Effect of Annealing on Magnetic Properties of Ultrafine Jet-Milled Nd-Fe-B Powders

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This paper reports the effects of annealing on the magnetic properties of ultrafine Nd-Fe-B powders with an average particle size of 0.67 μm . The powder was fabricated from hydrogenation–disproportionation–desorption–recombination (HDDR)-treated Nd-Fe-B alloys by hydrogen decrepitation and helium jet milling. The coercivity of the ultrafine powders was slightly increased by annealing below 500°C, and was drastically increased by annealing above 600°C. These two stepwise increases in coercivity were attributed to hydrogen desorption and formation of a liquid Nd-rich phase. In addition, after annealing below 500°C, the coercivity ($\mu_0 H_c$) of the ultrafine powder was higher than that of the conventional powder, which was prepared from a strip-cast Nd-Fe-B alloy powder with a particle size of 1.12 μm , because of a decrease in particle size. In contrast, after annealing above 600°C, the $\mu_0 H_c$ of the ultrafine powder was smaller than that of the conventional powder. The rare earth element content (Nd + Pr) was lower in the ultrafine powders than in the conventional powder. These results indicate that the rare earth element content was insufficient in the ultrafine powders. [doi:10.2320/matertrans.MAW201402]

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1. Introduction

Nd-Fe-B sintered magnets are used in many products, such as hard disk drives and hybrid electric vehicles. Because the temperature coefficient of coercivity is large, the magnets require a high coercivity of about 3 T at room temperature in order to work under high temperatures around 200°C. Addition of Dy increases the coercivity of Nd-Fe-B sintered magnets, but decreases their saturation magnetization and increases their price. Grain refinement of the Nd₂Fe₁₄B phase increases the coercivity of Nd-Fe-B sintered magnets;^{1–4)} therefore, preparation of finer Nd-Fe-B powders is needed in order to obtain high coercivity in sintered magnets. Une and Sagawa^{5–7)} used He jet milling to prepare fine Nd-Fe-B powders with a particle size of approximately 1.1 μm from strip-cast (SC) Nd-Fe-B alloys. This was considerably smaller than the particle size of approximately 3 μm for the powder prepared by conventional N₂ jet milling. Furthermore, they also reported the preparation of grain-refined Nd-Fe-B sintered magnets with a high coercivity of 2.0 T without Dy addition. To further improve the coercivity of Nd-Fe-B sintered magnets, it is necessary to prepare ultrafine Nd-Fe-B powders of less than 1 μm in size. In addition, the ultrafine Nd-Fe-B powders must consist of Nd₂Fe₁₄B and Nd-rich phases. The Nd-rich phase liquefies and spreads along the grain boundaries during sintering and subsequent heat treatment, and is reported to decrease the number of nucleation sites.⁸⁾ Hence, the Nd-rich phase needs to be homogeneously distributed over the surface of the Nd₂Fe₁₄B phase in order to obtain high coercivity in Nd-Fe-B sintered magnets. Simultaneously achieving 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), development of a Nd-Fe-B alloy consisting of homoge-

neous Nd₂Fe₁₄B grains smaller than 1 μm covered with the Nd-rich phase is necessary.

Against this background, we focused on the hydrogenation–disproportionation–desorption–recombination (HDDR) and hydrogen decrepitation processes. It is well known that the HDDR process refines the grain size of the Nd₂Fe₁₄B phase in Nd-Fe-B alloys, and it produces ultrafine Nd₂Fe₁₄B grains approximately 0.3 μm in size.^{9,10)} During hydrogenation–disproportionation (HD), heating at 650–1000°C under a hydrogen atmosphere decomposes the Nd₂Fe₁₄B phase into NdH₂, Fe, and Fe₂B. During desorption–recombination (DR), hydrogen is removed from NdH₂ by heating in a vacuum, and NdH₂, Fe, and Fe₂B recombine into fine Nd₂Fe₁₄B grains. As a result, HDDR gives a homogeneous microstructure consisting of Nd₂Fe₁₄B and Nd-rich grain boundary phases.^{11–13)}

We have previously reported the fabrication of ultrafine Nd-Fe-B powders with an average particle size of 0.33 μm from HDDR-treated Nd-Fe-B alloy through hydrogen decrepitation and He jet milling.¹⁴⁾ However, no reports have covered the effects of annealing on ultrafine Nd-Fe-B powders. Understanding the effect of annealing on the magnetic properties and morphology of ultrafine Nd-Fe-B powders provides useful information for using these powders in sintering because the sintering conditions strongly depend on particle size.^{15,16)} Therefore, in this study, we investigated the effects of annealing on the magnetic properties and morphology of ultrafine Nd-Fe-B powders.

