Effects of Hydrogenation-Disproportionation-Desorption-Recombination Processing Parameters on the Particle Size of Ultrafine Jet-Milled Nd-Fe-B Powders

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The effects of variations in the hydrogenation-disproportionation-desorption-recombination (HDDR) processing parameters on the size of Nd-Fe-B ultrafine powders were investigated. The ultrafine powders were fabricated by hydrogen decrepitation and jet milling of the HDDR alloys. Before pulverization, the crystal grain size of the HDDR alloys obtained by changing the HD processing temperature ($T_{HD}$) varied from 0.27 to 0.55 µm, and decreased as $T_{HD}$ was lowered. The ultrafine powder of the HDDR alloy became finer as $T_{HD}$ decreased, with sizes in the range of 0.33 to 0.58 µm.

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1. Introduction

The most common type of rare earth magnets are Nd-Fe-B sintered magnets. They are essential for various products, including generators, electric motors, and hard disk drives. However, their temperature coefficient of coercivity is large, and thus to work at temperatures around 200°C they require a high coercivity of about 3 T at room temperature. The addition of Dy can increase the coercivity of Nd-Fe-B sintered magnets; however, this is expensive and decreases the saturation magnetization. The coercivity can also be increased by grain refinement of the Nd$_2$Fe$_{14}$B phase.¹-⁴ Fine Nd-Fe-B powders about 1.1 µm in size have been prepared from strip-cast (SC) Nd-Fe-B alloys by He jet milling.⁵-⁷ The powders have been used to prepare grain-refined Nd-Fe-B sintered magnets that achieved a high coercivity of 2.0 T without Dy. However, to improve the coercivity of Nd-Fe-B sintered magnets further, ultrafine Nd-Fe-B powders less than 1 µm in size are now required.

In ultrafine Nd-Fe-B powders, Nd$_2$Fe$_{14}$B and Nd-rich phases must be present together in individual particles or in a mixture of particles. The Nd-rich phase melts and diffuses along the grain boundaries during sintering and heat treatment, and reduces the number of nucleation sites.⁸ Therefore, the Nd-rich phase needs to be homogenously distributed over the surface of the Nd$_2$Fe$_{14}$B phase to obtain a high coercivity in Nd-Fe-B sintered magnets. Achieving both grain refinement and homogeneous distribution of the Nd-rich phase is necessary for improving the coercivity of Nd-Fe-B sintered magnets. To prepare ultrafine Nd-Fe-B jet-milled powders (<1 µm), a Nd-Fe-B alloy consisting of homogeneous Nd$_2$Fe$_{14}$B grains smaller than 1 µm covered with the Nd-rich phase is required.

Ultrafine Nd$_2$Fe$_{14}$B grains with an average size of about 0.3 µm in Nd-Fe-B powders are produced by hydrogenation-disproportionation-desorption-recombination (HDDR).⁹,¹⁰ During hydrogenation-disproportionation (HD), the Nd$_2$Fe$_{14}$B phase is decomposed into NdH$_2$, Fe, and Fe$_2$B at 650–1000°C under a hydrogen atmosphere. During desorption-recombination (DR), hydrogen is removed from NdH$_2$ by heating in a vacuum, and NdH$_2$, Fe, and Fe$_2$B recombine into fine Nd$_2$Fe$_{14}$B grains, creating a homogeneous microstructure consisting of Nd$_2$Fe$_{14}$B and Nd-rich grain boundary phases.¹¹-¹³ A promising combination of HDDR and hydrogen decrepitation has been identified as a fabrication method for ultrafine Nd-Fe-B powders: hydrogen decrepitation and jet milling was used to obtain ultrafine Nd-Fe-B powders with an average particle size of 0.33 µm from a HDDR-treated Nd-Fe-B alloy.¹⁴ However, the relationship between the HDDR processing parameters and the grain size of the resulting HDDR alloy has not been reported thus far, and the effects of these parameters on the particle size of the ultrafine jet-milled powder obtained when the HDDR alloy is pulverized is not known. In this study, the effects of different HDDR processing parameters on the grain size of the HDDR alloy and the particle size of the jet-milled powder obtained from it were investigated.¹⁵

