Magnetic Properties of Nd–Fe–B Sintered Magnets Produced by Reduction-Grain Boundary Diffusion Process with Heavy Rare-Earths Compounds and Ca Metal Vapor

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The grain boundary region of NdFeB sintered magnets were modified by reduction-grain boundary diffusion (r-GBD) process using Heavy Rare-Earths (HRE = Dy or Tb) metal which generated via reduction of HRE compounds such as oxide or fluoride with Ca metal vapor. After modification, magnetic properties were measured accurately by superconducting magnet-based vibrating sample magnetometer (SCM-VSM). The coercivity of DyF3 and TbF3 treated magnets with the assistance of reduction by Ca metal vapor (HJ = 1580 kA/m, respectively) were effectively enhanced compared to untreated magnets (HJ = 1003 kA/m) without decreasing of remanence value. The resultant coercivity was higher than that of the magnets modified by DyF3 (HJ = 1319 kA/m) and TbF3 (HJ = 1580 kA/m) without using any reducing agent such as Ca metal vapor. [doi:10.2320/matertrans.MT-MBW2019006]

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1. Introduction

NdFeB sintered magnets have been widely used for as key materials of voice coil motors (VCM), magnetic resonance imaging (MRI), and many kind of motors, because they have excellent magnetic properties. In addition to this, with interest in environmental problems being heightened, demand for the application of driving motors such as electric vehicles (EV) and hybrid vehicles (HEV) are significantly increased. It has been strongly demanded for permanent magnets having a high coercivity for driving them at high temperatures since they are self-heated when driving at high speed or long distance.

It is well known that addition of heavy rare-earths (HRE = Dy or Tb) is effectively enhance their coercivity (HJ), because (Nd, Dy or Tb)2Fe14B phase has a higher magnetic anisotropy field (HJ) than that of Nd2Fe14B main phase. However, in this process, while the coercivity is enhanced with increasing in the amount of HRE, there is a problem that the remanence (BR) and maximum energy ((BH)max) is considerably decreased, because the anti-parallel coupling between the magnetic moments of HRE element with Fe element.

On the other hand, the magnetic reversal mechanism of NdFeB sintered magnets are generally understood to be nucleation type, magnetic reversal occurs from the localized lower anisotropy regions such as defective surface of magnetic domains. Therefore, if it is possible to substitute HRE element only magnetic domain surface and grain boundary region which possesses low magnetic anisotropy, it can be enhanced coercivity without decreasing their intrinsic remanence.

Based on this concept, the technique for increasing of coercivity of NdFeB sintered magnets has been reported in which the magnets are coated with HRE material and then heat treatment around the melting point of the grain boundary region. This technique is generally referred to as Grain Boundary Diffusion (GBD) process. In this technique, HRE element is selectively concentrated at the Nd-rich grain boundary region among Nd2Fe14B main phase particles in the magnets, and consequently the coercivity of these magnets is considerably enhanced almost kept their intrinsic high remanence.

In our previous papers, the authors have reported GBD process with sputtered Tb metal and reduction-GBD process involving reduction of Dy2O3 or DyF3 with CaH2 powder. Later, similar GBD processes using various HRE-compounds powder vapor deposition, and alloy powder have been reported. However, when the HRE compounds are used, the increase in coercivity is small, and the decrease in squareness with respect to the untreated magnets are large, and when HRE- vapor deposition or alloy powder is used, efficiently increase in coercivity is obtained, but the decrease in remanence value is serious. In addition, HRE- metal and alloy is expensive, and there is a concern that manufacturing costs will increase because of the need for large-scale equipment investment.

