Microstructure and Magnetic Property of Sm$_2$Fe$_{17}$ Nanopowder Synthesized by Modified Reduction-Diffusion Process

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A modified reduction-diffusion (MRD) process at low temperature was performed on the microstructure and magnetic property of a base alloy nanopowder of Sm$_2$Fe$_{17}$ for high performance Sm$_2$Fe$_{17}$N$_3$ magnetic materials. The Sm$_2$Fe$_{17}$ nanopowder with a particle size distribution of 100–500 nm was synthesized by MRD process at 700°C. The measurement of magnetic property revealed that the Sm$_2$Fe$_{17}$ nanopowders had a saturation magnetization ($M_s$) of 128 A·m$^2$/kg and a high coercivity ($H_c$) of 91.8 kA/m. It is expected that the magnetic property of Sm$_2$Fe$_{17}$ nanopowder provides a superior base alloy material for fabricating high performance Sm$_2$Fe$_{17}$N$_3$ magnetic materials by subsequent nitriding treatment. [doi:10.2320/matertrans.M2014152]

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1. Introduction

Samarium-iron nitride (Sm$_2$Fe$_{17}$N$_3$) is a promising hard magnetic material which is generally utilized in the form of a resin-bonded magnet. However, thermal instability issues of Sm$_2$Fe$_{17}$N$_3$ powder due to its low Curie temperature (470°C) and thermal decomposition into SmN and α-Fe phase at elevated temperature make it difficult to process a sintered Sm$_2$Fe$_{17}$N$_3$ hard magnet. For this reason many efforts are being paid to consolidation of Sm$_2$Fe$_{17}$N$_3$ powder by pressure-assisted sintering methods.

Sm$_2$Fe$_{17}$N$_3$ nanopowder is generally produced in two ways such as the pulverization and nitrogenation of Sm$_2$Fe$_{17}$ ingot material and the reduction of Sm$_2$O$_3$ into Sm by liquid Ca and a diffusion reaction with Fe and finally nitrogenation of Sm$_2$Fe$_{17}$. However, both processes are not suitable for making Sm$_2$Fe$_{17}$ nanopowder due to its high-temperature process above 1000°C. As a breakthrough for solving this problem, recently the authors reported that the nanoscale Sm$_2$Fe$_{17}$ intermetallic phase at elevated temperature make it difficult to process a sintered Sm$_2$Fe$_{17}$N$_3$ hard magnet. For this reason many efforts are being paid to consolidation of Sm$_2$Fe$_{17}$N$_3$ powder by pressure-assisted sintering methods.

Sm$_2$Fe$_{17}$N$_3$ powder was produced by mixing Sm$_2$O$_3$ and Fe$_2$O$_3$ powders and then ball-milled by SPEX mill in an argon atmosphere for 1 h to produce Sm$_2$O$_3$-Fe powders. The partially reduced Sm$_2$O$_3$-Fe powders were then mixed with CaH$_2$ and subsequently ball-milled by SPEX mill in an argon atmosphere for 1 h to finally produce Sm$_2$O$_3$-Fe-CaH$_2$ nanopowders. The compositions of the oxide powders corresponded to 1.1 for Sm$_2$O$_3$, 1.1 for Fe$_2$O$_3$ and 4.5 for CaH$_2$, respectively, the chemical equivalent in excess of stoichiometry to compensate for their loss during the MRD process.

The MRD process for the Sm$_2$O$_3$-Fe-CaH$_2$ powder mixtures was conducted in a switched atmosphere consisting of Ar-5 vol.%H$_2$ and then in a vacuum (1 Pa). The powder mixture was put in a stainless steel container (50 × 50 × 30 mm) with a covering lid to prevent the evaporating loss of Sm$_2$O$_3$ and CaH$_2$ during reaction. Then the sample in the container was heated to 600, 650, 700 and 800°C at a rate of 5°C/min and held at each temperature for 3 h in Ar-5 vol.%H$_2$. The chamber was continuously evacuated using a rotary pump, held for 2 h, and allowed to cool in the furnace. The MRD processed powders were recovered by washing the product three times with D.I. water to remove CaO.

