Modified Process for High-Performance Anisotropic Sm$_2$Fe$_{17}$N$_3$ Magnet Powder

To cite this article: T Ishikawa et al 2011 J. Phys.: Conf. Ser. 266 012033

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Modified Process for High-Performance Anisotropic Sm$_2$Fe$_{17}$N$_3$ Magnet Powder

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Abstract. The magnetic properties of an anisotropic Sm$_2$Fe$_{17}$N$_3$ magnet powder were improved by enhancement of nitrogenation homogeneity. We made the Sm$_2$Fe$_{17}$ parent material powder by a reduction-diffusion method which contains a reduction-diffusion heat treatment and a subsequent wet process for removal of a CaO by-product. In the present study, as the modified process for the magnet powder, the nitrogenation heat treatment was done between the reduction-diffusion heat treatment and the wet process, though the nitrogenation was normally done after the wet process. The surface of the Sm$_2$Fe$_{17}$ powder before the wet process is rather clean than the surface after the wet process. It was found that the modified process seemed to promote the nitrogenation and decreased the number of Sm$_2$Fe$_{17}$N$_3$ particles with un-nitrogenated phase. The magnetic properties of the magnet powder through this process reached $B_r = 1.46$ T, $H_c = 874$ kA/m and $(BH)_{max} = 353$ kJ/m$^3$ without demagnetizing field correction and $(BH)_{max} = 371$ kJ/m$^3$ with the correction assuming the density 7.67 Mg/m$^3$.

1. Introduction
An anisotropic Sm$_2$Fe$_{17}$N$_3$ magnet powder is a key material for high-performance rare-earth bonded magnets. It is mass-produced by nitrogenation of an Sm$_2$Fe$_{17}$ parent material powder made by a reduction-diffusion method and its maximum energy product $(BH)_{max}$ was up to 323 kJ/m$^3$ without a surface treatment for stabilization [1] and 290 kJ/m$^3$ for the surface-treated stabilized powder [2]. The saturation magnetization $J_s$ of the Sm$_2$Fe$_{17}$N$_3$ compound was reported to be 1.54 - 1.57 T [3], [4], and therefore the theoretical $(BH)_{max} = J_s^2/4\mu_0$ is 472 - 490 kJ/m$^3$. There is much difference between these values.

In the reduction-diffusion process, the mixture of Sm$_2$O$_3$ powder and Fe powder is heat-treated with Ca metal granule. The reaction product is a sintered composite which consists of Sm$_2$Fe$_{17}$ alloy particles and a CaO by-product. In the conventional process shown in figure 1(a), the composite is subjected to water and it turns to be a slurry of the alloy particles and Ca(OH)$_2$. For separation of the Sm$_2$Fe$_{17}$ alloy powder, the slurry is washed and rinsed several times. After the decantation and drying, the powder is nitrogenated and the Sm$_2$Fe$_{17}$N$_3$ coarse powder was obtained. There is a case that the Sm$_2$Fe$_{17}$N$_3$ powder contains a un-nitrogenated Sm$_2$Fe$_{17}$ phase which degrades the saturation magnetization and the squareness ratio of demagnetization curve. In the conventional process, the...
Sm$_2$Fe$_{17}$ parent material powder has to be treated very carefully in order to avoid the residue of un-nitrogenated phase. The surface contamination of the Sm$_2$Fe$_{17}$ alloy powder by water-washing and rinsing operation can be a barrier against homogeneous nitrogenation and it causes particles with the un-nitrogenated phase. The purpose of this study is to develop a fabrication process which reduces these undesirable particles effectively.

