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Magnetic properties of Sm$_5$Fe$_{17}$-based magnets produced by spark plasma sintering method

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Abstract. Sm$_5$Fe$_{17}$-based magnets, one of the newer permanent magnetic materials, were successfully produced from Sm$_{12.5+X}$Fe$_{87.5-X}$(x=0-17.5) melt-spun ribbons by the spark plasma sintering (SPS) method. X-ray diffraction and thermomagnetic studies revealed that the resultant Sm-Fe magnets contained the metastable Sm$_5$Fe$_{17}$ phase. From further studies, it was found that the amount of Sm$_5$Fe$_{17}$ phase and the resultant coercivity of the Sm-Fe magnets were highly dependent on the Sm content of the Sm-Fe melt-spun ribbon. The Sm$_{22.5}$Fe$_{77.5}$ magnet consisted of the Sm$_5$Fe$_{17}$ phase and exhibited a large coercivity of 34.2 kOe with a remanence of 46.2 emu/g (0.423T).

1. Introduction

The Nd$_5$Fe$_{17}$ phase is a new stable ferromagnetic phase in the binary Nd-Fe system [1-3]. Although the Nd$_5$Fe$_{17}$ phase has a high saturation magnetization of 1.61 T at 4 K and a Curie temperature above 500 K, it does not possess c-axis anisotropy, which is essential for permanent magnet materials [4]. The R$_5$Fe$_{17}$ (R: rare-earth) structure can be obtained with various rare-earth elements, as found with other rare-earth compounds such as the R$_2$Fe$_{14}B$ phase [5]. In fact, the magnetic phase found in Sm-Fe-Ti alloys was characterized by Stadelmaier et al. as isomorphic with the Nd$_5$Fe$_{17}$ phase [6]. Since Sm has a Stevens factor $\alpha_j$ with a different sign from that of Nd, the Sm$_5$Fe$_{17}$ phase is expected to show c-axis anisotropy. The formation of the Sm$_5$Fe$_{17}$ phase has only been reported in sputtered films, and the films exhibited a large coercivity [7,8]. Since the formation of several metastable phases has been reported in binary Sm-Fe alloys, the Sm$_5$Fe$_{17}$ phase may be produced by rapid solidification processing such as melt-spinning [9]. Recent studies have revealed that the Sm$_5$Fe$_{17}$ phase can be obtained by annealing a Sm-Fe melt-spun ribbon [10]. It was found that the Sm$_5$Fe$_{17}$ melt-spun ribbon exhibits a high coercivity [11].

In the production of high-performance Nd-Fe-B permanent magnets, Nd-Fe-B alloy powders have been consolidated into green compact and then sintered at high temperatures [12]. However, this sintering technique cannot be applied to the production of Sm-Fe bulk magnets because the Sm$_5$Fe$_{17}$ phase is metastable and is transformed into the stable phase at high temperatures [13,14]. The recently developed spark plasma sintering (SPS) method can consolidate powders at relatively lower temperatures with a short consolidating period [15]. It has been demonstrated that Sm-Fe melt-spun ribbon can be consolidated into bulk form by the spark plasma sintering method [16]. In the present investigation, Sm$_{12.5+X}$Fe$_{87.5-X}$(x=0-17.5) alloys produced by melt-spinning were consolidated into bulk materials by the SPS method. The structures and magnetic properties of Sm-Fe bulk magnets produced by the SPS method are discussed.
2. Experiment
Sm\(_{12.5+X}\)Fe\(_{87.5-X}\) alloy ingots were prepared by induction melting of Sm (99.9 wt%) and Fe (99.9 wt%) under an argon atmosphere. An alloy ingot with a mass of 20 g was induction melted under an argon atmosphere in a quartz crucible having an orifice 0.6 mm in diameter at the bottom. The molten metal was ejected through the orifice with argon onto a chromium-plated copper wheel rotating at a surface velocity of 50 ms\(^{-1}\). The resultant melt-spun ribbon was brittle and could be mechanically comminuted and subsequently sieved to particle sizes ranging from 40 to 210 µm. The powder was placed in a carbon die and then sintered under a vacuum by SPS. The temperature of the specimen was increased from room temperature to the consolidating temperature of 873 K for 300 s and the consolidating temperature was then held for 300 s by applying a pulsed electric current of 500 A at intervals of 2.4 ms. The temperature was measured by a thermocouple placed on the surface of the specimen. A pressure of 100 MPa was applied during the heating and cooling of the specimen. The consolidation behavior was monitored by the change in the specimen height during the SPS treatment. After the SPS treatment, the specimens were cooled to room temperature under a vacuum.

