Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

HDDR process and Nd-Fe-B magnet powders

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We have been studying Nd-Fe-B magnets produced by HDDR (Hydrogenation-Decomposition-Desorption-Recombination) process. $Nd_2Fe_{14}B$ undergoes the reversible phase transition in hydrogen and vacuum atmosphere. This phenomenon was first observed in the sintering study of the Nd-Fe-B magnet in an atmospheric hydrogen gas. By the HDDR process, magnet powders consisting of fine crystalline grains with the high coercivity are produced. The addition of elements such as Ga, Zr and Hf in a small amount is very effective for producing magnetically anisotropic powders with large BH_{max}'s about 43 MGOe. Bonded magnets with BH_{max} of 20 MGOe and full dense magnets with BH_{max} of 38 MGOe are obtained from these anisotropic magnet powders.

1. INTRODUCTION

The most powerful practical permanent magnet, Nd-Fe-B magnet, is produced by many metallurgical techniques such as the powder metallurgy [1], the rapid quenching [2], the mechanical alloying [3], the hot working [4], the HDDR (Hydrogenation-Decomposition-Desorption-Recombination) process [5] and etc. Anisotropic Nd-Fe-B bonded magnets with the high energy product could be produced if good anisotropic magnet powders are available. These are obtained by; 1) simple grinding of alloy ingots or sintered magnets [6-7], 2) grinding of hot deformed bodies of rapidly quenched powders or mechanically alloyed powders [8-9], and 3) the HDDR process [10].

We studied the sintering process of Nd-Fe-B magnet in hydrogen atmosphere [11], and found the HDDR process for producing the isotropic and the anisotropic magnet powder [12-13]. The HDDR process makes good use of the phase transition at temperatures higher than 650 °C as follows; $Nd_2Fe_{14}B(H_x) + H_2 \leftrightarrow NdH_2 + Fe + Fe_2B$. In this paper, we describe the HDDR process and report the use of HDDR powders for anisotropic Nd-Fe-B bonded magnets and full dense magnets (bulk magnets) production.

2. EXPERIMENT

Nd-Fe-B alloys of various composition were prepared by the plasma arc-melting technique in Ar. The alloys were first homogenized and crushed into blocks of the size less than 20 × 20 × 20 mm before the HDDR process. They were treated at temperatures from 750 °C to 900 °C in hydrogen of 1 atm, and then evacuated to a high vacuum (10^{-5} Torr), and finally quenched by Ar gas. The magnet powder of the size less than 420 μm was prepared by crushing the HDDR treated alloy blocks above. Bonded magnets were made by mixing the magnet powders and the epoxy resin and molding the compound into the green compacts with or without the applied magnetic field of 25 kOe at the pressure of 6 Ton/cm^2, and hardening them at 100 °C for 2 hours. Densities of bonded magnets were between 6.0 and 6.1 g/cm^3. Full dense magnets were made by molding the HDDR magnet powders into the green compacts with or without the applied magnetic field of 25 kOe, pressing them with the pressure of 0.5 Ton/cm^2 at temperatures from 720 °C to 840 °C for 10 min in a high vacuum (10^{-4} Torr), and cooling them. These production processes are shown in Figure 1. Magnetic properties of magnet powders, bonded magnets and full dense magnets were obtained by VSM and B-H curve tracer methods after magnetization with the applied

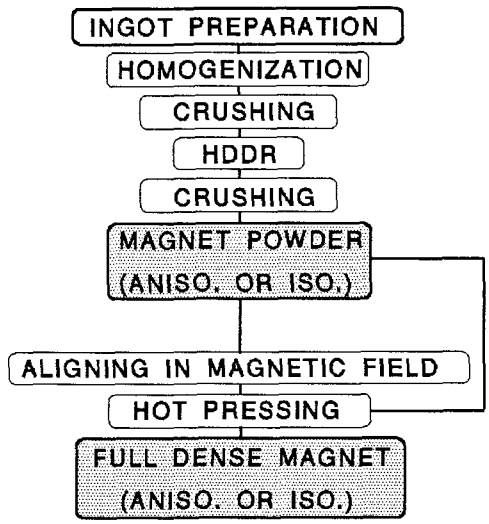

Figure 1. Flow chart of the Nd-Fe-B magnet powder and the full dense magnet production by the HDDR process.

