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Coercivity enhancement of hot-deformed Nd-Fe-B magnets by the eutectic grain boundary diffusion process using $Nd_{62}Dy_{20}Al_{18}$ alloy

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ABSTRACT

The eutectic grain boundary diffusion process was applied to a 2-mm-thick hot-deformed Nd-Fe-B magnets using $Nd_{62}Dy_{20}Al_{18}$ alloy as a diffusion source, realizing the coercivity enhancement from 0.91 T to 2.75 T with relatively small remanence deterioration from 1.50 T to 1.30 T. In contrast, the conventional grain boundary diffusion process using Dy-vapor resulted in the degradation of coercivity as the grains are catastrophically coarsened at the processing temperature of 900 °C. Scanning transmission electron microscopy showed the formation of Dy-rich shell at the sides of the $Nd_2Fe_{14}B$ grains and the diffusion of Al into the $Nd_2Fe_{14}B$ grains, explaining the significant improvement in coercivity.

Nd-Fe-B based permanent magnets have been used for traction motors in (hybrid) electric vehicles owing to its ability to induce strong magnetic flux density. Since the application environment causes temperature increase under demagnetization fields, not only high remanence but also high coercivity is required. In order to attain the coercivity around 0.8 T at the operation temperature of 200 °C, about 10 wt% Dy is alloyed in commercial Nd-Fe-B sintered magnets with room temperature coercivity higher than 3 T. The partial substitution of Nd with Dy increases the anisotropy field of $(Nd_{1-x}Dy_x)_2Fe_{14}B$, thereby increasing the coercivity of the magnet [1]. However, the magnetic moment of Dy is antiferromagnetically coupled with that of Fe atom in the $(Nd_{1-x}Dy_x)_2Fe_{14}B$ compound, resulting in a deterioration of magnetization as coercivity increases [2]. Since the natural abundance of Dy is quite limited compared to that of Nd, the development of Dy-free or Dy-saving high coercivity Nd-Fe-B permanent magnets is strongly needed.

Grain size refinement of Nd-Fe-B sintered magnets is one of the effective methods to increase the coercivity without using Dy [3–5]. Sagawa et al. [6] have developed the press-less process (PLP) for sintering the submicron sized powders that were processed by helium-jet milling, realizing the coercivity of 2 T in the sintered magnets with 1 μm grain size. However, further refinement of grain size is difficult using the conventional powder metallurgy route considering the severe oxidation of Nd-rich phases. On the other hand, hot-deformed magnets produced from isotropic melt-spun ribbons followed by proper hot-press and hot-deformation exhibit strong [001] texture and the fine grain size that is comparable to the single domain size of $Nd_2Fe_{14}B$ phase [7–9]. Unlike the conventional sintering process, powder size can be larger than 100 μm, inside which nano-sized grains are dispersed; therefore, individual grain are not exposed to oxygen even if the process is carried out without rigorous control of oxygen. The typical coercivity value, $\mu_0 H_c$, of hot-deformed magnets is around 1.2 T with a remanence, $\mu_0 M_r$, of 1.4 T, which are comparable to those of sintered magnets [10,11]. Strong exchange interaction between $Nd_2Fe_{14}B$ grains through ferromagnetic intergranular phase is the main reason for this relatively low coercivity of the hot-deformed magnets [12–15]. More recently, Liu et al. reported a good correlation between the Nd content in the intergranular phase and the coercivity using atom probe tomography [11], and they suggested that the modification of the intergranular phase would enhance the coercivity further.

Sepehri-Amin et al. demonstrated a dramatic enhancement of coercivity by the eutectic grain boundary diffusion (GBD) process for hydrogen-disproportionation-decomposition-recombination (HDDR) processed Nd-Fe-B powders using $Nd_{70}Cu_{30}$ eutectic alloy as a diffusion source [4]. This eutectic GBD process was later extended to Nd-Fe-B hot-deformed magnets [16], which enhanced the coercivity from 1.5 T to 2.3 T without using Dy. In order to explore the extent of coercivity enhancement by this eutectic GBD process, Liu et al. [17] applied various $Nd_{1-x}M_x$ eutectic alloys to the 2-mm-thick Nd-Fe-B hot-deformed magnets, obtaining the highest coercivity of 2.5 T at room temperature using $Nd_{90}Al_{10}$ as a diffusion source. However, the coercivity measured at 200 °C was only 0.6 T because of poor temperature dependence of

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$\mu_0 H_c$ partly due to the dissolution of Al in the $Nd_2Fe_{14}B$ phase. A higher level of coercivity is required for the applications such as automotive traction motors and wind turbines.