In this paper, grain boundary region of NdFeB sintered magnets were modified via reduction-GBD (r-GBD) process using HRE compounds such as oxide or fluoride with Ca metal vapor, for the purpose of effective use of inexpensive and stable HRE compounds and establishing a simple process. Ca metal has a low boiling point (b.p. = 1757 K) and can easily be vapor deposition under vacuum condition, so it is expected to serve as a reducing agent that reduces HRE compounds to HRE metals during heat treatment.
2. Experimental

A typical experimental procedure of r-GBD process is shown in Fig. 1. Commercially available NdFeB sintered magnets \( (B_r = 1.43 \text{T}, H_{c,J} = 1003 \text{kA/m}) \) were cut into a number of pieces square shape with dimensions of \( 3.0 \times 3.0 \times 2.8 \text{mm}^3 \) or cylindrical shape with dimensions of \( \phi 10 \times 3.5 \text{mm}^3 \) by machining. Then the magnets surface were etched with dilute nitric acid to remove the oxide film layer.

Powder of DyF\(_3\), Dy\(_2\)O\(_3\), TbF\(_3\) and TbO\(_3\) (99.9% in purity) with mean particle size of several microns was mixed with anhydrous-butanol in a ratio of 50:50 in weight. The magnets were uniformly coated by dipping in these slurry solutions in the air atmosphere.

After drying, the powder-coated magnets were wrapped in Mo foil to prevent contact with Ca metal grains (99% in purity) used as the reducing agent, and then vacuum sealed in a quartz tube with dimension of about \( 2.8 \times 10^{-3} \text{Pa} \). And then, the quartz tube which coated magnets and Ca metal grains were vacuum sealed was heated at 1173–1223 K for 6 h and subsequently annealed at 923 K for 2 h. After heat treatment, obtained magnets were washed with dilute nitric acid and subsequently with ethanol under supersonic for a minute to remove the impurity on the surface of magnets such as Ca oxide or fluoride.

The magnetic properties were measured by pulse-excitation type BH tracer (PBH) or superconducting magnet-based vibrating sample magnetometer (SCM-VSM) in a range of magnetic fields \( \pm 6.0 \text{T} \) at room temperature. SCM-VSM measurement method was described in detail in previous papers. Micro-structural observations were performed by X-ray diffractometer (XRD), field emission electron probe micro-analyzer (FE-EPMA), field emission scanning electron microscope (FE-SEM), and quantitative analysis was performed by inductively coupled plasma (ICP).

3. Results and Discussions

During heat treatment such as 1223 K, Ca metal is vapor deposition on the magnets surface and reacts with DyF\(_3\), Dy\(_2\)O\(_3\), TbF\(_3\), and TbO\(_3\) powder which previously coated on the magnets and to generate Dy or Tb metal as follows:

\[
\begin{align*}
2\text{DyF}_3 + 3\text{Ca} & \rightarrow 2\text{Dy} + 3\text{CaF}_2 \\
\text{Dy}_2\text{O}_3 + 3\text{Ca} & \rightarrow 2\text{Dy} + 3\text{CaO} \\
2\text{TbF}_3 + 3\text{Ca} & \rightarrow 2\text{Tb} + 3\text{CaF}_2 \\
\text{Tb}_2\text{O}_3 + 7\text{Ca} & \rightarrow 4\text{Tb} + 7\text{CaO}
\end{align*}
\]

Typical XRD patterns measured on the surface of magnets (a) untreated and (b) treated by r-GBD process with DyF\(_3\) + Ca at 1223 K for 6 h are shown in Fig. 2. From this figure, it found that DyF\(_3\) were almost completely reduced to Dy metal by Ca metal vapor, because the peak attributed to CaF\(_2\) was confirmed, on the other hand, the peak attributed to DyF\(_3\) was not confirmed. In addition, Dy metal generated by the reduction reaction progressed with substitutional diffusion with Nd metal present at the grain boundary region. Therefore, it seems that peaks attributed to Nd\(_2\)O\(_3\) were generated on the magnet surface. This result is similar to the surface of a magnet that has been coated with Nd metal and then heat treatment, as reported by Fukagawa et al., and Dy metal also can recover a deteriorated magnet surface in the same way as Nd metal.