A phase analysis was conducted by X-ray diffraction using a CuK$_{α1}$ target at a scanning speed of 4°/min. The powder morphology and cross section were examined by scanning electron microscopy. The elemental compositions of the powder were analyzed by energy dispersive spectroscopy. The crystal structure of the SmFe intermetallic phase was examined by transmission electron microscopy. The magnetization hysteresis curves were measured on a vibrating sample magnetometer with a maximum magnetic field of 119 kA/m at room temperature.

2. Experimental Procedure

As starting materials, samarium oxide powder (Sm$_2$O$_3$, 99.9% purity, 1 µm on average particle size), calcium hydride powder (CaH$_2$, 94% purity) and iron oxide powder (Fe$_2$O$_3$, 99.9% purity, 1 µm on average particle size) were used to fabricate Sm$_2$O$_3$-Fe-CaH$_2$ mixture. First, the mixture of Sm$_2$O$_3$-Fe$_2$O$_3$ powders was ball-milled using a SPEX mill at a speed of 1060 revolutions/min for 1 h. And then, the ball-milled powders were reduced at 450°C in H$_2$ gas atmosphere for 1 h to produce Sm$_2$O$_3$-Fe$_2$O$_3$ powders.

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3. Results and Discussion

3.1 Microstructure and phase analysis

Figure 1 shows the X-ray diffraction patterns of the produced powders at various temperatures. It was found that...
the Sm$_2$Fe$_{17}$ phase is formed above 650°C and its peak intensity gradually increases with increasing temperature up to 800°C. The lower temperature phase of SmH$_2$ vanished above 700°C. This phenomenon was interpreted in terms of the switching atmosphere effect in our previous work.\textsuperscript{7)} The switching atmosphere from Ar-5 vol% H$_2$ to a vacuum was found to enhance the decomposition of SmH$_2$ and as a consequence promoted a diffusion reaction between Sm and Fe to form Sm$_2$Fe$_{17}$. According to the temperature-pressure phase diagram of the Sm$_2$Fe$_{17}$H$_x$H$_2$ system,\textsuperscript{11)} the Sm$_2$Fe$_{17}$ phase is only formed at a low hydrogen pressure of 0 Pa at 630°C. This thermodynamic feature is in agreement with the switching atmosphere effect on the formation of Sm$_2$Fe$_{17}$ in this study. Based upon the XRD results, the optimal temperature of our MRD process was determined at 700°C.

Figure 2(a) shows the X-ray diffraction pattern of the powder sample synthesized at 700°C and washed with D.I. water. The powder is found to consist of Sm$_2$Fe$_{17}$ and residual Fe phase. The relative volume fraction, which was estimated by the X-ray intensity data of the two peaks of (303) for Sm$_2$Fe$_{17}$ and (110) for Fe,\textsuperscript{12)} amounts to 84 : 16 (Sm$_2$Fe$_{17}$:Fe in at%). The presence of residual Fe phase might be due to raw powder losses of Sm$_2$O$_3$, Fe$_2$O$_3$ and CaH$_2$ during the powder preparation. In this respect, the Sm$_2$Fe$_{17}$ powder can be fabricated by optimizing the contents of Fe$_2$O$_3$ powders and Sm$_2$O$_3$ powders.\textsuperscript{13)} SEM micrograph of Fig. 2(b) reveals the Sm$_2$Fe$_{17}$ powders having 100–300 nm in size are much finer compared to a previous study.\textsuperscript{7)} The TEM-micrograph of Fig. 2(c) also confirms this observation. Its phase analysis using a SAED pattern identifies that the Sm$_2$Fe$_{17}$ phase has a rhombohedral Th$_2$Zn$_{17}$-type (2:17 R) crystal structure, which is the typical crystal structure of the Sm$_2$Fe$_{17}$ alloy phase.\textsuperscript{14)}

