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

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Abstract. We have investigated the magnetic property and the microstructure of Nd₈Fe₈₅B₅Zr₂ bulk nanocomposite magnets consolidated by Spark Plasma Sintering (SPS) method with various sintering temperatures. The volume fractions of a soft magnetic phase (α-Fe) and a hard magnetic phase (Nd₂Fe₁₄B) are found to vary sensitively with the quenching speed, i.e., the surface velocity of the Cu wheel, as well as the sintering temperature. The optimal magnetic property of \((BH)_{\text{max}} = 100 \text{ kJ/m}^3\) has been obtained when sintered at 650 °C with the surface velocity of 25 m/s, and the high performance is attributed to a combined effect of grain refinement and reduction of non magnetic regions such as grain boundaries.

1. INTRODUCTION

Nanocomposite magnets are composed of hard and soft magnetic phases which are coupled by exchange interaction. They are expected to have a high potential as permanent magnets because of their high magnetic flux density arising from the soft magnetic phase such as α-Fe [1][2]. In particular, Nd-Fe-B nanocomposite magnets have a great advantage over the conventional sintered magnets prepared at compositions near stoichiometric Nd₂Fe₁₄B with respect to the production cost because of their low rare earth content. One successful application of the nanocomposite magnets is bond magnets, which are synthesized by heat treatment of amorphous powders prepared by the melt spinning technique. However, the volume density of the bond magnets is not high enough, about 80 % of the full density, because of the unavoidable usage of binders for the formation of bond magnets. For this reason, it is preferable to synthesize full density bulk nanocomposite magnets in order to substantially improve the magnetic performance such as the magnetic flux density.

Spark Plasma Sintering (SPS) method is a unique technique which allows us to obtain full-density bulk nanocomposite magnets in a short time. In SPS, powder material is consolidated into bulk by simultaneous application of electrical current and pressure. Its advantages over other sintering techniques exist in its high sintering speed and low sintering temperature, which inhibits an excessive grain growth during sintering, making it possible to obtain a bulk sample in an amorphous or nano grains state.

Recently, various bulk nanocomposite magnets have been synthesized by using 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 increased greatly due to the reduction of the grain size [5]. More recently, the influence of SPS sintering conditions such as the sintering temperature and the heating speed has been systematically investigated [6]. Following the previous works, the role of sintering conditions such as the sintering temperature, the quenching speed, i.e., the surface velocity of Cu wheel (vₚ), in the magnetic properties and the microstructure were investigated in detail for Nd-Fe-B-Zr nanocomposite magnets prepared by the SPS method in this study.
2. EXPERIMENTAL

Alloy ingots with nominal composition Nd$_8$Fe$_{85}$B$_5$Zr$_2$ 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 velocities ($v_s$) of 12-37 m/s. The melt spun ribbons were then crushed into powder, packed into a carbon die, and consolidated by SPS in vacuum under the applied pressure of 100 MPa. For the sintering conditions, the sintering temperature was varied between 500 and 750 °C and the heating speed was set to be 250 °C/min. After reaching the sintering temperature, the specimens were furnace-cooled with no holding time. Characterization of the phases was performed by X-ray diffraction (XRD) using Cu-Kα and the magnetic properties of the specimens were measured by using a vibrating sample magnetometer (VSM) in the magnetic field up to 2 T. The shape of the bulk samples is a disc of 10 mm × 2 mm. 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$_2$ melt spun ribbons with different surface velocities ($v_s$ = 12-37 m/s) together with a calculated diffraction pattern of Nd$_2$Fe$_{14}$B on the bottom. For $v_s$ = 12-25 m/s, the peaks marked by solid circles are attributed to those from α-Fe and the positions of the remaining peaks are in agreement with those of Nd$_2$Fe$_{14}$B. The volume fraction of α-Fe is found to increase with decreasing the surface velocity $v_s$. On the other hand, the melt spun ribbon prepared with $v_s$ = 37 m/s is found to be in a nanocrystalline state.

