd-Cu and Pr-Cu diffusion-processed magnets. The details of the magnetic properties and microstructure studies of the Nd-Cu diffusion processed magnet were reported in our previous report [13]. The temperature coefficient of coercivity, $\beta = [\Delta H_c / (H_c \Delta T)] \times 100$, calculated from 23°C to 197 °C for the as hot-deformed, Nd-Cu diffusion-processed, and the Pr-Cu diffusion-processed magnets were $-0.48\%/^{\circ}\text{C}$, $-0.40\%/^{\circ}\text{C}$, and $-0.45\%/^{\circ}\text{C}$, respectively. Although the thermal stability of the coercivity is improved by the diffusion-process, the Pr-Cu diffusion processed sample shows a larger $|\beta|$ compare to that of the Nd-Cu diffusion processed sample.

3.2. Overall microstructure

Figure 3 (a) and (b) show back scattered electron (BSE) SEM images of the hot-deformed and Pr-Cu diffusion processed samples. C-axes of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are aligned to the upward direction as indicated by the arrow. Figure 3 (c) and (d) show SEM BSE images of the hot-deformed and Pr-Cu diffusion processed samples, in which c-axes are aligned out of the plane. The areal fraction of RE-rich intergranular phase in the hot-deformed and the Pr-Cu diffusion processed samples estimated from the SEM BSE images were 4.6 and 27.7 %, respectively. Bright field (BF) TEM images of the hot-deformed and Pr-Cu diffusion processed samples are shown in Fig. 3 (e) and (f). The grain sizes of these two samples are comparable, indicating that the Pr-Cu diffusion process at 580°C did not cause substantial grain growth. Strain contours are more frequently observed in the BF-TEM image of the Pr-Cu diffusion processed sample, suggesting the introduction of the Pr-rich intergranular phase induced strains in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains.

STEM-EDS maps of Fe, Pr, Nd, Cu, Ga, and Co obtained from the Pr-Cu diffusion processed sample are shown in Fig. 4 (a) to (f). Most of the intergranular phases are depleted from Fe and a good isolation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains by the Pr-rich intergranular phase can be observed from the EDS map of Pr. The distribution of Cu and Pr indicates that there are mainly two phases existing in the intergranular phase, one is enriched with Pr and Cu with some content of Co and Ga and the other is mainly Pr with some content of Cu and Ga. Note that the Nd dissolution can also be observed in the intergranular phase. This macro-scale phase separation within the intergranular phase due to the eutectic solidification was also reported in our previous study in the Nd-Cu diffusion processed hot-deformed Nd-Fe-B magnets [13]. Figure 4 (g) shows nano-beam diffraction patterns obtained from the intergranular phases, indicating that the phase

enriched with Pr and Cu correspond to orthorhombic PrCu phase and the Pr-rich phase with some Cu and Ga has the fcc structure.

Figure 5 (a) shows higher magnification STEM-EDS maps for Fe, Nd, Co, and Pr of the Pr-Cu diffusion processed sample. A platelet shaped $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain can be seen in the Fe map. Fe is not dissolved in the intergranular phase. Note that Nd is depleted from the faceted side of the platelet shaped grain, in which Pr is enriched. This indicates that $(\text{Nd}_{1-x},\text{Pr}_x)_2\text{Fe}_{14}\text{B}$ phase form in contact with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain. However, the $(\text{Nd}_{1-x},\text{Pr}_x)_2\text{Fe}_{14}\text{B}$ phase does not envelope the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain. A particular interest is that Co is rejected from the $(\text{Nd}_{1-x},\text{Pr}_x)_2(\text{Fe}_{1-y},\text{Co}_y)_{14}\text{B}$ region. Higher magnification STEM-HAADF images and STEM-EDS maps of Pr, Co, and Cu obtained from region i and ii in Fig. 5 (a) are shown in Fig. 5 (b) and (c). Non-uniform distributions of Co and Cu in the intergranular phase and their segregation at the interface between the intergranular phase and the $(\text{Nd},\text{Pr})_2\text{Fe}_{14}\text{B}$ phase can be seen in region (i) (Fig. 5 (b)). In region ii, where $(\text{Nd},\text{Pr})_2\text{Fe}_{14}\text{B}$ is not formed (Fig. 5 (c)), no Co segregation is found at the interface; only Cu is segregated there. However, around 8 nm far from the interface, Cu and Co rich phase can be found in the intergranular phase.

