Magnetic properties of Sm$_5$Fe$_{17}$ melt-spun ribbons and their borides

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Abstract: Sm$_5$Fe$_{17}$ melt-spinning ribbons exhibited low coercivity and partly or mostly consisted of the amorphous phase. Annealing of Sm$_5$Fe$_{17}$ melt-spinning ribbon resulted in the formation of the Sm$_5$Fe$_{17}$ phase. The annealed Sm$_5$Fe$_{17}$ melt-spinning ribbon exhibited a high coercivity. It was found that the addition of B to the Sm$_5$Fe$_{17}$ alloy resulted in the promotion of the Sm$_2$Fe$_{14}$B phase. Annealed Sm$_5$Fe$_{17}$B$_x$ ($x = 0.5$) melt-spinning ribbons consisted of the Sm$_5$Fe$_{17}$ phase together with the Sm$_2$Fe$_{14}$B and SmFe$_2$ phases. On the other hand, annealed Sm$_5$Fe$_{17}$B$_x$ ($x = 1.0−1.5$) melt-spinning ribbons consisted of the Sm$_2$Fe$_{14}$B and SmFe$_2$ phases without the Sm$_5$Fe$_{17}$ phase. The resultant Sm$_5$Fe$_{17}$B$_x$ ($x = 1.0−1.5$) melt-spinning ribbons still showed a coercivity of around 2 kOe. The annealed Sm$_5$Fe$_{17}$ melt-spinning ribbon exhibited a high coercivity over 25 kOe and a remanence of 40 emu/g, whereas the annealed Sm$_5$Fe$_{17}$B$_{1.0}$ melt-spinning ribbon exhibited a high remanence of 65 emu/g and a coercivity of 2.0 kOe.

Keywords: Sm-Fe alloys; rare-earth magnet; melt-spinning; coercivity; microstructures

1. Introduction

The Sm$_5$Fe$_{17}$ phase is a ferromagnetic phase in the binary Sm-Fe system [1,2]. It is a metastable phase and its formation has been reported only in sputtered films [3,4]. Through the intensive studies to produce the Sm$_5$Fe$_{17}$ phase as bulk materials, it was found that the Sm$_5$Fe$_{17}$ phase can be obtained by annealing of amorphous melt-spinning ribbons [5]. Sm$_5$Fe$_{17}$ melt-spinning ribbon shows a large coercivity exceeding 25 kOe and a remanence of 40 emu/g, which is significantly lower than the remanence of Nd-Fe-B magnets. For the application in the motors of electric vehicles and
wind-turbine generators, the temperature of the magnets rises to nearly 473 K due to the evolution of eddy currents. Nd-Fe-B magnets cannot be used for the motors and instead Nd-Dy-Fe-B magnets, which the Dy was added to increase the coercivity, are applied. At such a high temperature, the magnetic properties of the Sm$_5$Fe$_{17}$ melt-spun ribbon were almost comparable to those of the Nd-Fe-B melt-spun ribbon (The results are discussed later in the results and discussion section). Thus, the high coercivity magnets are required for the high temperature applications. Since the Sm$_5$Fe$_{17}$ melt-spun ribbon possesses the high coercivity, it can be suitable for a hard magnet component in the nanocomposite magnets, which is the most promising candidate for the new types of the permanent magnets. In any case, the increase of the remanence of the Sm$_5$Fe$_{17}$ melt-spun ribbon is almost always beneficial. There have been several efforts to increase the remanence of Sm$_5$Fe$_{17}$-type melt-spun ribbons, but the reported values are not yet satisfactory [6,7,8]. It is known that the magnetic properties of Sm-Co-based magnets can be improved by the addition of B to the Sm-Co-based alloy [9,10,11]. In this study, small amounts of B were added to Sm$_5$Fe$_{17}$ melt-spun ribbon in order to increase the remanence. The structures and magnetic properties of the Sm-Fe and Sm-Fe-B melt-spun ribbons were then examined.

2. Materials and Method

Sm$_5$Fe$_{17}$ and Sm$_5$Fe$_{17}$B$_x$ (x = 0.5–1.5) alloy ingots were induction melted in an argon atmosphere in a quartz crucible having an orifice of 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 40 ms$^{-1}$. The resultant melt-spun ribbons were annealed under an argon atmosphere at temperatures between 773 K and 1073 K for 1 h. The phases in the specimens were examined by X-ray diffraction (XRD) using Cu Kα radiation. The microstructures of the specimens were examined using a transmission electron microscope (TEM) after ion beam thinning. The thermomagnetic properties of the specimens were examined in a vacuum using a vibrating sample magnetometer (VSM) with an applied field of 500 Oe. The magnetic properties of the specimens were measured by the VSM with a maximum applied field of 25 kOe after premagnetization in a pulsed field of 70kOe. Some of the specimens were further examined by VSM using a superconducting magnet with a maximum applied field of 100 kOe.

