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Coercivity of Hot-pressed Compacts of Nd-Fe-B-type HDDR-treated Powder

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$Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ HDDR-treated powder was compacted by hot-pressing using different configurations of dies and heating rates. The die configurations were especially different in terms of the evacuation system that was used in heating for hot-pressing. The coercivity in the compacts was influenced by the evacuation system of the die and heating rate. In spite of the identical hot-pressing temperature and heating rate, coercivity was radically reduced above 600 °C in the compacts prepared in the closed-type die compared to that in the compacts prepared in the open-type die. The coercivity in the compacts prepared in the closed-type die decreased with increasing heating rate and the value further increased when extreme high heating rate was employed. $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ HDDR-treated powder contained a significant amount of residual hydrogen (approx. 1500 ppm) in the form of $Nd_2Fe_{14}BH_x$ hydride. The dramatic coercivity decrease in the compact prepared in the closed die is attributed to the disproportionation of $Nd_2Fe_{14}BH_x$ hydride. High coercivity is mainly due to the effective desorption of hydrogen or the suppression of hydrogen-related disproportionation upon hot-pressing.

Keywords : HDDR, hot-pressing, residual hydrogen, disproportionation, coercivity

1. Introduction

The key feature of Nd-Fe-B-type HDDR (hydrogenation, disproportionation, desorption and recombination)-treated powder is its unique microstructure, consisting of ultra fine $Nd_2F_{14}B$ grains of about single-domain size (~300 nm for $Nd_2F_{14}B$) [1-4]. This fine grain structure can be exploited particularly to achieve high coercivity in a permanent magnet. It would be desirable to consolidate an HDDR-treated material, generally in powder form, into a high density bulk magnet while its fine grain structure maintained [5-8]. Our previous work revealed that the Nd-Fe-B-type HDDR material lost coercivity dramatically when it was consolidated by hot-pressing at an elevated temperature [9]. Radical coercivity loss in the Nd-Fe-B-type HDDR material was also witnessed when it was heated in vacuum without pressing load [10]. This radical coercivity reduction is considered to be one of the technical barriers against the consolidation of the Nd-Fe-B-type HDDR material without loss in magnetic performance. The coercivity of the Nd-Fe-B-type HDDR material is influenced significantly by many factors, such as temperature, heating rate, evacuating system etc. It is important from a technological point of view, therefore, to fully understand the effect of radical coercivity reduction on the consolidation of the Nd-Fe-B-type HDDR powder. In the present study, the Nd-Fe-B-type HDDR-treated powder was consolidated by hot-pressing using different die configurations and heating rates. The coercivity variations in the hot-pressed compacts were studied emphasizing the role of residual hydrogen in the Nd-Fe-B-type HDDR-treated powder.

2. Experimental Work

Small $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy slabs (approx. 5 × 5 × 5 mm^3) were exposed to hydrogen ($P_{H2} = 1$ bar) at room temperature, and disproportionation was carried out at 740 °C in hydrogen (P_{H2} = 0.35 bar) for 3 hr. Desorption and recombination occurred at 820 °C for 40 min under vacuum. This HDDR-treated powder (iHc =13.5 kOe, 100-150 μm) was used as the starting material for the present study. The powder was then compacted by hot-pressing (1 Ton/cm^2) in vacuum (1.2×10^{-5} mbar at

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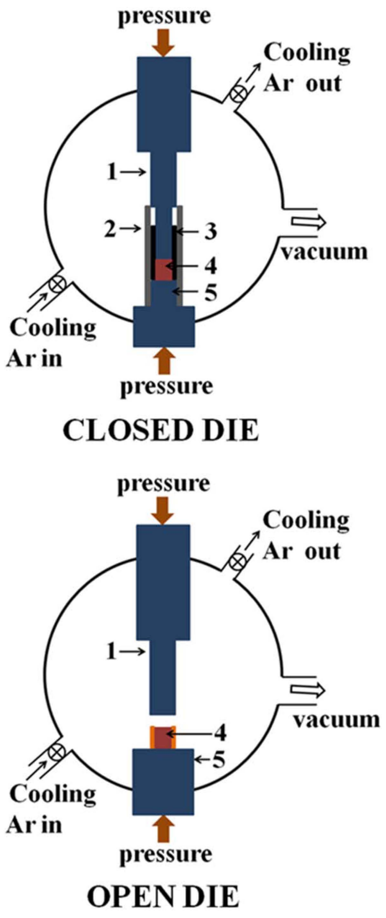

Fig. 1. (Color online) Schematic diagram of die: (1) upper punch, (2) WC die, (3) graphite bushing, (4) sample powder, (5) bottom punch.