The powder was successfully compacted into a bulk material by the SPS method. Typical dimensions of the specimens were 10-15 mm in diameter and 1-3 mm in thickness. After the surface of the specimens was ground to remove carbon contamination, they were cut for further processing and property measurements. Furthermore, the phases of the specimens were examined by performing X-ray diffraction (XRD) using Cu K\(_\alpha\) radiation, and the magnetization of the specimens was examined in a helium atmosphere by using a vibrating sample magnetometer (VSM). The magnetic properties of the specimens were measured at room temperature by both the VSM with a maximum applied field of 25 kOe and a pulsed field magnetometer with a maximum applied field of 100 kOe. In the calculations of magnetization, the value obtained by Archimedes’ method was used as the density of the specimen.

3. Results and Discussion

Figure 1 shows the XRD patterns of the Sm-Fe melt-spun ribbons. The corresponding thermomagnetic curves of the Sm-Fe melt-spun ribbons are shown in Figure 2. Narrow and broad diffraction peaks can be seen in the XRD patterns of the Sm\(_{12.5}\)Fe\(_{87.5}\) and Sm\(_{15}\)Fe\(_{85}\) melt-spun ribbons.
The Sm$_{12.5}$Fe$_{87.5}$ melt-spun ribbon consists of the SmFe$_7$ phase. The thermomagnetic curve of the Sm$_{12.5}$Fe$_{87.5}$ melt-spun ribbon shows a large magnetic transition at around 450 K, which corresponds to the Curie temperature of the SmFe$_7$ phase. This confirms that the specimen consists of the SmFe$_7$ phase. The Sm$_{15}$Fe$_{85}$ melt-spun ribbon consists of the SmFe$_7$ phase together with the Sm$_2$Fe$_{17}$ and SmFe$_{12}$ phases. The thermomagnetic curve of the Sm$_{15}$Fe$_{85}$ melt-spun ribbon shows two magnetic transitions at around 400 K and 450 K, which correspond to the Curie temperature of the Sm$_2$Fe$_{17}$ phase and the SmFe$_7$ phase, respectively. However, no clear magnetic transition of the SmFe$_{12}$ phase is noted in the thermomagnetic curve. This implies that the amount of the SmFe$_{12}$ phase in the specimen is limited and that the specimen contains mainly of Sm$_2$Fe$_{17}$ and SmFe$_7$ phases. Since the Sm$_{15}$Fe$_{85}$ melt-spun ribbon has a higher Sm content than the observed Sm$_2$Fe$_{17}$ and SmFe$_7$ phases, it is believed that the ribbon should consist of another phase which is enriched in Sm. In the XRD patterns of the Sm$_{17.5}$Fe$_{82.5}$ and Sm$_{20}$Fe$_{80}$ melt-spun ribbons, the diffraction peaks are embedded in the halo-like peak and are too weak to be indexed to any crystalline phase. The thermomagnetic curves of the Sm$_{17.5}$Fe$_{82.5}$ and Sm$_{20}$Fe$_{80}$ melt-spun ribbons show a large magnetic transition at around 450 K, which corresponds to the Curie temperature of the SmFe$_7$ phase. This indicates that these specimens consist of the SmFe$_7$ phase. On the other hand, the XRD pattern of the Sm$_{22.5}$Fe$_{77.5}$ melt-spun ribbon shows a fairly broad halo-like peak, which is characteristic of an amorphous structure. The thermomagnetic curve of the Sm$_{22.5}$Fe$_{77.5}$ melt-spun ribbon shows a large magnetic transition at around 500 K. Since this specimen consisted of the amorphous phase, the magnetic transition at around 500 K is believed to be the Curie temperature of amorphous Sm-Fe alloy. This indicates that the increase in the Sm content in the Sm-Fe melt-spun ribbon markedly increases the glass formability. Although formation of the amorphous phase in binary alloys is rather difficult, the Sm-Fe melt-spun ribbons consist of the fully or partially amorphous phase. The XRD pattern of the Sm$_{25}$Fe$_{75}$ melt-spun ribbon also shows a fairly broad halo-like peak. Although a clear magnetic transition at around 500 K is seen in the thermomagnetic curve of the Sm$_{25}$Fe$_{75}$ melt-spun ribbon, it shows an additional small magnetic transition at around 550 K, which corresponds to the Curie temperature of the Sm$_5$Fe$_{17}$ phase. This suggests that the specimen consists of the Sm$_5$Fe$_{17}$ phase together with the amorphous phase. The thermomagnetic curves of the Sm$_{27.5}$Fe$_{72.5}$ and Sm$_{30}$Fe$_{70}$ melt-spun ribbons also show two magnetic transitions at around 500 K and 550 K, which correspond to the Curie temperature of the amorphous phase and the Sm$_5$Fe$_{17}$ phase, respectively. These results indicate that these specimens consist of the Sm$_5$Fe$_{17}$ phase together with the amorphous phase.