Figure 6 (a) and (b) show high resolution STEM-HAADF images obtained from the intergranular phases (IGP) of the as hot-deformed magnet lying parallel to the flat surface of platelet and the one inclined from the c-plane. A ~2 nm-thick layer of amorphous intergranular phase is observed along the grain boundaries. Figure 6 (c) shows a thick crystalline intergranular phase in the Pr-Cu diffusion processed magnet. A majority of the intergranular phases in the Pr-Cu diffusion processed magnet is this type. Fig. 6 (d) shows high resolution STEM-HAADF image taken from an interface between a $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain and the PrCu phase, showing a step like interface of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase with Pr-rich intergranular phase. Based on STEM-EDS analysis

(data not shown here), both of the intergranular phases shown in Fig. 6 (c) and (d) are free from Fe suggesting that most of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are well isolated with Pr-rich intergranular phase. STEM-EDS maps of Fe, Pr, Nd, Cu, Co, and Ga of a thick intergranular phase and corresponding STEM-HAADF image are shown at Fig. 6 (e). Co, Cu and Ga are strongly segregated at the interface. The comparison of high resolution STEM-HAADF image with STEM-EDS maps indicates that the segregation of Co and Cu is in the intergranular phase at the interface rather than inside of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

3.3. Pr content in $(\text{Nd},\text{Pr})_2\text{Fe}_{14}\text{B}$

Fig. 7 (a) shows atom probe tomography of Nd, Pr, Co, and Cu obtained from the Pr-Cu diffusion processed sample. The c-axis of the sample is parallel to the probing direction (longitudinal direction of the specimen). The concentration profiles calculated from inset box 1 and 2 show a $(\text{Nd}_{1-x},\text{Pr}_x)_2\text{Fe}_{14}\text{B}$ phase presents in contact with a $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain. However, the elemental maps in Fig. 7 (a) indicate that the $(\text{Nd}_{1-x},\text{Pr}_x)_2\text{Fe}_{14}\text{B}$ phase does not envelope the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains continuously in agreement with the STEM-EDS result in Fig. 5 (a). No oxygen was found at the intergranular phase. The concentration of the $(\text{Nd},\text{Pr})_2\text{Fe}_{14}\text{B}$ was quantified to be $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ (Fig. 7 (c)). The composition profiles in Fig. 7 (b) and (c) show that $\text{Pr}_{0.6}\text{Nd}_{0.4}$ and Nd phases coexist in the RE-rich phase. In addition, a segregation of Pr, Co, and Cu was found in the intergranular phase at the interface with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain, *i.e.*, 45 at.% Co, 10 at.% Cu, and 45 at.% Nd+Pr at the interface in the inset box 1 and 10 at. % Co and 4 at. % Cu at the interface of the inset box 2. Note that the amount of Co in the $(\text{Nd},\text{Pr})_2\text{Fe}_{14}\text{B}$ phase is just 1.2 at. % while it increases to 3.5 at.% at the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain as shown in Fig. 7 (c).

Figure 8 shows atom probe tomography taken along the probing direction perpendicular to the c-axis of the Pr-Cu diffusion processed sample. The intergranular phase in this atom probe data is located at the side of the platelet shaped $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain as illustrated in Fig. 8 (a). Figure 8 (b) shows 3D atom maps of Fe, Nd, Pr, and Co. Composition profiles calculated from the selected box drawn in the Co map is shown in Fig. 8 (c). The chemical composition of the $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ at the left side of this thick intergranular phase was $(\text{Nd}_{0.8}\text{Pr}_{0.2})_2\text{Fe}_{14}\text{B}$ and the one at the right side of the thick NdPr-rich intergranular phase was $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$. Segregations of Cu was found at the interface between the intergranular phase and the $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ phase. No Fe was detected from the intergranular phase, indicating a good magnetic isolation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains by Nd and NdPr. Note that the chemical composition of the intergranular phase observed at the side of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelet-like grains in the Nd-Cu diffusion processed sample was Fe-rich amorphous phase, which is considered to be ferromagnetic [13]; so the Pr-Cu diffusion process appears to give better magnetic isolation in the longitudinal direction of the platelets compared to the Nd-Cu diffusion processed sample.