3.2 Magnetic properties

Figure 3 shows a hysteresis loop of the Sm$_2$Fe$_{17}$ nanopowder sample measured in the magnetic field of 119 kA/m. It is found that the Sm$_2$Fe$_{17}$ nanopowder has saturation magnetization ($M_s$) of 128 A·m$^2$/kg. This value is about 9% larger than that of pure Sm$_2$Fe$_{17}$ (117 A·m$^2$/kg at room temperature) fabricated by the induction melting process.\textsuperscript{15)} Intuitively, such an increment in the $M_s$ value can be attributed to the presence of a residual Fe phase. According to a report by Konishi et al.,\textsuperscript{16)} the total $M_s$ of Sm$_2$Fe$_{17}$ can be increased by the presence of a small amount of the residual Fe phase in which the pure Fe phase has the $M_s$ of 200 A·m$^2$/kg somewhat higher than the major phase of Sm$_2$Fe$_{17}$. As described above, the MRD processed powder in this study contains 16% of the residual Fe phase. Considering the contribution of this residual phase, the apparent $M_s$ value of the powder sample can be simply estimated by a rule of mixture of both phases of Sm$_2$Fe$_{17}$ and Fe from the XRD patterns.\textsuperscript{17)} The calculated $M_s$ value exists in the range of 123–131 A·m$^2$/kg is in good agreement with the experimental result of this study (128 A·m$^2$/kg). This consistency between both $M_s$ from the experimental and calculation implies that the Sm$_2$Fe$_{17}$ nanopowder sample has the $M_s$ value for the Sm$_2$Fe$_{17}$ phase regardless of its particle size and residual iron phase.

Figure 3 discloses that the coercivity ($H_c$) of the present Sm$_2$Fe$_{17}$ nanopowder sample amounts to 91.8 kA/m. As
depicted in Table 1, most of the reported coercivity values for the Sm$_2$Fe$_{17}$ powders, which are produced in different processes and so have much larger grain or particle size in the range of 0.3–20 µm, apparently have much lower coercivity of 19.1–38.2 kA/m. This result is basically due to the size effect of the Sm$_2$Fe$_{17}$ nanopowder. To interpret this argument, the size dependence of the coercivity of the Sm$_2$Fe$_{17}$ nanopowder should first be discussed in terms of a single domain limit, which was reported to have approximately 300 nm for the Sm$_2$Fe$_{17}$ based intermetallics. Such Sm$_2$Fe$_{17}$ intermetallics having a grain size of this single domain range was also reported to have the highest value of coercivity. In the grain size range above the single domain limit, the $H_c$ of Sm$_2$Fe$_{17}$ decreased sharply as the particle size in a multi domain state increased. This tendency can be seen from the data in Table 1.

Based on these results, it is expected that Sm$_2$Fe$_{17}$N$_x$ nanopowder having an excellent structural integrity and high magnetic properties can be synthesized using Sm$_2$Fe$_{17}$ nanopowder through a subsequent nitrogenation process.

4. Conclusions

We investigated the fabrication of Sm$_2$Fe$_{17}$ nanopowder by a MRD process using a homogeneous powder mixture of Sm$_2$O$_3$–Fe–CaH$_2$. The Sm$_2$Fe$_{17}$ phase could be synthesized in a low temperature range below 800°C by an MRD process. It was found that the 700°C processed powder sample with an average particle size of 100–300 nm consisted of Sm$_2$Fe$_{17}$ and a residual Fe of 16%. The Sm$_2$Fe$_{17}$ powder was identified with a rhombohedral Th$_2$Zn$_{17}$-type (2:17 R) structure. The result of the magnetic property revealed that the $M_s$ and $H_c$ of the Sm$_2$Fe$_{17}$ nanopowder were 128 A·m$^2$/kg and 91.8 kA/m, respectively. The somewhat higher value of the $M_s$ is attributed to the presence of residual Fe ferromagnetic particles. However, the much higher coercivity of the Sm$_2$Fe$_{17}$ nanopowder sample in this study compared to the literature data is basically due to the size effect of the Sm$_2$Fe$_{17}$ nanopowder.

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