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EFFECT OF THE DESORPTION-RECOMBINATION TEMPERATURE ON THE MICROSTRUCTURE AND MAGNETIC PROPERTIES OF HDDR PROCESSED Nd-Fe-B POWDERS

WPŁYW TEMPERATURY DESORPCJI-REKOMBINACJI NA MIKROSTRUKTURĘ I WŁAŚCIWOŚCI MAGNETYCZNE PROSZKÓW Nd-Fe-B PRZETWARZANYCH METODĄ HDDR

The effect of the desorption-recombination temperature on the microstructure and magnetic properties of hydrogenation-disproportionation-desorption-recombination (HDDR) processed Nd-Fe-B powders was studied. The $Nd_xB_{6.4}Ga_{0.3}Nb_{0.2}Fe_{bal}$ (x=12.5-13.5, at.%) casting alloys were pulverized after homogenizing annealing, and then subjected to HDDR treatment. During the HDDR process, desorption-recombination (DR) reaction was induced at two different temperature, 810°C and 820°C. The higher Nd content resulted in enhanced coercivity of the HDDR powder, and which was attributed to the thicker and more uniform Nd-rich phase along grain boundaries. But this uniform Nd-rich phase induced faster grain growth. The remanence of the powder DR-treated at 820°C is higher than that DR-treated at 810°C. In addition, it was also confirmed that higher DR temperature is much more effective to improve squareness.

Keywords: Nd-Fe-B, HDDR, permanent magnet, grain boundary

1. Introduction

Recently, there is a strong demand for high coercive Nd-Fe-B permanent magnets in the application of green technology such as the traction motor of hybrid electric vehicles (HEVs) or electric vehicles (EVs) [1]. For the high coercivity, heavy rare-earth (HRE) elements such as Dy or Tb should be substituted for Nd in Nd-Fe-B magnets to increase the anisotropy magnetic field. However, the content of HRE elements needs to be reduced in Nd-Fe-B magnets due to the limitations of their natural resources. Moreover, the substitution of HRE elements for Nd reduces the saturation magnetization and energy product ($(BH)_{max}$) due to the anti-ferromagnetic coupling between Fe and them. Therefore, developing high coercivity Nd-Fe-B permanent magnets without HRE elements have drawn a great deal of attention [2]. Actually, the coercivity of the commercial Nd-Fe-B permanent magnets without HRE elements (H_{ci} ~12 kOe) is considerably lower than that expected from their anisotropic magnetic field (H_A ~73 kOe) [3], which can be attributed to insufficient microstructure control [3,4]. Accordingly, the control of microstructures such as grain size and grain boundary is of significant importance to improve magnetic properties of Nd-Fe-B permanent magnets without HRE elements. The hydrogenation-disproportionation-desorption-recombination (HDDR) process is a well-known method to produce anisotropic Nd-Fe-B magnetic powders with submicron grains

(200-400 nm) which is close to single magnetic domain size (~300 nm) [5-7]. However, most of studies on HDDR have been focused on the hydrogenation- disproportionation (HD) stage although the desorption- recombination (DR) stage is also thought to be important for improvement of magnetic properties [3,8]. In our previous study, it was confirmed that there is a large temperature reduction of ~30°C during DR stage due to an endothermic reaction and which can be suppressed by slow DR speed [9]. This result suggests that the temperature control during DR stage has a decisive effect on the magnetic properties of HDDR treated Nd-Fe-B powders.

In the present study, the influence of DR temperature and Nd content on the microstructure and magnetic properties of HDDR treated Nd-Fe-B powders.

2. Experimental procedure

The alloys with a composition of $Nd_xB_{6.4}Ga_{0.3}Nb_{0.2}Fe_{bal}$ (x=12.5-13.5, at.%) were prepared as starting materials by vacuum arc melting process. They were heat-treated at 1000°C for 27 h under Ar atmosphere in the tube furnace for homogenization. After heat treatment, they were transferred directly to the glove box and then crushed into powders of 200-300 μm under Ar atmosphere with less than 1 ppm oxygen and water contents. After being transferred to the furnace again, they were subjected to Modified Solid HDDR (MS-HDDR) treat-