3.4. Micromagnetic simulation study on temperature dependency of coercivity

Micromagnetic simulation was employed to study the effect of the presence of the $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ phase on the temperature dependence of the coercivity. For simplicity, the rejection of Co from the $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ regions and Co segregations at the interface of the intergranular phase was not considered in our micromagnetic model. Figure 9 (a) shows the modeled hot-deformed Nd-Fe-B magnet with platelet shaped grains. $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ phase is placed in contact with $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelet grain as shown with green color in Fig. 9 (a). Demagnetization curves of the following three models were simulated; (i) $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains

separated with a ferromagnetic grain boundary phase ($\mu_0 M_s^{\text{GB}}=0.5$ T), (ii) $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains enveloped with a non-ferromagnetic grain boundary phase ($\mu_0 M_s^{\text{GB}}=0.0$ T) representing an exchange decoupled hot-deformed Nd-Fe-B magnet, and (iii) $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelet shaped grains with $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ surface area separated with non-ferromagnetic grain boundary phase ($\mu_0 M_s^{\text{GB}}=0.0$ T). The demagnetization curves of these three samples were simulated using the literature values of $\mu_0 M_s$ and K_u of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ at temperatures of 27, 67, 107, 147, and 187 °C [16,17]. Coercivity versus temperature for the three models are plotted in Fig. 9 (b). The isolation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains with non-ferromagnetic intergranular phase led to a large increase of coercivity. The formation of $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phase in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains induces a higher room temperature coercivity compared to the samples without the $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ grains. The coercivity of the sample with the $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phase remains larger than that without the $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phase up to 107°C. Thereafter, the coercivity of the sample with the $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phase becomes lower than that of the sample without $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$, suggesting that the formation of the $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phase at some surfaces of the platelet shaped $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains causes steeper reduction of the coercivity with temperature.

Figure 10 (a) shows magnetic configuration of the exchange coupled model without $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ at 27 °C and 187 °C under an external demagnetization field (applied parallel to $-Z$) of 3.41 T and 1.98 T, respectively. Note that the magnetization configurations are shown with the same view direction as the model shown in Fig. 9 (a). The nucleation of reversed magnetic domains occurs at the corner of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain, at the interface with ferromagnetic grain boundary phase.

Figure 10 (b) shows the magnetic configuration of the exchange decoupled model without $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ at 27 °C and 187 °C under the demagnetizing field of 4.15 T and 2.32 T, respectively. The nucleation of reversed magnetic domains occurs at the interfaces between the intergranular phase and $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains at both temperatures. Figure 10 (c) shows magnetic configuration of the exchange decoupled model with Pr-rich surface area at 27 °C and 187 °C under the demagnetizing field of 4.21 T and 2.24 T, respectively. Although the magnetization reversal starts the interface between the intergranular phase and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain at 27°C, the nucleation site changes to the interface between the intergranular phase and the $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phase at 187 °C. Note that the nucleation field at 187 °C is -2.32 T for the exchange-decoupled model without the $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ while it decreases to -2.24 T for the exchange-decoupled model with Pr-rich surface area indicating that the nucleation at the $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phase is easier at elevated temperatures. As temperature increases, the anisotropy field of the $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phase becomes lower than that of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, then reversed domain nucleates at the interface between the intergranular phase and the $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phase at a lower demagnetizing field.

