

IMPROVEMENT OF THE MAGNETIC PROPERTIES OF $\text{Nd}_2\text{Fe}_{14}\text{B}$ POWDERS BY DYSPROSIUM DIFFUSION

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Received: February 17, 2011

Abstract. Dysprosium powders were diffused into $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic powders to improve their magnetic properties. Initial powders, $\text{Nd}_{12.5}\text{Ga}_{0.3}\text{Nb}_{0.2}\text{B}_{6.4}\text{Fe}_{\text{bal}}$ alloys, were prepared by HDDR process. For diffusion, DyH_x powders were pulverized by zirconia-ball under Ar gas for 5-20 hours. The powders were mixed at a ratio of $\text{DyH}_x:\text{Nd}_2\text{Fe}_{14}\text{B}=3.4:96.6$ and heated to 700-800 °C under vacuum ($\leq 10^{-6}$ torr) for 0.5-16 hours. Their magnetic properties were then measured by VSM, Phases and resulting microstructures were analyzed by XRD and SEM-EDX. The optimum diffusion condition occurred with heating to 800 °C for 2 hr, the resulting magnetic powders had the high coercivity of > 12.2 kOe.

1. INTRODUCTION

Recently, hybrid and electric vehicles have attracted attention because of reduction of fossil fuel and energy reduction. Such vehicles are used electricity, so they have to be adopted by permanent magnet motors or generators. From this reason, permanent magnets were demand for excellent magnetic properties because of improvement energy efficiency [1]. Compared with conventional permanent magnets, Nd-Fe-B ternary rare earth magnets have advantages in terms of coercivity, remanance, maximum energy products [2]. $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets, one of the Nd-Fe-B ternary rare earth magnets, widely used motor industry field. Of these materials, $\text{Nd}_2\text{Fe}_{14}\text{B}$ ternary rare earth magnets produced by hydrogenation-disproportionation-desorption-recombination (HDDR) process have advantages of improvement coercivity (H_c) and maximum energy products ($(\text{BH})_{\text{max}}$) [3~5]. From $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic powders with HDDR process, their magnetic properties were lower than theoretical properties because magnetic material

depends sensitively on a material's microstructure, such as grain size, particle shape, grain boundary type, Curie temperature, and distribution secondary phase [6]. Especially, multi-component materials such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ can have their magnetic properties decreased by low Curie temperature (310 °C), non-magnetic phases (Nd-rich), soft-magnetic phases (α -Fe), and surface defects (surface cracks, pits) [7]. Such defects were limited to the use of applications made by $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic powders.

For elimination or reduction of defects, it is suggested to defects coating by Dysprosium diffuse in $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic powders.

The magnetic properties of $\text{Nd}_2\text{Fe}_{14}\text{B}$ can be highly improved through the addition of dysprosium (Dy), resulting in $\text{Dy}_2\text{Fe}_{14}\text{B}$ on the $\text{Nd}_2\text{Fe}_{14}\text{B}$ surface, because Dy has a greater magnetism than Nd [8]. Furthermore, the effects of defects can be reduced by the dysprosium coating.

Therefore to increase magnetic properties and decrease surface defects, magnetic powder's sur-

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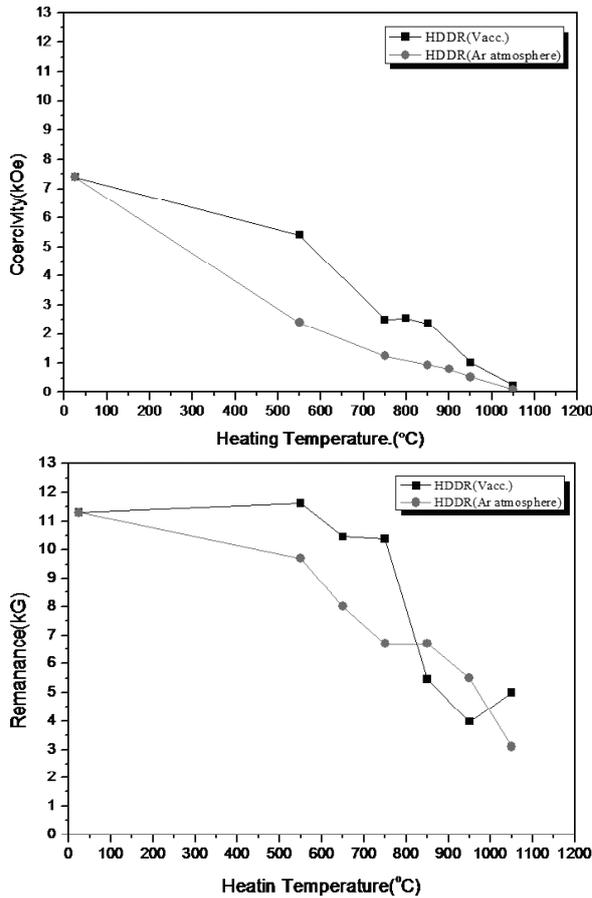