The magnetic properties of the Sm-Fe melt-spun ribbons were examined by VSM. The results are shown in Figure 3. Both the saturation magnetization and remanence of the Sm-Fe melt-spun ribbon monotonically decreases up to 22.5 at% and then rapidly decreases, reaching a plateau with increasing Sm content. However, the coercivity of the Sm-Fe melt-spun ribbon remains the same.
even though the Sm content of the Sm-Fe melt-spun ribbon increases. The Sm$_{27.5}$Fe$_{72.5}$ and Sm$_{30}$Fe$_{70}$ melt-spun ribbons exhibit a small coercivity, because they contain some of the Sm$_{3}Fe_{17}$ phase together with the amorphous phase.

It has been reported that the annealing of amorphous Sm-Fe melt-spun ribbons results in a formation of the metastable Sm$_{3}Fe_{17}$ phase and a large coercivity is exhibited [11]. Thus, sintering of the Sm-Fe melt-spun ribbons was performed by the SPS method. It is believed that the Sm-Fe melt-spun ribbons are annealed during the sintering. The Sm-Fe melt-spun ribbons were successfully consolidated into bulk materials by the SPS method regardless of the Sm content. For instance, the density of the Sm$_{22.5}$Fe$_{77.5}$ magnets was 7.23 g/cm$^3$ (approximately 91% of the ingot density). Virtually the same density was obtained from the other Sm-Fe magnets produced by the SPS method. Thus, the structures of the resultant Sm-Fe magnets were examined by XRD and thermomagnetic studies. Figure 4 shows XRD patterns of the Sm-Fe magnets produced by the SPS method. The corresponding thermomagnetic curves of the Sm-Fe magnets produced by the SPS method are shown in Figure 5.

The Sm-Fe magnets produced by the SPS method showed crystalline peaks which may be assigned to the Sm$_{3}Fe_{17}$ phase. Heat exposure during the sintering process resulted in the formation of the crystalline phase. According to the phase diagram, the Sm$_{12.5+x}Fe_{87.5-x}$ (x=0-17.5) alloys are located in the region of two phases: Sm$_{3}Fe_{17}$ and Sm$_{5}Fe_{2}$ or Sm$_{5}Fe_{2}$ and Sm$_{2}$Fe. Since the XRD pattern of the Sm$_{3}Fe_{17}$ phase is similar in appearance to that of the Sm$_{5}Fe_{2}$ phase and that of the Sm$_{2}$Fe phase, it is difficult to eliminate the possibility that these phases exist in the Sm-Fe magnets. Unlike in the XRD studies, clear changes in the magnetic transition temperature are noted in the thermomagnetic curve of the Sm$_{12.5}$Fe$_{87.5}$ magnet. The thermomagnetic curve of the Sm$_{12.5}$Fe$_{87.5}$ magnet shows three magnetic transitions at around 450 K, 550 K, and 650K, which correspond to Curie temperature of the Sm$_{5}Fe_{2}$ phase, Sm$_{3}Fe_{17}$ phase, and Sm$_{2}$Fe$_{3}$ phase, respectively. Since the Sm$_{2}$Fe$_{3}$ phase is not the equilibrium phase but the metastable phase, the Sm$_{5}Fe_{2}$ and Sm$_{2}$Fe$_{3}$ phases are formed from the Sm$_{5}Fe_{2}$ phase during the sintering of the Sm$_{12.5}$Fe$_{87.5}$ melt-spun ribbon. It was found that changes in the magnetic phase can be more effectively determined by the thermomagnetic studies than the XRD studies.