2. Experimental Procedure

An SC Nd-Fe-B alloy with a composition of Nd$_{26.2}$Pr$_{4.7}$Fe$_{59.8}$B$_{0.9}$Al$_{0.2}$Cu$_{0.1}$Co$_{0.99}$ (mass%) was used as the starting material. The HDDR treatment conditions were as follows. Figure 1 shows a schematic of the overall treatment process and its parameters. The HDDR treatment consists of two steps. The first step is the HD process, where the alloy is annealed at 850–1000°C for 60 min under a 0.1 MPa hydrogen atmosphere. In this paper, the temperature used for HD treatment is referred to as $T_{HD}$ and a material that has been HD processed and rapidly cooled is referred to as an HD alloy. The second step is the DR process, where the alloy is annealed at 800°C for 10 min in an argon atmosphere, then the furnace is evacuated to a vacuum of 10 Pa or less for 60 min, and the alloy is subsequently cooled to room temperature. An HDDR-treated Nd-Fe-B alloy is thus produced. Table 1 presents a summary of the various HD and HDDR alloys, labeled by the HD processing temperature. Each of the resulting HDDR alloys was hydrogen
decrepitated for 5 h at 200°C and then helium jet milled to produce a series of ultrafine jet-milled Nd-Fe-B powders. For comparison, the original SC alloy was also pulverized by hydrogen decrepitation and helium jet milling. Here, jet-milled powders from the HDDR alloy are referred to as jet-milled HDDR alloy powder and those from the SC alloy are referred to as jet-milled SC alloy powder. The magnetic properties of the powders were measured by a vibrating sample magnetometer (VSM). The powders were aligned with a magnetic field of 2.0 T and fixed with paraffin wax, then magnetized in a pulsed magnetic field of 8.0 T before VSM measurements. We identified phases in the sample by X-ray diffraction (XRD). The microstructure was observed by field-emission scanning electron microscopy (FE-SEM). Grain (particle) size distributions were quantified at cumulative 10%, 50%, and 90% fractions as $d_{10}$ ($D_{10}$), $d_{50}$ ($D_{50}$), and $d_{90}$ ($D_{90}$), respectively. The average grain and particle sizes were defined as the median diameters ($d_{50}$ and $D_{50}$, respectively) and the dimensionless value of the grain and particle size distribution was defined as the relative span ($RS_{\text{grain}}$ and $RS_{\text{particle}}$, respectively) as

$$RS_{\text{grain}} = \frac{(d_{90} - d_{10})}{d_{50}},$$

$$RS_{\text{particle}} = \frac{(D_{90} - D_{10})}{D_{50}}.$$

The values of $d_{50}$, $D_{50}$, $RS_{\text{grain}}$ and $RS_{\text{particle}}$ were calculated from the electron microscope images.

3. Results and Discussion

3.1 Effects of HDDR processing parameters on grain size of the HDDR alloy

Figure 2 shows the XRD patterns for the four HD alloys and the SC alloy. The peaks obtained from the SC alloy correspond to its main phase, Nd$_2$Fe$_{14}$B. In contrast, these Nd$_3$Fe$_{14}$B peaks are not visible in the HD$_{850}$, HD$_{900}$, and HD$_{950}$ alloy, in which NdH$_2$, Fe, and Fe$_2$B peaks are present instead. This shows that a disproportionation reaction occurred upon HD processing at 850–950°C. Furthermore, for the HD$_{1000}$ alloy, NdFe$_4$B$_4$ peaks are observed instead of Fe$_2$B peaks.

Figure 3 shows the XRD patterns for the HDDR alloys, all of which were DR processed at 800°C. In this figure, no NdH$_2$, Fe, or Fe$_2$B peaks are present, indicating that disproportionation occurred. Instead, only Nd$_3$Fe$_{14}$B phase peaks are present. Furthermore, the HDDR$_{1000}$ alloy does not show the NdFe$_4$B$_4$ phase peaks that are present in the HD alloy. This indicates that regardless of $T_{\text{HD}}$, DR processing at 800°C produces a recombination reaction leading to Nd$_3$Fe$_{14}$B phase formation.

