Structure and magnetic properties of $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ thin films by adding light elements

M. Kambayashi*, H. Kato**, Y. Mori**, M. Doi*** and T. Shima*,***

* Graduate School of Engineering, Tohoku Gakuin Univ., 1-13-1 Tagajo 985-8537 Japan

** Department of Engineering, Tohoku Gakuin Univ., 1-13-1 Tagajo 985-8537 Japan

*** Elements Strategy Initiative Center for Magnetic Materials (ESICMM), National Institute for Materials Science, 1-2-1 Sengen Tsukuba 305-0047, Japan

The effect of light elements such as B, C and N on $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ alloy was investigated in detail. The highest coercivity H_c of 11.1 kOe was obtained for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films with the thickness of 100 nm and B content of 11.2 at.%. From X-ray diffraction patterns, peaks from (002) and (004) of ThMn_{12} -type phase were clearly observed for the films. However, no significant improvement in magnetic properties was observed with the addition of C and N to the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ alloy, as was the case with the combined addition with B. It was confirmed that only the addition of B contributes significantly to the improvement of magnetic properties from the result of adding light elements to this series of $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ alloy.

Keywords: RFe_{12} compound, ThMn_{12} -type structure, $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ alloy, light elements, coercivity

1. Introduction

RFe_{12} (R : rare-earth elements) compounds¹⁾⁻³⁾ with a tetragonal ThMn_{12} -type crystal structure are expected to surpass the magnetic properties of Nd-Fe-B sintered magnets, since RFe_{12} compounds possess high saturation magnetization M_s and high anisotropy field H_A by the largest composition ratio 1:12 of R atom versus Fe atoms which have high molar fraction among Rm-nFe_{5m+2} systems. However, the RFe_{12} compounds are known to be very unstable from a thermodynamic point of view, and it has been realized that the RFe_{12} phase have been successfully stabilized only by substitution of the element M ($M = \text{Cr}, \text{V}, \text{Ti}, \text{Mo}, \text{W}, \text{Si}$ and Fe)⁴⁾⁻⁷⁾. Unfortunately, the substitution of Fe with a large amount of M causes a reduction in saturation magnetization M_s . Therefore, there is a strong demand for the realization of $\text{R}(\text{Fe}, M)_{12}$ compounds having high phase stability by substituting a small amount of elements.

In recent years, Hirayama et al. reported that the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ thin films with a film thickness of 595 nm deposited on a MgO (100) single crystal substrate with V underlayer grow epitaxially, and their representative magnetic properties of M_s of 1.78 T, anisotropy field H_A of 120 kOe and Curie temperature T_C of 586 °C, which surpasses that of $\text{Nd}_2\text{Fe}_{14}\text{B}$ compound. Since then, a lot of studies have been performed on $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ compound with changing the fabrication conditions⁸⁾⁻¹⁰⁾. Previously, we have successfully reported that the large coercivity of 1.2 T can be achieved by the addition of B to an anisotropic $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ thin film¹¹⁾. It is thought that additive elements will play an important role for improving the magnetic properties of the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ compounds.

Since the light elements B, C and N have small atomic radii, they are expected to be alloyed by interstitial or substitutional position in the ThMn_{12} -type main phase or grain boundary phase and it is considered to have a great influence on the structure and magnetic properties of $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ compound. The effect of light elements on this compound has not been fully studied yet, although the effect of N addition for R-Fe compounds have been

widely investigated¹²⁾. In this study, in order to see the effect of light elements on the structure and magnetic properties for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ thin films, $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ - X ($X = \text{B}, \text{C}, \text{N}, \text{B-C}$ and B-N) have been fabricated and their structure and magnetic properties have also been investigated.

2. Experimental procedure

The samples were prepared by using ultra-high vacuum magnetron sputtering system with base pressure of less than 1.0×10^{-8} Pa. First of all, a V underlayer of 20 nm was deposited onto the MgO (100) single crystal substrate at substrate temperature T_s of 350 °C. Then, the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ - X ($X = \text{B}, \text{C}, \text{N}, \text{B-C}$ and B-N) layer was deposited. Film thickness of $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films was changed from 5 to 200 nm, while it was fixed to 100 nm for another samples with C or N addition. The composition of B and C was designed and calculated by the deposition rate of co-deposition of the targets. On the other hand, the amount of N addition was adjusted by the ratio of Ar gas and N_2 gas during deposition. Highly accurate elemental analysis of light element is not easy, however, B content has been analyzed by inductively coupled plasma (ICP) spectroscopy to be $\text{Sm}_{7.3}\text{Fe}_{67.6}\text{Co}_{16.0}\text{B}_{9.1}$

Fig. 1. Effect of film thickness on the XRD patterns for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films. The film thickness t_{SFCB} was changed from 5 to 200 nm. Enlarged view of the high-angle (004) peak is also shown.

Corresponding author: T. Shima

(e-mail: shima@mail.tohoku-gakuin.ac.jp).