2. Experimental Procedure

The starting material was an SC Nd-Fe-B alloy with a composition of Nd_{27.5}Pr_{4.15}Fe_{bal.}B_{1.0}Al_{0.23}Cu_{0.1}Co_{0.96} (mass%). The HDDR treatment conditions were as follows. HD treatment was performed under a hydrogen atmosphere (0.1 MPa) at 950°C for 60 min. The alloy was annealed at 800°C for 10 min under Ar atmosphere, and then it was also annealed under vacuum (<10 Pa) for 60 min. Finally, the

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alloy was cooled to room temperature, and the DR treatment was performed. The HDDR alloy was subjected to hydrogen decrepitation for 5 h at 200°C under a hydrogen atmosphere, and then pulverized to a powder by He jet milling. For comparison, the original SC alloy was also pulverized by hydrogen decrepitation and He jet milling. Here, jet-milled powders from the HDDR alloy and SC alloy are referred to as “jet-milled HDDR alloy powder” and “jet-milled SC alloy powder”, respectively. The jet-milled HDDR and SC alloy powders were annealed from 100 to 1000°C for 30 min under high vacuum (10^{-4} Pa), and were quenched to room temperature. 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, and then magnetized in a pulsed magnetic field of 8.0 T before VSM measurements. The composition of the powders was determined by X-ray fluorescence (XRF) analysis. The microstructure was observed by field-emission scanning electron microscopy (FE-SEM). The average particle size and particle size distribution are defined as the median diameter (D_{50}) and relative span (RS), respectively. These values were evaluated from the electron microscopy images.

3. Results and Discussion

Figure 1 shows the secondary electron (SE) images of the jet-milled HDDR and SC alloy powders. The jet-milled HDDR alloy powders were more spherical and smaller than the jet-milled SC alloy powders. Figure 2 shows the particle size distribution of the jet-milled HDDR and SC alloy powders. The cumulative distribution (Q) of the jet-milled HDDR alloy powder increased drastically from 10% to 90% as the particle size (D) increased from 0.43 to 1.00 μm . The particle sizes for cumulative distributions of 10% and 90% are defined as D_{10} and D_{90} , respectively. The average particle size is defined as D_{50} for a cumulative distribution of 50%. In addition, the RS , which is a dimensionless value describing the distribution width of the particle size, is defined as

$$RS = \frac{(D_{90} - D_{10})}{D_{50}} \quad (1)$$

As the particle size distribution narrows, the relative span (RS) approaches zero. From Fig. 2, the average particle size was 0.67 μm , and the RS was calculated as 0.85 for the jet-milled HDDR alloy powder. In contrast, the cumulative curve of the jet-milled SC alloy powder increased gradually, and the average particle size (D_{50}) was 1.12 μm . D_{10} and D_{90} were 0.61 and 2.32 μm , respectively, and the RS was calculated as 1.53. Thus, the average particle size of the jet-milled SC alloy powder was approximately twice that of the jet-milled HDDR alloy powder. In addition, the jet-milled SC alloy powder exhibited a wider particle size distribution than the jet-milled HDDR alloy powder.

The jet-milled HDDR and SC alloy powders were annealed at 100–1000°C for 30 min under high vacuum (10^{-4} Pa). Figure 3 shows the annealing temperature dependence of magnetic properties of the jet-milled HDDR and SC alloy powders. In this paper, the value of magnetization measured under an applied field of 2 T is denoted as $\mu_0 M_{2T}$.

Fig. 1 SE images of the jet-milled (a) HDDR and (b) SC alloy powders.

Fig. 2 Particle size distributions of jet-milled (a) HDDR and (b) SC alloy powders.

Fig. 3 Annealing temperature dependence of the (a) magnetization and (b) coercivity of jet-milled HDDR and SC alloy powders.

Without annealing, the value of $\mu_0 M_{2T}$ for both the jet-milled HDDR and SC alloy powders was 1.32 T. The value of $\mu_0 M_{2T}$ for both the jet-milled HDDR and SC alloy powders was slightly decreased by annealing at a low temperature, and was sharply decreased by annealing around 600°C. The

Fig. 4 Demagnetization curves of the jet-milled (a) HDDR and (b) SC alloy powders before and after annealing at 300 and 600°C.

annealing temperature dependence of the coercivity ($\mu_0 H_c$) of the jet-milled HDDR and SC alloy powders is also shown in Fig. 3(b). Before annealing, the value of $\mu_0 H_c$ for the jet-milled HDDR alloy powders was 0.14 T, which was higher than that of the jet-milled SC alloy powders (0.06 T). Annealing at 300–500°C increased the value of $\mu_0 H_c$ of both powders slightly. The coercivity value reached 0.64 and 0.27 T for the jet-milled HDDR and SC alloy powders annealed at 500°C, respectively. Consequently, the value of $\mu_0 H_c$ was larger for the jet-milled HDDR alloy powder than the jet-milled SC alloy powder by annealing below 500°C.