RT) at a temperature range from 500 to 800 °C with heating rate 70 °C/min. Different die configurations, namely closed- and open-type shown in Fig. 1, were used in the hot pressing. Die configurations were distinctively different in terms of the evacuation system of the desorbed hydrogen from the HDDR material due to thermal processing.

The HDDR powder was also compacted at 750 °C at different heating rates. Induction heating was employed for rapid heating in hot-pressing. The powder was compressed to make green compacts at room temperature. Each green compact was then dropped into a preheated die and hot-pressed at 750 °C under pressure (1 Ton/cm^2). Heating from room temperature to the hot-pressing temperature was carried out within 2 min under pressure and then rapid cooling with Ar gas quenching. The magnetic characterization of the hot-pressed compacts was carried out by using a vibrating sample magnetometer (VSM) with a maximum field of 12 kOe. Prior to the VSM measurement, the compact was cut into small pieces and then wax bonded and magnetized in a 4.5 T pulsing field. The microstructures of the compacts prepared in the closed-type die were observed by SEM. Differential thermal analysis (DTA) was also carried out to investigate the phase change in the material during heating under different atmospheres at the heating rate of 7 °C/min. X-ray diffraction (XRD) (Cu-K$_\alpha$ radiation) was used to study the change in the crystallographic lattice parameter in the tetragonal $Nd_2Fe_{14}B$-type phase in the compacts due to the desorption of residual hydrogen.

3. Results and Discussion

$Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ HDDR-treated powder was compacted by hot-pressing under vacuum in a closed-type die at a temperature in the range from 500 to 800 °C with a heating rate 70 °C/min. The coercivity and density of the compacts were measured. The results are shown in Fig. 2. Coercivity was reduced dramatically above 600 °C. At least 750 °C was required for nearly full densification of the compacts under an applied load of 1 Ton/cm^2.

One of the possible causes for coercivity reduction may be the excessive grain growth due to the hot-pressing at an elevated temperature. The grain structures of the HDDR-treated powder and hot-pressed compacts observed by SEM are shown in Fig. 3. There was no appreciable grain growth in the compacts prepared at 750 °C; therefore, grain coarsening was not the cause for the sharp coercivity loss in the compacts. The Nd-Fe-B-type HDDR-treated powder contained a significant amount (1500 ppm) of residual hydrogen in the form of $Nd_2Fe_{14}BH_x$ hydride [9, 10]. The temperature at which coercivity started to decrease was close to the typical disproportionation temperature (650 °C) of $Nd_2Fe_{14}BH_x$ hydride [11, 12].

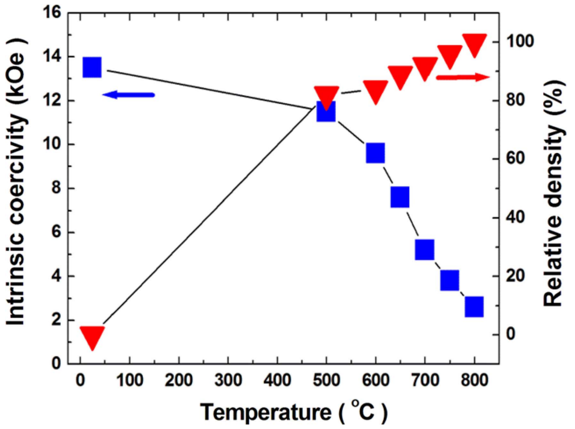

Fig. 2. (Color online) Variations of coercivity and relative density as a function of hot-pressing temperature in the hot-pressed compacts of $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ HDDR-treated powder prepared in the closed-type die.