Fig. 1. Magnetic properties of heated $\text{Nd}_2\text{Fe}_{14}\text{B}$ powders produced by HDDR process under Ar- and under vacuum (a) coercivity, (b) remanance.

faces and grain boundaries were coated by a Dy layer using a diffusion process at high temperatures up to 800 °C under high vacuum.

2. EXPERIMENTAL PROCEDURE

Starting alloys of $\text{Nd}_{12.5}\text{Ga}_{0.3}\text{Nb}_{0.2}\text{B}_{6.4}\text{Fe}_{\text{bal}}$ were prepared by mold casting. $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic powders were produced by subsequent HDDR process with starting alloys. Dy diffusion precursors were prepared from DyH_x powder ball-milled in an Ar atmosphere for 5-20 hr. Both powders were mixed with the ratio $\text{DyH}_x:\text{Nd}_2\text{Fe}_{14}\text{B} = 3.4:96.6$ and heated to either 700 or 800 °C for 0.5-16hr at 6×10^{-6} torr, resulting in Dy-treated powders after quenching to room temperature.

These powders' magnetic properties were measured by a vibrating sample magnetometer (VSM, Lakeshore-7400) with a 12 T maximum field. Their phases were analyzed by X-ray diffraction (XRD) with monochromatic $\text{Cu } K_\alpha$ radiation. Microstructure observation and composition analysis were performed by field emission scanning electron microscopy (FE-

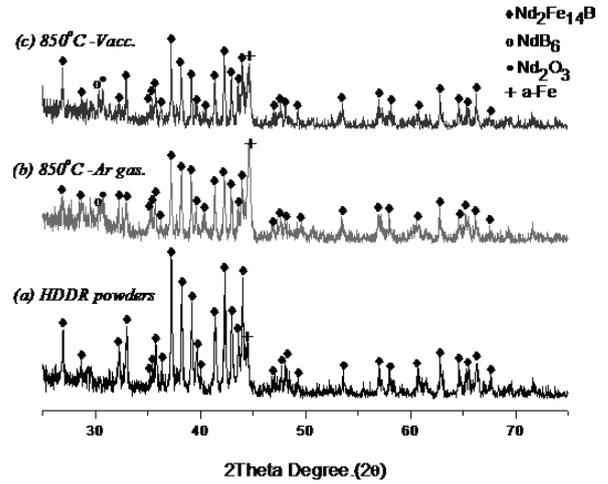


Fig. 2. XRD patterns of heat-treated $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic powders. (a) original HDDR powders, and powders after heating under (b) Ar, and (c) vacuum.

SEM) and energy dispersive X-ray spectroscopy (EDX).

3. RESULTS AND DISCUSSION

$\text{Nd}_2\text{Fe}_{14}\text{B}$ magnetic powders were produced by HDDR process [$H_c = 7.3$ kOe, $B_r = 12.2$ kG] and heated to between 550 and 1050 °C for 1 hr under both Ar gas and vacuum then quenched to room temperature. VSM and XRD analyses of the heated $\text{Nd}_2\text{Fe}_{14}\text{B}$ powders studied their magnetic properties at high temperature. Fig. 1 shows the VSM results of heated HDDR powders. Powders' coercivity and remanance drastically decreased under both Ar and vacuum with heating. Furthermore, the lowest coercivity and remanance were observed at 1050 °C under both Ar and vacuum.