Heavy rare earth (HRE) grain boundary diffusion process was developed for enhancing the coercivity of sintered magnets with the grain size of about 5 μm using Dy-vapor, Dy_2O_3, DyF_3, Tb_3O_4 and TbF_4 [18–21]. However, this method cannot be employed to ultrafine-grain-sized hot-deformed Nd-Fe-B magnets since the high temperature annealing required for the HRE GBDP results in catastrophic grain growth. Recently, Sepehri-Amin reported that Dy-rich interface can be developed without any grain coarsening in Nd-Fe-B hot-deformed magnet using $Nd_{60}Dy_{20}Cu_{20}$ powder as a diffusion source followed by annealing at low temperature of 650 °C [22].

On the other hand, along with the remarkable enhancements of coercivity by using Nd-Cu [4,16,23], Nd-Al [17], Pr-Cu [23–25] or Nd-Dy-Cu [22] as the diffusion source, the diffusion-processed magnets always experienced a significant degradation in remanence due to the infiltration of excessive non-ferromagnetic RE-rich liquid phase into the magnet. Akiya et al. [26] applied an expansion constraint on the c-plane of the magnet during infiltration of RE-rich liquid phase and achieved coercivity enhancement while retaining a relatively high level of remanent magnetization, suggesting controlling the volume fraction of Nd-rich intergranular phase and its distribution would be key factors to obtain high-performance hot-deformed Nd-Fe-B magnets.

The aim of this work is to enhance the coercivity of the hot-deformed Nd-Fe-B magnet with a thickness of 2 mm by the diffusion of Nd-Dy-Al eutectic alloy and to modify the composition of the grain boundary phase by introducing Dy-rich shells in $Nd_2Fe_{14}B$ grains. The mechanism of the coercivity enhancement is also addressed by microstructure studies using scanning electron microscopy (SEM) and aberration corrected scanning transmission electron microscopy (STEM).

Hot-deformed magnet used in this study was in the size of $4 \times 4 \times 2$ mm^3 with the composition of $Nd_{13.2}Fe_{76}Co_{5.6}B_{4.7}Ga_{0.5}$ (at.%). The height reduction of the hot-deformation was 75% at 780 °C. $Nd_{62}Dy_{20}Al_{18}$ alloy ribbons were prepared by the melt-spinning technique. The hot-deformed Nd-Fe-B magnets with entire surface completely covered by the ribbons were heat treated at 700 °C, which was selected based on the melting temperature of the $Nd_{62}Dy_{20}Al_{18}$ alloy, for 1 h. The amount of ribbons was controlled to be about 20 wt% of the starting material. For comparison, Dy-vapor diffusion process was applied to the hot-deformed magnets at 900 °C. All the samples were diffusion processed without any stress or constraint applied. Inductively coupled plasma analysis showed that about 0.27 wt% Dy was introduced in the sample after the process.

0.5-mm-thick plate-like specimens were sliced from the sample parallel to the c-planes from the surface and the center of the sample. Magnetic measurements were carried out using a superconducting quantum interface device vibrating sample magnetometer (SQUID-VSM) applying a maximum magnetic field of 7 T. The magnetization value was determined using the magnetic moment from SQUID-VSM which was calibrated with Ni standard sample, and the density value measured by Gas Displacement Pycnometry System; in this work AccyPyc II 1340 Pycnometer with helium as the inert gas was used for obtaining accurate density measurement. Overall microstructural characterization was conducted using Carl ZEISS CrossBeam 1540EsB and the surfaces of the samples were cleaned using focused ion beam (FIB) before SEM observation. Scanning transmission electron microscopy energy-dispersive spectroscopy (STEM EDS) maps were constructed using Nd-*L*α, Dy-*M*α, Fe-*K*α, Co-*K*α and Cu-*K*α spectra. TEM specimens were prepared with the lift-out method by a focused ion beam on FEI Nanolab Helios 650.

