

The Influence of Dehydrogenation Speed on the Microstructure and Magnetic Properties of Nd-Fe-B Magnets Prepared by HDDR Process

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The influence regarding the dehydrogenation speed, at the desorption-recombination state during the hydrogenation-disproportionation-desorption-recombination (HDDR) process, on the microstructure and magnetic properties of Nd-Fe-B magnetic powders has been studied. Strip cast Nd-Fe-B-based alloys were subjected to the HDDR process after the homogenization heat treatment. During the desorption-recombination stage, both the pumping speed and time of hydrogen were systematically changed in order to control the speed of the desorption-recombination reaction. The magnetic properties of HDDR powders were improved as the pumping speed of hydrogen at the desorption-recombination stage was decreased. The lower pumping speed resulted in a smaller grain size and higher DoA. The coercivity and the remanence of the 200-300 μm sized HDDR powder increased from 12.7 to 14.6 kOe and from 8.9 to 10.0 kG, respectively. In addition, the remanence was further increased to 11.8 kG by milling the powders down to about 25-90 μm , resulting in $(\text{BH})_{\text{max}}$ of 28.8 MGOe.

Keywords : grain size, hard magnetic materials, HDDR, Nd-Fe-B, anisotropy

1. Introduction

Nd-Fe-B permanent magnets have been used for various applications due to their high maximum energy product $[(\text{BH})_{\text{max}}]$ ever since Sagawa's invention in 1984 and thus, they are now indispensable in our daily life [1]. In particular, the traction motor of hybrid electric vehicles (HEVs) or electric vehicles (EVs) is one of the rapidly growing demands for high performance permanent magnets [1]. On the other hand, their low Curie temperature ($T_c \sim 310^\circ\text{C}$) and high temperature coefficient of coercivity ($\beta \sim -0.6\%/^\circ\text{C}$) impose restrictions on their application in high temperatures above 100°C . In addition, it is quite difficult to modify the intrinsic magnetic properties, such as T_c and β . The most effective method for increasing the coercivity at room temperature (RT) as well as maintain it at a high operating temperature of HEVs or EVs is the partial substitution of a heavy rare-earth (HRE) element, such as Dy or Tb, for Nd in $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets

[3]; further, it should actually be employed in the permanent magnet industry. However, due to the magnets' uneven distribution in the earth crust, low output and high price, HRE-free high-coercivity Nd-Fe-B permanent magnets have drawn great attention [2]. In order to achieve high coercivity without heavy rare earth elements, the control of microstructures, such as grain size and grain boundary, is of significant importance. With regard to grain size, it is desirable to decrease the size down to a single domain size (~ 250 nm) [3]. Hydrogenation-disproportionation-desorption-recombination (HDDR) process is one of the simple methods to obtain Nd-Fe-B magnetic powders with single domain-sized grains [3, 4]. Furthermore, under optimal conditions, the powders show anisotropic magnetic properties, which are explained by the texture memory effect (TME) model [5]. Therefore, the HDDR process has been expected to become useful in realizing HRE-free high-coercivity Nd-Fe-B permanent magnets. Moreover, many studies have been focused on the consolidation of anisotropic HDDR powders in order to form a bulk permanent magnet with submicron-sized grains by using either hot-pressing or spark plasma sintering (SPS) technique [6-9]. On the other hand, most studies

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on HDDR have been focused on the hydrogenation-disproportionation (HD) stage; however, the desorption-recombination (DR) stage is also regarded as important for the improvement of magnetic properties [10, 11]. In the present study, the influence of dehydrogenation speed, at the DR stage during the HDDR process, on the microstructure and magnetic properties of Nd-Fe-B magnetic powders, which were produced by strip casting, has been studied.