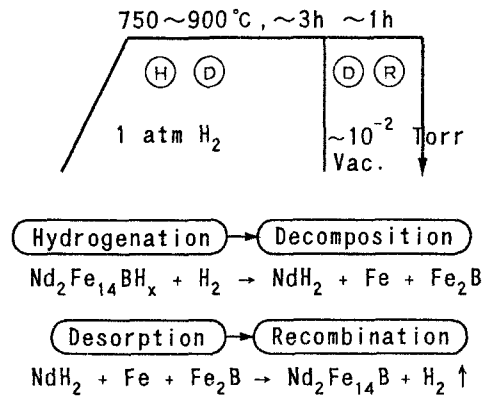

Figure 2. HDDR process of the Nd-Fe-B system.

magnetic field of 70 kOe.

3. RESULTS AND DISCUSSIONS

3.1. HDDR process and magnet powders

It is well known that $Nd_2Fe_{14}B$ intermetallic compound absorbs hydrogen at temperatures from room temperature to 650 °C in 1 atm H_2 and forms the compound hydride $Nd_2Fe_{14}BH_x$ [14]. We have studied the phenomenon of Nd-Fe-B system in hydrogen atmosphere at high temperatures [10]. In the temperature range between 650 °C and 1000 °C and in 1 atm H_2, the compound $Nd_2Fe_{14}B$ or the compound hydride $Nd_2Fe_{14}BH_x$ absorbs more hydrogen and decomposes into NdH_2, Fe and Fe_2B, and $Nd_2Fe_{14}B(H_x)$ is again stable at temperature higher than 1000 °C. When hydrogen is desorbed from the system consisting of NdH_2, Fe and Fe_2B at the temperatures from 650 °C to 1000 °C, NdH_2, Fe and Fe_2B recombine into $Nd_2Fe_{14}B$. Figure 2 shows the HDDR process and the phase transition of the Nd-Fe-B system. The HDDR process makes good use of the phase transition that $Nd_2Fe_{14}B$ undergoes, i.e., $Nd_2Fe_{14}B(H_x) + H_2 \rightarrow NdH_2 + Fe + Fe_2B$ in hydrogen and $NdH_2 + Fe + Fe_2B \rightarrow Nd_2Fe_{14}B(H_x) + H_2$ in vacuum atmosphere at temperatures from 650 °C to 1000 °C. At from 750 °C to 900 °C, magnet powder particles consisting of fine crystalline grains (~ 10^{-1} μm) with the high coercivity and the good magnetic properties can be produced from original cast ingots or homogenized ingots with large crystalline grains (≥ 10 μm). Recently, it is reported that Sm-Fe-N, Sm-Fe-(Ti,V) and Nd-Fe-(V,Mo)-N systems also undergo the HDDR process [15-16]. It is indicated that there exist unique microstructures of those ferromagnetic intermetallic compounds in these system treated by the HDDR process. It is now established that the HDDR process is one of techniques to prepare unique microstructures of intermetallic compounds.

Figure 3 shows magnetic properties of isotropic bonded magnet made from the HDDR powders of $Nd_xFe_{94-x}B_6$ and $Nd_x(Fe_{0.9}Co_{0.1})_{94-x}B_6$ [17]. $4\pi I$ means the magnetization intensity obtained in the magnetic field of 20 kOe. For both the Nd-Fe-B system and the Nd-Fe-Co-B system, the maximum value of, the remanence, B_r are obtained at about 12 at % Nd. The coercivity, ${}_iH_c$, varies from 8 to 12 kOe for 12 - 14 at % Nd, and decreases for Nd less than 12 at % Nd. In the case of $Nd_{13}Fe_{87-x}B_x$ composition, the maximum values of $4\pi I$ and B_r are

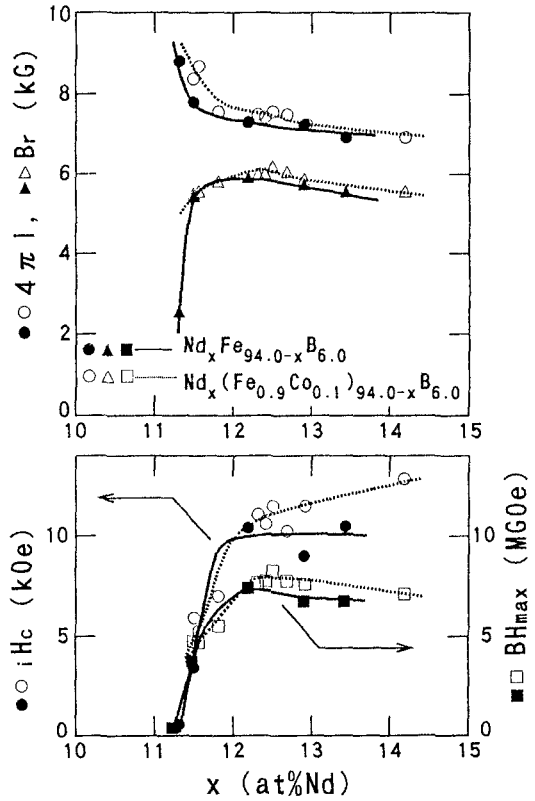

Figure 3. Magnetic properties of the isotropic bonded magnet made from the HDDR powders.

