Preparation of Sm−Fe−N bulk magnets with high maximum energy products

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In an effort to increase the maximum energy product ((BH)max) and coercivity (Hc) of Zn-bonded Sm−Fe−N magnets, we developed a process for preparing Sm−Fe−N and Zn powders with low oxygen contents and subjected them to spark plasma sintering. The oxygen content, remanence, and coercivity of the Sm−Fe−N powder were 0.22 wt%, 151 A m^-2 kg^-1, and 0.72 MA m^-1, respectively. The oxygen content and secondary average particle size of the Zn powder were 0.083 wt% and 0.93 μm, respectively. The magnetic properties of the Zn-free Sm−Fe−N magnets included an Hc of 0.86 MA m^-1 and a (BH)max of 188 kJ m^-3, while the Zn-bonded (10 wt%) Sm−Fe−N magnets exhibited excellent magnetic properties with a (BH)max of 200 kJ m^-3 and an Hc of 1.28 MA m^-1. Compared with previous studies, this is the high (BH)max observed for a Sm−Fe−N bulk magnet simultaneously displaying a high Hc. The (BH)max of the Zn-bonded magnets was greater than that of the Zn-free magnets owing to the higher relative density of the former. Therefore, Zn is an effective binder for increasing not only the coercivity but also the density of Sm−Fe−N magnets. Consequently, the procedure reported herein permits the successful preparation of high-performance Sm−Fe−N bulk magnets.

Key words: Sm−Fe−N magnets, Zn binder, maximum energy products, low oxygen content, fine Zn powder, spark plasma sintering