2. Experimental procedures

The water-washing and rinsing operation makes the Sm$_2$Fe$_{17}$ alloy surface oxidized [1]. We thought that the alloy surface just after the reduction-diffusion heat treatment would be rather clean. Therefore it was tried to nitrogenate the sintered composite which consists of Sm$_2$Fe$_{17}$ alloy particles and a CaO by-product. The modified fabrication process we proposed is shown in figure 1(b) [5]. The particle size of raw materials was under 300 mesh for the Sm$_2$O$_3$ powder and under 150 mesh for the Fe powder. The size of Ca metal granule was under 4 mesh. These were mixed together and heated at 1000-1190 °C under an Ar atmosphere for the reduction-diffusion reaction. In this experiment, the input composition of raw materials was in the range of Sm$_2$Fe$_{17}$ to Sm$_2$Fe$_{17}$ and the amount of Ca was 1.2 times the chemical equivalent for reducing the Sm$_2$O$_3$. The reacted product was heated at 435-480 °C under the NH$_3$-H$_2$ mixed gas flow for the nitrogenation. The flow ratio of NH$_3$/H$_2$ was in the range of 0.2 to 1.0. After the nitrogenation heat treatment, the product was put into water and washed in the same way as the conventional process to remove Ca(OH)$_2$. The Sm$_2$Fe$_{17}$N$_3$ coarse powder was obtained after drying and it was ball milled in ethanol down to 2-3 μm in average particle size.

The nitrogen and samarium content was determined by a thermal conductivity detector and an inductively-coupled plasma atomic emission spectrometry respectively. The phases in the samples were examined by an X-ray diffraction (XRD) apparatus using Cu Kα radiation. The microstructure of the samples was observed with a scanning electron microscope (SEM). The magnetic properties of Sm$_2$Fe$_{17}$N$_3$ magnet powder were measured by a vibrating sample magnetometer (VSM) after pulse magnetization of 3.2 MA/m. In order to align the crystal axis, the powder sample was made put in a wax, heated up to 70 °C and cooled down to room temperature in a magnetic field of 1.6 MA/m. The magnetization was calibrated by a Ni cylinder with saturation magnetization of 485.6 kA/m [6]. The density of Sm$_2$Fe$_{17}$N$_3$ magnet powder was determined as 7.67 Mg/m$^3$ by the XRD analysis.

Figure 1. Manufacturing process of Sm$_2$Fe$_{17}$N$_3$ magnet powder: (a) conventional, (b) modified.

3. Results and discussion

Figure 2(a) shows an appearance of the reduction-diffusion reaction product. It is a mass of the sintered composite comprised of Sm$_2$Fe$_{17}$ alloy particles and CaO. The SEM (BEI) photograph of the cross section in the product is shown in figure 2(b). It is observed that the Sm$_2$Fe$_{17}$ alloy particles of several ten microns are surrounded by CaO particles of a few microns and a lot of voids. Though the
reaction product is a bulky material, these voids seem to play an important role in nitrogenation as a diffusion pass of NH$_3$ and H$_2$ gasses. Moreover, the bulky product was crushed and turned to be a granule under 1 mm in size during the nitrogenation heat treatment as shown in figure 2(c). Hence we believed that the nitrogenation was possible even if the Sm$_2$Fe$_{17}$ particles were embedded in the sintered composite.

The dependence of coercive force $H_c$ and nitrogen content of Sm$_2$Fe$_{17}$N$_3$ magnet powder on nitrogenation time are shown in figure 3. The nitrogen content increases with increasing the nitrogenation time. As the anisotropy field $H_A$ takes the maximum value at $x=3$ for Sm$_2$Fe$_{17}$N$_x$ [4], the coercive force also indicates a peak at a certain nitrogenation time. The optimum nitrogenation time is in the range of 120 to 180 minutes for the modified process, which is shorter than 180 minutes for the conventional process. Thus the modified process seems to nitrogenate the Sm$_2$Fe$_{17}$ alloy more easily than the conventional process, which indicates that the voids worked as the diffusion pass of the nitrogenation gasses.

![Figure 2](image1.png)  
**Figure 2.** Photographs of the samples: (a) the reduction-diffusion reaction product, (b) SEM back-scattering electron image of fracture cross section in the product (a), (c) the reaction product after the nitrogenation heat treatment.