Fig. 2. Effect of film thickness on the M - H curves for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films measured in applied field perpendicular (solid line) and parallel (dotted line) to the film plane. The film thickness t_{SFCB} was changed from 5 to 200 nm.

(at.%) for the film with B = 9.1 at.% was determined in a previous report¹¹). Although the exact amount of C and N addition is uncertain at this moment, it was confirmed that the tendency can be understood because the amount of addition is continuously changed. The amount of B was changed from 0 to 11.3 at.%, the addition of C was designed by the deposition rate of each target and it was changed from 0 to 4.0 %, while for the addition of N, the flow rate ratio of N_2 gas to Ar gas was changed from 0 to 1.0 %. According to an energy dispersive X-ray spectroscopy (EDX) analysis, 14 at.% N was determined to the film with a flow rate ratio of N of 0.5 %, and it was about 22 at.% N to that of 1.0 %. It was confirmed that the amount of nitrogen became constant when the flow rate exceeded that. Accurate elemental analysis of C and N will be performed later. Finally, the V layer of 10 nm was deposited as a cap layer for the prevention of oxidation. The structural analysis was performed by the XRD with Cu-K α radiation from the out-of-plane configuration, the magnetization curves were measured by using a superconducting quantum interference device (SQUID) magnetometer, the film composition was determined by EDX, and in some cases an ICP spectroscopy analysis and APFIM was performed. All measurements were performed at room temperature.

3. Results and discussion

In order to investigate the effect of film thickness on the structure and magnetic properties for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films, $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ thin films with B content of 9.1 at.% were prepared. XRD patterns of $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films with different film thickness are shown in Fig. 1. The enlarged view of high-angle (004) peak was also shown. The peaks from (002) and (004) of ThMn_{12} -type phase with the strongly texture toward (001) direction were began to observe for the film with t_{SFCB} of 20 nm and they shifted to higher angle, indicating that c -axis shrank. Further increasing the film thickness, the intensity of these peaks increased and the position of the peak hardly changed up to 120

Fig. 3. XRD patterns for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B (100 nm) thin films with different B content of 0 to 11.3 at.%. Enlarged view of the high-angle (004) peak is also shown.

Fig. 4. M - H curves for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B (100 nm) thin films with different B content of 0 to 11.3 at.%.

nm, but changed to a low angle beyond that.

The magnetization curves for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films with different film thickness are shown in Fig. 2. The solid and dotted lines denote the curve measured in applied field perpendicular and parallel to the film plane, respectively. It was confirmed that the H_c was increased with increasing the film thickness, and high H_c of 9.4 kOe, high M_s of 1230 emu/cm³ and moderate high uniaxial magnetic anisotropy K_u of 34.7 Merg/cm³ were obtained for the film with t_{SFCB} of 100 nm (f). With further increasing of film thickness, H_c was slightly decreased to 8.2 kOe for the film with t_{SFCB} of 200 nm (h).

Subsequently, the effect of B content to $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films with the film thickness of 100 nm was investigated. The XRD patterns and their enlarged view of the high-angle (004) peak for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B (100 nm) thin films are shown in Fig. 3. The peaks from (002) and (004) of ThMn_{12} -type compound can be observed for all the samples. With increasing B content, the intensity of these peaks decreased and shifted to higher angle for

Fig. 5. XRD patterns for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}\text{-C}$ (100 nm) thin films with different C content of 0 to 4.0 %. Enlarged view of the high-angle (004) peak is also shown.

Fig. 6. M - H curves for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}\text{-C}$ (100 nm) thin films with different C content of 0 to 4.0 %.

the film with B of 6.3 at.% (c), indicating that the lattice constant of c -axis slightly shrank. Also, the peaks from (004) became sharper as the amount of B increased. It is considered that this is because a columnar structure having an average grain size of about 40 nm was formed¹¹⁾.

The magnetization curves for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}\text{-B}$ (100 nm) thin films with different B content are shown in Fig. 4. Without B addition, low H_c of 1.3 kOe was obtained for the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ thin film. However, it was confirmed that the H_c was increased with increasing B content and high H_c of 11.1 kOe, high M_s of 1260 emu/cm^3 and moderate high K_u of 32.2 Merg/cm^3 were obtained for the film with B of 11.2 at.% (g). By a slightly increase of B content, H_c was decreased to 10.1 kOe for the film with B of 11.3 at.% (h).

XRD patterns and their enlarged view of the high-angle (004) peak for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}\text{-C}$ (100 nm) thin films with different C content of 0 to 4.0 % are shown in Fig. 5. The peaks from (002) and (004) of ThMn_{12} -type compound were observed for all the samples. With increasing C content, the intensity of these peaks decreased and the position was almost unchanged up to $C = 2.0$ % (d), and shifted to lower angle when it reached 3.0 or higher, indicating that the lattice constant of c -axis was slightly increased for the film with $C = 3.0$ % (e). At 3.0 % or higher C content,

Fig. 7. XRD patterns for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}\text{-N}$ (100 nm) thin films with different N content of 0 to 1.0 %. Enlarged view of the high-angle (004) peak is also shown.