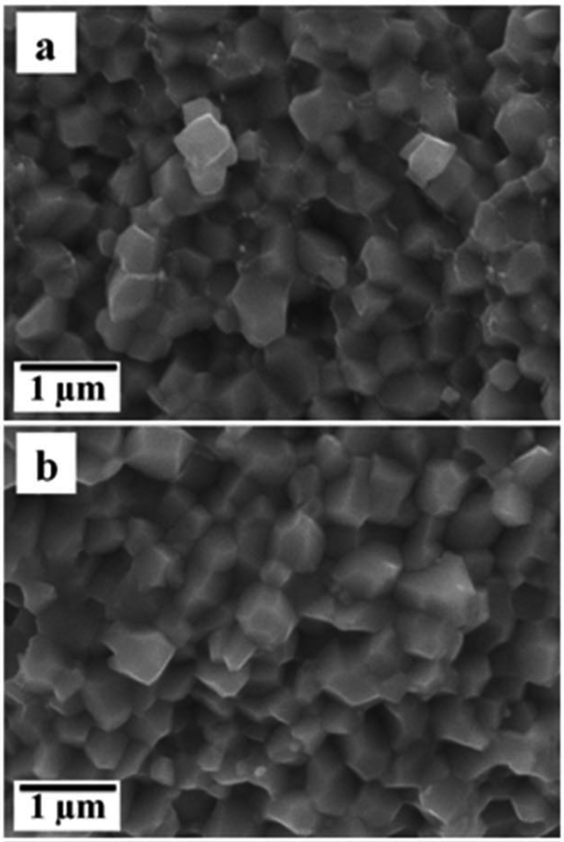

Fig. 3. SEM micrographs showing the grain structure (a) $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ HDDR-treated initial powder and (b) compacted powder at 750 °C in closed-type die.

Our previous TEM and XRD studies demonstrated the effect of disproportionation of the $Nd_2Fe_{14}BH_x$ hydride in the HDDR-treated powder on thermal processing [9, 10]. The disproportionation of the $Nd_2Fe_{14}BH_x$ hydride in the HDDR-treated powder was also verified by DTA during heating in Ar and in vacuum. As shown in Fig. 4, while no thermal event occurred during heating in vacuum, a noticeable exothermic event occurred at the temperature range of 620 °C-655 °C during heating in Ar atmosphere. This exothermic event is believed to correspond to the disproportionation of the $Nd_2Fe_{14}BH_x$ hydride in the HDDR-treated powder.

Consolidation of the HDDR-treated powder without loss of magnetic properties would be promising. The coercivity of the Nd-Fe-B-type HDDR-treated powder did not decrease upon heating without load if the evacuation system worked effectively [10]. So we expected the powder to be compacted without loss of magnetic performance, provided that the evacuation system worked effectively during heating for hot-pressing. In order to see whether the compacts would show distinctive coercivity variations depending on the hot-pressing die configuration, the HDDR-treated powder was hot-pressed in the open-type effective evacuation die. Hot-pressing was performed at a temperature range from 650 to 800 °C with heating rate of 70 °C/min. The coercivity and relative density of the compacts were measured. The results are shown in Fig. 5. The coercivity in the compacts prepared in the open die decreased gradually and full dense compacts were obtained at 750 °C. The coercivity was 10.8 kOe in the full dense compact prepared in the open die, and was only 3.8 kOe (Fig. 2) in the compact prepared in the closed die at 750 °C. In spite of the identical temperature and heating rate, the coercivity was significantly higher in the compacts prepared in the open die than in the compacts prepared in the closed die. The markedly different coercivity

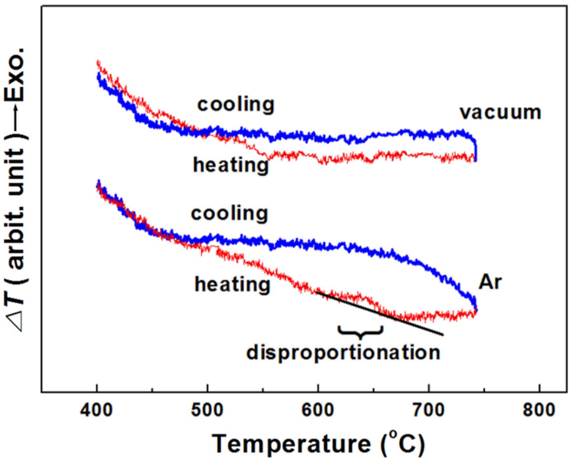

Fig. 4. (Color online) DTA results for the $Nd_{12.5}Fe_{80.6}B_{6.4}$-$Ga_{0.3}Nb_{0.2}$ HDDR-treated powder in different atmospheres.

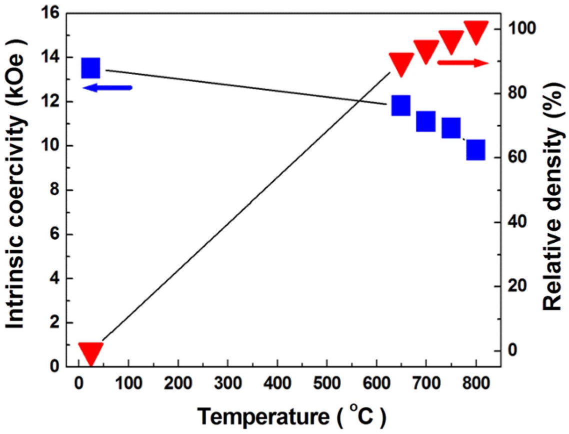

Fig. 5. (Color online) Variations of coercivity and relative density as a function of hot-pressing temperature in the hot-pressed compact of $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ HDDR-treated powder prepared in the open die.