For both the jet-milled powders, $\mu_0 H_c$ was drastically increased by annealing above 600°C. The value of $\mu_0 H_c$ increased from 0.64 to 1.52 T for the jet-milled HDDR alloy powder, and from 0.27 to 1.60 T for the jet-milled SC alloy powder. For annealing temperatures above 600°C, the value of $\mu_0 H_c$ for the jet-milled SC alloy powder was higher than that of the jet-milled HDDR alloy powder. Annealing above 950°C resulted in $\mu_0 H_c$ of the jet-milled HDDR alloy powder dropping to about 0.19 T.

Figure 4 shows the demagnetization curves of the jet-milled HDDR and SC alloy powders before and after annealing at 300 and 600°C. Annealing at 300°C increased the remanence ($\mu_0 M_r$) of both the powders as a result of increasing their $\mu_0 H_c$. In contrast, annealing at 600°C increased $\mu_0 H_c$ dramatically, although it decreased $\mu_0 M_r$ and squareness ($\mu_0 M_r / \mu_0 M_{2T}$) for both jet-milled powders.

Figure 5 shows the SE images of the jet-milled HDDR and SC alloy powders after annealing at 300°C. Comparing Fig. 1 and 5, the morphology and particle size of both powders were almost unchanged by annealing at a low temperature. This indicates that the slight increase in $\mu_0 H_c$ for both the jet-milled powders was not caused by the appearance of the liquid Nd-rich phase but by hydrogen

Fig. 5 SE images of the jet-milled (a) HDDR and (b) SC alloy powders annealed at 300°C.

desorption. The HDDR and SC alloys were crushed by hydrogen decrepitation before jet-milling; therefore, the jet-milled powders still absorbed hydrogen. Book and Harris¹⁷ reported that the desorption of hydrogen from the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase peaks around 150°C, and that the partial desorption of hydrogen from neodymium hydride ($\text{NdH}_{2.7} \rightarrow \text{NdH}_2$) peaks around 250°C. In this study, the slight increase in $\mu_0 H_c$ was obtained by annealing around 300°C without an accompanying change of morphology. These results into consideration, the increase in $\mu_0 H_c$ we observed was caused by hydrogen desorption from the jet-milled HDDR and SC alloy powders.

As shown in Fig. 3(b), $\mu_0 H_c$ of the jet-milled HDDR alloy powder was larger than that of the jet-milled SC alloy powder annealed below 500°C. This is because the morphology of powders was almost unchanged by annealing below 500°C; below 500°C, the liquid Nd-rich phase is not formed. The average particle sizes of the jet-milled HDDR and SC alloy powders annealed at 300°C were evaluated from Fig. 5. The D_{50} of the jet-milled HDDR and SC alloy powders was 0.67 and 1.12 μm , respectively. These results mean that the decrease in particle size is the main factor in the increased $\mu_0 H_c$ of the jet-milled HDDR alloy powder.

Figures 3 and 4 show that the $\mu_0 M_{2T}$ and squareness for both the jet-milled powders decreased by annealing at 600°C. In contrast, $\mu_0 H_c$ was drastically increased by annealing at 600°C for both jet-milled powders. Then, the microstructure was observed. Figure 6 shows the BSE images of the polished surface of the jet-milled HDDR and SC alloy powders before and after annealing at 600°C. The dark and bright regions in the BSE images correspond to the $\text{Nd}_2\text{Fe}_{14}\text{B}$ and Nd-rich phases, respectively. Each particle was dispersed in both the unannealed jet-milled powders (Fig. 6(a) and (b)). After annealing at 600°C, several particles adhered to each other in both the jet-milled powders as shown in Fig. 6(c) and (d). Moreover, the Nd-rich phase (bright contrast), was observed at some grain boundaries in the annealed jet-milled powders. These results indicated that annealing the jet-milled HDDR and SC alloy powders at 600°C melted the Nd-rich phase and bound the individual Nd-Fe-B particles together. The bound particles act as polycrystalline particles, thus they cannot be aligned by an external magnetic field. Therefore, the bound particles decreased the squareness of the hysteresis curves, and consequently decreased the $\mu_0 M_{2T}$.