The magnetic properties of the SC alloy and HDDR alloys are shown in Table 2. The value of the magnetization measured under an applied field of 2 T is denoted as $\mu_0M_\text{T}$. For the SC alloy, $\mu_0M_\text{T}$ was measured as 0.94 T and the coercivity ($\mu_0H_c$) as 0.10 T. In contrast, for the HDDR alloys, $\mu_0M_\text{T}$ was 0.95–0.97 T, indicating that it remains similar to that the SC alloy, whereas $\mu_0H_c$ increased to 1.12–1.38 T. The $\mu_0H_c$ value of the HDDR alloys tends to be higher for lower $T_{\text{HD}}$, and the HDDR$_{850}$ alloy achieved the highest $\mu_0H_c$ of 1.38 T.

Next, FE-SEM was used to examine the microstructural changes that occur during HDDR processing. Figure 4 shows
a backscattered electron (BSE) image of the SC alloy, and Fig. 5 shows BSE images of HDDR alloys after processing at different values of $T_{\text{HD}}$. In Fig. 4 a lamellar structure is evident, consisting of a bright contrast Nd-rich phase and a gray contrast Nd$_2$Fe$_{14}$B phase. The lamellar spacing between these Nd-rich phases was measured as approximately 3.2 µm on average. Furthermore, the Nd$_2$Fe$_{14}$B phase recombination reaction reached completion in each of the HDDR alloys. This suggests that the gray contrast regions visible in the BSE images of Fig. 5(a)–(d) correspond to the Nd$_2$Fe$_{14}$B phase and that the light contrast regions visible along grain boundaries correspond to the Nd-rich phase. These images show that, relative to the Nd$_2$Fe$_{14}$B phase in the SC alloy, the Nd$_2$Fe$_{14}$B phase in the HDDR alloys has been refined to a submicrometer size and that the Nd-rich phase is present along the grain boundaries. Furthermore, with higher values of $T_{\text{HD}}$, the Nd-rich phase in the HDDR alloys tends to segregate, producing successively larger Nd-rich pools. Figure 5(a)–(d) also shows that the Nd-rich phase is most uniformly distributed in the HDDR850 alloy, for which an average Nd-rich phase spacing of approximately 0.28 µm is calculated from the SEM image, which is less than one-tenth of the 3.2 µm spacing observed in the SC alloy.

Figure 6 shows SEM images of the fracture surface of each of the HDDR alloys and how the grain size increases with higher $T_{\text{HD}}$. Figure 7 shows the grain size distribution of the Nd$_2$Fe$_{14}$B phase in each of the HDDR alloys measured from the SEM images. The distribution profiles shift to the left and become sharper for lower values of $T_{\text{HD}}$ (1000, 950, 900, 850°C); in other words, at lower $T_{\text{HD}}$, the grain size distribution is narrower and the average grain size is smaller. The $d_{10}^\text{grain}$, $d_{50}^\text{grain}$, and $d_{90}^\text{grain}$ fractions and $R_S^\text{grain}$ for each of the HDDR alloy grain size distributions were calculated and are summarized in Table 3. As the grain size distribution becomes narrower, the $R_S^\text{grain}$ value becomes smaller. As the table shows, the average grain size ($d_{50}^\text{grain}$) for the HDDR850 alloy ($T_{\text{HD}} = 850°C$) was measured as 0.27 µm, with a $d_{10}^\text{grain}$–$d_{90}^\text{grain}$ grain size distribution of 0.15–0.38 µm and $R_S^\text{grain}$ of

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{\text{HD}}$ (°C)</th>
<th>$\mu_0M_T$ (T)</th>
<th>$\mu_0M_r$ (T)</th>
<th>$\mu_0H_c$ (T)</th>
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<td>SC</td>
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<td>0.94</td>
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<tr>
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<td>0.97</td>
<td>0.74</td>
<td>1.12</td>
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0.85. As $T_{HD}$ increases, the average grain size increases, the grain size distribution widens, and $RS_{grain}$ increases. These parameters reach their maxima in the HDDR1000 alloy ($T_{HD}=1000^\circ C$), which has an average grain size of 0.55 $\mu m$, a particle size distribution of 0.34–0.99 $\mu m$, and $RS_{grain}$ of 1.18. Thus, the decrease in the coercivity of the HDDR alloy with the increase in $T_{HD}$ (see Table 2) can be attributed to an increase in the grain size of the Nd$_2$Fe$_{14}$B phase in the HDDR alloy. As seen from the table, the average grain size increases from 0.27 to 0.55 $\mu m$ as $T_{HD}$ increases.