2. Experimental Procedure

Strip-cast alloy with the nominal composition $\text{Nd}_{12.5}\text{-B}_{6.4}\text{Ga}_{0.3}\text{Nb}_{0.2}\text{Fe}_{\text{bal}}$ was employed as a starting material. The alloy was first heat treated at 1000 °C for 12 h under Ar atmosphere, then transferred to a glove box, which was directly connected to the furnace; it was then crushed into powder with particle sizes of 200-300 μm . Figure 1 shows a schematic diagram of the experimental equipment that was employed in the present study. After being

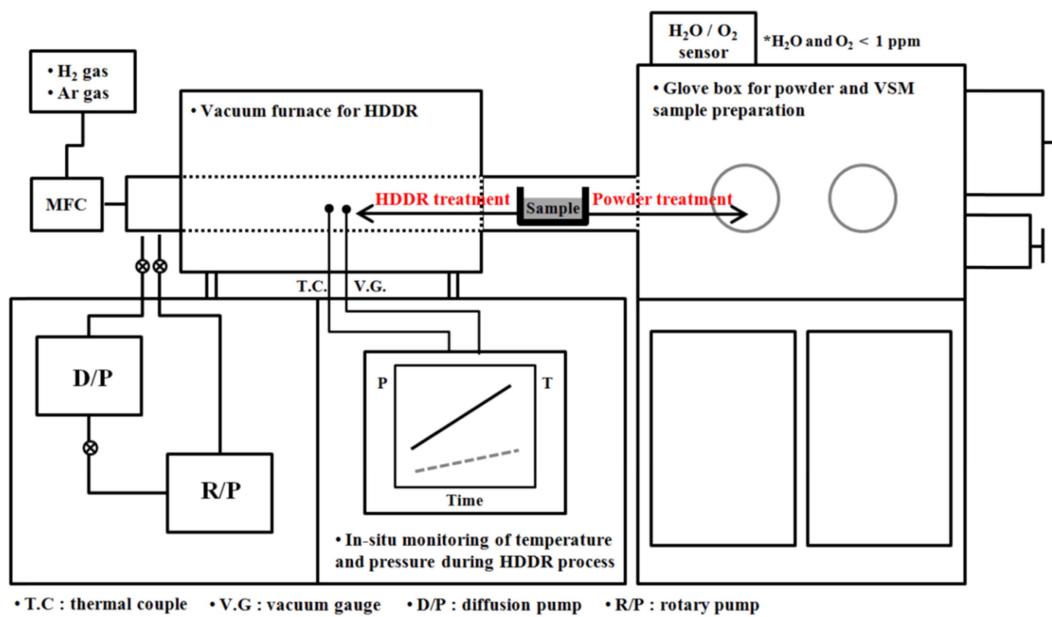


Fig. 1. (Color online) Schematic diagram of experimental equipment.