obtained at x = 6. It is established that the HDDR powders with the good magnetic properties can be obtained at nearly the stoichiometric composition of $Nd_2Fe_{14}B$ or $Nd_2(Fe,Co)_{14}B$. These HDDR powders are almost magnetically isotropic. We have already reported that microstructures of HDDR powder particles consist of fine crystalline grains of the $Nd_2Fe_{14}B$ type intermetallic compound with the size of about 0.3 μm, and there exist almost no boundary layer phases between $Nd_2Fe_{14}B$ crystalline grains [12]. The high coercivity of the magnet powder is considered to be due to the size of fine crystalline grains of recombinated $Nd_2Fe_{14}B$. We will report the reason why fine $Nd_2Fe_{14}B$ crystalline grains are produced by the HDDR process, elsewhere [17].

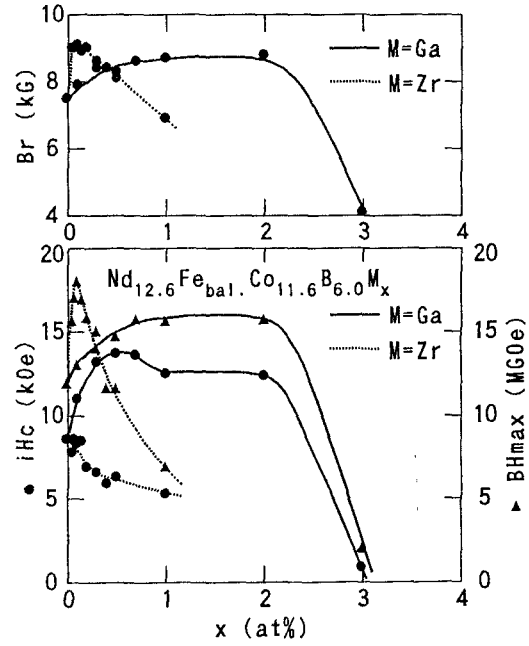

Figure 4. Magnetic properties of the anisotropic bonded magnet made from the HDDR powders.

3.2 Anisotropic magnet powders and bonded magnets

In the Nd-Fe-B system, good anisotropic magnet powder are obtained by the HDDR process from Nd-Fe-Co-B alloy with an addition of a small amount of Ga, Zr, Nb, Hf and Ta [13]. Figure 4 shows magnetic properties of bonded magnets made from Nd-Fe-Co-B-Ga and Nd-Fe-Co-B-Zr anisotropic HDDR magnet powders. B_r of bonded magnets possess the maximum value for the alloys with 0.5 ~ 2.0 at % Ga and 0.1 at % Zr, respectively. $_iH_c$ increases up to 13 kOe at 0.5 at % to 2.0 at % Ga and decreases with the Zr addition. The more favorable HDDR magnet powder possessing high B_r and high $_iH_c$ is obtained from the Nd-Fe-Co-B alloy co-added with Ga and Zr. The typical demagnetization curve of the anisotropic bonded magnet made from Nd-Fe-Co-B-Zr-Ga magnet powder is shown in Figure 5. The bonded magnet with $_iH_c$ of 13.3 kOe and BH_{max} of 20.1 MGOe is obtained.

Figure 6 shows magnetic properties of anisotropic

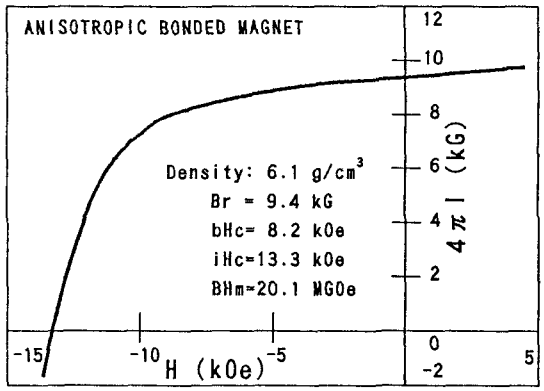

Figure 5. Demagnetization curve of an anisotropic bonded magnet.

