Magnetic Properties of Nd-Fe-B-Zr Bulk Nanocomposite Magnets Prepared by Spark Plasma Sintering Method

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Abstract. We have investigated the magnetic properties and the microstructure of Nd₈Fe₈₅B₅Zr₂ bulk nanocomposite magnets consolidated by Spark Plasma Sintering (SPS) method with various sintering temperatures and heating speeds. The volume fractions of a soft magnetic phase (α-Fe or Fe₃B) and a hard magnetic phase (Nd₂Fe₁₄B) are found to vary sensitively with the sintering temperature, and the samples sintered at 600-650 °C show optimum hard magnetic properties. At the same sintering temperature of 600 °C, the sample with a higher heating speed of 2400 °C/min exhibits larger coercivity and remanence than that with a lower heating speed of 244 °C/min, which is attributed to the difference in the grain size.

1. INTRODUCTION

Nanocomposite magnets are composed of a mixture of hard and soft magnetic phases which are magnetically coupled by exchange interaction. They are expected to have a high potential as permanent magnets because of the high magnetic flux density of the soft magnetic phase such as α-Fe [1][2]. In particular, Nd-Fe-B nanocomposite magnets have a great advantage over the conventionally sintered magnets prepared at the composition near Nd₂Fe₁₄B in view of the production cost because of their reduced rare earth content. One successful application of the nanocomposite magnets is bond magnets, which are prepared by annealing amorphous powders produced by the melt spinning technique. However, the density of the bond magnets is not high enough, e.g., about 80% of the full density, and therefore it is necessary to synthesize full density bulk nanocomposite magnets in order to improve their magnetic performance.

Spark Plasma Sintering (SPS) method allows us to obtain full-density bulk nanocomposite magnets. SPS is one of the sintering techniques, by which powder material is consolidated into bulk by applying current and pressure simultaneously. Its advantages over other sintering techniques exist in its high sintering speed and low sintering temperature, which inhibits unfavorable grain growth during the sintering process.

Up to now, various bulk nanocomposite magnets have been prepared by SPS, where the hard phase is Nd₂Fe₁₄B and the soft phase is either α-Fe or Fe₃B [3][4]. In the case of α-Fe/Nd₂Fe₁₄B nanocomposite magnets prepared by annealing melt-spun ribbons, the addition of Zr has been found to be very effective in improving the glass forming ability and, as a result, the coercivity of nanocomposite magnets has been increased successfully via the reduction of the grain size [5]. In this study, attempts have been made to produce α-Fe/ Nd₂Fe₁₄B full density bulk nanocomposite magnets by using the SPS method, and comparison of the magnetic properties and the microstructure has been made among bulk magnets prepared under different sintering conditions such as different heating speeds and different sintering temperatures.

2. EXPERIMENTALS

Alloy ingots with the nominal composition Nd₈Fe₈₅B₅Zr₂ were prepared by melting pure elements...
in an arc furnace and the ingots were then melt spun onto a copper wheel rotating with the surface velocity of 50m/s. The thickness of the obtained melt spun ribbons is about 20 \( \mu \)m. The melt spun ribbons were then crashed into powder and packed into a carbon die, and consolidated by SPS under vacuum. For the sintering conditions, the sintering temperature was varied between 500 and 750°C, and the heating speed was set to be either 244°C/min or 2400°C/min. After reaching the sintering temperature, the specimens were furnace-cooled with no holding time. Characterization of the phase was performed by X-ray diffraction (XRD) using Cu-K\( \alpha \) and the magnetic properties of the specimens were measured by using a vibrating sample magnetometer (VSM). The sizes of the bulk samples are either discs of 10mm\( \phi \times 2\)mm or cubes of \( 2 \times 2 \times 2 \)mm\(^3\). The microstructure was investigated by using a field emission scanning electron microscope (FE-SEM).

3. RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of Nd\(_8\)Fe\(_{85}\)B\(_5\)Zr\(_2\) bulk nanocomposite magnets consolidated at 500-750°C with the constant heating speed of 244°C/min. Their magnetic properties are presented in Figs. 2(a)-(c), where Ms is the saturation magnetization, Br is the remanent magnetic flux density and iHc is the coercivity.

![Figure 1: XRD patterns of Nd\(_8\)Fe\(_{85}\)B\(_5\)Zr\(_2\) bulk nanocomposite magnets consolidated at (a)500, (b)550, (c)600, (d)650, (e)700 and (f)750°C with the heating speed of 244°C/min.](image1)

![Figure 2: Magnetic properties of Nd\(_8\)Fe\(_{85}\)B\(_5\)Zr\(_2\) bulk nanocomposite magnets as a function of sintering temperature; (a)saturation magnetization, (b)remanent magnetic flux density and (c)coercivity.](image2)
As seen from Fig. 1, the bulk nanocomposite magnets consolidated at 500 and 550 °C are composed mostly of the Fe₃B phase, and no peaks of the Nd₂Fe₁₄B phase are observed. It explains their low coercivities observed in Fig.2(c). In contrast, when consolidated at 600 °C, the XRD pattern reveals the coexistence of both the α-Fe and the Nd₂Fe₁₄B phases and, at above 650 °C, the peak intensity of the Nd₂Fe₁₄B phase decreases relatively to those of α-Fe, showing that the volume fraction of the α-Fe phase increases when consolidated at higher temperatures above 650 °C. Thus, the increase of Ms with increasing sintering temperature above 650 °C (Fig.2 (a)) is understood by the increase of the volume fraction of the α-Fe phase. The present results have shown that the volume fraction of the Nd₂Fe₁₄B phase is maximized when consolidated at temperatures around 600 °C.