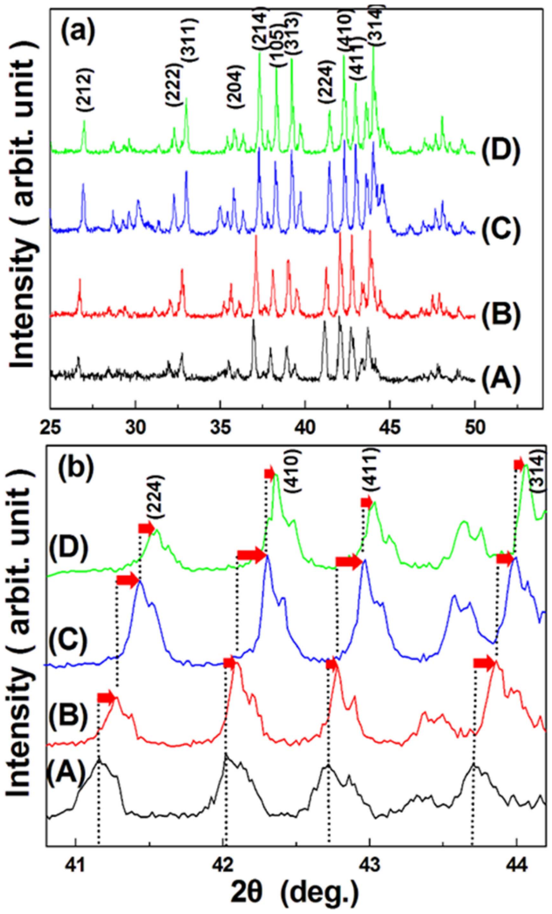

Fig. 6. (Color online) (a) XRD patterns of $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy (A) after HDDR-treatment, (B) HDDR-treated powder compacted at 750 °C in closed die, (C) HDDR-treated powder compacted at 750 °C in open die, (D) before HDDR treatment, and (b) enlarged view of angle shift.

variations were attributed only to the different evacuation systems of the hot-pressing dies (Fig. 1). Residual hydrogen may be confined in the closed-type die during heating for hot-pressing, resulting in the disproportionation of the HDDR-treated powder, which dramatically reduced the coercivity above 600 °C in the compacts. In the open die, residual hydrogen could be desorbed effectively, mitigating the detrimental effect of hydrogen-related disproportionation to result insignificant coercivity loss in the hot-pressed compacts.

Residual hydrogen in the hot-pressed compacts was also verified by the lattice shrinkage, studied by XRD. Fig. 6 shows the XRD patterns of the compacts prepared in the closed and open dies at 750 °C. Also included in Fig. 6 are the patterns of the HDDR-treated initial powder and the alloy before HDDR-treatment with no history of hydrogen for comparison. The diffraction peaks were shifted toward a higher angle as the hydrogen content decreased, indicating that the expanded lattice of the tetragonal $Nd_2Fe_{14}B$-type phase in the materials was shrunk by the extent of dehydrogenation. Furthermore, the peaks for the compacts hot-pressed in the open die shifted more than those of the compacts hot-pressed in the closed die. This indicated that residual hydrogen was desorbed more effectively in the open die than in the closed die. The lattice constants, calculated from the corresponding XRD patterns, decreased with increasing dehydrogenation, as shown in Table 1. It was seen that lattice parameters a (8.8580 Å) and c (12.3076 Å) of the $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ alloy after HDDR-treatment were significantly higher than a (8.8168 Å) and c (12.1999 Å) values for the alloy before HDDR-treatment. However, the lattice parameters a (8.8181 Å) and c (12.2212 Å) of the compacts prepared in the open die were lower than a (8.8319 Å) and c (12.2562 Å) values for the compacts hot-pressed in the closed die. This result can be explained by the fact that the lattice constant variations for the compacts hot-pressed in different dies were due largely to the effective desorption of residual hydrogen in the HDDR-treated powder upon hot pressing.