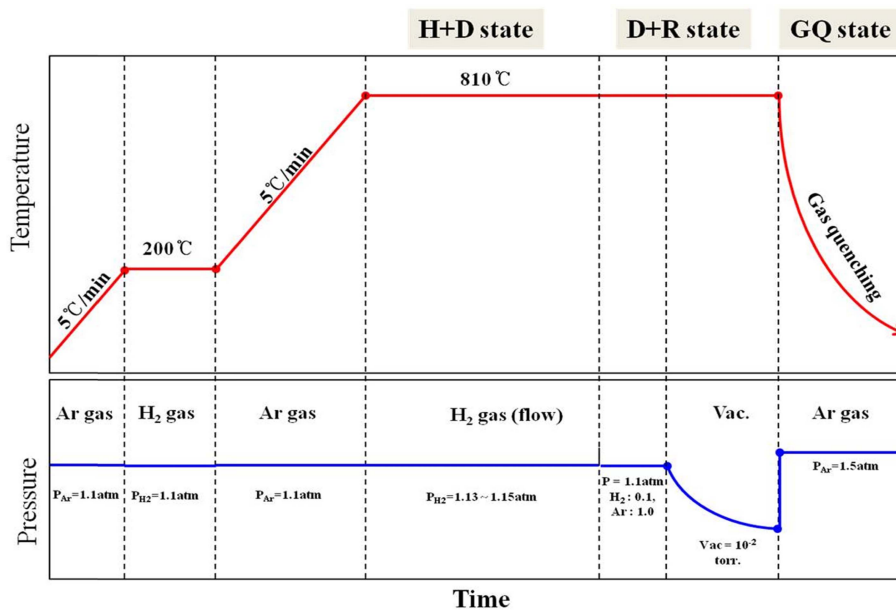


Fig. 2. (Color online) Schematic diagram of MS-HDDR process employed in the present study.

transferred to the furnace again, the powders were subjected to a modified solid HDDR (MS-HDDR) treatment, as schematically shown in Fig. 2. The powders were heated up to 200 °C and maintained for 30 min in H₂ atmosphere. The furnace was then evacuated in order to remove H₂ gas. This hydrogenation-desorption (HDe) treatment, prior to solid HDDR (S-HDDR) treatment, helps the subsequent HD reaction to uniformly take place inside and outside of the powders [12, 13]. After the HDe stage, the powders were again heated up to 810 °C under Ar atmosphere; then, H₂ gas was introduced up to the pressure of 1.1 atm in order to induce an HD reaction. This HD reaction was carried out for 90 min. In the DR stage, the furnace was maintained for 10 min under the Ar-H₂ mixed gas (1.1 atm, (the partial pressure of H₂ was 0.1 atm)). Then, the furnace was evacuated in a different manner. First, it was evacuated directly to a low vacuum under 0.1 atm with a rotary pump (N-DR, hereafter). Second, it was gradually evacuated down to 0.6 and 0.1 atm and maintained for 2 min or 5 min at each step (2M-DR or 5M-DR, hereafter). Finally, the powders were quenched using Ar gas down to RT. The magnetic properties of the powders were measured using a vibrating sample magnetometer (VSM) after pre-magnetizing with a 5 T pulsing field. Anisotropy of the HDDR powder was determined by the degree of alignment (DoA), which is defined by $(B_r(\parallel) - B_r(\perp)) / B_r(\parallel) \times 100$ (%), where $B_r(\parallel)$ and $B_r(\perp)$ are the remanence along the direction parallel and perpendicular to the aligning direction, respectively. The microstructure of the powders was examined with a scanning electron microscope (SEM). Finally, any changes in temperature and pressure during the MS-HDDR process were monitored in real-time.

3. Results and Discussion

Figure 3 shows the microstructural change of the strip-cast alloy by homogenization heat treatment. The typical microstructure of the strip-cast alloy perpendicular to the direction of the solidification observed with an optical microscope is shown in Fig. 3(a). It is well known that the strip-cast alloy consists of a hard magnetic phase (Nd₂Fe₁₄B), which is indicated as a white columnar grain. The thickness of the columnar grains is approximately 5 μm, as shown in Fig. 3(a). Thin dark regions at the grain boundaries consist of the Nd-rich phase. There is no indication of a formation of dendritic α-Fe or other phases. The grain size of the strip-casting alloy is not suitable to obtain high-performance magnetic powders via HDDR treatment. Even if these powders were subjected to HDDR treatment, they should be pulverized down to 5 μm in

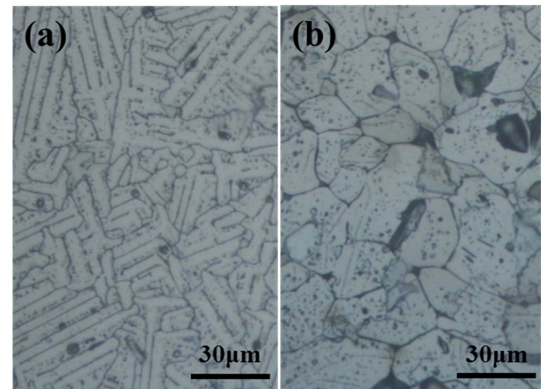


Fig. 3. (Color online) Cross-section images of strip cast alloy (a) before heat treatment (b) after heat treatment at 1000 °C for 12 h under Ar atmosphere.