3. Results and Discussion

3.1. Sm-Fe melt-spun ribbon

The Sm$_5$Fe$_{17}$ melt-spun ribbons were amorphous and exhibited a low coercivity value, less than 1 kOe. It is known that crystalline phases can be produced by rapid solidification processing and subsequent heat treatment [6]. In the previous studies [7,8], the annealed samples consisted of the Sm$_5$Fe$_{17}$ phase but also contained some other phase such as the SmFe$_{12}$ phase and the SmFe$_3$ phase. As the result of the extensive study of the annealing conditions, the optimal annealing condition to obtain the Sm$_5$Fe$_{17}$ phase was established in this paper. Figure 1 shows the XRD patterns of the annealed Sm-Fe melt-spin ribbons. The amorphous melt-spin ribbon should be annealed at relatively high heating rates of 0.5–1.0 K/s to 873–973 K and then kept for 1 h. As shown in Figure 1, the optimal annealed specimens consisted of the Sm$_5$Fe$_{17}$ (hexagonal) phase. However, the Sm-Fe
ribbon annealed at 1073 K consisted of the SmFe$_3$ (rhombohedral) phase together with the Sm$_3$Fe$_{17}$ phase.

Figure 2 shows the dependence of the coercivity of the Sm$_3$Fe$_{17}$ melt-spun ribbons on the annealing temperature. The specimens annealed at 873 K and 973 K showed high coercivity values. According to the results of the XRD studies, those annealed melt-spun ribbon consists of the Sm$_3$Fe$_{17}$ phase. This indicates that the observed high coercivity in the annealed melt-spun ribbon is due to the existence of the Sm$_3$Fe$_{17}$ phase.

Figure 1. XRD patterns of (a) the Sm-Fe melt-spun ribbon and the specimens annealed at (b) 773 K, (c) 873 K, (d) 973 K, and (e) 1073 K.

Figure 2. Dependence of the coercivity of the Sm-Fe melt-spun ribbons on the annealing temperature.

The hysteresis loops of the Sm$_3$Fe$_{17}$ melt-spun ribbon and the specimen annealed at 973 K are shown in Figure 3. Since the applied field of 25 kOe is far lower than the field required to fully saturate the Sm$_3$Fe$_{17}$ melt-spun ribbon, the hysteresis curve is not closed (i.e., it is a minor loop), and
it is not symmetrical with respect to either coordinate. The actual coercivity of the annealed specimen was measured as 40 kOe using a superconducting magnet with a maximum applied field of 100 kOe.

Figure 3. Hysteresis loops of (a) the Sm-Fe melt-spun ribbon and (b) the specimen annealed at 973 K. The demagnetization curve of the annealed specimen measured using a superconducting magnet with a maximum applied field of 100 kOe is also shown in the insert.

Figure 4 shows the hysteresis loops of the Sm$_2$Fe$_{17}$ melt-spun ribbon and the Nd$_{15}$Fe$_{77}$B$_8$ melt-spun ribbon measured at 473 K under the applied magnetic field of 20 kOe. Although the Sm$_2$Fe$_{17}$ melt-spun ribbon ribbons showed a much smaller remanence than the Nd$_{15}$Fe$_{77}$B$_8$ melt-spun ribbon at room temperature, it exhibits a much smaller difference in remanence at 473 K. Therefore, the magnetic properties of the Sm$_2$Fe$_{17}$ melt-spun ribbon are comparable to those of Nd$_{15}$Fe$_{77}$B$_8$ melt-spun ribbon at 473 K.

Figure 4. Hysteresis loops of (a) the Nd$_{15}$Fe$_{77}$B$_8$ melt-spun ribbon and (b) the Sm$_5$Fe$_{17}$ melt-spun ribbon measured at 473 K. The high-temperature measurements were made by VSM under a maximum applied magnetic field of 20 kOe.
3.2. Sm-Fe borides

The Sm$_5$Fe$_{17}$B$_x$ ($x = 0.5–1.5$) melt-spun ribbon showed a low coercivity, as was the case for the Sm$_5$Fe$_{17}$ melt-spun ribbon. Figure 5 shows the dependence of the coercivity of the Sm$_5$Fe$_{17}$B$_x$ ($x = 0.5–1.5$) melt-spun ribbons on the annealing temperature. The coercivity of the Sm$_5$Fe$_{17}$B$_x$ ($x = 0.5–1.5$) alloys shows a similar temperature dependence, but their maximum coercivity, achieved by annealing at 973 K, decreases with increasing B content of the alloy. This indicates that the addition of B to the Sm$_5$Fe$_{17}$ alloy results in a decrease in coercivity.

