Coercivity enhancement of Nd-Fe-B sintered magnets by grain boundary modification via reduction-diffusion process

To cite this article: D S Li et al 2009 IOP Conf. Ser.: Mater. Sci. Eng. 1 012020

View the article online for updates and enhancements.

Related content
- Relation between domain wall motion and coercivity in Nd-Fe-B sintered magnets prepared in various conditions
  K Kobayashi, Y Ochiai, K Hayakawa et al.
- Enhancement of coercivity in Al and Cu added Nd-Fe-B sintered magnets by high field annealing
  Takahiro Akiya, Hiroaki Kato, Masato Sagawa et al.
- Effect of Cu addition on coercivity and interfacial state of Nd-Fe-B/Nd-rich thin films
  M Matsuura, S Sugimoto, T Fukada et al.

Recent citations
- Coercivity enhancement mechanism in Dy-substituted Nd-Fe-B nanoparticles synthesized by sol-gel base method followed by a reduction-diffusion process
  Hamed Rahimi et al
- Interface state and coercivity in Nd-Fe-B/Dy films
  Jin Umezawa et al
- Oxide evolution in NdDy-Fe-B magnet during aging process
  Jingdai WANG et al
Coercivity Enhancement of Nd-Fe-B Sintered Magnets by Grain Boundary Modification via Reduction-diffusion Process

D S Li, M Nishimoto, S Suzuki, K Nishiyama, M Itoh and K Machida*
Center for Advanced Science and Innovation, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan
Email: machida@casi.osaka-u.ac.jp

Abstract. The interface between the Nd$_2$Fe$_{14}$B particles and the grain boundary surrounding them in Nd-Fe-B sintered magnets was modified by diffusion Dy metal selectively through the grain boundary involving the reduction of Dy$_2$O$_3$ or DyF$_3$ with CaH$_2$ and the coercivity of them was effectively enhanced from 0.98 MA/m to 1.42 MA/m with keeping the high value of remanence. The resultant coercivity was higher than that of the magnets modified with Dy$_2$O$_3$ ($H_c = 1.10$ MA/m) and DyF$_3$ ($H_c = 1.24$ MA/m) without using any reductant such as CaH$_2$, respectively.

1. Introduction
It is well known that Nd-Fe-B sintered magnets have been widely used as key parts for voice coil motors (VCMs), magnetic resonance imaging (MRI) analyzers, many kinds of motors or actuators and so on because they have excellent magnetic properties as well as the cost performances. With extending the application to high efficient generator and motors, particularly for hybrid electric vehicles and air conditioners, high-performance permanent magnets are strongly demanded for driving them at high temperatures since they are self-heated under high load conditions. The magnetic properties of Nd-Fe-B sintered magnets may meet the requirement of such demand but the coercivity values are still low and must be increased without decreasing their own high residual magnetization ($B_r$). The most conventional method to increase the coercivity of Nd-Fe-B sintered magnets is to add Dy or Tb metal to the mother alloys, since Dy$_2$Fe$_{14}$B or Tb$_2$Fe$_{14}$B possesses the higher magnetic anisotropy than Nd$_2$Fe$_{14}$B [1, 2]. However, the anti-parallel coupling between the magnetic moments of Dy or Tb and Fe elements lowers the magnetization. Meanwhile, the coercivity of Nd-Fe-B sintered magnets usually alternates according to the nucleation-controlled mechanism and so, the flux reversal of the magnets usually is usually induced by structural defects around the surface of magnetic domain particles, so that the coercivity of magnets is usually smaller than their own anisotropic field [3].

Recently, the authors have reported that Dy or Tb element is selectively enriched by diffusing their metals selectively through the Nd-rich grain boundary region among Nd$_3$Fe$_{14}$B grains in the magnets, so that the coercivity is effectively enhanced on the premise that only a small amount of Dy or Tb element is used and the remanence is almost kept at the original level [4, 5]. The similar results have also been reported by Kim et al. [6] for Nd-Fe-B sintered magnet powders and Nakamura or Hirota et al. [7-9] for thin plates using oxides or fluorides of Dy or Tb. However, the lanthanide metal-based method is more effective to increase the coercivity than the treatments using Ln$_2$O$_3$ or LnF$_3$ (Ln=lanthanides).
In this paper, the grain boundary modification was made on the Nd-Fe-B sintered magnets by developing the reduction-diffusion process method using Dy_2O_3 or DyF_3 and CaH_2 and the magnetic properties of the modified magnets were characterized for aiming the industrial applications for them.

2. Experiments
Commercially available Nd-Fe-B sintered magnets (\(B_r = 1.44\) T, \(H_{cj} = 0.98\) MA/m and \((BH)_{max} = 379\) kJ/m^3) were cut into a number of pieces with dimensions of 3.0×3.0×2.8 mm^3. Powders of DyF_3, Dy_2O_3, TbF_3 and Tb_2O_7 (99.9% in purity) with mean particle size of several microns were mixed with CaH_2 powders (95.0% in purity) respectively according to different molar ratio (MR). The magnets were coated with the powder mixtures uniformly by dipping the magnet in the slurry solutions composed of the powder mixtures and anhydrous butanol. After drying, the powder-coated magnets were heated at 1073-1273 K for 0.5-3 h and subsequently annealed at 873 K for 20 min in a vacuum system at \(8 \times 10^{-3}\) Pa. Then, the obtained magnets were washed with dilute nitric acid and subsequently with ethanol under supersonic conditions to remove the impurity on the surface such as Ca-metal and calcium compounds.