1. Introduction

Sm2Fe17N3 is well known for its high saturation magnetization (M), anisotropy field (Hk), and Curie temperature (Tc). Therefore, Sm2Fe17N3-based bulk magnets are expected to exhibit a high thermal stability and maximum energy product (BH)max. However, at temperatures exceeding 600 °C, Sm2Fe17N3 decomposes into α-Fe and Sm−N. Consequently, Sm2Fe17N3 powders are typically used for bonded magnets. Although resins are widely applied as the binder in bonded magnets, metal binders have also been explored. Otani et al. reported that the use of Zn as the binder can increase the coercivity (Hc) of bonded magnets, which was attributed to reaction of the Zn with the soft magnetic α-Fe phase during annealing to form a non-magnetic Fe-Zn phase. As the soft magnetic α-Fe phase acts as a nucleation site for reversed magnetic domains, reducing the α-Fe phase is essential for obtaining high Hc. To improve the (BH)max of Sm-Fe-N magnets, it is crucial to increase the relative density and volume fraction of the Sm-Fe-N powder. Numerous researchers have tried to improve the (BH)max of Sm-Fe-N magnets. For example, Mashimo et al. prepared Zn-free Sm-Fe-N magnets using shock compression and reported a density of 6670 kg m^-3, a (BH)max of 179 kJ m^-3, and a coercivity of 0.40 MA m^-1 for the resulting magnets. Ito et al. prepared Zn-bonded Sm-Fe-N magnets by hot isostatic pressing and obtained a (BH)max and coercivity of 168 kJ m^-3 and 0.56 MA m^-1, respectively, for a 5 wt% Zn-bonded magnet. Our group has also reported Zn-bonded Sm-Fe-N magnets fabricated by mechanical processing. Ishihara et al. prepared Zn-bonded Sm-Fe-N magnets by hot-rolling and obtained a relative density of 97%, a (BH)max of 132 kJ m^-3, and a coercivity of 1.36 MA m^-1 for a 5 wt% Zn-bonded magnet. Kataoka et al. prepared Zn-bonded Sm-Fe-N magnets by swaging and reported a (BH)max of 67.8 kJ m^-3, and a coercivity of 1.89 MA m^-1 for a 15 wt% Zn-bonded magnet. Furthermore, Saito and Prabhu et al. obtained Zn-bonded Sm-Fe-N magnets via spark plasma sintering (SPS). Saito used magnetic-field-assisted SPS to prepare 5 and 10 wt% Zn-bonded Sm-Fe-N magnets with relative densities of 88.7−92.5%. In particular, a (BH)max of 158 kJ m^-3 and a coercivity of 0.64 MA m^-1 were achieved for the 5 wt% Zn-bonded magnet. Prabhu et al. reported a high coercivity of 2.19 MA m^-1, a high density of 6200 kg m^-3, and a (BH)max of approximately 70 kJ m^-3 for a 15 wt% Zn-bonded Sm-Fe-N magnet. In addition, decreasing the oxygen content is important for improving the coercivity of Zn-bonded Sm-Fe-N magnets because oxygen at the surface of the Sm-Fe-N powder can decrease the coercivity by mediating the decomposition of the Sm2Fe17N3 phase. Therefore, reducing the oxygen content in Sm-Fe-N magnets suppresses the decrease in coercivity. We previously reported the preparation of high-coercivity Zn-bonded Sm-Fe-N magnets using Zn powder with a low oxygen content and fine particle size, which was obtained via the hydrogen plasma–metal reaction (HPMR) method. The HPMR approach is useful for preparing fine Zn particles with a low oxygen content, and the primary and secondary average particle sizes of the obtained Zn powder were 0.23 and 0.93 μm, respectively, while the oxygen content was only 0.068 wt%. The oxygen content of the Zn-bonded Sm-Fe-N magnets prepared using HPMR Zn and commercial...
Sm–Fe–N powders also decreased, and high coercivities of 2.66 and 2.41 MA m\(^{-1}\) were observed for the 15 and 10 wt% Zn-bonded Sm–Fe–N magnets, respectively. To further reduce the oxygen content of Zn-bonded Sm–Fe–N magnets, it is necessary to use a Sm–Fe–N powder with a low oxygen content. Soda et al.\(^{11}\) reported that decreasing the oxygen content of the Sm–Fe–N powder was effective for suppressing the decrease in the coercivity of Sm–Fe–N bulk magnets. Recently, our group has also demonstrated that decreasing the oxygen content in Sm\(_{2}\)Fe\(_{17}\)N-based magnets is effective for suppressing the deterioration of coercivity during heat treatment\(^{50}\). In our previous study, Sm–Fe–N powder was synthesized without exposure to air. The resulting oxygen content was 0.23 wt\%, which is one-third of that of commercial Sm–Fe–N powder. Subsequently, fine Zn particles with a diameter of several tens of nanometers were deposited on the Sm–Fe–N powder under vacuum conditions via arc plasma deposition (APD). The application of APD avoided an increase in the oxygen content of the Zn-deposited Sm–Fe–N powder, which was then subjected to sintering via SPS. The resulting 3.3 wt\% Zn-bonded and Zn-free Sm–Fe–N magnets displayed \((BH)_{\text{max}}\) values of 153 and 179 kJ m\(^{-3}\) and \(H_d\) values of 1.14 and 0.80 MA m\(^{-1}\), respectively. Despite these promising magnetic properties obtained via a combination of APD and SPS, the APD process used for Zn deposition was complex. Thus, in this study, we investigated the use of the HPMR process to synthesize fine Zn powder with a low oxygen content and the subsequent application of this Zn powder and the Sm–Fe–N powder with low oxygen content to the fabrication of high-\((BH)_{\text{max}}\) Zn-bonded Sm–Fe–N magnets via SPS.

2. Experimental procedure

Low-oxygen-content (low-O) Sm–Fe–N powder was prepared from Sm\(_{2}\)Fe\(_{17}\)N-based coarse Sm–Fe powder without exposure to air. The coarse Sm–Fe powder was obtained via a reduction-diffusion process and pulverized by ball milling in organic solvent with a rotational speed of 400 rpm and a milling time of 45 min. The resulting fine Sm–Fe powder was subjected to nitridation under \(N_2\) gas at 450 °C for 25 h. Zn powder was prepared via the HPMR method with an arc current of 100 A and a hydrogen gas partial pressure of 20%. The low-O Sm–Fe–N powder and 10 wt\% Zn powder were mixed via ball milling and the mixed powder was then pressed at 200 MPa under an applied magnetic field of 2.3 MA m\(^{-1}\) in an argon atmosphere. The green compacts were subjected to SPS under a sintering pressure of 750 MPa and a sintering temperature of 300–500 °C. Zn-free Sm–Fe–N magnets were also prepared from the low-O Sm–Fe–N powder via SPS.