Figure 2 presents FE-SEM back scattering images of Nd$_8$Fe$_{85}$B$_5$Zr$_2$ melt spun ribbons with $v_s$ = 12-37 m/s. In figure 2(a), the dark regions represent α-Fe and its grain size is estimated to be about 50-100 nm from the contrast observed in the figure. It is seen that the grain size becomes finer with increasing the surface velocity. For $v_s$ = 18 m/s, white regions are attributed to Nd$_2$Fe$_{14}$B, which accounts for the high coercivity (457 kA/m) of the sample. For $v_s$ = 25 m/s, the grain size is very fine and is not well distinguished from the image, i.e., dark and light regions are not clearly resolved on several 10 nm scale such as seen in figure 2(a). Since both the α-Fe and the Nd$_2$Fe$_{14}$B phases are recognized in the X-ray diffraction pattern (figure 1(a)), it suggests that the sample with $v_s$ = 25 m/s consists of very fine grains of the soft and the hard phases.

![Figure 1](image1.png)

**Figure 1.** XRD patterns of Nd$_8$Fe$_{85}$B$_5$Zr$_2$ melt spun ribbons prepared with the surface velocities of (a) 12m/s, (b) 18m/s, (c) 25m/s and (d) 37m/s. On the bottom is shown the calculated diffraction pattern using the structural model of Nd$_2$Fe$_{14}$B.

![Figure 2](image2.png)

**Figure 2.** FE-SEM back scattering images of Nd$_8$Fe$_{85}$B$_5$Zr$_2$ melt spun ribbons prepared with the surface velocities of (a) 12m/s, (b) 18m/s, (c) 25m/s, (d) 37m/s.
Figure 3 shows XRD patterns of Nd$_8$Fe$_{85}$B$_5$Zr$_2$ bulk nanocomposite magnets prepared with $v_s = 12$-$37$ m/s together with a calculated pattern of Nd$_2$Fe$_{14}$B on the bottom. As seen from the figures 3 (a)-(c), peaks from the α-Fe phase are observed in the samples consolidated at temperatures above 550 °C and the remaining broad peaks are in agreement with those of the Nd$_2$Fe$_{14}$B phase. Note that no other phase is recognized from the patterns, suggesting that the samples are mostly composed of α-Fe and Nd$_2$Fe$_{14}$B. In addition, the relative peak intensity of the Nd$_2$Fe$_{14}$B phase decreases with increasing sintering temperature, indicating that the volume fraction of α-Fe increases with increasing sintering temperatures. From the figure 3 it is also seen that the relative intensity of the α-Fe peak becomes larger for lower $v_s$, implying that the volume fraction of the α-Fe becomes higher for a lower quenching speed. On the other hand, for the highest quenching speed ($v_s = 37$ m/s), the samples consolidated at 500 and 550 °C are composed mostly of the Fe$_3$B phase as seen from the figure 3(d), which is in contrast with the case of the sample consolidated at 600 °C where the α-Fe and the Nd$_2$Fe$_{14}$B phases coexist. When consolidated above 650 °C, the peak intensity of the Nd$_2$Fe$_{14}$B phase decreases relatively to those of α-Fe, showing that the volume fraction of α-Fe phase increases when consolidated at higher temperatures above 650 °C. The above results indicates that lower sintering temperatures are favorable for obtaining higher volume fraction of Nd$_2$Fe$_{14}$B.

![XRD patterns of Nd$_8$Fe$_{85}$B$_5$Zr$_2$ bulk nanocomposite magnets](image)

**Figure 3.** XRD patterns of Nd$_8$Fe$_{85}$B$_5$Zr$_2$ bulk nanocomposite magnets prepared with the surface velocities of (a) 12m/s, (b)18m/s, (c)25m/s and (d)37m/s, and sintered at 500-750°C. On the bottom is shown the calculated diffraction pattern using the structural model of Nd$_2$Fe$_{14}$B.

