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Effect of substituting Pr for Nd on magnetic properties of Nd–Fe–B HDDR powder

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ABSTRACT

The effect of partially substituting Nd by Pr on magnetic properties of HDDR (hydrogenation-decomposition-desorption-recombination)-processed Nd–Fe–Co–B–Ga–Zr powder was studied. It was found that coercivity H_{cJ} of the $(Nd_{1-x},Pr_x)_{12.9}Fe_{bal.}Co_{5.8}B_{6.3}Ga_{0.5}Zr_{0.1}$ ($x = 0–0.40$) powder at room temperature is increased with increasing Pr content x, while residual induction was kept almost constant. The increase in H_{cJ} is larger than that expected from the increase in magnetocrystalline anisotropy field H_a of the magnetic phase $(Nd,Pr)_2Fe_{14}B$. This can be attributed to change in grain-boundary microstructures. Temperature-dependence of H_{cJ} in the injection-molded-bonded magnets made from the powders was also examined. It was confirmed that the decrease in H_{cJ} of the magnet with $x = 0.24$ is kept almost the same as the magnet with no Pr addition in the temperatures ranging from room temperature to 150 °C.

1. Introduction

It is well established that the hydrogenation-decomposition-desorption-recombination (HDDR) process can produce anisotropic Nd–Fe–B magnet powders [1,2], and the modifications of the process have achieved remarkable improvements in the magnetic properties of the powders [3–6]. Some of the present authors recently reported that a high coercivity up to 1760 kA/m can be induced in the Nd–Fe–Co–B–Ga–Zr HDDR powder by the addition of Al and the increase in Nd content [7,8]. The Al addition, however, lowers residual induction of the powder, since Al is soluble in the magnetic phase $Nd_2Fe_{14}B$, and decreases its saturation magnetization [9].

In this study, the magnetic properties of the HDDR powders with partial substitution of Nd by Pr were studied. Since the magnetic phase $Pr_2Fe_{14}B$ possesses high magnetocrystalline anisotropy field H_a and similar saturation magnetization in comparison with $Nd_2Fe_{14}B$ [10], it can be expected that replacing Nd with Pr can enhance the coercivity of the powders without causing a decrease in residual induction. McGuiness et al. reported that the Pr substitution can effectively improve coercivity of the Nd(–Dy)–Fe–B(–Zr) HDDR powders [11]. However, their powders were magnetically isotropic due to the HDDR treatment conditions, and only coercivity was shown as the resultant magnetic properties. In this study, the HDDR conditions for inducement of high anisotropy in the powders [12] were employed, and residual induction of the powders was also examined varying the Pr content. As a result, in the studied range of Pr content, coercivity of the powder at room temperature was found to be increased with increasing Pr content, while residual induction was kept almost constant. The increase in coercivity is larger than that expected from the increase in H_a of the magnetic phase. This can be ascribed to change in grain-boundary microstructures. Temperature-dependence of coercivity in the injection-molded-bonded magnets made from the powders was also examined.

2. Experimental procedure

The $(Nd_{1-x},Pr_x)_{12.9}Fe_{bal.}Co_{5.8}B_{6.3}Ga_{0.5}Zr_{0.1}$ ($x = 0–0.40$) alloy ingots were prepared by induction melting of constituent elements in an argon-gas atmosphere. They were subjected to homogenization heat treatment in an argon atmosphere, and then crushed into powders of particle sizes of <150 μm. The alloy powders thus obtained were HDDR-treated as follows. The hydrogenation-decomposition (HD) process was carried out by heating the

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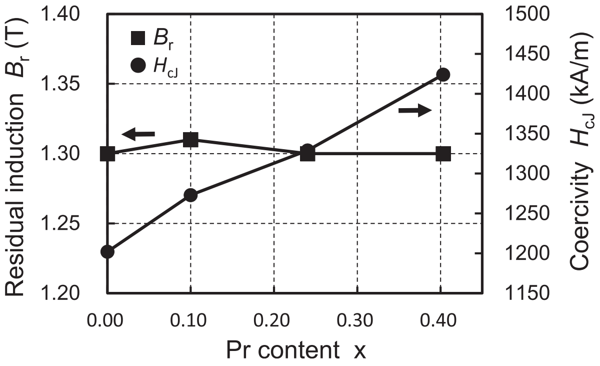

Fig. 1. Pr content x versus B_r and H_{cJ} of the $(Nd_{1-x},Pr_x)_{12.9}$ $Fe_{bal}Co_{5.8}B_{6.3}Ga_{0.5}Zr_{0.1}$ powder at room temperature.