The magnetic properties of the Zn-free and Zn-bonded Sm–Fe–N magnets were measured using a pulsed \(B-H\) loop tracer and a DC \(B-H\) loop tracer. The magnetic properties of the raw powders were measured using a vibrating-sample magnetometer. The oxygen content was measured using an O/N analyzer, and the microstructure was examined via field-emission scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (TEM). The powder composition was determined via X-ray fluorescence. The secondary particle size distribution was measured by laser diffraction. The relative densities of the Zn-free and Zn-bonded magnets were evaluated using the reported density of Sm\(_2\)Fe\(_{17}\)N (7.68 Mg m\(^{-3}\))\(^{10}\) and theoretical density of Zn (7.13 Mg m\(^{-3}\)).

3. Results and discussion

The oxygen content of the low-O Sm–Fe–N powder was 0.22 wt\%, which is one-third of that of commercial Sm–Fe–N powder, whereas the nitrogen content was almost the same at 3.20 wt\%. Figure 1 shows the particle size distribution of the low-O Sm–Fe–N powder. The average particle size (\(d_{50}\) and \(d_{90}\), which were evaluated from cumulative distribution, for low-O Sm–Fe–N powder were 2.47 and 5.68 μm, respectively. For comparison, the \(d_{50}\) and \(d_{90}\) of commercial powder were evaluated and these values were 2.99 and 5.26 μm, respectively. Therefore, it is suggested that the low-O Sm–Fe–N powder has smaller average particle size than commercial powder, while the low-O powder has larger amount of coarse powder than the commercial one. The oxygen content and secondary average particle size of the Zn powder fabricated via HPMR were evaluated, and these values were 0.083 wt\% and 0.93 μm, respectively.

Figure 2 shows the hysteresis loops for the low-O and commercial Sm–Fe–N powders. The saturation magnetization and remanence of the low-O Sm–Fe–N powder were 154 A m\(^{-2}\) kg\(^{-1}\) and 151 A m\(^{-2}\) kg\(^{-1}\), respectively, which were higher than those of the commercial Sm–Fe–N powder. The coercivity of the low-O Sm–Fe–N powder was 0.72 MA m\(^{-1}\), which was slightly less than that of the commercial Sm–Fe–N powder. The reason for the low-O Sm–Fe–N powder

![Figure 1](image-url) Particle size distribution of the low-O Sm–Fe–N powder.
showing slightly lower coercivity than the commercial Sm–Fe–N powder is thought that the low-O powder has coarse powders. As described above, the \( d_{50} \) of the low-O powder was larger than that of the commercial powder, therefore it can cause decrease in the coercivity. In addition, the local stray field could also decrease coercivity of the low-O Sm–Fe–N powder. The low-O Sm–Fe–N powder had angular shape because it was prepared by ball milling. The angular shape particles have high local stray field, therefore the coercivity of the low-O powder could be slightly less than that of commercial one.