Figure 4 presents FE-SEM back scattering images of Nd$_8$Fe$_{85}$B$_5$Zr$_2$ bulk magnet prepared with $v_s = 12$-$37$ m/s sintered at 650 °C. The grain size of the magnet prepared with $v_s = 12$ m/s is considerably larger than those of the magnets with the higher surface velocities $v_s$ and it becomes finer with increasing $v_s$. Figure 5 shows FE-SEM back scattering images of Nd$_8$Fe$_{85}$B$_5$Zr$_2$ sintered at 650 and 700 °C. The grain size of the magnet sintered at 650 °C is about 50 nm whereas that of the magnet sintered at 700 °C is about 100 nm, showing that the grain size varies sensitively with the sintering temperature. A lower sintering temperature is effective in the suppression of the grain growth during sintering.
From these observations we can conclude that the quenching speed, i.e., the surface velocity, and the sintering temperature are two important factors in determining the volume fraction of $\alpha$-Fe and Nd$_2$Fe$_{14}$B and the grain size of the nanocomposites.

Figure 6 presents sintering temperature dependence of the maximum energy product (BH)$_{\text{max}}$ of the Nd$_8$Fe$_{85}$B$_5$Zr$_2$ bulk nanocomposite magnets prepared with $v_s$=12-37 m/s. The sample sintered at 650 °C exhibits highest energy product (BH)$_{\text{max}}$ among those prepared with the other temperatures for all the surface velocities ($v_s$=12-37 m/s). The high (BH)$_{\text{max}}$ for the 650 °C sintered samples is attributed to strong exchange coupling effect between the soft and hard grains since the grain growth is effectively suppressed for the 650 °C–sintered samples. Figure 7 shows M-H curves of the bulk magnets sintered at 650 °C with different surface velocities. The highest saturation magnetization of 1.38 T and the highest energy product of 100 kJ/m$^3$ are obtained for $v_s$=25 m/s. The reason for the best magnetic performance for $v_s$=25 m/s is considered to be twofold. One is the high Mr/Ms ratio of 0.75, which is attributed to effective exchange coupling effect between the soft and the hard phases, and the other is high coercivity, which indicates that the volume fraction of Nd$_2$Fe$_{14}$B is the highest for the sintering condition. The latter result means that the volume fraction of Nd$_2$Fe$_{14}$B can be controlled by tuning the surface velocities. The present work has shown that the quenching speed i.e. the surface velocity of the Cu wheel, is a very important factor to determine the volume fraction of nonmagnetic regions such as grain boundaries, the volume fraction of Nd$_2$Fe$_{14}$B and the grain size.

It is noted that concerning the saturation magnetization, one might expect much higher saturation magnetization exceeding 1.6 T for nanocomposite magnets entirely composed of $\alpha$-Fe and Nd$_2$Fe$_{14}$B since the saturation magnetization is determined by the volume fraction and the saturation magnetization of the constituent phases. However, the observed saturation magnetizations are less than 1.6 T for all the samples, suggesting that the samples sintered at 650 °C with $v_s$=12-37 m/s contain either nonmagnetic or weak magnetic regions within the specimens. Such a phase has not been recognized in the present work, however, grain boundaries might be responsible for the loss of the magnetization. The present results suggest that the volume fraction of nonmagnetic regions is the lowest for the bulk magnet prepared with $v_s$ = 25 m/s and sintered at 650 °C.
4. CONCLUSIONS

We have investigated the magnetic properties and the microstructure of Nd₈Fe₈₅B₅Zr₂ bulk nanocomposite magnets consolidated by spark plasma sintering (SPS) method at various temperatures as well as with various quenching speeds. It has been demonstrated that the grain size and the volume fraction of Nd₂Fe₁₄B and weak or non magnetic regions such as grain boundaries can be controlled by the sintering temperature and the quenching speed, respectively. As a result of the optimization by the two sintering conditions, the highest energy product of (BH)_{max}=100 kJ/m³ has been obtained at the surface velocity of 25 m/s and the sintering temperature of 650 °C for the Nd₈Fe₈₅B₅Zr₂ nanocomposite magnet.

5. ACKNOWLEDGMENTS

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Figure 6. Sintering temperature dependence of (BH)_{max} for the Nd₈Fe₈₅B₅Zr₂ bulk nanocomposite magnets prepared at v_s =12-37 m/s

Figure 7. Magnetization curves of the Nd₈Fe₈₅B₅Zr₂ bulk nanocomposite magnets sintered at 650 °C with the various surface velocities of (a) 12 m/s, (b) 18 m/s, (c) 25 m/s and (d) 37 m/s.