Fig. 2 shows the heated $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet powders' XRD patterns at 850 °C under both Ar and vacuum. Compare to HDDR powder, boron-rich (NdB_6), oxidation (Nd_2O_3) and soft magnet ($\alpha\text{-Fe}$) phases were observed by each heating conditions. Their magnetic properties drastically decreased ($H_c \leq 3$ kOe, $B_r \leq 7$ kG, 850 °C) owing to secondary phases [10].

Fig. 3a shows XRD patterns of the as-received DyH_x powders. From this, Dy precursors of 23.1–1 μm (Figs. 3b-3f) were prepared by ball-milling with hexane for 5-20 hr at 40 rpm under Ar.

To improve their magnetic properties, dysprosium was diffused into them at high temperatures 700 and 800 °C for 0.5–20 hr under a 6×10^{-6} torr vacuum. These powder' XRD patterns and VSM results are shown in Figs. 4 and 5.

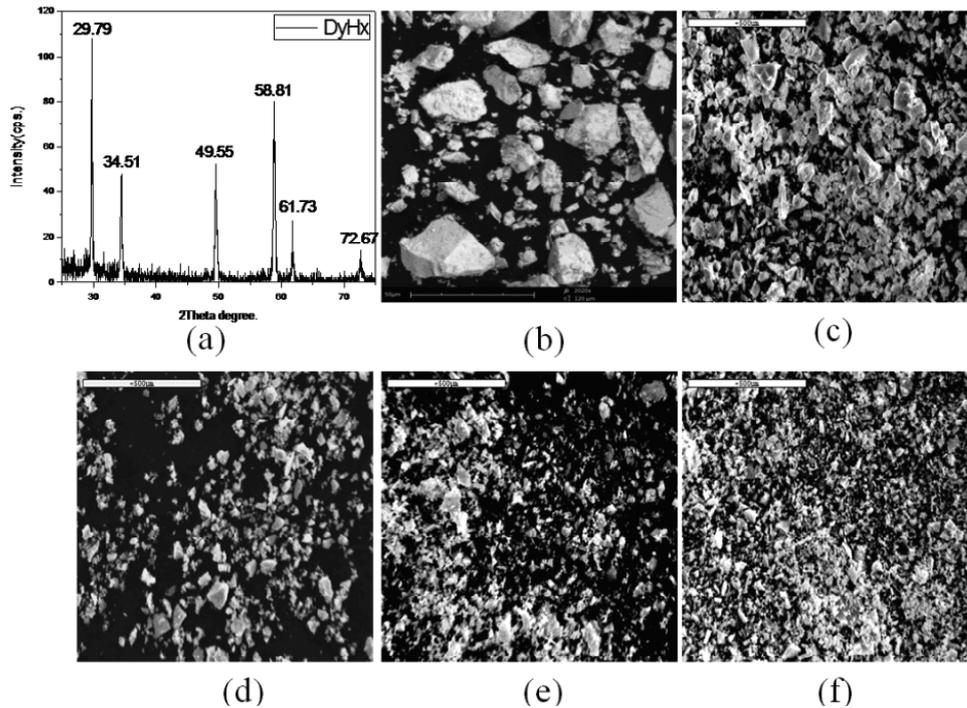


Fig. 3. XRD and SEM analyses of DyH_x . (a) XRD results before ball-milling. SEM images (b) as-received and (c-f) after ball-milling for 5, 10, 15, 20 hr, respectively.

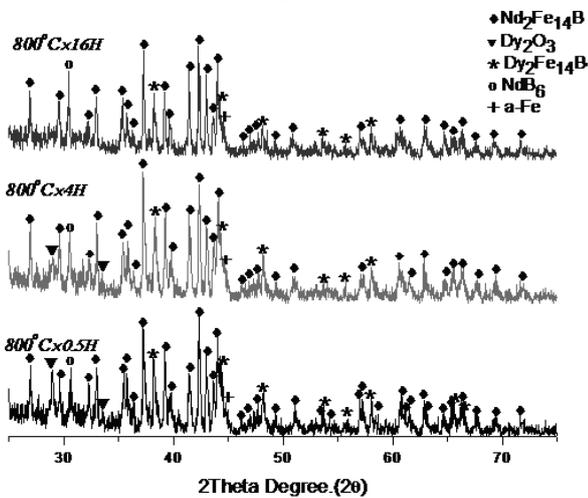


Fig. 4. XRD patterns of Dy diffusion-treated $Nd_2Fe_{14}B$ magnet powders heated at 800° for 0.5 – 16 hr under 6×10^{-6} torr vacuum.