4. Discussion

The microstructure analyses of the Pr-Cu diffusion processed sample showed $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are well isolated with Pr-rich intergranular phase that is free from ferromagnetic elements, Fe and Co. Hence, the magnetic isolation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains is considered to be the main reason for the substantial enhancement of coercivity by the Pr-Cu grain boundary diffusion process. On the other hand, the platelet-shaped $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains in the Nd-Cu diffusion processed sample is ferromagnetically coupled in the longitudinal direction [13]. Thus, the Pr-Cu diffusion source appears to be better for the perfect magnetic isolation of the grains in hot-deformed magnets.

This explains the higher coercivity of the Pr-Cu diffusion processed sample ($\mu_0 H_c = 2.6$ T) compared to that of the Nd-Cu diffusion processed sample ($\mu_0 H_c = 2.3$ T). At temperature above $\sim 107^\circ\text{C}$, the anisotropy field of the $(\text{Nd}_{1-x}\text{Pr}_x)_2\text{Fe}_{14}\text{B}$ phase becomes lower than that of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, resulting in a lower coercivity in the Pr-Cu diffusion processed sample above 140°C . The atom probe tomography result (Fig. 7 (c)) and the STEM-EDS maps (Fig. 5 (a)) has shown that Co is depleted from the $(\text{Nd}_{1-x}\text{Pr}_x)_2\text{Fe}_{14}\text{B}$ phase, which leads to a decrease of Curie temperature. This may also cause a steeper decrease of the anisotropy field of the $(\text{Nd}_{1-x}\text{Pr}_x)_2\text{Fe}_{14}\text{B}$ phase. These two microstructure features account for the larger temperature dependence of the coercivity in the Pr-Cu diffusion processed sample ($-0.45\%/^\circ\text{C}$) compared to the Nd-Cu diffusion processed sample ($-0.40\%/^\circ\text{C}$).

Here, we consider how the Pr-rich surface region is formed during the Pr-Cu diffusion process based on the experimental observations. The eutectic temperature of Pr/PrCu is 470°C , 50°C lower than that for Nd/NdCu, 520°C , and $\text{Pr}_{90}\text{Cu}_{10}$ can infiltrate into the hot-deformed magnets only at 580°C [19,20]. This suggests that during the diffusion process, Pr-Cu alloy melts and infiltrates into the hot-deformed magnets by reacting with the Nd-rich intergranular phase. This would make molten (Nd,Pr)-Cu phase at the reaction front even at 580°C . Based on Nd-Fe-B phase diagram, there is a low temperature eutectic reaction between Nd and $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase at temperature of $\sim 680^\circ\text{C}$ [21]. This suggests that existence of molten Nd-rich at the surface of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains cannot react with $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains by a eutectic reaction at temperature of 580°C . However, the molten intergranular phase is (Nd,Pr)-Cu phase in which existence of Pr and Cu may reduce the eutectic reaction temperature between molten (Nd,Pr)-Cu and $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, leading to melting of the surface region of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains at the processing temperature of 580°C . Hence, Pr diffuses into the magnet through liquid intergranular phase and intermixes

with the liquid phase on the surface of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain. On cooling the magnet, the liquid phase containing the higher amount of Pr solidifies to $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ surface region templated from the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain by rejecting excess RE to the remaining liquid phase. During the solidification, Co is also rejected from the solidified $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ phase (Fig. 5 (a) and Fig. 7 (c)), resulting in the formation of the Co-depleted $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ phase. The atom probe result obtained from an intergranular phase in Fig. 8 supports this mechanism. The intergranular phase does not have a uniform Pr composition; *i.e.*, the Pr content in the right side of the intergranular phase was ~38 at.% while that in the left side was ~50 at.%. The $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ phase at the right side of the intergranular phase has the composition of $(\text{Nd}_{0.5},\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ while the one at the left side of the intergranular phase is $(\text{Nd}_{0.8},\text{Pr}_{0.2})_2\text{Fe}_{14}\text{B}$. Thus, the Pr content in the $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ phase appears to be influenced by the Pr content in the neighboring intergranular phase.