order to obtain a high DoA. The texture of HDDR-treated powders strongly depends on that of parent powders. Therefore, if the texture of the parent powders is random, HDDR-treated powders also have an isotropic microstructure. For this reason, the HDDR process is useful for a single crystalline parent powder to obtain an anisotropic microstructure. In the case of polycrystalline parent powders, they should be pulverized down to the grain size of the parent powders after HDDR treatment in order to obtain a high DoA. However, in this case, such a small-sized powder can be easily oxidized, thereby resulting in a significant decrease of coercivity. Hence, the grains need to be made bigger by heat treatment prior to HDDR treatment. Fig. 3(b) shows the microstructure of the same alloy after heat treatment at 1000 °C for 12 h under Ar atmosphere. The grain size increased to about 20-30 μm.

Figure 4 presents the demagnetization curves of the HDDR powders in the size range of 200-300 μm, obtained by using two different DR rates. It should be noted that

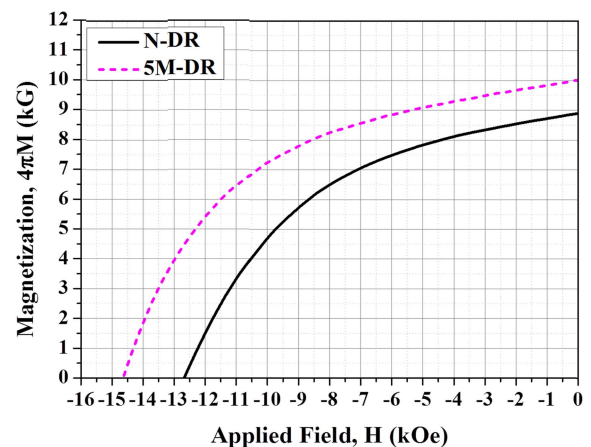


Fig. 4. (Color online) Demagnetization curves of the HDDR powders produced by different hydrogen desorption rates.

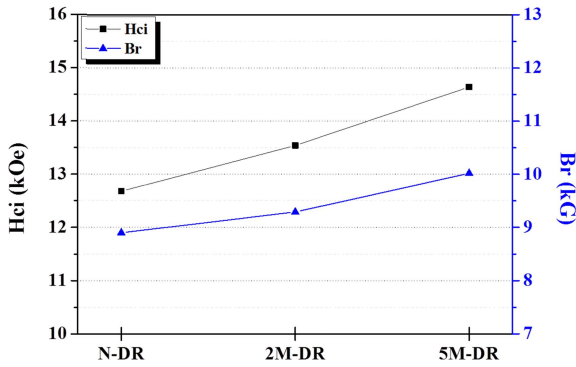


Fig. 5. (Color online) Dependence of HDDR powders' magnetic properties on DR process.

the remanence and coercivity of the HDDR powder obtained by the 5M-DR process is higher than that of the powder obtained by the N-DR process. Figure 5 depicts the dependence of remanence and coercivity on the DR process. The remanence gradually increased from 8.9 to 10.0 kG, with a decreasing hydrogen desorption rate during the DR stage. In addition, the coercivity also increased from 12.7 to 14.6 kOe. From the results in Fig. 4 and Fig. 5, it can be concluded that a slower hydrogen desorption during the DR stage results in a simultaneous enhancement in both the remanence and coercivity of the HDDR powders. This simultaneous increase in both the remanence and coercivity is probably due to a higher DoA and smaller grain size.