Figure 3 shows the heat treatment temperature dependence of the magnetic properties of 3.0 \( \times 3.0 \times 2.8 \text{mm}^3 \) magnets treated by r-GBD process with DyF\(_3\) + Ca. Magnetic properties were simply evaluated by PBH. From this figure, the coercivity enhances as the heating temperature increases. In particular, when treated at 1273 K, the coercivity of the magnets improved to 1450 kA/m. However, when the heating temperature reached 1273 K, the maximum energy tended to decrease as the remanence reduced. This is because, under high temperature conditions of 1273 K or higher, Dy metal produced by the reduction reaction is also actively diffused into the Nd\(_2\)Fe\(_{14}\)B main phase, and Dy- and Fe- element become ferrimagnetic inside the (Dy, Nd)\(_2\)Fe\(_{14}\)B phase. From the results, considering the increase in coercivity and decrease in remanence, 1223 K is the optimum heating...
temperature for this study. However, since these magnetic properties were measured by PBH, the demagnetizing field correction is insufficient, for details on magnetic properties, we will evaluate cylindrical magnets which dimension of \(10 \, \text{mm} \times 7.0 \, \text{mm}^3\) (stack two pieces of magnets dimension of \(10 \, \text{mm} \times 3.5 \, \text{mm}^3\)) using SCM-VSM thereafter.

Demagnetization curves of (a) untreated magnet and GBD or r-GBD magnets with (b) DyF\(_3\), (c) Dy\(_2\)O\(_3\) + Ca, (d) DyF\(_3\) + Ca, (e) TbF\(_3\), (f) Tb\(_2\)O\(_3\) + Ca, and (g) TbF\(_3\) + Ca, measured by SCM-VSM.

Regardless of which diffusion materials were used for GBD or r-GBD process, coercivity was improved while suppressing a decrease in remanence. On the other hand, compared with the GBD process that did not use Ca metal vapor as the reducing agent, the amount of increase in coercivity was larger and the squareness was higher in the r-GBD process using the reducing agent. This is because that oxygen or fluorine contained in the diffusing materials can be prevented from being taken into the magnet by using a reducing agent. Further, regardless of whether Dy- or Tb-compound is used, the increase in coercivity is higher when fluoride is used than when oxide is used. This is because fluorine has higher reactivity with Ca metal vapor than oxygen, and CaF\(_3\) (\(\Delta G^0 = -1228 \, \text{kJ} \cdot \text{mol}^{-1}\)) generated during the reduction reaction is more stable than CaO (\(\Delta G^0 = -635 \, \text{kJ} \cdot \text{mol}^{-1}\)) and has less chemical influence on the magnets. Thus, the present r-GBD process with Ca metal vapor as a reducing agent can effectively improve the coercivity while using an inexpensive HRE compounds.

Figure 5 shows the demagnetization curve of (a) untreated magnet and conventional r-GBD or GBD magnets with (b) DyF\(_3\) + CaH\(_2\), (c) Dy vapor deposition, and the present r-GBD magnet with (d) DyF\(_3\) + Ca, measured by SCM-VSM.

![Fig. 3 Heat treatment temperature dependence of the magnetic properties of magnets treated by r-GBD process with DyF\(_3\) + Ca.](image1)

![Fig. 4 Demagnetization curves of (a) untreated magnet and GBD or r-GBD magnets with (b) DyF\(_3\), (c) Dy\(_2\)O\(_3\) + Ca, (d) DyF\(_3\) + Ca, (e) TbF\(_3\), (f) Tb\(_2\)O\(_3\) + Ca, and (g) TbF\(_3\) + Ca, measured by SCM-VSM.](image2)

![Fig. 5 Demagnetization curves of (a) untreated magnet and conventional r-GBD or GBD magnets with (b) DyF\(_3\) + CaH\(_2\), (c) Dy vapor deposition, and the present r-GBD magnet with (d) DyF\(_3\) + Ca, measured by SCM-VSM.](image3)