Segregation of Co was found at the interface between the intergranular phase and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (Figs. 5-7). Woodcock et al. [22] reported that Co substitutes for Fe at the terminal {001} plane of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ crystal in the Nd-Cu diffusion processed hot-deformed Nd-Fe-B magnets leading to the formation of a distorted region at the (001) surface of $\text{Nd}_2(\text{Fe,Co})_{14}\text{B}$ phase based on molecular dynamic simulations. However, the atom probe tomography and STEM-EDS maps of this work have revealed that Co is segregated in intergranular phase at the interface with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, not in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase (Fig. 5-7). The difference in the observations of the Co distribution might be due to the analyzed samples, Pr-Cu diffusion processed in this work and Nd-Cu diffusion processed magnet by woodcock et al [22]. The formation of Co enriched layer at the interface between the intergranular phase and the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains may cause a local reduction in the magnetic anisotropy, which may act as nucleation sites for magnetic reversed domains during

magnetization reversals. Further studies by first principle calculations will shed light on the influence of Co segregation on the local anisotropy at the surface of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains.

5. Conclusions

The coercivity of a hot-deformed Nd-Fe-B magnet was enhanced from 1.0 T to 2.6 T by the Pr-Cu eutectic diffusion process. A good isolation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains with Pr-rich intergranular phase was found in the Pr-Cu diffusion processed magnet. Atom probe tomography showed that most of the intergranular phases were free from ferromagnetic elements, suggesting $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are magnetically isolated. STEM-EDS and atom probe tomography results showed the formation of Co-rich layer at the interface between intergranular phases and $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains which can act as nucleation sites for reversed magnetic domains during demagnetization process. $(\text{Nd}_{1-x}, \text{Pr}_x)_2\text{Fe}_{14}\text{B}$ phase ($x=0$ to 0.5 at.%) was found at the outer region of $\text{Nd}_2\text{Fe}_{14}\text{B}$ platelet shaped grains, from which Co was depleted. The good isolation of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains with Pr-rich intergranular phase combined with the formation of the $(\text{Nd}, \text{Pr})_2\text{Fe}_{14}\text{B}$ account for the higher room temperature coercivity of the Pr-Cu diffusion processed hot-deformed Nd-Fe-B magnets compared to that of Nd-Cu diffusion processed magnets. The depletion of Co from the Pr-rich surface region and the steeper temperature dependence of the anisotropy field of the $(\text{Nd}_{1-x}, \text{Pr}_x)_2\text{Fe}_{14}\text{B}$ phase account for the large temperature degradation of coercivity for the Pr-Cu diffusion processed magnet ($\beta=-0.45\text{ }^\circ\text{C}^{-1}$) compare to the Nd-Cu diffusion processed magnet ($\beta=-0.40\text{ }^\circ\text{C}^{-1}$).

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Table 1: Magnetic parameters ($\mu_0 M_s$, K_1 , and A) of $\text{Nd}_2\text{Fe}_{14}\text{B}$ and $(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$ phases at different temperatures used for the micromagnetic simulation [16,17]. It was assumed that saturation magnetization and magnetic anisotropy filed changes linearly from $\text{Nd}_2\text{Fe}_{14}\text{B}$ to $\text{Pr}_2\text{Fe}_{14}\text{B}$ for $(\text{Nd}_{1-x}\text{Pr}_x)_2\text{Fe}_{14}\text{B}$.

Temperature (°C)	$\text{Nd}_2\text{Fe}_{14}\text{B}$			$(\text{Nd}_{0.5}\text{Pr}_{0.5})_2\text{Fe}_{14}\text{B}$		
	$\mu_0 M_s$ (T)	K_1 (MJ/m ³)	A (pJ/m)	$\mu_0 M_s$ (T)	K_1 (MJ/m ³)	A (pJ/m)
27	1.61	4.3	12.5	1.59	4.99	12.5
67	1.54	3.89	12.0	1.51	4.07	12.0
107	1.46	3.33	11.3	1.43	3.26	11.3
147	1.37	2.64	10.6	1.33	2.48	10.6
207	1.25	1.92	9.7	1.21	1.76	9.7

Figure 1: Maximum energy product, remanent magnetization, and coercivity of Pr-Cu diffusion processed magnets versus the mass fraction content of Pr-Cu covered on hot-deformed Nd-Fe-B magnet prior to the heat treatment.