HDDR magnet powders, from which the bonded magnet with BH_{max} of 20 MGOe is made. These magnetic properties were obtained by VSM methods and were corrected for the demagnetizing field; powder samples were dispersed in the liquidized wax at 50 °C, were aligned in the magnetic field of 15 kOe, and were fixed at room temperature. The maximum value of B_r is obtained for magnet powders with the size of 50 ~ 200 μm. $_iH_c$ is almost constant at about 13.5 kOe for magnet powders with the size between 50 μm and 420 μm, but decrease for magnet powers with the size less than 50 μm. It is considered that the decrease in B_r and $_iH_c$ values in magnet powders with the size less than 50 μm is due to the surface oxidation of the powder particle and the stress introduced during crushing. A typical demagnetization curve of anisotropic HDDR magnet powders is shown in Figure 7. BH_{max} of magnet powders of the size between 50 μm and 100 μm possesses 43.2 MGOe.

The morphology of fine $Nd_2Fe_{14}B$ type crystalline grains in the anisotropic HDDR magnet powders is almost the same as that of the isotropic HDDR magnet powders, except for crystallographic orientation of fine crystalline grains [18]. From results shown in Figure 6, it is seen that magnetic properties of magnet powders are dependent on the particle sizes and that the optimum powder particle size of magnet powders is roughly the same as the size of original large crystalline grains of alloy ingots. This indicates that the crystallographic *c*-axis orientation of original large crystalline grains of alloy

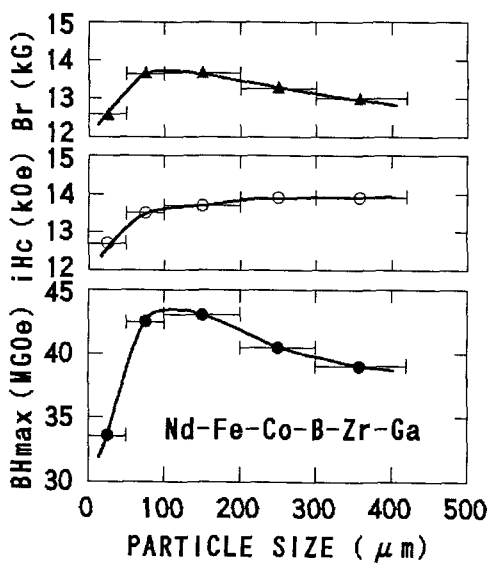

Figure 6. Magnetic properties of anisotropic HDDR magnet powders, from which the bonded magnet with BH_{max} of 20 MGOe is made.

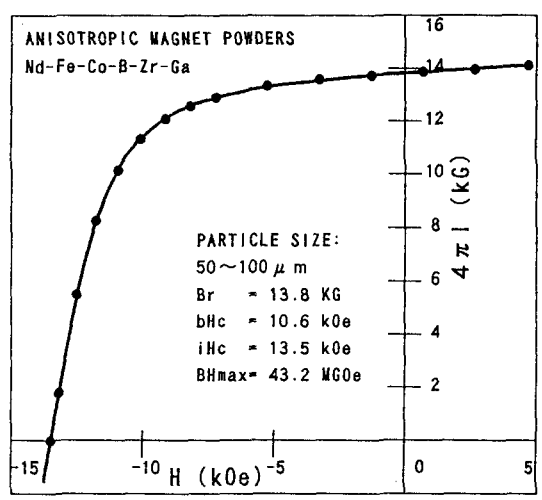

Figure 7. Demagnetization curve of the anisotropic HDDR magnet powder.

ingots may be maintained during the HDDR process. There are reports that possible memory sites are related to the types of additive elements [13, 19-20]. We are now studying the mechanism of this interesting HDDR phenomenon.

3.3. Full dense magnets

The powerful full dense magnet (the bulk magnet) can be prepared from anisotropic or isotropic HDDR magnet powders by the hot pressing technique [21]. Anisotropic full dense magnets can be obtained by the hot pressing only (no hot working) since magnet powders are anisotropic. Figure 8 shows densities and magnetic properties of full dense magnets produced by the hot pressing of Nd-Fe-Co-B-Zr-Ga anisotropic HDDR magnet powders, versus hot pressing temperature. Magnetic properties of anisotropic magnet powder used for the hot pressing are ${}_iH_c$ = 13.7 kOe and BH_{max} = 19.0 MGOe (as the bonded magnet). Densities and B_r reach to the maximum value while ${}_iH_c$ decrease at the temperature higher than 760 °C. Optimum values of BH_{max} are obtained at temperatures between 760 °C and 800 °C. Figure 9 shows a demagnetization curve of the HDDR full dense magnet. BH_{max} of the magnet is 38.0 MGOe.