The formation of $Dy_2Fe_{14}B$ was confirmed by the XRD patterns of the resulting Dy-treated powders (Fig. 4). Typical diffraction patterns of $Nd_2Fe_{14}B$ and $Dy_2Fe_{14}B$ phases were observed all the Dy-treated powders. The Dy-treated powders had reduced intensity of the α -Fe peak compared with $Nd_2Fe_{14}B$ powders that were only heat treated. The powders Dy-treated for 16 hr showed an increased boron-rich (NdB_6) peak compared with the Dy-treated powders for 0.5 and 4 hr.

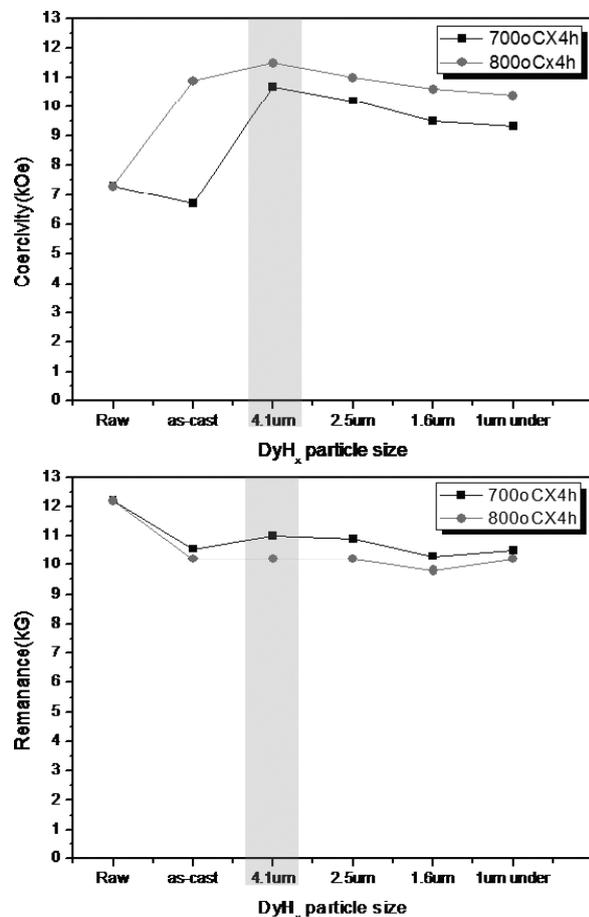


Fig. 5. (a) Coercivity and (b) remanance after treatment with different sized Dy precursors at 700 and 800 °C for 4 hr under 6×10^{-6} torr vacuum.