![Figure 5. Dependence of the coercivity of the Sm$_5$Fe$_{17}$B$_x$ ($x = 0.5–1.5$) melt-spun ribbons on the annealing temperature.](image)

Figure 6 shows the hysteresis loops of the Sm$_5$Fe$_{17}$B$_x$ ($x = 0.5–1.5$) melt-spun ribbons annealed at 973 K. For comparison, the hysteresis loop of the Sm$_5$Fe$_{17}$ melt-spun ribbon annealed at 973 K is also shown in the each figure.

![Figure 6. Hysteresis loops of the Sm$_5$Fe$_{17}$B$_x$ ($x = 0.5–1.5$) melt-spun ribbons annealed at 973 K. For comparison, the hysteresis loop of the Sm$_5$Fe$_{17}$ melt-spun ribbon annealed at 973 K is also shown in the each figure.](image)
alloys is much smaller than that of the Sm₅Fe₁₇ alloy. The remanence increases with increasing B content from 40 emu/g for the Sm₅Fe₁₇ alloy to 65 emu/g for the Sm₅Fe₁₇B₁.₀ alloy and then decreases to 60 emu/g for the Sm₅Fe₁₇B₁.₅ alloy. The remanence of 65 emu/g exhibited by the annealed Sm₅Fe₁₇B₁.₀ alloy is much higher than that of the annealed Sm₅Fe₁₇ melt-spun ribbon.

The Sm₅Fe₁₇ and Sm₅Fe₁₇Bₓ (x = 0.₅–1.₅) melt-spun ribbons annealed at 973 K were examined by XRD and thermomagnetic studies to evaluate the differences in the coercivity value. Figure 7 shows the XRD patterns of the annealed Sm-Fe-B melt-spun ribbons. The diffraction peaks of the Sm₅Fe₁₇ alloy were determined to be the Sm₅Fe₁₇ phase. Virtually the same XRD patterns were obtained from the Sm₅Fe₁₇B₀.₅ alloy. This indicates that the small addition of B to the Sm₅Fe₁₇ alloy did not alter the XRD pattern. On the other hand, the XRD pattern of the Sm₅Fe₁₇B₁.₀ alloy is quite different from that of the Sm₅Fe₁₇ alloy. The diffraction peaks of the Sm₅Fe₁₇ alloy were determined to be the Sm₂Fe₁₄B and SmFe₂ phases. The XRD pattern of the Sm₅Fe₁₇B₁.₅ alloy is similar to that of the Sm₅Fe₁₇B₁.₀ alloy, indicating that the Sm₅Fe₁₇B₁.₅ alloy also consisted of the Sm₂Fe₁₄B (tetragonal) and SmFe₂ (cubic) phases. These results reveal that the large addition of B to the Sm₅Fe₁₇ alloy resulted in the formation of the Sm₂Fe₁₄B and SmFe₂ phases instead of the Sm₅Fe₁₇ phase, and hence the decrease in coercivity.

Figure 7. XRD patterns of the annealed melt-spun ribbons: (a) Sm₅Fe₁₇, (b) Sm₅Fe₁₇B₀.₅, (c) Sm₅Fe₁₇B₁.₀, and (d) Sm₅Fe₁₇B₁.₅ alloys.

Figure 8 shows the thermomagnetic curves of the annealed Sm-Fe-B melt-spun ribbons. The thermomagnetic curve of the Sm₅Fe₁₇ alloy exhibits one magnetic transition at around 550 K, which corresponds to the Curie temperature of the Sm₅Fe₁₇ phase. Unlike in the case of the XRD studies, the thermomagnetic curve of the Sm₅Fe₁₇B₀.₅ alloy is quite different from that of the Sm₅Fe₁₇ alloy. The thermomagnetic curve exhibits three magnetic transitions at around 550 K, 620 K, and 680 K. It has been reported that the Curie temperatures of the Sm₂Fe₁₄B phase and SmFe₂ phase are 616 K and 675 K, respectively [12,13,14]. Therefore, the Sm₅Fe₁₇B₀.₅ alloy contains the Sm₂Fe₁₄B and SmFe₂ phases together with the Sm₅Fe₁₇ phase. The thermomagnetic curve of the Sm₅Fe₁₇B₁.₀ alloy exhibits
two magnetic transitions at around 620 K and 680 K, indicating that the Sm$_3$Fe$_{17}$B$_{1.0}$ alloy has no Sm$_3$Fe$_{17}$ phase. The Sm$_3$Fe$_{17}$B$_{1.5}$ alloy also exhibits two magnetic transitions at around 620 K and 680 K, which correspond to the Curie temperatures of the Sm$_2$Fe$_{14}$B and SmFe$_2$ phases. This is consistent with the results of the XRD studies.