![Figure 3](image2.png)  
**Figure 3.** The dependence of coercive force $H_c$ and nitrogen content of Sm$_2$Fe$_{17}$N$_3$ magnet powder on nitrogenation time. (input composition Sm$_{2.5}$Fe$_{17}$, r-d temperature 1190°C, nitrogenation temperature 465°C, flow ratio of NH$_3$/H$_2$=1.0, pulverized down to 2.5 μm)

In order to improve the magnetic properties of the magnet powder, the optimum conditions were examined for each operation in the modified process. In consequence, the conditions were set as shown in table 1. In particular, the temperature of the reduction-diffusion heat treatment affected the shape of Sm$_2$Fe$_{17}$ alloy particles. Figure 4 indicates SEM photographs of the alloy particles reacted at 1050°C and 1190°C. The powder morphology for 1050°C was botryoidally-aggregated in contrast with that for 1190°C and the grain under 10 μm in size was observed. The specific surface area and the number of the grain boundary is obviously large for 1050°C, which appears to enhance the homogeneous nitrogenation. Though a slight α-Fe peak in the XRD profile was detected for the Sm$_2$Fe$_{17}$N$_3$ magnet powder made of a 1050°C-reaction product, 1050°C was the best in the range of 1000-1190°C in terms of both the residual flux density $B_r$ and the coercive force $H_c$ of the powder.

<table>
<thead>
<tr>
<th>Input composition</th>
<th>Reduction-diffusion heat treatment Temperature</th>
<th>Nitrogenation heat treatment Temperature</th>
<th>Flow ratio of NH$_3$/H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm$<em>{2.5}$Fe$</em>{17}$</td>
<td>1050°C</td>
<td>450°C</td>
<td>0.50</td>
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</table>

Table 1. Optimum conditions for the modified process.
Figure 4. SEM photographs of Sm$_2$Fe$_{17}$ alloy particles reacted at different reduction-diffusion heat treatment temperatures: (a) 1050°C, (b) 1190°C. (input composition Sm$_{2.3}$Fe$_{17}$)

Figure 5. Demagnetization curves of Sm$_2$Fe$_{17}$N$_3$ magnet powder fabricated by the modified process with optimum conditions with and without demagnetizing correction.

Figure 5 indicates the demagnetization curve of Sm$_2$Fe$_{17}$N$_3$ magnet powder fabricated by the modified process with optimum conditions. The residual flux density $B_r$ and the maximum energy product $(BH)_{max}$ reached 1.46 T and 353 kJ/m$^3$ respectively without demagnetizing field correction. We evaluated the demagnetizing coefficient $N$ with Ni fine powder (2-3 μm in size) and the value 0.07 was obtained as the coefficient $N$. After the demagnetizing field correction with $N = 0.07$, the magnetic properties of the powder were $B_r = 1.47$ T, $H_c = 874$ kA/m, $(BH)_{max} = 371$ kJ/m$^3$ respectively. The Sm and N contents were determined before pulverizing the Sm$_2$Fe$_{17}$N$_3$ coarse powder and they were 23.6 wt% and 3.3 wt% respectively. In order to identify the number of particles with un-nitrogenated phase, cross sections of the Sm$_2$Fe$_{17}$N$_3$ coarse powder was observed by SEM. Figure 6(a) is a back-scattering electron image of the cross section for the coarse powder made by the conventional process. The core with the white contrast inside dark-gray particles corresponds to the un-nitrogenated Sm$_2$Fe$_{17}$ phase. The cross section image for the powder made by the modified process is shown in figure 6(b). It is clearly observed that the number of the particles with the un-nitrogenated phase was reduced drastically for the modified process. The image analysis showed that the ratio of white area to the whole was 0.04 % for the modified process in contrast with 0.73 % for the conventional process. This result shows that the modified process could promote the homogeneous nitrogenation.