Fig. 1(a) shows the magnetization curves of the hot-deformed magnets diffusion-processed by $Nd_{62}Dy_{20}Al_{18}$ eutectic alloy at 700 °C and Dy-vapor at 900 °C. The coercivity ($\mu_0 H_c$) of the hot-deformed magnet is enhanced from 0.91 T to 2.75 T by the $Nd_{62}Dy_{20}Al_{18}$ grain boundary diffusion process, while the remanence drops from 1.50 T to 1.30 T. In contrast, the hot-deformed magnet treated by the Dy vapor at 900 °C for 4 h showed a slight change in coercivity to 1.0 T without much change in remanence ($\mu_0 M_r$). The S-shaped initial magnetization curve of the hot-deformed magnet has a high-susceptibility region up to around 0.9 T, followed by a lower susceptibility part then increases again to saturation. This kind of behavior indicates the magnetization process takes place by the domain wall displacement in the multi-domain grains; i.e., the domain walls are pinned at the intergranular phase, and then get depinned to reach saturation at a higher external magnetic field [27]. The depinning field increases substantially in the sample diffusion processed with $Nd_{62}Dy_{20}Al_{18}$. On the other hand, the Dy-vapor diffusion processed sample is magnetized in one stage, suggesting all grains are multi-domain particles that can be reversed with domain wall displacements.

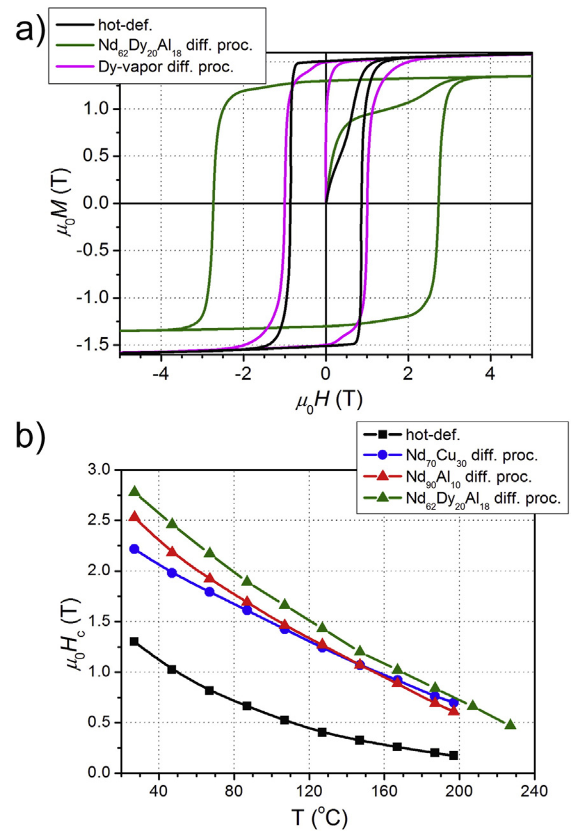

Fig. 1. (a) Magnetization curves of the hot-deformed, $Nd_{62}Dy_{20}Al_{18}$ eutectic diffusion processed and Dy-vapor diffusion processed hot-deformed magnets, and (b) temperature dependence of the coercivity of the hot-deformed, $Nd_{70}Cu_{30}$, $Nd_{90}Al_{10}$ and $Nd_{62}Dy_{20}Al_{18}$ diffusion-processed samples.

Fig. 1(b) shows the temperature dependence of coercivity for the hot-deformed magnets and the samples diffusion processed with $Nd_{62}Dy_{20}Al_{18}$. For comparison, the data of the samples diffusion processed with $Nd_{70}Cu_{30}$ and $Nd_{90}Al_{10}$ are also shown [17]. The sample diffusion processed with Nd-Cu shows $\mu_0 H_c$ of 0.82 T at 180 °C. The Nd-Al diffusion-processed magnet exhibits only 0.76 T at 180 °C while its room temperature coercivity is higher than that of the Nd-Cu diffusion processed sample, 2.52 T [17]. This is because Al is dissolved in the $Nd_2Fe_{14}B$ phase to form $Nd_2(Fe,Al)_{14}B$ phase, by which the Curie temperature decreases while the anisotropy field is increased due to the reduction of M_s. The $Nd_{62}Dy_{20}Al_{18}$ diffusion-processed sample shows the highest coercivity 2.75 T at room temperature, and the coercivity at 180 °C is also the highest, 0.91 T.

Fig. 1(a), (b) and (c) are the backscattered electron SEM images of the samples (a) as hot-deformed, (b) $Nd_{62}Dy_{20}Al_{18}$ diffusion processed, and (c) Dy-vapor diffusion-processed samples, respectively, observed with the c-axis in-plane upward direction. The as hot-deformed sample