The resultant products obtained by the grain boundary modification were identified on a conventional powder X-ray diffractometer (Rigaku, RINT2200) with monochromated Cu Kα radiation. Magnetization hysteresis curves of the magnets before and after modification were recorded on a vibrating sample magnetometer (Tamakawa, TM-VSM2014-MHR type) in a range of magnetic fields up to ±1.6 MA/m at room temperature after magnetization at 6.4 MA/m by a pulsed field generator and pulsed high field magnetometer (NIHON DENJI SOKKI, PHB-1000) by monitoring the decay of magnetization in an alternated pulsed magnetic field between −6.4 and +6.4 MA/m. Micro-structural observations for magnets were performed by a conventional electron probe microanalyzer (JEOL, JXA-8100).

3. Results and Discussion
Calcium hydride, CaH_2 decomposed into Ca metal and H_2 gas only at the temperatures higher than 973 K [10]. At the higher temperature such as 1173 K, consequently, Ca metal reacts with Dy_2O_3 as follows:

\[\text{Dy}_2\text{O}_3 + 3\text{CaH}_2 \rightarrow 2\text{Dy} + 3\text{CaO} + 3\text{H}_2\]  (1)

Typical XRD patterns measured on the mixtures of (a) Dy_2O_3 or (b) DyF_3 with CaH_2 as heated at 1173 K for 1 h are shown in Fig.1, respectively. From this figure, one can see that Dy_2O_3 and DyF_3 were almost completely reduced by the Dy metal derived from CaH_2.
Figure 2 shows EPMA images of (a) untreated magnet and (b) magnet treated via reduction-diffusion process (Dy$_2$O$_3$+CaH$_2$). From the mapping image of Dy element, one can see that Dy metal formed from the reduction of Dy$_2$O$_3$ with CaH$_2$ mainly was diffused from the magnet surface into the magnet through the grain boundary region. Consequently, the Dy element was enriched at the interface between Nd$_2$Fe$_{14}$B primary phase particles and the Nd-rich boundary phase surrounding.

Figure 2 shows EPMA images of (a) untreated magnet and (b) magnet treated via reduction-diffusion process (Dy$_2$O$_3$+CaH$_2$). From the mapping image of Dy element, one can see that Dy metal formed from the reduction of Dy$_2$O$_3$ with CaH$_2$ mainly was diffused from the magnet surface into the magnet through the grain boundary region. Consequently, the Dy element was enriched at the interface between Nd$_2$Fe$_{14}$B primary phase particles and the Nd-rich boundary phase surrounding.

Demagnetization curves of (a) untreated magnet and (b) magnets treated with (b) Dy$_2$O$_3$, (c) DyF$_3$, (d) Dy$_2$O$_3$+ CaH$_2$ and (e) DyF$_3$+CaH$_2$ at 1173 K for 3 h are shown in Fig. 3, and the magnetic properties are summarized in Table 1. For both of the magnets treated with Dy element via the reduction-diffusion process, the coercivity increased drastically and almost was the same value ($H_c$ = 1.42 MA/m) as that of the magnet treated with the Dy metal deposited by sputtering, while the remanence values of them almost kept the similar level to those of the untreated magnets.

Figure 3. Demagnetization curves of (a) the untreated magnet and the magnets treated with (b) Dy$_2$O$_3$, (c) DyF$_3$, (d) Dy$_2$O$_3$+ CaH$_2$ and (e) DyF$_3$+CaH$_2$ at 1173 K for 3h.
Also the reduction-diffusion process of Dy metal made the Nd-Fe-B sintered magnets to be high coercive more effectively than the magnets treated with Dy₂O₃ ($H_c J = 1.10 \text{ MA/m}$) and DyF₃ ($H_c J = 1.24 \text{ MA/m}$) respectively. The mechanism for the coercivity enhancement of Nd-Fe-B sintered magnets treated via reduction-diffusion process of Dy metal is understood as follows: The Dy metal formed from the reduction of Dy₂O₃ or DyF₃ with CaH₂ mainly was diffused into the magnets and enriched at the interface between the Nd₂Fe₁₄B particles and the grain boundary surrounding them selectively through the grain boundary region. Such Dy-enriched phase around primary phases increase the magnetic anisotropy at the grain surface to stabilize the state of aligned magnetic domains.

### 4. Conclusion

The reduction-diffusion process is effective method to enhance the coercivity of Nd-Fe-B sintered magnets without any decrease in the original high remanence. By optimizing the process conditions, the coercivity of magnets increases by more than 40% than that of the untreated magnet, and so this process is noted to meet the requirements for the Nd-Fe-B sintered magnets to produce high-coercive permanent magnets for the practical uses.

### References


### Table 1. Magnetic properties of the untreated magnet and grain-boundary modified magnets via different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>$B_r$ (T)</th>
<th>$H_c J$ (MA/m)</th>
<th>$(BH)_{max}$ (kJ/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As is</td>
<td>1.44</td>
<td>0.98</td>
<td>379</td>
</tr>
<tr>
<td>Dy-metal (sputter)</td>
<td>1.43</td>
<td>1.45</td>
<td>394</td>
</tr>
<tr>
<td>Dy₂O₃</td>
<td>1.43</td>
<td>1.10</td>
<td>386</td>
</tr>
<tr>
<td>DyF₃</td>
<td>1.44</td>
<td>1.24</td>
<td>389</td>
</tr>
<tr>
<td>Dy₂O₃+CaH₂</td>
<td>1.44</td>
<td>1.42</td>
<td>390</td>
</tr>
<tr>
<td>DyF₃+CaH₂</td>
<td>1.43</td>
<td>1.42</td>
<td>393</td>
</tr>
</tbody>
</table>