3.2 Ultrafine jet-milled Nd-Fe-B powders: particle sizes and magnetic properties

A series of HDDR alloys was prepared with an average Nd$_2$Fe$_{14}$B crystal grain size from 0.27 to 0.55 $\mu m$ by HDDR processing at $T_{HD}$ of 850 to 1000$^\circ C$. Next, a helium jet mill was used to pulverize each of the HDDR alloys and produce a series of submicrometer ultrafine jet-milled Nd-Fe-B powders.

First, each of the alloys was subjected to hydrogen decrepitation for 5 h at 200$^\circ C$. Figure 8 shows a BSE image of the HDDR$_{900}$ alloy after hydrogen decrepitation. Comparing Figs. 8 with 5(b) and 6(b) reveals the presence of cracks along the grain boundaries caused by hydrogen decrepitation of the HDDR$_{900}$ alloy. Next, a helium jet mill was used to pulverize the cracked HDDR alloy finely. SEM images of the jet-milled HDDR powders obtained by pulverizing each of the HDDR alloys are presented in Fig. 9(a)–(d). For comparison, Fig. 10 shows an SEM image of the jet-milled SC alloy powder produced by hydrogen decrepitation of the SC alloy. The jet-milled HDDR alloy powder produced from the HDDR$_{850}$ alloy (Fig. 9(a)) has a relatively coarse particle size of about 2 $\mu m$. Such coarse grains larger than 1 $\mu m$ in size were not observed in the HDDR$_{850}$ alloy prior to pulverization. As a result, the coarse particles observed in Fig. 9(a) are thought to be unpulverized particles. The HDDR$_{850}$ alloy was the finest of the HDDR alloys, with an average grain size of 0.27 $\mu m$, and had the largest volume fraction of the grain boundary phase. A large number of unpulverized particles remained because the hydrogen decrepitation treatment at 200$^\circ C$ for 5 h before pulverization was short and did not induce sufficient cracks in the grain boundaries. Therefore, the alloy could be made easier to pulverize by increasing the hydrogen pulverization time to induce more crack formation. Comparing Fig. 9(a)–(d) and Fig. 10 reveals the jet-milled HDDR alloy powders have smaller particle sizes than those produced from the jet-milled SC alloy powder. The particle size distributions of these jet-milled HDDR and SC alloy powders are shown in Fig. 11, and their corresponding $D_{10}$, $D_{50}$, and $D_{90}$ cumulative fractions and $RS_{particle}$ values are listed in Table 4. In Fig. 11, the jet-milled SC alloy powder has a wide particle size distribution (0.64–1.64 $\mu m$), an average particle size of 1.07 $\mu m$, and $RS_{particle}$ of 0.93. In contrast, for the jet-milled HDDR alloy powders, the particle size distribution profile shifts to the left, and the average particle sizes are smaller. Table 4 shows that the average particle size ($D_{50}$) of these powders ranges from 0.33 to 0.58 $\mu m$, which is roughly half that the 1.07 $\mu m$ particle size obtained by pulverizing the SC alloy. Furthermore, down to a $T_{HD}$ of 900$^\circ C$, a lower $T_{HD}$ is accompanied by a smaller average particle size and a smaller value of $RS_{particle}$ in the jet-milled HDDR alloy powder. This demonstrates the effectiveness of the helium jet mill for
pulverizing the HDDR alloy to produce jet-milled HDDR alloy powder that is finer and has a more consistent size than that produced by the conventional method of pulverizing an SC alloy. Comparing the average grain size and $R_{S_{\text{particle}}}$ values of the HDDR alloys (Table 4) with those of the jet-milled HDDR alloy powders (Table 5) reveals that for the HDDR alloys, the average grain size and $R_{S_{\text{particle}}}$ are increased considerably by pulverization. This is because of the presence of a large number of unpulverized particles (also visible in Fig. 9(a)), leading to a wider particle size distribution. In contrast, at a $T_{\text{HD}}$ of 900°C or above, the values after pulverization remain almost unchanged compared with those before pulverization for all HDDR alloys and regardless of HD temperature. This, together with the observation that hydrogen decrepitation promotes grain boundary fracture (Fig. 8), shows that helium jet milling tends to pulverize HDDR alloys along their grain boundaries.