Figure 6 shows the microstructure of the HDDR powders. In Fig. 6, it is clearly shown that the grain size of the powders produced by the 5M-DR process is more uniform and smaller than that produced by the N-DR

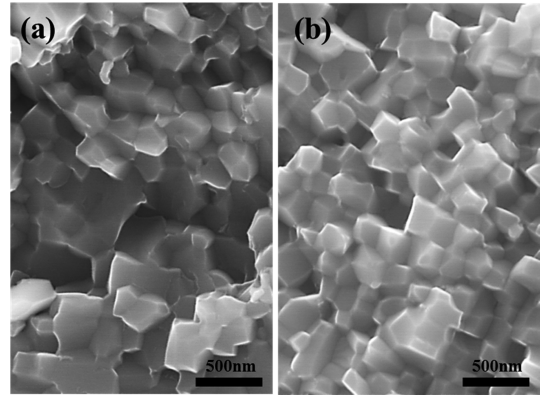


Fig. 6. SEM image of the HDDR powder produced by (a) N-DR, (b) 5M-DR process.

Table 1. Typical magnetic properties of the powders produced by different DR conditions.

DR condition	Particle size (μm)	H_{ci} (kOe)	B_r (kG)	$(BH)_{\text{max}}$ (MGOe)	DoA (%)
N-DR	200-300	12.7	8.9	16.6	51.4
2M-DR	200-300	13.5	9.3	18.4	
5M-DR	200-300	14.6	10.0	21.2	66.7
	25-90	13.9	11.8	28.8	77.2

process. Further, it is close to a single domain size of the $\text{Nd}_2\text{Fe}_{14}\text{B}_2$ phase, which is approximately 250 nm. It is well known that as the grain size decreases, the coercivity increases; it goes through a maximum at the single domain size and then tends toward zero [14]. In fact, it has been recently reported that the coercivity (H_c) of Nd-Fe-B permanent magnets increased as the grain size

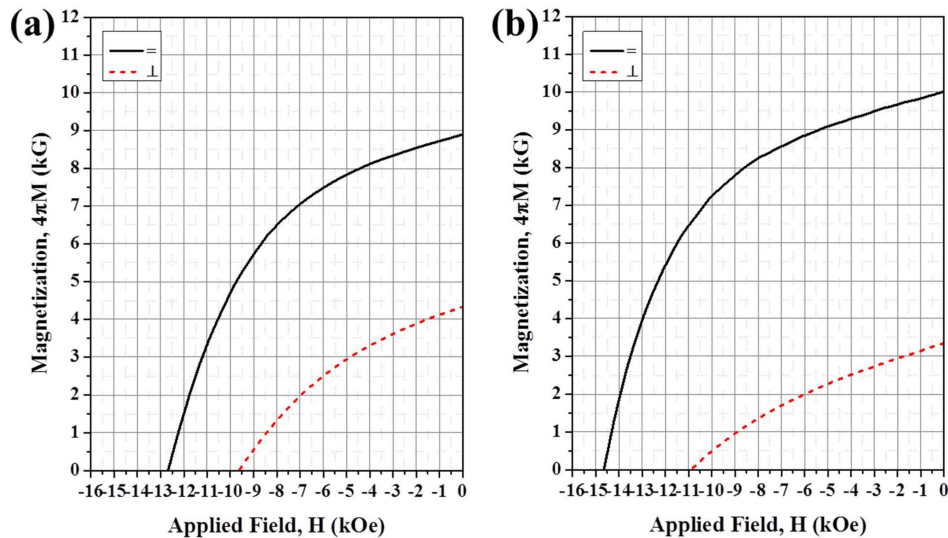


Fig. 7. (Color online) Demagnetization curves of the HDDR powder measured both parallel and perpendicular to the aligning direction. (a) N-DR (b) 5M-DR process.