Figure 4. XRD patterns of the Sm-Fe magnets produced by the SPS method:
(a) Sm$_{12.5}$Fe$_{87.5}$, (b) Sm$_{15}$Fe$_{85}$, (c) Sm$_{17.5}$Fe$_{82.5}$, (d) Sm$_{20}$Fe$_{80}$, (e) Sm$_{22.5}$Fe$_{77.5}$, (f) Sm$_{25}$Fe$_{75}$, (g) Sm$_{27.5}$Fe$_{72.5}$, (h) Sm$_{30}$Fe$_{70}$.

Figure 5. Thermomagnetic curves of the Sm-Fe magnets produced by the SPS method:
(a) Sm$_{12.5}$Fe$_{87.5}$, (b) Sm$_{15}$Fe$_{85}$, (c) Sm$_{17.5}$Fe$_{82.5}$, (d) Sm$_{20}$Fe$_{80}$, (e) Sm$_{22.5}$Fe$_{77.5}$, (f) Sm$_{25}$Fe$_{75}$, (g) Sm$_{27.5}$Fe$_{72.5}$, (h) Sm$_{30}$Fe$_{70}$.
Further studies were therefore carried out by thermomagnetic studies. Virtually the same thermomagnetic curves are obtained from the Sm$_{15}$Fe$_{85}$ and Sm$_{17.5}$Fe$_{82.5}$ magnets. This suggests that these magnets contain some Sm$_5$Fe$_{17}$ and SmFe$_3$ phases together with the SmFe$_7$ phase. The thermomagnetic curve of the Sm$_{20}$Fe$_{80}$ magnet shows two magnetic transitions at around 550 K and 650 K, which correspond to the Curie temperature of the Sm$_5$Fe$_{17}$ phase and SmFe$_3$ phase, respectively. A trace of the SmFe$_7$ phase is seen in the thermomagnetic curve, indicating that the Sm$_{20}$Fe$_{80}$ magnet consists of the Sm$_5$Fe$_{17}$ and SmFe$_3$ phases together with a small amount of the SmFe$_7$ phase. A clear magnetic transition at around 550 K is seen in the thermomagnetic curve, suggesting that this magnet is mostly composed of the Sm$_5$Fe$_{17}$ phase. Unlike in the case of the Sm$_{22.5}$Fe$_{77.5}$ magnet, the thermomagnetic curves of the Sm$_{25}$Fe$_{75}$, Sm$_{27.5}$Fe$_{72.5}$, and Sm$_{30}$Fe$_{70}$ magnets show two magnetic transitions at around 550 K and 650 K, which correspond to the Curie temperatures of the Sm$_5$Fe$_{17}$ phase and SmFe$_3$ phase, respectively. This suggests that these magnets contain some SmFe$_3$ phase together with the Sm$_5$Fe$_{17}$ phase. This indicates that the increase in the Sm content in the Sm-Fe magnet promotes the formation of the Sm$_5$Fe$_{17}$ phase up to 22.5 at%Sm. Above this point, the formation of the SmFe$_3$ phase is favored compared to that of the Sm$_5$Fe$_{17}$ phase. It was found that only the Sm$_{22.5}$Fe$_{77.5}$ magnet consists mostly of the Sm$_5$Fe$_{17}$ phase in the Sm$_{12.5+X}$Fe$_{87.5-X}$ (x=0-17.5) magnets produced by the SPS method.