![Fig8](image1)

Figure 8. Thermomagnetic curves of the annealed Sm-Fe-B melt-spun ribbons.

![Fig9](image2)

Figure 9. TEM micrographs of the (a) Sm$_3$Fe$_{17}$B$_{0.5}$ and (b) Sm$_3$Fe$_{17}$B$_{1.5}$ annealed melt-spun ribbons and corresponding X-ray mappings for iron and samarium.
Figure 9 shows TEM micrographs of the annealed Sm$_3$Fe$_{17}$B$_{0.5}$ and Sm$_3$Fe$_{17}$B$_{1.5}$ melt-spun ribbons. The grain size of the annealed Sm$_3$Fe$_{17}$B$_{0.5}$ alloy was around 50 nm in diameter, which is almost comparable to the reported grain size of annealed Sm$_3$Fe$_{17}$ alloy [8]. Samarium and iron were detected in most of the grains of the annealed Sm$_3$Fe$_{17}$B$_{0.5}$ alloy, except for the centrally located grain that were rich in samarium but poor in iron. According to the results of the thermomagnetic studies, the specimens contained some of the Sm$_2$Fe$_{14}$B (Sm11.7 at%) and SmFe$_2$ (Sm33.3 at%) phases together with the Sm$_3$Fe$_{17}$ (Sm22.7 at%) phase. Thus, the samarium-rich centrally located grain consisted of the SmFe$_2$ phase and the surrounding grains were either the Sm$_2$Fe$_{14}$B or SmFe$_2$ phase. The upper-left grain region, which was rich in iron but slightly poor in samarium, may be the Sm$_2$Fe$_{14}$B phase. In the TEM micrograph of the annealed Sm$_3$Fe$_{17}$B$_{1.5}$ alloy, an increase was seen in the amount of the SmFe$_2$ phase, where is poor in iron but rich in samarium. The grain size of the SmFe$_2$ phase was found to be larger than that in the annealed Sm$_3$Fe$_{17}$B$_{0.5}$ alloy. Since the Sm$_3$Fe$_{17}$B$_{1.5}$ alloy consisted of the Sm$_3$Fe$_{14}$B and SmFe$_2$ phases, the surrounding grains are considered to be the Sm$_2$Fe$_{14}$B phase. This confirms that the addition of B to Sm$_3$Fe$_{17}$ alloy results in the formation of the SmFe$_2$ and Sm$_2$Fe$_{14}$B phases, instead of the formation of a Sm$_5$Fe$_{17}$B$_x$ phase. Since the Sm$_3$Fe$_{14}$B phase does not possess uniaxial anisotropy [12], the observed coercivity of the annealed Sm-Fe-B melt-spun ribbons is considered to be the fine SmFe$_2$ phase.

4. Conclusion

The structures and magnetic properties of Sm$_3$Fe$_{17}$B$_x$ (x = 0–1.5) melt-spun ribbons annealed at 973 K were examined. The annealed Sm$_3$Fe$_{17}$ melt-spun ribbon consisted of the Sm$_3$Fe$_{17}$ phase and exhibited a high coercivity. The annealed Sm$_3$Fe$_{17}$B$_{0.5}$ melt-spun ribbon consisted of the Sm$_3$Fe$_{17}$ phase together with the Sm$_2$Fe$_{14}$B and SmFe$_2$ phases. In contrast, the annealed Sm$_3$Fe$_{17}$B$_x$ (x = 1.0–1.5) melt-spun ribbons consisted of the Sm$_2$Fe$_{14}$B and SmFe$_2$ phases. The coercivity of the annealed Sm$_3$Fe$_{17}$B$_x$ (x = 0–1.5) melt-spun ribbons decreased as the B content increased. On the other hand, the annealed Sm$_3$Fe$_{17}$B$_x$ (x = 0.5–1.5) melt-spun ribbons exhibited a higher remanence than the Sm$_3$Fe$_{17}$ melt-spun ribbon.

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Conflict of Interest

All authors declare no conflicts of interest in this paper.

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