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<th>Sample</th>
<th>(B_r) / T</th>
<th>(H_{cj}) / kA/(\text{m}^2)</th>
<th>(H_e/H_{cj})</th>
<th>((BH)_{max}) / kJ/(\text{m}^3)</th>
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subjected to optimized heat treatment respectively. Compared with the conventional r-GBD process with DyF$_3$ + CaH$_2$ mixed powders, which we previously reported,$^{14}$ the increase in coercivity is the almost same in the present r-GBD process with Ca metal vapor. However, CaH$_2$ powder has higher activity than bulk Ca metal, therefore, DyF$_3$ + CaH$_2$ mixed powders must be handled and coated in inert atmosphere, which is problematic in terms of operability and equipment investment. On the other hand, the present r-GBD process has advantages that the processes of slurry preparation and coating these slurries to magnets can be performed in the air atmosphere, because only the stable DyF$_3$ powder is coated on the surface of magnets. While the process with Dy vapor deposition can achieve high coercivity, it is difficult to supply uniform Dy vapor to the magnets surface, therefore it caused a significant reduction in the squareness. Such low squareness magnets can’t be used for driving motors of automobiles. Further, DyF$_3$ is cheaper than Dy metal, and its uniform coating and diffusion on the magnets achieve a diffusion efficiency of about 70%, which is also advantageous in terms of material costs.

Figure 6 shows BSE images and EPMA images at various depth from surface of (a) untreated magnet and (b) r-GBD magnets treated with TbF$_3$ + Ca, and the quantitative analysis of Nd, Tb, and Ca by ICP was summarized in Table 3. From the EPMA images, Tb metal generated from the reduction of TbF$_3$ by Ca metal vapor slightly diffuses inside the Nd$_2$Fe$_{14}$B main phase particles near the surface layer, but Tb diffuses continuously into the magnet mainly through the grain boundary region. As a result, Tb was concentrated at the interface between the Nd$_2$Fe$_{14}$B main phase particles and the surrounding Nd-rich boundary region, which effectively enhanced the coercivity while suppressing the decrease in remanence.

While, diffusion of Ca used as a reducing agent was confirmed at the partially concentrated grain boundary triple points near the surface layer, but almost no diffusion into the magnet was confirmed. Figure 7 shows cross-sectional SEM images at various depth from surface of (a) untreated magnet and (b) r-GBD magnet treated with TbF$_3$ + Ca, and Table 4 shows a summary of quantitative analysis of Nd, Tb, Ca, O, Fe, Co, and Cu in the region indicated by arrow points in Fig. 7. Each arrow point in Fig. 7 is Nd-rich grain boundary

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<th>Process</th>
<th>Sample</th>
<th>$B_s$ / T</th>
<th>$H_c$ / kA•m$^{-1}$</th>
<th>$H_e$ / $H_c$</th>
<th>$(BH)_{Mrt}$ / kJ•m$^3$</th>
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<th>Sample</th>
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Fig. 6 BSE images and EPMA images of at various depth from surface of (a) untreated magnet and (b) r-GBD magnet treated with TbF$_3$ + Ca.
region near the surface of magnet. The present r-GBD treatment with TbF3 + Ca clearly increased the Tb content in the grain boundary region of the magnet surface, which effectively increased the coercive force. On the other hand, for Ca, the content increased only near the surface layer, and no increase could be confirmed inside the magnet. This result is consistent with the EPMA images in Fig. 6. From these results, it is presumed that the Ca metal used as the reducing agent did not affect the magnetic properties.

4. Summary

The improved r-GBD process with Ca metal vapor is an effective process to enhance the coercivity of NdFeB sintered magnets, while using inexpensive and stable HRE compounds as raw material. Also, this r-GBD process is superior in operability with a simple process as compared with conventional r-GBD process using CaH2 powder as a reducing agent, and has an advantage in terms of capital investment costs. By optimizing the process conditions, the coercivity of magnets treated by TbF3 with Ca metal vapor increases by more than 70% ($H_{cJ} = 1778 \text{kA/m}$) than that of the untreated magnet ($H_{cJ} = 1003 \text{kA/m}$) without severe reducing the original high remanence and squareness. Such an effective coercivity improvement is because that the HRE metal generated by the reduction reaction at the surface of magnets is continuously diffused to the grain boundary region of magnets and enriched between the Nd2Fe14B main phase and the Nd-rich grain boundary region.

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REFERENCES