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ment [9,10]. The powders were heat treated at 200°C for 30 min in H_2 atmosphere. The furnace was then evacuated to remove H_2 gas. This hydrogenation-desorption (HDe) treatment before Solid HDDR (S-HDDR) can help the subsequent HD reaction to take place uniformly inside and outside of the powders. After HDe stage, the powders were heated up to 810°C under Ar atmosphere, and then H_2 gas was introduced up to a pressure of 1.1 atm 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-H_2 mixed gas (1.1 atm, (the partial pressure of H_2 was 0.1 atm)) without changing the temperature. And then the furnace was evacuated directly to a low vacuum (2×10^{-2} mbar) at 810°C (810°C-DR, hereafter) or 820°C (820°C-DR, hereafter). And finally, the powders were quenched using Ar gas down to room temperature (RT). The changes in temperature and pressure during the MS-HDDR process were monitored in real-time. The magnetic properties of the powders were measured using a vibrating sample magnetometer (VSM). For VSM measurement, the powders were fixed with paraffin wax under a magnetic field of 1.2 T and pre-magnetized with a 6 T pulsing magnetic field. The microstructure of the powders was examined with a scanning electron microscope (SEM).

3. Results and discussion

Fig. 1 shows the demagnetization curves of 810°C-DR and 820°C-DR treated HDDR powders with 12.5 at.% Nd. It can be seen that the squareness of the demagnetization curves was improved by increasing the DR temperature from 810°C to 820°C and the coercivity and remanence were also slightly increased at 820°C. Actually, the maximum energy product is considered to be the best single index of quality of permanent magnet material, and an increase in the maximum energy product can be achieved via remanence enhancement and improved squareness of demagnetization curve. In our result, the remanence increased from 9.4 to 9.7 kG but maximum energy product was largely increase from 16.1 to 19.3 MGOe due to the improved squareness of demagnetization curve by increasing only 10°C of DR temperature (Tab. 1).
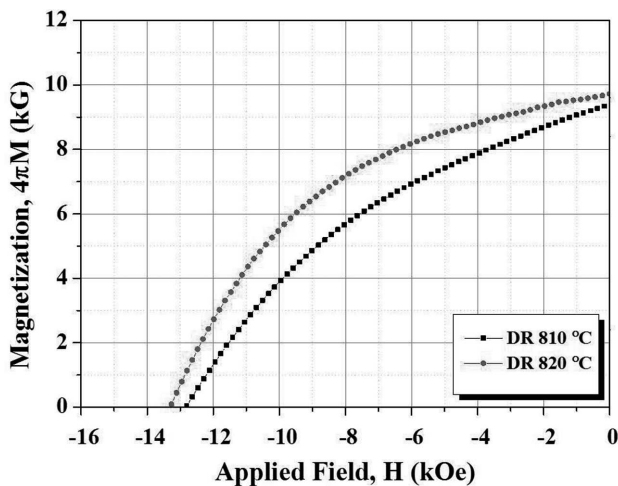

Fig. 1. Demagnetization curves of HDDR powders treated at different DR temperature of 810 and 820°C

Fig. 2 shows the dependence of magnetic properties of HDDR powders on Nd content. The coercivity was increased with Nd content and the dependency on Nd content is stronger at higher DR temperature as shown in Fig. 2 (a). On the other hand, the remanence remained almost same regardless of Nd content. It should be however noted that the remanence of 820°C-DR treated HDDR powders is higher than that of 810°C-DR treated HDDR powders in the Nd content range from 12.5 to 13.5 at.%. This result is consistent to our previous result in which slow DR speed suppressed temperature drop during DR stage and resultingly enhanced remanence due to highly textured microstructure [11]. Based upon these results, it can be concluded that higher temperature during DR stage results in higher degree of anisotropy of the HDDR powders.

TABLE 1

Typical magnetic properties of the powders produced at two different DR temperatures with various Nd contents

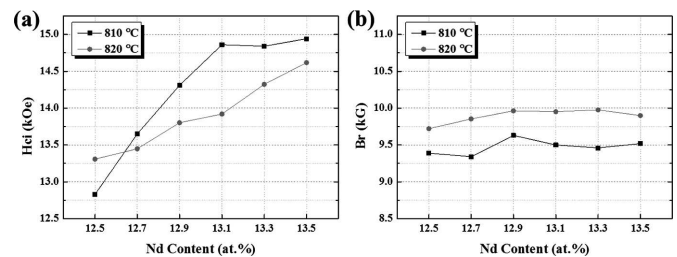| DR temperature (°C)	Nd content (at.%)	H_{ci} (kOe)	B_r (kG)	$(BH)_{max}$ (MGOe)
810	12.5	12.8	9.4	16.1
	13.5	15.0	9.5	18.4
820	12.5	13.3	9.7	19.3
	13.5	14.6	9.9	20.5