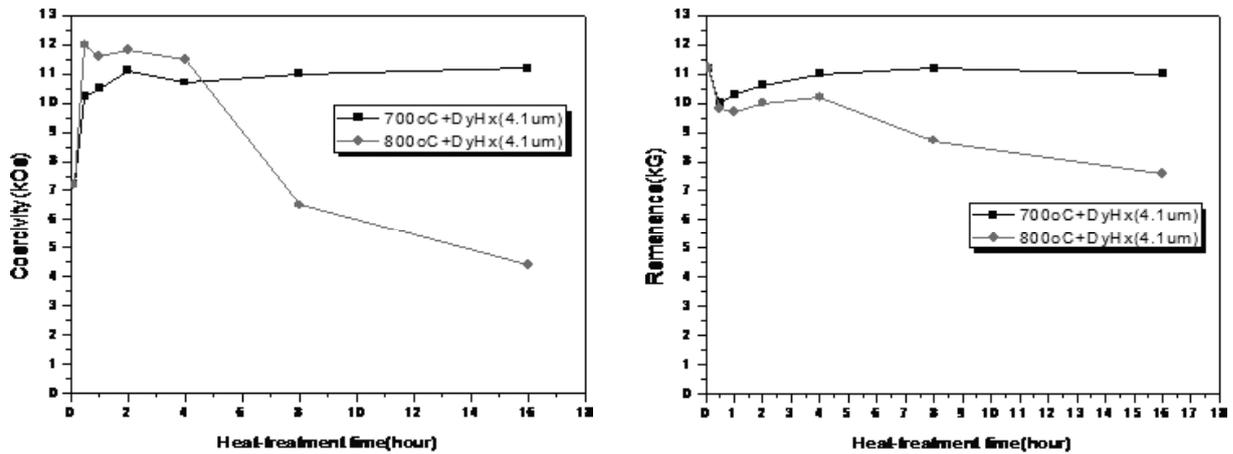


Fig. 6. (a) Coercivity and (b) remanence after diffusion treatment with 4.1 μm Dy at 700 and 800 $^{\circ}\text{C}$ for 0.5 – 16 hr under 6×10^{-6} torr vacuum.

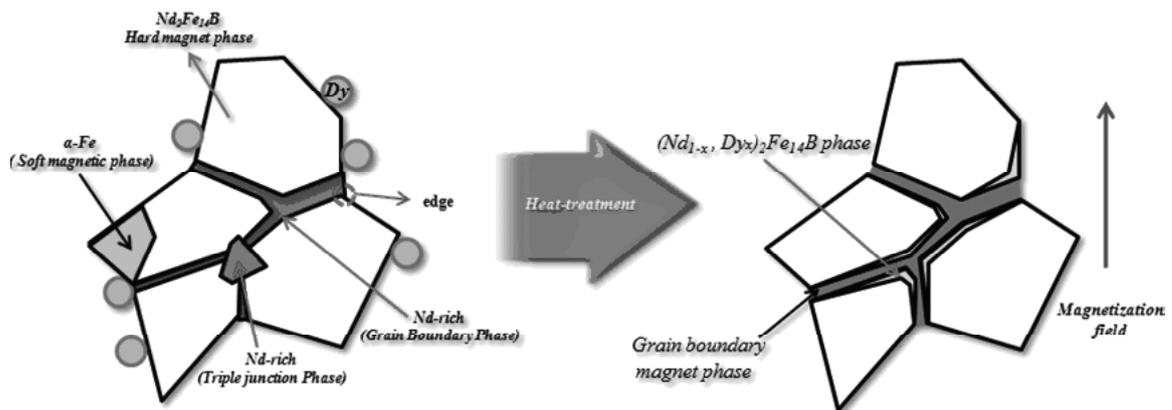


Fig. 7. Schematic illustration for the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains of Dy diffusion-treated magnets.

Fig. 5 shows the efficacy of Dy diffusion in increasing magnetic properties. The diffusion process with Dy precursors ($< 23 \pm 1 \mu\text{m}$) at 800 $^{\circ}\text{C}$ for 2 hr resulted in a significant improvement of the coercivity. In particular, Dy-treatment using the 4.1 μm (5 hr milled) precursor gave maximum coercivity at 800 $^{\circ}\text{C}$ (11.5 kOe, Fig. 5a). However, remanance slightly decreased when Dy diffused into the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet powder. Dy diffusion treatment generally lowered remanance by ca. 10% because the volume fraction of Fe in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase decreased as Dy atoms substituted the Fe [11] and the antiparallel magnetic moment alignment of Dy and $\text{Nd}_2\text{Fe}_{14}\text{B}$ also decreased remanance [12]. The magnetic properties of powders diffusion treated with 4.1 μm Dy precursor for different durations are shown in Fig. 6. Coercivity was optimized at 12.2 kOe with heating to 800 $^{\circ}\text{C}$ for 0.5 hr, compared with the 7.3 kOe of the original $\text{Nd}_2\text{Fe}_{14}\text{B}$. With heat-treatment longer than 4 hr, coercivity decreased by 7 kOe (Fig. 6a). Dy diffusion treatment decreased remanance by ca. 10%, as described under (Fig. 6b).

Dy treatment of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ powders facilitated the partial replacement of Nd atoms in the $\text{Nd}_2\text{Fe}_{14}\text{B}$

phase with Dy atoms at the interface of the grain boundary (Fig. 7), and it formed both $\text{Dy}_2\text{Fe}_{14}\text{B}$ and grain boundary magnet phase. The surface defects (grain boundary edge, pits, surface cracks) that decrease magnetic properties were coated by Dy as it diffused into the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets' grain boundaries, thus increasing the material's magnetic properties. Therefore, only a small amount of Dy precursor was required to improve markedly the coercivity of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ powders [13].