Figure 6 shows the dependence of the saturation magnetization, remanence, and coercivity of the Sm-Fe magnets produced by the SPS method on the Sm content. The saturation magnetization of the Sm-Fe magnets monotonically decreases with increasing Sm content, as was the case for the Sm-Fe melt-spun ribbon. However, the Sm-Fe magnets exhibit coercivity depending on the Sm content in the Sm-Fe magnets. Although a slight increase in the coercivity value is observed in the Sm-Fe magnets with the Sm content in the range of 12.5 at% to 20 at%, the Sm-Fe magnets with a Sm content in the range of 22.5 at% to 25 at% exhibited attractively high coercivities of over 30 kOe. This is because the Sm-Fe magnets with a Sm content in the range of 22.5 at% to 25 at% mainly consist of the Sm$_5$Fe$_{17}$ phase. According to the XRD and thermomagnetic studies, the Sm$_{30}$Fe$_{80}$ magnet consisted of the Sm$_5$Fe$_{17}$ phase together with the SmFe$_3$ phase. Although the Sm$_{30}$Fe$_{80}$ magnet contains the hard magnetic Sm$_5$Fe$_{17}$ phase, the amount of the hard magnetic Sm$_5$Fe$_{17}$ phase in the Sm$_{30}$Fe$_{80}$ magnet is limited and does not exhibit a large coercivity. The Sm$_{27.5}$Fe$_{22.5}$ and Sm$_{30}$Fe$_{70}$ magnets exhibit a small coercivity, because they contain some of the Sm$_5$Fe$_{17}$ phase. These Sm-Fe magnets consisted of the
Sm$_{5}$Fe$_{17}$ and SmFe$_{3}$ phases, as was the case for the Sm$_{25}$Fe$_{75}$ magnet. However, the amount of the soft magnetic SmFe$_{3}$ phase is relatively high and thus deteriorates the coercivity of the Sm-Fe magnets. It is known that the remanence of the magnets is usually determined by both the saturation magnetization and coercivity. Since the Sm$_{22.5}$Fe$_{77.5}$ and Sm$_{25}$Fe$_{75}$ magnets exhibit large coercivity values, they show large remanence values compared to other Sm-Fe magnets.

Figure 7 shows the demagnetization curves of the Sm$_{22.5}$Fe$_{77.5}$ magnet produced by the SPS method together with the Sm$_{22.5}$Fe$_{77.5}$ melt-spun ribbon. The Sm-Fe melt-spun ribbon showed a low coercivity of less than 1 kOe, as expected for an amorphous material. On the other hand, the Sm$_{22.5}$Fe$_{77.5}$ magnet produced by the SPS method showed a high coercivity of 34.2 kOe with a remanence of 46.6 emu/g (0.423 T). Since that Sm$_{22.5}$Fe$_{77.5}$ magnet consisted of the Sm$_{5}$Fe$_{17}$ phase, the observed coercivity is due to the existence of the Sm$_{5}$Fe$_{17}$ phase. Although the remanence of the annealed Sm-Fe melt-spun ribbon is not yet comparable to that of Nd-Fe-B melt-spun ribbon, the annealed Sm-Fe melt-spun ribbon exhibits a much higher coercivity than a Nd-Fe-B melt-spun ribbon.

4. Conclusion

Sm$_{12.5+x}$Fe$_{87.5-x}$ (x=0-17.5) melt-spun ribbons mainly consisted of either amorphous phase or SmFe$_{7}$ phase and showed low coercivity. The Sm-Fe melt-spun ribbons were successfully consolidated into bulk materials by the SPS method. The resultant Sm-Fe magnets contained the metastable Sm$_{5}$Fe$_{17}$ phase. The amount of Sm$_{5}$Fe$_{17}$ phase and the resultant coercivity of the Sm-Fe magnets were highly dependent on the Sm content of the Sm-Fe melt-spun ribbon. The Sm$_{22.5}$Fe$_{77.5}$ magnet almost entirely consisted of the Sm$_{5}$Fe$_{17}$ phase and exhibited a large coercivity of 34.2 kOe.

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