Table 5 shows the magnetic properties of jet-milled HDDR and SC alloy powders. Compared with the jet-milled SC alloy powders that exhibited a $\mu_{0}H_{c}$ of 0.06 T, all the jet-milled HDDR alloy powders exhibited high $\mu_{0}H_{c}$ (0.13 to 0.17 T) except that prepared at a $T_{\text{HD}}$ of 1000°C. This can be explained by the smaller particle size. Although the jet-milled powder obtained from the HDDR900 alloy had a mean particle size of 0.33 µm, which is near the theoretical value for the size of a single-domain particle, $\mu_{0}H_{c}$ was only 0.17 T. The following two reasons may explain this. First, the jet-milled powder contains adsorbed hydrogen because hydrogen decrepitation was performed before pulverization. Second, many defects are introduced during pulverization by helium jet-milling. We investigated the annealing temperature dependence of the magnetic properties of jet-milled powder, and we confirmed that $\mu_{0}H_{c}$ of the jet-milled powder could be increased by desorption of hydrogen from the jet-milled powder and smoothing the surface of Nd$_{2}$Fe$_{14}$B grain by the liquid Nd-rich phase. Similarly, although the $\mu_{0}M_{MT}$ was 1.36 T for the SC alloy powder, it was 1.27–1.36 T for the HDDR alloy powder. The $\mu_{0}M_{MT}$ was lowest in the jet-milled HDDR alloy powder for a $T_{\text{HD}}$ of 850°C in which many unpulverized particles were observed after pulverization (see Fig. 9(a)). Although the $\mu_{0}M_{MT}$ was 1.36 T, the same as the SC alloy powder, for a $T_{\text{HD}}$ of 900°C the $\mu_{0}M_{MT}$ decreased slightly as $T_{\text{HD}}$ increased. This shows that jet-milled powders can be fabricated from the HDDR alloy prepared at a $T_{\text{HD}}$ of 900°C without degrading the $\mu_{0}M_{MT}$ and with a particle size less than half that of the jet-milled SC alloy powder.

4. Conclusion

The effect of various HDDR processing parameters on the grain size of a Nd$_{2}$Fe$_{14}$B phase in HDDR alloys was investigated. The effect of those parameters on the particle size distribution of jet-milled powders produced by pulverizing those alloys was examined. The results are summarized below.

(1) Upon HDDR processing at a $T_{\text{HD}}$ of 850, 900, 950, or 1000°C, the average grain size of the Nd$_{2}$Fe$_{14}$B phase in the HDDR alloy increased with higher $T_{\text{HD}}$ to 0.27, 0.33, 0.41, or 0.55 µm, respectively. $R_{S_{\text{grain}}}$ also increased with $T_{\text{HD}}$ reaching 0.85, 0.88, 0.90, or 1.18, respectively. However, the coercivity of the HDDR alloy decreased to 1.38, 1.36, 1.23, or 1.12 T, respectively.

(2) By subjecting the HDDR alloys processed at each $T_{\text{HD}}$ to hydrogen decrepitation followed by helium jet milling, a corresponding set of ultrafine jet-milled HDDR alloy powders were obtained. The average particle size was 0.42 µm for the jet-milled HDDR$_{850}$ alloy powder (from the HDDR alloy processed at a $T_{\text{HD}}$ of 850°C), 0.33 µm for the HDDR$_{900}$ alloy powder, 0.47 µm for the HDDR$_{950}$ alloy powder, and 0.58 µm for the HDDR$_{1000}$ alloy powder. Similarly, the values of $R_{S_{\text{particle}}}$ were 1.07, 0.88, 0.91, and 1.21, respectively.

(3) For HDDR at $T_{\text{HD}}$ of 900°C or above, the $d_{50}$ and $R_{S_{\text{particle}}}$ in the HDDR alloys were the same as the $D_{50}$ and $R_{S_{\text{particle}}}$ of the jet-milled HDDR alloy powders from which they were pulverized.

<table>
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<th>Sample</th>
<th>$T_{\text{HD}}$ (°C)</th>
<th>$\mu_{0}M_{MT}$ (T)</th>
<th>$\mu_{0}H_{c}$ (T)</th>
<th>$\mu_{0}M_{c}$ (T)</th>
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<tr>
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<tr>
<td>SC</td>
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<td>1.36</td>
<td>0.59</td>
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Table 5 Magnetic properties of jet-milled HDDR and SC alloy powders.15)
Acknowledgments

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