However, the formation of the liquid Nd-rich phase substantially increased the coercivity. The value of $\mu_0 H_c$ for both the jet-milled powders was increased drastically by

Fig. 6 BSE images of the polished surface of the jet-milled (a) (c) HDDR and (b) (d) SC alloy powders before and after annealing at 600°C.

annealing at 600°C (Fig. 3(b)). The liquid Nd-rich phase can smooth the surface of $\text{Nd}_2\text{Fe}_{14}\text{B}$ grain, and the coercivity increases. Therefore, the reason for the drastic increase in $\mu_0 H_c$ of the jet-milled powders was thought to be the formation of the liquid Nd-rich phase during annealing at 600°C.

Figure 3(b) shows that the $\mu_0 H_c$ of the jet-milled SC alloy powder was higher than that of HDDR alloy powder annealed above 600°C. The amount of the Nd-rich phase is strongly related to the change in coercivity during annealing for the Nd-Fe-B system. For this reason, the rare earth element content (Nd and Pr, which are found in the Nd-rich phase) in the jet-milled powders was analyzed by XRF. The rare earth element content in the jet-milled HDDR alloy powder was 30.0 mass%, and that in the jet-milled SC alloy powders was 31.1 mass%. The rare earth element content in the jet-milled HDDR alloy powder was decreased by 1.65 mass% by jet-milling, and the rare earth element content in the jet-milled HDDR alloy powder is lower than that in the jet-milled SC alloy powder. In contrast, the specific surface area (S_m) was found to be considerably higher in the HDDR alloy powder than in the SC alloy powder as a result of the decrease in particle size. The value of S_m of the powders was calculated as follows:

$$S_m = \frac{6}{\rho D_{50}}, \quad (2)$$

where ρ is the density of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. The jet-milled HDDR alloy powder had S_m of $1.18 \text{ m}^2 \text{ g}^{-1}$, which is 1.7-fold that of the SC alloy powder, $0.71 \text{ m}^2 \text{ g}^{-1}$. To cover the surface of jet-milled particles with the Nd-rich phase, a higher S_m value requires a higher rare earth element content. However, as described above, the rare earth element content was lower in the jet-milled HDDR alloy powder than the SC alloy powder. These results mean that the amount of the Nd-rich phase was insufficient for the jet-milled HDDR alloy powder, leading to a lower coercivity than that of the jet-milled SC alloy powder.

Fig. 7 BSE images of the jet-milled (a) HDDR and (b) SC alloy powders annealed at 950°C.

Annealing above 950°C resulted in a drastic drop in $\mu_0 H_c$ for only the jet-milled HDDR alloy powder (Fig. 3(b)). Figure 7 shows BSE images of the jet-milled HDDR and SC alloy powders after annealing at 950°C. Some coarse $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains several tens of micrometers in size were observed in the jet-milled HDDR alloy powders. In contrast, this abnormal grain growth was not observed in the jet-milled SC alloy powder. Consequently, the large drop in $\mu_0 H_c$ for the jet-milled HDDR alloy powder annealed at 950°C was attributed to the abnormal grain growth.

These results indicate that the sintering temperature must be less than 950°C to prevent abnormal grain growth in jet-milled HDDR alloy powders for sintered magnets. In addition, although the particle size of the jet-milled HDDR alloy powder is smaller than that of the jet-milled SC alloy powder, the amount of rare earth elements is also smaller. Therefore, the addition of an extra Nd-rich phase is necessary for preparing sintered magnets from the jet-milled HDDR alloy powder. Powder preparation conditions need to be determined so that the amount of Nd-rich phase in the jet-milled HDDR alloy powder is at least similar to that in the jet-milled SC alloy powder.

4. Conclusion

In this study, the effects of annealing on the magnetic properties and morphology of ultrafine Nd-Fe-B powder were investigated. The average particle size (D_{50}) of jet-milled HDDR and SC alloy powders was 0.67 and 1.12 μm , and the rare earth element (Nd + Pr) content in these powders was 30.0 and 31.1 mass%, respectively. The coercivity of both the jet-milled powders was slightly increased by annealing at 300°C, and was drastically increased by annealing at 600°C. The increase in coercivity by low- and high-temperature annealing was explained by hydrogen desorption and formation of the liquid Nd-rich phase, respectively. Furthermore, the coercivity of the jet-milled HDDR alloy powder was higher than that of the SC alloy powder after annealing at low temperatures, owing to the decrease in particle size. In contrast, coercivity was higher in the jet-milled SC alloy powder than in the HDDR alloy powder after annealing at high temperatures. The lack of rare earth elements and the increase in the surface area (S_m) of the jet-milled HDDR alloy powder suggest the low coercivity of this powder after annealing at 600°C is caused by an insufficient amount of the Nd-rich phase.

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