And multi domain particles like $\text{Nd}_2\text{Fe}_{14}\text{B}$ are subdivided into homogeneously magnetized domains, in which magnetization is oriented along an easy axis. The transition region between two domains, which ranges over several lattice planes, is the domain wall. By applying reversed magnetic fields to the multi domain particles, domains with weaker magnetization compared with others were rotated (Fig. 8.1). The rotated domains interacted with their neighbors through coupling effects and made these neighboring domains more easily rotated by the applied reversed magnetic field (Fig. 8.2). Eventually under a continuous reverse field,

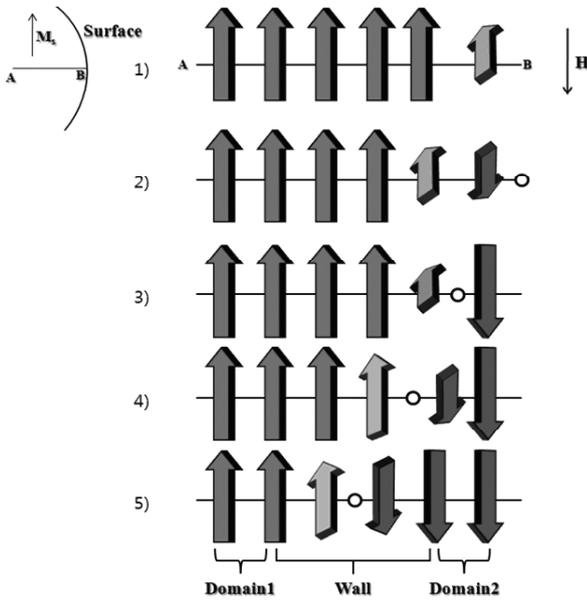


Fig. 8. Schematic illustration for the exchange interaction between $Nd_2Fe_{14}B$ domains.

two distinct domains emerge by “Barkhausen jump” that are separated domain walls [14].

However, when Dy diffused into the grain boundaries, grain boundary magnet phases were created that eliminated coupling effects between adjacent, oppositely magnetized domains. Dy diffused grain boundaries are created a locally hard magnet phase of $Dy_2Fe_{14}B$, which allows better coercivity than in un-treated magnets [15].

Fig. 9 shows FE-SEM images of Dy-treated and un-treated $Nd_2Fe_{14}B$ powders’ microstructures. Powders that only underwent HDDR process had an average particles size of 400 nm. The powders Dy-treated at 800 °C for 0.5 hr with 4.1 μm Dy precursor were slightly larger (450 nm). However, those treated for 16 hr much larger still (850 nm).

Generally, the magnetic properties were influenced by particles’ sizes. Coercivity gradually increased with diminishing particle size until a critical point, after which it tended to zero with further shrinking by thermal effects (Fig. 10). The relation between particle’s size and coercivity, multi-domain particle can be expressed as [14]

$$H_{ci} = a + b/D, \tag{1}$$

where a and b are constant value while D is diameter of particle. In particular, particles’ larger surface areas have a lot magnet defects that would decrease the magnetic properties. Magnet defects can arise more easily when domains can be rotated with lower demagnetization fields. From this follows