Fig. 8. M - H curves for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}\text{-N}$ (100 nm) thin films with different N content of 0 to 1.0 %.

SmFe_2 (220) and (440) peaks and ThMn_{12} -type superlattice (132) peaks began to observe at 34.5° , 72.1° and 52.0° .

The magnetization curves for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}\text{-C}$ (100 nm) thin films with different C content are shown in Fig. 6. The out-of-plane magnetic anisotropy and low H_c was obtained for the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}\text{-C}$ thin film. It was confirmed that the H_c was slightly increased with increasing C content, however, with further increasing C content to 3.0 %, H_c was decreased and magnetic anisotropy was changed from the out-of-plane to the in-plane anisotropy.

XRD patterns and their enlarged view of the high-angle (004) peak of ThMn_{12} -type compound for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}\text{-N}$ (100 nm) thin films with different N content of 0 to 1.0 % are shown in Fig. 7. The peaks from (002) and (004) of ThMn_{12} -type compound were observed for the films with N content up to 0.25 %. With increasing N content as in the case of the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}\text{-B}$ thin films, the intensity of these peaks decreased and shifted to higher angle, indicating the lattice constant of c -axis slightly shrank. It is also thought that peaks from the SmN (200) and (400) began to observe at 35.6° and 74.8° when N content was reached 0.2 % or higher, and the SmN (220) peak began to observe at 51.2° when it reached 0.25 % or higher. On the contrary to the results from B added films, C and N added samples are seemed to be almost

Fig. 9. XRD patterns and M - H curves for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B (100 nm) thin films by adding C to 2.0 % and N to 0.2 %.

same width of the (004) peak, this is because the ThMn_{12} -type structure has hardly changed.

The magnetization curves for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -N (100 nm) thin films with different N content are shown in Fig. 8. It was confirmed that the H_c was slightly increased with increasing N content, and high H_c of 3.9 kOe was obtained for the film with N of 0.2 % (c). However, H_c was decreased and magnetic anisotropy was changed from the out-of-plane to the in-plane anisotropy for the film with N of 0.25 % (d). Furthermore, H_c decreased at the film with N of 0.5 % (e).

From the detail microstructural observation by 3D atom probe, the addition of B to the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ film leads to the formation of amorphous intergranular phase and B rich shell can be observed in the vicinity of the grain boundaries. It was also found that C was abundantly present in the V buffer layer for C added films and it was also confirmed that N was present in the vicinity of the precipitated Sm and Fe. Therefore, no grain boundary phase was formed by the addition of C and N. The detailed microstructural results will be reported in the future¹³⁾.

Since H_c was increased by the addition of B, the films were prepared by adding C and N to the B content in which H_c was improved. XRD patterns for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ (100 nm) thin films with B, B-C and B-N addition are shown in Fig. 9 (a). The amount of B content to $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ thin film was fixed at 11.2 at.%, while C and N were combined added to 2.0 % and 0.2 %, respectively. The peaks from (002) and (004) of ThMn_{12} -type phase were clearly observed for all the films, indicating that the strongly textured structure toward (00 l) direction was obtained. However, by the combined addition of the B-C and B-N, the intensity of the peak was significantly reduced, and the position of the peak was slightly shifted to lower angle for the film with B-C addition, while it shifted to higher angle for the film with B-N addition. The magnetization curves for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ (100 nm) thin films with B, B-C and B-N addition are shown in Fig. 9 (b). H_c was decreased remarkably by adding C of 2.0 % and N of 0.2 %, and the magnetic anisotropy of $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films was changed from the out-of-plane to the in-plane anisotropy.

4. Summary

In this study, the effect of light elements such as B, C and N to

the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ alloy was investigated. From XRD patterns, the peaks from (002) and (004) of ThMn_{12} -type compound were clearly observed for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films. High H_c of 11.1 kOe, high M_s of 1260 emu/cm³ and moderate high K_u of 32.2 Merg/cm³ were obtained for the film with B content of 11.2 at.% and t_{SFCB} of 100 nm. It was found that the B addition was very effective in improving the magnetic properties for $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ compounds. However, no significant improvement in magnetic properties was observed with the addition of C and N to the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ thin film. Magnetic anisotropy was changed from the out-of-plane to the in-plane and H_c was decreased with the combined addition of C and N to the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ -B thin films. It was confirmed that only the addition of B contributes significantly to the improvement of magnetic properties of $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ alloy. From the results of this study, the addition of C and N is not suitable for further improving H_c in the $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ compound. However, in order to further improve the magnetic properties of $\text{Sm}(\text{Fe}_{0.8}\text{Co}_{0.2})_{12}$ thin film, it is considered that not only the addition of B but also the grain boundary diffusion effect of the non-magnetic material plays a major role.

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