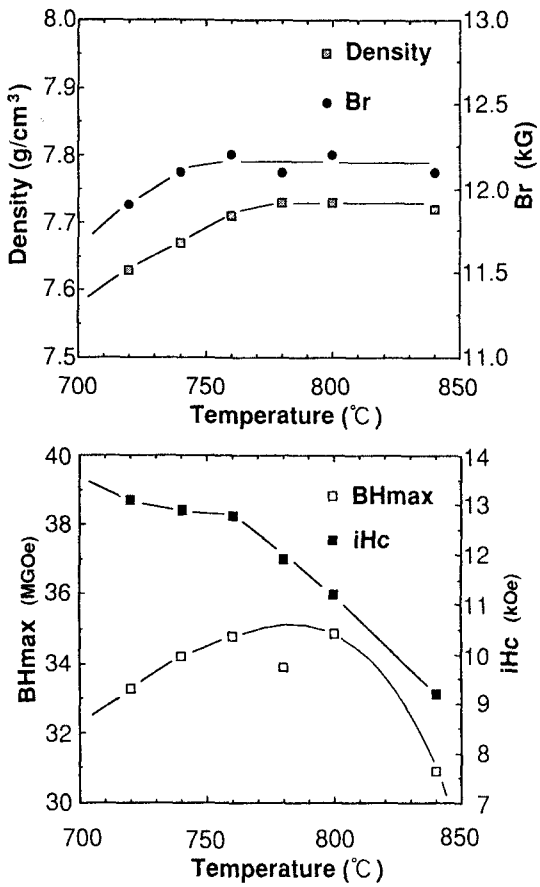

Figure 8. Magnetic properties of anisotropic full dense magnet made from the HDDR powders, versus hot pressing temperature.

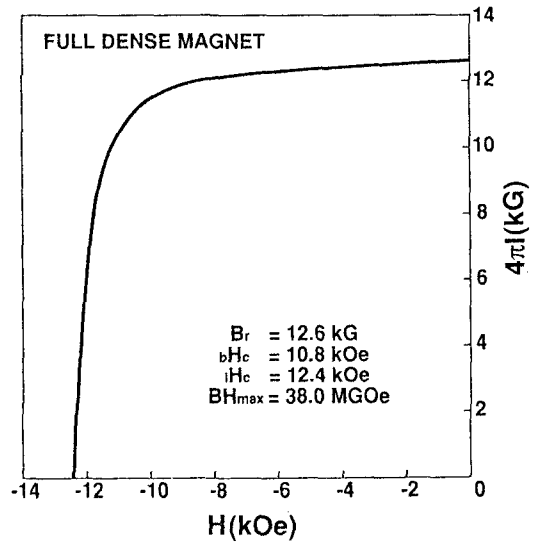

Figure 9. Demagnetization curve of a full dense magnet.

Magnetic properties of full dense magnets are slightly decreased as compared with those of the magnet powder used. It is possible that magnetic properties of full dense magnets can be made comparable with those of magnet powders if experimental conditions are optimized.

4. CONCLUSIONS

The HDDR process makes good use of the phase transition that $Nd_2Fe_{14}B$ undergoes, i.e., $Nd_2Fe_{14}B(H_x) + H_2 \leftrightarrow NdH_2 + Fe + Fe_2B$, in hydro-

gen and vacuum at temperatures from 650 °C to 1000 °C. It is expected that the HDDR process is one of techniques to prepare unique microstructures of intermetallic compounds, not only Nd-Fe-B but also so other intermetallics. The HDDR magnet powder possessing high B_r and high $_iH_c$ is obtained from the Nd-Fe-Co-B alloy co-added with Ga and Zr. From them, the bonded magnet with $_iH_c$ of 13.3 kOe and BH_{max} of 20.1 MGOe is obtained. BH_{max} of anisotropic magnet powders with the size between 50 μm and 100 μm possesses 43.2 MGOe. The powerful full dense magnet can are prepared from anisotropic or isotropic HDDR magnet powders by the hot pressing technique. BH_{max} of the anisotropic full dense magnet is 38.0 MGOe.

ACKNOWLEDGMENT

We wish to thank Mr. H. Mori and Mr. T. Ogawa for their experimental assistance.

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