As seen from Fig. 2 (b), Br exhibits a sharp increase at 600 °C exhibiting a maximum at 650 °C. The behavior of Br is similar to that of iHc as mentioned below and the increase of Br is attributed to the increase of the remanence enhancement effect. When consolidated at higher temperatures above 650 °C, i.e., 700 °C and 750 °C, Br begins to decrease, due to weakened exchange coupling between the hard and the soft phases because of the occurrence of excessive grain growth. For the coercivity, iHc is very small at 500 °C and 550 °C as seen in Fig. 2 (c), which is attributed to the absence of the Nd₂Fe₁₄B hard phase: iHc increases sharply with the formation of Nd₂Fe₁₄B and exhibits a maximum when consolidated at 600 °C. The reduction of iHc above 600 °C is ascribed to the excessive grain growth of the hard phase.

Figure 3 shows examples of FE-SEM back scattering images of Nd₈Fe₈₅B₅Zr₂ bulk nanocomposite magnets sintered at (a) 650 °C and (b) 700 °C.

Figure 3 shows examples of FE-SEM back scattering images of Nd₈Fe₈₅B₅Zr₂ sintered at (a) 650 °C and (b) 700 °C. The grain size of the magnet sintered at 650 °C is 50-100 nm whereas that of the magnet sintered at 700 °C is 80-200 nm. Thus, it justifies the above argument that the grain size becomes smaller when sintered at a lower temperature. The large iHc and the high Br of the magnets sintered at 600 and 650 °C are explained by effective exchange coupling, i.e., remanence enhancement.

Figure 4 shows M-H curves of the bulk magnets consolidated at 600 °C with different heating speeds of 244 °C/min and 2400 °C/min, and their XRD patterns are presented in Fig. 5.
Figure 4. Magnetization curves of Nd$_8$Fe$_{85}$B$_5$Zr$_2$ bulk nanocomposite magnets with the heating speeds of 2400 °C/min and 244 °C/min

![Magnetization curves](image)

Figure 5. XRD patterns of Nd$_8$Fe$_{85}$B$_5$Zr$_2$ bulk nanocomposite magnets consolidated at the heating speeds of (a) 2400 °C/min and (b) 244 °C/min

![XRD patterns](image)

For the magnet with the heating speed of 244 °C/min, Br, iHc and Ms are 0.79 T, 322 kA/m and 1.19 T, respectively, and for the magnet with 2400 °C/min, they are 0.88 T, 433 kA/m and 1.19 T, respectively. It is found that both iHc and Br are improved when consolidated with a higher heating speed. On the other hand, Ms shows no change with the variation of the heating speed. As seen in Fig. 5, both the magnets are composed of a mixture of α-Fe and Nd$_2$Fe$_{14}$B with similar relative intensities, which indicates that the volume fractions of α-Fe and Nd$_2$Fe$_{14}$B are nearly the same between the two magnets. Hence, no appreciable difference in the Ms value is attributed to nearly the same volume fractions of α-Fe between the two magnets. On the other hand, as seen from Fig. 4, the hysteresis curves shows that
the exchange coupling is weakened for the sample with 244 °C/min compared with the magnet with the higher heating speed, i.e., the curve for the sample with 244 °C/min is composed of each contribution from the soft and the hard phases. As seen in Fig. 5, the XRD peaks are broader for the sample with the heating speed of 2400 °C/min than those for 244 °C/min, which indicates that the grain size is smaller when prepared with a higher heating speed. Therefore, the heating speed during SPS process is also an important factor for the optimization of the grain size. In this respect, even larger coercivity and higher remanence are expected by controlling the grain growth during SPS process.

4. CONCLUSIONS
We have investigated the magnetic properties and the microstructure of Nd_{8}Fe_{85}B_{5}Zr_{2} bulk nanocomposite magnets consolidated by spark plasma sintering (SPS) method at various temperatures and with various heating speeds. It has been found that for the same heating speed, i.e., 244 °C/min, the optimum magnetic properties are obtained when consolidated at 600-650 °C, which is due to small grain sizes of the hard and the soft phases, i.e., effective exchange coupling effect between the two phases. For the same sintering temperature, i.e., 600 °C, both the remanence and the coercivity are found to be improved by consolidation with a higher heating speed, which is attributed to reduced grain sizes of the hard and soft phases at the higher heating speed.

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