powders up to 840 °C in an atmospheric hydrogen-argon gas mixture, and keeping them at this temperature for 230 min. In the desorption-recombination (DR) process, the powders were desorbed under a constant hydrogen partial pressure of 3 kPa at 840 °C for 100 min, and subsequently evacuated to a high vacuum of 1 Pa at the same temperature. This two-step desorption process can induce a large coercivity in the powder together with a high degree of magnetic anisotropy [12]. After this processing, the powders were quenched using argon gas to room temperature. The bonded magnets were prepared from the HDDR-treated powders as follows. The powders were coated with a silane coupling agent and then kneaded with 8 wt% nylon12 resin at 190 °C. The obtained mixtures were injection-molded into cylindrical pieces with a diameter of 10 mm and a length of 7 mm in an aligning magnetic field of 1260 kA/m at 260 °C. The magnetic properties of the powders and those of the bonded magnets were measured with a vibrating sample magnetometer (VSM) and a B–H curve tracer, respectively. The powders for the measurements were aligned with a magnetic field of 796 kA/m and fixed with paraffin wax. The density of the homogenized ingots, and a demagnetizing factor of 0.10, which was determined by measuring the pure Ni specimen with the same dimension as the HDDR powder specimens, was used for the VSM measurements. The powder specimens and the bonded magnets were magnetized in a pulsed magnetic field of 5.6 MA/m before the measurements. The microstructures of the powders were examined with a transmission electron microscope (TEM). TEM specimens were fabricated by Ga focused ion beam (FIB) mill with a micro-sampling unit. Composition analyses of the phases in the powders were performed using energy-dispersive X-ray spectroscopy (EDX).

3. Results and discussion

3.1. Magnetic properties and microstructures

Fig. 1 shows the Pr content x versus coercivity H_{cJ} and residual induction B_r of the $(Nd_{1-x},Pr_x)_{12.9}Fe_{bal.}Co_{5.8}B_{6.3}Ga_{0.5}Zr_{0.1}$ (x = 0–0.40) powder at room temperature. It was found that H_{cJ} of the powder increases monotonously as the Pr content x increases from 0 to 0.40, while B_r was kept almost constant. This is much more effective than the 1.5 at% Al addition to the same base alloy composition, which brings a 0.05 T decline of B_r with an increase in H_{cJ} to 1350 kA/m [8].

Table 1 shows the percentage increase in H_a of the magnetic phase and that in H_{cJ} of the powder as a function of Pr content x. The increments of H_a were calculated on the assumption that with increasing Pr content, H_a increases linearly from the literature H_a data at room temperature for x = 0, $Nd_2Fe_{14}B$ (5.33 MA/m) to that for x = 1, $Pr_2Fe_{14}B$ (6.93 MA/m) [10]. The increase in H_{cJ} was experimentally obtained as shown in Fig. 1. It can be seen that the percentage increase in H_{cJ} is larger than that in H_a. This indicates that the improvement of H_{cJ} can be due to not only the increase in H_a but change in microstructures of the powder.

Table 2 lists the EDX analysis data of Pr:(Nd + Pr) content ratio in magnetic phase and in rare-earth (R)-rich phase at the triple points of the grain boundaries (cf. the inset photo) for the powders with the overall composition of x = 0.24 and x = 0.40. It was observed that in each powder, Pr:(Nd + Pr) ratio in the R-rich phase is much higher than the overall material composition, while this ratio in the magnetic phase was similar to the overall composition.

High-resolution TEM observations on several grain boundaries of the x = 0 and x = 0.40 powders revealed that the Pr substitution increases the thickness of thin R-rich grain-boundary layer between adjacent $(Nd,Pr)_2Fe_{14}B$ grains. The typical TEM images are shown in Fig. 2. One can see that the thicknesses of the thin R-rich grain-boundary layer is increased from approximately 0.8 nm to 2.0 nm by the Pr addition of x = 0.40.

These observation results suggest the following mechanism of the grain-boundary phase development. (1) Pr is selectively distributed to the R-rich grain-boundary phase. (2) This lowers melting point of the R-rich phase, i.e., eutectic temperature of Pr–Fe system is approximately 70 °C lower than that of Nd–Fe system, which would lead to improving the fluidity of the R-rich phase and promoting its uniform spread along the grain boundaries. Such a change in chemistry and microstructures of the grain boundaries is thought to be closely related to the increase in H_{cJ}. Sepehri-Amin et al. observed a similar grain-boundary phase in the Nd–Cu diffusion-processed HDDR powders, and proposed that the coercivity enhancement of the powders is attributed to the domain wall pinning at the grain-boundary phase [13].

3.2. Temperature-dependence of coercivity

To evaluate H_{cJ} of the powders at elevated temperatures, the injection-molded-bonded magnets were made from the powders, and their temperature-dependent coercivity was examined. The magnetic properties of the bonded magnets at room temperature are shown in Fig. 3. They are consistent with the magnetic properties of the powders, i.e., B_r of these magnets is similar, and the order of increasing H_{cJ} for the magnets is the same as that for the original powders. It can be also seen that the Pr substitution does not affect the demagnetization curve squareness of the magnet. The temperature-dependence of H_{cJ} in the magnets is shown in Fig. 4.

Table 1
Percentage increase in H_a of the magnetic phase (calculated) and that in H_{cJ} of the powder (experimental) as a function of Pr content x.

Pr content x	Percentage increase in H_a of the magnetic phase (%) (calculated)	Percentage increase in H_{cJ} of the powder (%) (experimental)
0.10	3.0	6.0
0.24	7.0	10.6
0.40	12.1	18.5