After mixing the low-O Sm–Fe–N and Zn powders, the oxygen content of the mixed Sm–Fe–N/Zn powder was 0.27 wt%, corresponding to an increase in the oxygen content during the mixing process of only 0.05 wt%. The saturation magnetization and Zn content of the mixed Sm–Fe–N/Zn powder were 140 A m\(^2\) kg\(^{-1}\) and 10.4 wt%, respectively. The decrease in the saturation magnetization corresponds to the amount of Zn addition. Next, the mixed Sm–Fe–N/Zn powder was subjected to SPS to prepare Zn-bonded Sm–Fe–N magnets. Figure 3 presents the coercivity and \((BH)_{\text{max}}\) values of the Zn-free and Zn-bonded Sm–Fe–N magnets as functions of the sintering temperature. As shown in Fig. 3(a), the coercivity of the Zn-free Sm–Fe–N magnets decreased with increasing sintering temperature above 400 °C, while the \((BH)_{\text{max}}\) increased with increasing sintering temperature to 400 °C and thereafter decreased. The highest value of \((BH)_{\text{max}}\) was obtained upon sintering at 440 °C, which was accompanied by a relatively high \( H_c \) of 1.28 MA m\(^{-1}\). Compared with the previous studies\(^{7,12,16,17,20}\), the \((BH)_{\text{max}}\) and coercivity obtained in this study are higher. Figure 4 presents demagnetization curves for the Zn-free and Zn-bonded Sm–Fe–N magnets sintered at 400 °C. The relative densities of the Zn-free and Zn-bonded Sm–Fe–N magnets were 81% and 91%, respectively. The \((BH)_{\text{max}}\) of the Zn-bonded magnets was higher than that of the Zn-free magnets in this study owing to the higher relative density of the former. Therefore, Zn is an effective binder for increasing not only the coercivity but also the density of the magnets. The oxygen content of the Zn-bonded magnets was only 0.28 wt%, which is only a slight increase from the value measured for the mixed Sm–Fe–N/Zn powder (0.27 wt%). This oxygen content of the Zn-bonded Sm–Fe–N magnets is lowest than those reported in previous papers\(^{11,12}\).
As thermal stability is an important property for Sm–Fe–N magnets, the temperature coefficient of coercivity \(d(H_c)/dT\) was evaluated for the Zn-free and Zn-bonded Sm–Fe–N magnets. Figure 5 shows the temperature dependences of coercivity for the Zn-free and Zn-bonded magnets measured using a pulsed \(B–H\) loop tracer over the temperature range from 25 to 200 °C. The open square and triangle indicate the coercivities measured at room temperature after the measurements at 200 °C, which were almost identical to the initial values. This result indicates that the influence of oxygen in the Zn-free and Zn-bonded magnets on their coercivities was negligible. The \(d(H_c)/dT\) values from 25 to 200 °C for the Zn-free and Zn-bonded magnets were \(-0.40\%/°C\) and \(-0.34\%/°C\) respectively. In previous papers\(^{9,14,15}\), the \(d(H_c)/dT\) values reported for Sm–Fe–N magnets without additional elements ranged from \(-0.45\%\) to \(-0.47\%/°C\), demonstrating the superiority of the Zn-free Sm–Fe–N magnets prepared in this study. In regard to the Zn-bonded magnet, Wall et al.\(^{16}\) reported an \(d(H_c)/dT\) value from 25 to 150 °C of \(-0.36\%/°C\) for a 5 wt% Zn-bonded Sm–Fe–N magnet. Furthermore, Kou et al.\(^{17}\) fabricated Zn-bonded magnets containing 5 and 15 wt% Zn, which displayed \(d(H_c)/dT\) values of approximately \(-0.36\%/°C\) and \(-0.37\%/°C\), respectively (we should note that \(d(H_c)/dT\) values were not reported in this paper; therefore, we estimated these \(d(H_c)/dT\) values from the published data). In addition, our group\(^{18}\) previously reported an \(d(H_c)/dT\) value of \(-0.32\%/°C\) for a 15 wt% Zn-bonded Sm–Fe–N magnet. Thus, the \(d(H_c)/dT\) value of \(-0.34\%/°C\) obtained for the 10 wt% Zn-bonded magnet in this study is reasonable considering its Zn content.

The Kronmüller equation\(^{18}\) is frequently applied to explain the coercivity of various samples by evaluating the values of the coefficient \(a\) and \(N_{eff}\). Here, the Kronmüller equation is expressed as follows:

\[
\mu_0H_c = a\mu_0H_{eff} - N_{eff}J_c.
\]  