Fig. 2. Dependence of (a) coercivity and (b) remanence of 810°C DR-treated and 820°C DR-treated HDDR powder with 12.5-13.5 at.% Nd

Fig. 3 shows the fractured surfaces of 810°C DR-treated and 820°C DR-treated HDDR powder with 12.5 (Fig. 3 (a), (c)) and 13.5 at.% Nd (Fig. 3 (b), (d)), respectively. It is well known that the coercivity strongly depends on the characteristics of grain size and grain boundary. The average grain size of HDDR-treated powders was close to the single domain size of the $Nd_2Fe_{14}B$ phase (~300 nm) and there is no significant difference among different temperature DR-treated HDDR powders with different Nd content as shown in Fig. 3. However, the characteristics of their grain boundaries were quite different, which made the difference in coercivity as shown in Fig. 2 (a). It is obvious that the volume fraction and distribution of the Nd-rich phase along grain boundary is quite different depending on DR temperature and Nd content. The thin and continuous Nd-rich phase can be observed along the grain boundary in the powder with 13.5 at.% Nd (Fig. 3(b),(d)). However, Nd-rich phase is difficult to observe in the powder with 12.5 at.% Nd (Fig. 3(a), (c)). This formation of a thin layer of Nd-rich phase along the grain boundary acted as strong pinning sites for domain wall motion [12] and resulted in coercivity enhancement [3]. In addition, the coercivity

and remanence of 820°C-DR treated powders was higher than those of 810°C-DR treated powders when the Nd content of the alloy was 12.5 at.%. On the other hand, the coercivity increased much more rapidly with the increasing Nd content in 810°C-DR treated powders than in 820°C-DR treated powders. As a result, 810°C-DR treated powder showed higher coercivity than 820°C-DR treated powder under the same Nd content from 12.7 at.% to 13.5 at.% in spite of thicker Nd-rich phase along the grain boundary. This is probably due to the slight grain growth related to the melting of the Nd-rich phase above 670°C [13]. Nd-rich phase exists more uniformly along the grain boundary of HDDR powders at higher temperature, but this uniform Nd-rich phase can induce faster grain growth due to enhanced Nd-rich phase diffusion at the grain boundary.
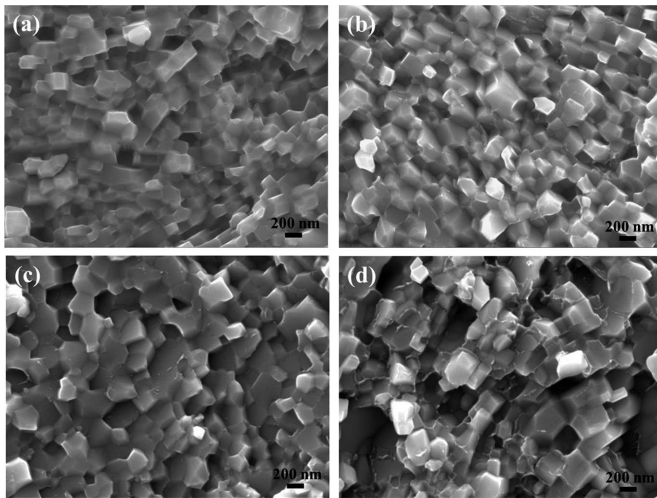

Fig. 3. SEM images of fractured surface of HDDR powders. DR-treated at 810°C with (a) 12.5 at.% Nd and (b) 13.5 at.% Nd and DR-treated at 820°C with (c) 12.5 at.% Nd and (d) 13.5 at.% Nd

4. Conclusions

The effect of the desorption-recombination temperature on the microstructure and magnetic properties of hydrogenation-disproportionation-desorption-recombination processed Nd-Fe-B magnetic powders was studied. The squareness of the demagnetization curves was improved by increasing the DR temperature from 810°C to 820°C, which resulted in the enhanced maximum energy product from 16.1 to 19.3 MGOe. And the higher Nd content was favorable to the magnetic properties of the HDDR powder, which could be attributed to the thicker and more uniform Nd-rich phase along grain boundaries.

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