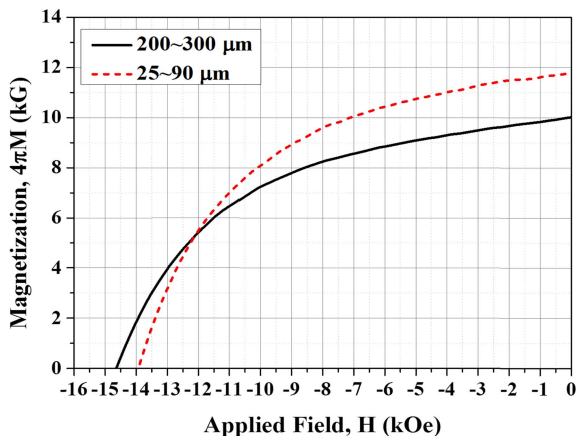


Fig. 8. (Color online) Demagnetization curves of the HDDR powder. (a) 200-300 μm sized powder produced by 5M-DR process (b) after milling down to 25-90 μm .

decreased, following $H_c = 24 - 2.6 \ln(D^2)$, where D stands for the average grain size [15]. However, the coercivity of the powders in Fig. 5(b) is much lower than that expected from the above equation. This seems due to the insufficient magnetic decoupling effect at the grain boundary [16]. The magnetic decoupling effect can be maximized when ultrafine grains of the $\text{Nd}_2\text{Fe}_{14}\text{B}_2$ hard phase are isolated by the Nd-rich phase. Thus, it seems that the content of Nd in the alloy employed in this study is not enough to induce a sufficient magnetic decoupling effect. Table 1 lists the typical magnetic properties of the HDDR powders produced by different DR conditions. It should be noted that a slower hydrogen desorption causes a higher DoA. This is the main reason for the increase of the remanence in Fig. 5.

Figure 7 shows the demagnetization curves measured both parallel and perpendicular to the aligning direction with the HDDR powders produced by different DR conditions. The remanence of the HDDR powder produced by the N-DR process both parallel and perpendicular to the aligning direction is 8.9 and 4.3 kG, respectively (Fig. 7(a)), which results in a DoA value of 51.4% (Table 1). Further, the remanence of the HDDR powder produced by the 5-DR process both parallel and perpendicular to the aligning direction is 10 and 3.3 kG, respectively (Fig. 7(b)). Here, DoA of the 5M-DR process is 66.7% and higher than that of the N-DR process. Hence, it is well known that the hydrogen pressure during the HD stage plays a key role for the high DoA [7]. On the other hand, it was confirmed that the DR speed also gives a significant effect on DoA. More specifically, a slower hydrogen desorption rate results in a higher DoA value.

Figure 8 portrays the additional milling effect on the

magnetic properties of the HDDR powder obtained by the 5M-DR process. When the particle size is decreased down to 25-90 μm from 200-300 μm , the remanence largely increased from 10.0 to 11.8 kG, although the coercivity slightly decreased from 14.6 to 13.9 kOe, thereby resulting in the highest $(BH)_{\text{max}}$, 28.8 MGOe in the present study. The powders employed in this study are not single crystalline, but polycrystalline. As aforementioned, the DoA value of the polycrystalline powder can increase via pulverization down to the grain size of the initial powders after the HDDR process. The increase in the remanence can be attributed to the increasing DoA by milling, as shown in Table 1, whereas the decrease in coercivity may result from oxidation due to the smaller particle size.

4. Conclusion

The influence of the hydrogen desorption rate, at the DR state during the HDDR process, on the microstructure and magnetic properties of Nd-Fe-B magnetic powders has been studied. The magnetic properties of HDDR powders were improved as the pumping speed of hydrogen at the DR stage was decreased. The coercivity and the remanence of 200-300 μm sized HDDR powder increased from 12.7 to 14.6 kOe and from 8.9 to 10.0 kG, respectively. The lower pumping speed resulted in a smaller and more uniform grain size, a higher DoA and a more distinct Nd-rich phase at the grain boundary. In addition, the remanence was further increased to 11.8 kG by milling the powders down to 25-90 μm , which resulted in $(BH)_{\text{max}}$ of 28.8 MGOe.

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