It is believed that residual hydrogen in the HDDR powder has a detrimental effect on the coercivity of the hot-pressed compacts. Therefore, the coercivity values of the compacts would be different depending on the heating rate because of the variances of time allowances for desorbing residual hydrogen during heating for hot-pressing. The HDDR-treated powder, iHc 13.5 kOe, was hot-pressed at 750 °C using different heating rates. The results are shown in Fig. 7. The coercivity was 6.8 kOe in the compacts prepared at a slow heating rate (40 °C/min). This value reduced to 1.1 kOe in the compacts prepared at a moderate heating rate (200 °C/min). On the other hand, the compacts prepared at a high heating rate (400 °C/min)

Table 1. Lattice parameters variations of $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ materials in different conditions.

Materials conditions	Lattice a (Å)	Lattice c (Å)	Unit cell volume v (Å)^3
$Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ HDDR-treated powder	8.8580	12.3076	965.7055
Hot-pressed compact of HDDR-treated powder prepared at 750 °C in closed die	8.8319	12.2562	956.0137
Hot-pressed compact of HDDR-treated powder prepared at 750 °C in open die	8.8181	12.2212	950.3069
$Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ Alloy	8.8168	12.1999	948.3710

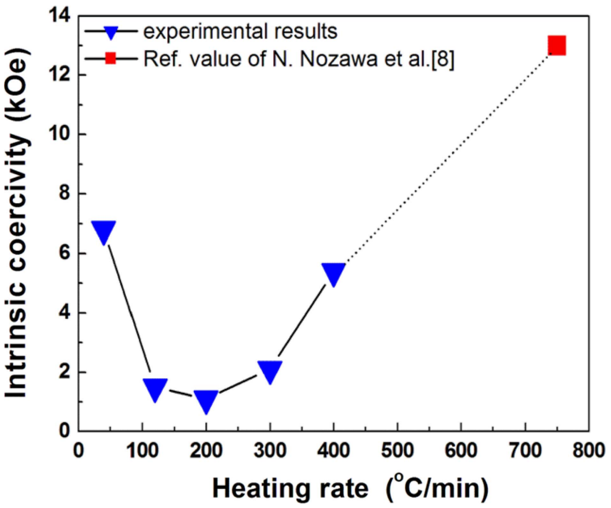

Fig. 7. (Color online) Coercivity variations as a function of heating rate in the compacts of $Nd_{12.5}Fe_{80.6}B_{6.4}Ga_{0.3}Nb_{0.2}$ HDDR-treated powder prepared at 750 °C. The value obtained by N. Nozawa *et al.* [8]

retained the coercivity 6.4 kOe. The results showed that the coercivity in the compacts decreased with increasing heating rate and the values were further increased when extreme high heating rate was employed. The fact can be explained that time allowance was much to be desorbed the residual hydrogen from HDDR-treated powder with slow heating rate which was likely getting slim with increasing the heating rate in the course of heating for hot-pressing. In a previous report, the HDDR-treated powder was compacted successfully at an extremely high heating rate ~750 °C/min under high pressure 586 MPa (~6 Ton/cm^2) within 1 min [8]. The extremely high heating rate (~750 °C/min) was employed to avoid the detrimental effect of the residual hydrogen-related disproportionation in the HDDR-treated powder. Therefore, it would be reasonable to assume that a high heating rate of 400 °C/min might have partially suppressed the hydrogen-related disproportionation in the HDDR-treated powder upon hot-pressing. As a result, the coercivity in the compact prepared at 400 °C/min was higher (6.4 kOe) than that in the compact prepared at 200 °C/min (1.1 kOe). The dotted line in Fig. 7 shows the assumption of coercivity improvement trend in the compact at an extremely high heating rate.

4. Conclusion

HDDR-treated powder was hot-pressed in closed and open-type dies. The closed-type die was less effective than the open-type die in terms of desorption of residual hydrogen during heating for hot-pressing. The coercivity was 10.8 kOe in the compacts prepared in the open die and was only 3.8 kOe in the compacts prepared in the closed-type die, in spite of the identical hot pressing conditions. The HDDR-treated powder contained a significant amount of residual hydrogen in the form of $Nd_2Fe_{14}BH_x$ hydride, which disproportionated into α-Fe, Fe_2B and NdH_2 phases in the closed-type die. Consequently, the compacts prepared in the closed-type die significantly lost coercivity. This finding is closely associated with residual hydrogen, which directly affects the coercivity of an HDDR-treated powder during heating for hot-pressing. Consolidation of an HDDR-treated powder without loss of magnetic performance is desirable. This may be possible by effective desorption of residual hydrogen or by suppression of hydrogen related problems during heating for hot-pressing of an HDDR-treated powder.

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