Table 2 lists the magnetic properties of Sm$_2$Fe$_{17}$N$_3$ magnet powder reported previously. Tajima et al. and Izumi et al. improved the coercive force by adding surfactants to a milling solvent [8], [9]. Sasaki et al. developed high coercivity by mild pulverizing [10]. On the other hand, Kawamoto et al. adopted the reduction-diffusion method for Sm$_2$Fe$_{17}$ parent material preparation and got high coercive force [1]. In this study, we have succeeded in reducing the particles with un-nitrogenated phase and improving the residual flux density $B_r$. However, the difference between 1.47 T in $B_r$ and 1.54 T in $J_s$ [3] is 5 % and the difference between 371 kJ/m$^3$ in $(BH)_{max}$ and 472 kJ/m$^3$ in $J_s^2/4\mu_0$ is 12 %, which are still large. One of the ways to close these values is to cut off the fine particles in the powder. Figure 7 shows the particle size distribution of the Sm$_2$Fe$_{17}$N$_3$ magnet powder made by the modified process. The volume ratio of the particle under 1 μm in size was 12 %. The powder was reported to be surrounded by an amorphous Oxygen-rich layer of about 10 nm in thickness [11]. As the volume ratio of the surface layer ("δr" in thickness) on the spherical particle ("2r" in diameter) is 3δr/2r, the volume ratio of the amorphous layer on a spherical 1 μm-Sm$_2$Fe$_{17}$N$_3$ magnet powder, for example, is 6 % (δr = 0.01 μm, r = 0.5 μm). Assuming that the amorphous layer is nonmagnetic, the saturation magnetization $J_s$ of 1.54 T drops to 1.45 T. In this manner it was found that the saturation magnetization of the spherical Sm$_2$Fe$_{17}$N$_3$ magnet powder was calculated to be 1.49 T based on the particle size distribution shown in figure 7. This value is close to the measured value 1.47 T in figure 5.
To cut off not only the fine particles but also coarse particles is an additional way to improve the magnetic properties. Since the particle size affects the coercive force, to sharpen the size distribution improves the squareness ratio of the demagnetization curves.

Figure 6. Back-scattering electron images of the cross section for the Sm$_2$Fe$_{17}$N$_3$ coarse powder made by (a) the conventional process, (b) the modified process. The white core inside the particles corresponds to the un-nitrogenated Sm$_2$Fe$_{17}$ phase.

Figure 7. Particle size distribution for the Sm$_2$Fe$_{17}$N$_3$ magnet powder made by the modified process.

Table 2. The magnetic properties of Sm$_2$Fe$_{17}$N$_3$ magnet powder.

<table>
<thead>
<tr>
<th></th>
<th>$B_r$ (T)</th>
<th>$H_c$ (kA/m)</th>
<th>(BH)$_{\text{max}}$ (kJ/m$^3$)</th>
<th>demagnetizing field correction</th>
<th>ref.</th>
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<td>Iriyama et al.  (1992)</td>
<td>-</td>
<td>-</td>
<td>279</td>
<td>N = 0.13</td>
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<tr>
<td>Tajima et al.   (1995)</td>
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<td>740</td>
<td>271</td>
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<td>860</td>
<td>313</td>
<td>N = 0.13</td>
<td>[9]</td>
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<tr>
<td>Kawamoto et al. (1999)</td>
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<td>899</td>
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<tr>
<td>Sasaki et al.   (1999)</td>
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<td>329</td>
<td>?</td>
<td>[10]</td>
</tr>
<tr>
<td>Ishikawa et al. (2010)</td>
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<td>353</td>
<td>none</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>1.47</td>
<td>874</td>
<td>371</td>
<td>N = 0.07</td>
<td></td>
</tr>
</tbody>
</table>

4. Conclusion
We have developed a fabrication process for high-performance Sm$_2$Fe$_{17}$N$_3$ magnet powder based on the reduction-diffusion method. In this process, the nitrogenation heat treatment is set between the reduction-diffusion heat treatment and the water-washing and rinsing operation. The undesirable particles with un-nitrogenated phase are readily reduced. The magnetic properties of the magnet powder through this process reached $B_r = 1.46$ T, $H_c = 874$ kA/m, (BH)$_{\text{max}} = 353$ kJ/m$^3$ without demagnetizing field correction and (BH)$_{\text{max}} = 371$ kJ/m$^3$ with the correction.

5. References