Figure 2: Coercivity versus temperature of the as hot-deformed, 20 wt. % Nd-Cu diffusion processed, and 20 wt.% Pr-Cu diffusion processed hot-deformed Nd-Fe-B magnet.

Figure 3: Back scattered electron (BSE) SEM and bright field (BF) TEM images of (a, c, e) the hot-deformed sample and (b, d, f) the Pr-Cu diffusion-processed sample. The c-axis direction for each image is shown in the inset.

Figure 4: STEM EDS maps of (a) Fe, (b) Pr, (c) Nd, (d) Cu, (e) Ga, (f) Co obtained from Pr-Cu diffusion processed sample. (g) Micro-beam diffraction pattern obtained from two types of Pr-rich intergranular phases of PrCu and Pr.

Figure 5: (a) STEM EDS maps of Fe, Nd, Co, and Pr obtained from the Pr-Cu diffusion processed sample. (b) and (c) Higher magnification STEM-HAADF images and STEM-EDS maps of Fe, Co, and Cu obtained from region i and ii shown in (a).

Figure 6: STEM-HAADF images obtained from intergranular phases of (a) and (b) as hot-deformed, (c) and (d) Pr-Cu diffusion processed sample. (e) STEM HAADF image and STEM-EDS maps of Fe, Pr, Nd, Cu, Co, and Ga obtained from a thick intergranular phase of the Pr-Cu diffusion processed magnet.

Figure 7: (a) 3D atom probe maps of Nd, Pr, Co, and Cu obtained from Pr-Cu diffusion processed sample. The probing direction is parallel to c-axis of the sample. (b) and (c) 3D atom maps of Nd, Pr, Co, and Cu and composition profile of constituent elements calculated from selected boxes 1 and 2 shown in Pr map in (a).

Figure 8: (a) Schematic illustration of how atom probe sample was prepared from Pr-Cu diffusion processed sample for this 3D atom probe analysis. (b) 3D atom probe maps of Fe, Nd, Pr, and Co. The probing direction is perpendicular to c-axis of the sample. (c) Composition profile of constituent elements calculated from selected box shown in 3D Co map in (b).

Figure 9: modeled hot-deformed Nd-Fe-B magnet with size of $100 \times 100 \times 100 \text{ nm}^3$. $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ surface area are shown in green and intergranular phase with thickness of 4nm is shown in dark red. (b) Simulated coercivity versus temperature of hot-deformed magnet with three conditions; exchange coupled $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (ferromagnetic grain boundary phase) and isolated $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains with non-ferromagnetic intergranular phase with and without $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ surface area.

Figure 10: The magnetization configuration of the modeled samples with a) exchange coupled $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains without $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ surface area, and magnetically isolated $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (b) without $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ surface region and (c) with $(\text{Nd,Pr})_2\text{Fe}_{14}\text{B}$ surface phase at 27 and 187 °C. The nucleation field for each magnetization configuration is shown in the inset.

Figure-1

Figure-2

Figure-3

Figure-4

Figure 5

Figure-6

Figure-7

Figure-8

Figure-9

Figure-10

a) GB : ferromagnetic

$T = 27^{\circ}\text{C}$, $\mu_0 H_N = -3.41 \text{ T}$

$T = 187^{\circ}\text{C}$, $\mu_0 H_N = -1.98 \text{ T}$

b) GB : non-ferromagnetic

$T = 27^{\circ}\text{C}$, $\mu_0 H_N = -4.15 \text{ T}$

$T = 187^{\circ}\text{C}$, $\mu_0 H_N = -2.32 \text{ T}$

c) GB : non-ferromagnetic+Pr-rich surface area

$T = 27^{\circ}\text{C}$, $\mu_0 H_N = -4.21 \text{ T}$

$T = 187^{\circ}\text{C}$, $\mu_0 H_N = -2.24 \text{ T}$