Sagawa and Hirohawa\(^{19}\) applied this equation to Nd–Fe–B and Pr–Fe–B sintered magnets, and they mentioned that the first term on the right-hand side of the equation represents the nucleation field of the reversed magnetic domains, while the second term takes into account the local stray fields. They also mentioned that it is presumed that \(a\) and \(N_{eff}\) are related to the microstructure of the magnet. Thus, the \(a\) and \(N_{eff}\) values of the Zn-free and Zn-bonded Sm–Fe–N magnets prepared in this study were evaluated from the temperature dependence of \(H_c\). Figure 6 presents a plot of \(\mu_0H_c/J_c\) against \(\mu_0H_{eff}/J_c\) for the Zn-free and Zn-bonded Sm–Fe–N magnets. In this study, we used the temperature dependence of \(H_c\) reported in a previous paper\(^{20}\). A linear relationship was observed between the two quantities, allowing the values of \(a\) and \(N_{eff}\) to be evaluated from the gradients and intercepts of the lines of best fit. The \(a\) and \(N_{eff}\) values of the Zn-free magnet were 0.065 and 0.42, respectively, whereas those of the Zn-bonded magnet were 0.088 and 0.32, respectively. Iriyama et al.\(^{20}\) reported \(a\) and \(N_{eff}\) values of 0.045 and 0.22, respectively, for a Zn-bonded Sm–Fe–N magnet containing 10 wt% Zn, and \(a\) and \(N_{eff}\) values of 0.084 and 0.23, respectively, for a Zn-bonded Sm–Fe–N magnet containing 30 wt% Zn. The \(a\) value of 0.088 obtained for the Zn-bonded magnet in this study is higher than the Zn-bonded magnet in the previous paper\(^{20}\). The \(N_{eff}\) values obtained for the magnets in this study are slightly higher than those reported in the
previous paper\textsuperscript{20}. These results suggested that the surface state of the Sm\textsubscript{2}Fe\textsubscript{17}N\textsubscript{x} phase may have been altered by the Zn addition. Thus, the microstructures of the Zn-free and Zn-bonded Sm–Fe–N magnets were examined via SEM and TEM. Figure 7 presents cross-sectional secondary electron and Zn-mapping images of the magnets. Zn was found to be present at the grain boundaries of the Zn-bonded magnet. Comparison of the Zn-free and Zn-bonded magnets in Figs. 7(a) and (b) revealed a higher density for the latter sample. Next, the detailed microstructure at the grain boundary was examined via TEM. Figure 8 presents a TEM image and Sm-, Fe- and Zn-mapping images of a grain boundary in the Zn-bonded magnet. As shown in Fig. 8(d), Zn was detected at the surface of the Sm–Fe–N phase. In contrast, as shown in Fig. 8(e), the Fe content in this region was low. Therefore, it is thought that Zn diffused along the grain boundary and reacted with the surface of the Sm\textsubscript{2}Fe\textsubscript{17}N\textsubscript{x} powder. It is suggested that this diffusion and reaction between the Zn and Sm\textsubscript{2}Fe\textsubscript{17}N\textsubscript{x} phase could be responsible for increasing the value of $a$ and coercivity of the Zn-bonded magnet.

Consequently, in this study, Zn-free and Zn-bonded Sm–Fe–N magnets exhibiting high $(BH)_{\text{max}}$ value were successfully prepared by using Sm–Fe–N and Zn powders with low oxygen contents in combination with SPS.

4. Summary

To increase the $(BH)_{\text{max}}$ of Zn-bonded Sm–Fe–N magnets, we applied a process for preparing Sm–Fe–N and Zn powders with low oxygen contents in combination with SPS. The oxygen content, remanence, and coercivity of the Sm–Fe–N powder were 0.22 wt\%, 151 A m\textsuperscript{2} kg\textsuperscript{-1}, and 0.72 MA m\textsuperscript{-1}, respectively, and the oxygen content and secondary average particle size of the Zn powder were 0.083 wt\% and 0.93 μm, respectively. The magnetic properties of the Zn-free Sm–Fe–N magnets included a $(BH)_{\text{max}}$ of 188 kJ m\textsuperscript{-3} and an $H_d$ of 0.86 MA m\textsuperscript{-1}, and the Zn-bonded (10 wt\%) Sm–Fe–N magnets exhibited excellent magnetic properties with a $(BH)_{\text{max}}$ of 200 kJ m\textsuperscript{-3} and an $H_d$ of 1.28 MA m\textsuperscript{-1}. Compared with previous studies, this is the high $(BH)_{\text{max}}$ observed for a Sm–Fe–N bulk magnet simultaneously displaying a high $H_d$. The oxygen content of the Zn-bonded Sm–Fe–N magnets was 0.28 wt\%, which was only a slight increase from the value observed for the mixed Sm–Fe–N/Zn powder (0.27 wt\%). This oxygen content is the lowest reported for a Zn-bonded Sm–Fe–N magnet. Furthermore, the temperature coefficients of coercivity of the magnets were evaluated, revealing values of $-0.40\%$°C\textsuperscript{-1} and $-0.34\%$°C\textsuperscript{-1} for the Zn-free and Zn-bonded magnets, respectively. Consequently, the procedure described in this paper allows the preparation of high-performance Sm–Fe–N bulk magnets.

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