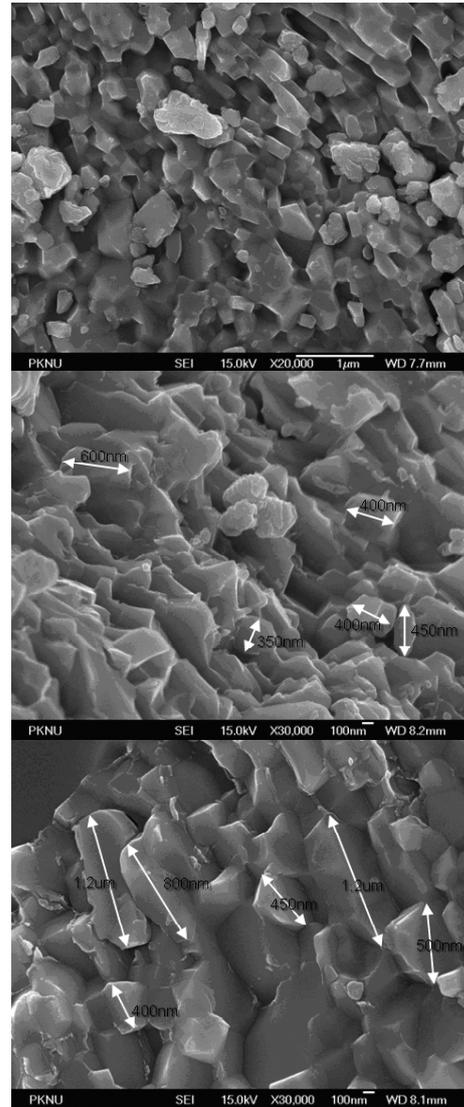


Fig. 9. FE-SEM images of Dy diffusion-treated $Nd_2Fe_{14}B$ surfaces heated at 800 °C for 0, 0.5, 16 hr (a, b, and c) under 6×10^{-6} torr vacuum.

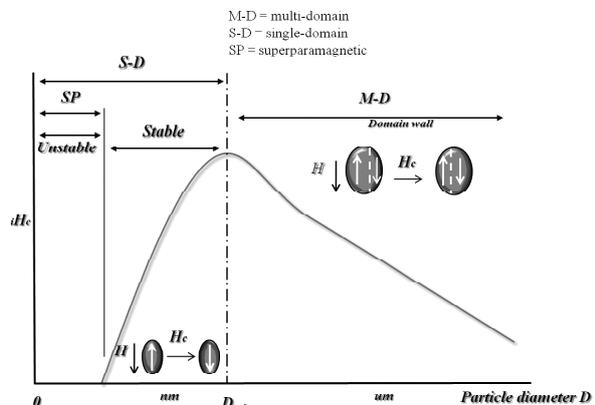


Fig. 10. Schematic representation of coercive field as a function of the particle size D .

that $Nd_2Fe_{14}B$ powders with larger grained particles had decreased magnetic properties [16].

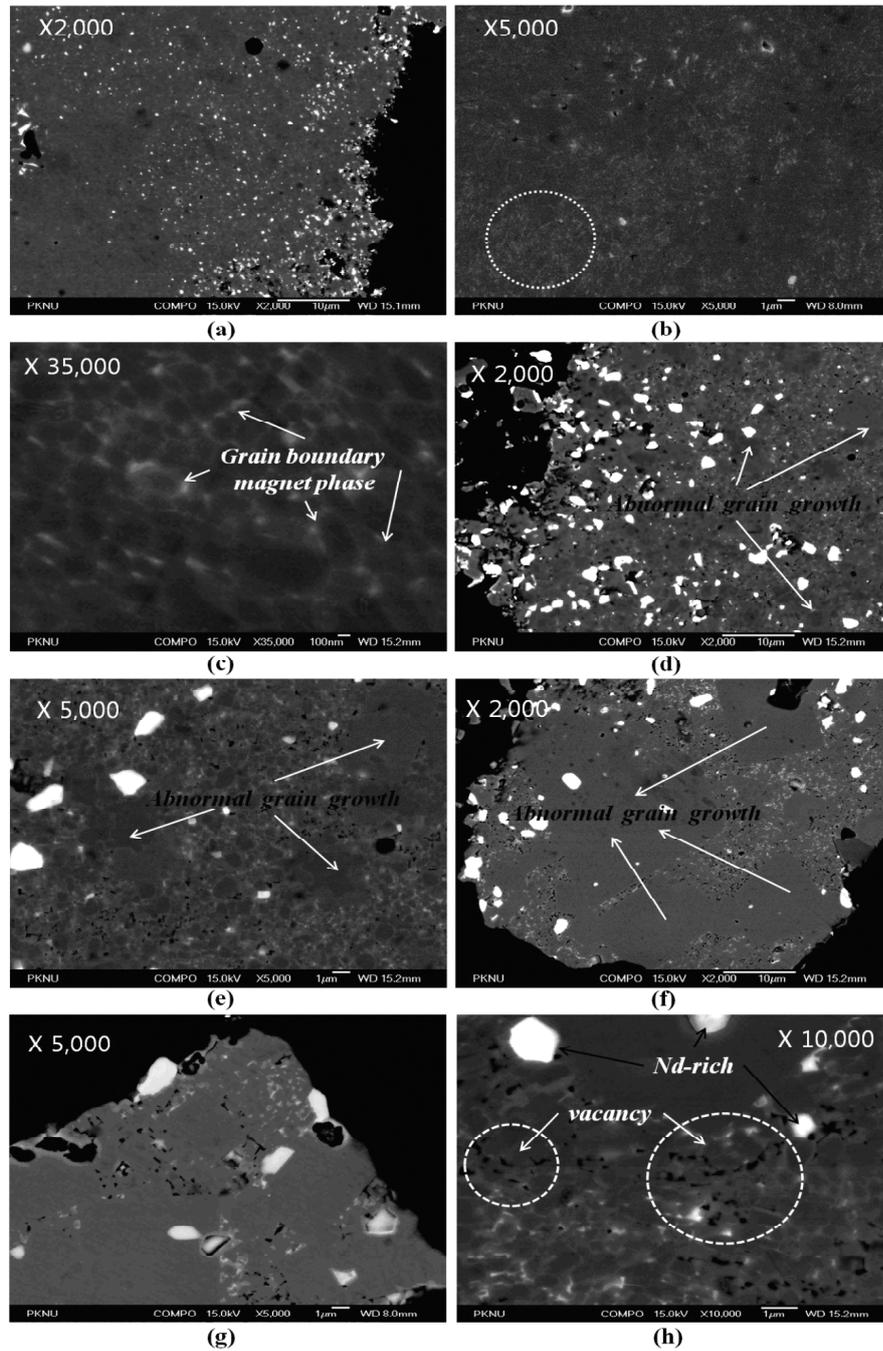


Fig. 11. Cross-sectional FE-SEM images of $\text{Nd}_2\text{Fe}_{14}\text{B}$ surfaces Dy diffusion treated at $800\text{ }^\circ\text{C}$ for (a,b,c) 0.5 hr, (d,e,f) 4 hr and (f,g,h) 16 hr under 6×10^{-6} torr vacuum.

Table 1. EDX measurements after Dy-treatment at $800\text{ }^\circ\text{C}$ for 0.5 hr (1-4) and 16 hr (5-7).

	Nd (weight%)	Fe (weight%)	Dy (weight%)	Totals
1	28.15	70.10	1.75	100
2	29.09	69.45	1.46	100
3	28.82	69.95	1.23	100
4	25.79	74.21	-	100
5	24.96	72.23	2.72	100
6	35.56	65.38	0.76	100
7	85.20	5.49	9.32	100

To clarify the effect of treatment time on the magnetic properties of Dy-treated $\text{Nd}_2\text{Fe}_{14}\text{B}$ powders, FE-SEM and EDX were used to analyze powders Dy-treated at 800 °C for 0.5, 4 and 16 hr. Figs. 11a-11c show the cross-sectional FE-SEM images of Dy-treated $\text{Nd}_2\text{Fe}_{14}\text{B}$ powders for 0.5 hr. In the surface region, Dy atoms made up 1.23 - 1.75 wt.% (Fig. 11a, Table 1). They were not found close to the cores of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ particles. Grain boundary diffusion magnet phase are confirmed in Fig. 11c. Compare with Dy-treated powders of 0.5 hr, both Nd-rich phases and vacancies were observed in the microstructure for 4 hr treatment (Figs. 11d and 11e). In addition, powders Dy-treated for 16 hr showed abnormal grain growth (Fig. 11f), with Nd-rich phases and vacancies being created because of the long treatment time (Figs. 11g and 11h). From above VSM results (Fig. 6), they therefore had, decreased magnetic properties.

4. CONCLUSIONS.

Dy diffusion process was studied and optimized to increase the magnetic properties of $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnet powders made by HDDR.

It effectively improved the powders' coercivity, which increased 64% from 7.3 to 12.2 kOe when 4.1 μm Dy precursor was used for treatment at 800 °C for 0.5 hr. A concurrent 10% decrease of remanance also occurred.

Longer duration treatment decreased the magnetic properties because it induced abnormal grain growth and defects in the magnets (vacancies, grain boundary edges, surface cracks).

ACKNOWLEDGEMENT

The authors would like to acknowledge support from a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

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