Structure and magnetic properties of Sm(Fe₀₈Co₀₂)₁₂ thin films by adding light elements

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The effect of light elements such as B, C and N on Sm(Fe₀₈Co₀₂)₁₂ alloy was investigated in detail. The highest coercivity $H_c$ of 11.1 kOe was obtained for Sm(Fe₀₈Co₀₂)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 ThMn₁₂-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 Sm(Fe₀₈Co₀₂)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 Sm(Fe₀₈Co₀₂)₁₂ alloy.

Keywords: RFe₁₂ compound, ThMn₁₂-type structure, Sm(Fe₀₈Co₀₂)₁₂ alloy, light elements, coercivity

1. Introduction

RFe₁₂ ($R$: rare-earth elements) compounds with a tetragonal ThMn₁₂-type crystal structure are expected to surpass the magnetic properties of Nd-Fe-B sintered magnets, since RFe₁₂ 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 $R$-Fe₄Sm₂ systems. However, the RFe₁₂ compounds are known to be very unstable from a thermodynamic point of view, and it has been realized that the RFe₁₂ phase have been successfully stabilized only by substitution of the element $M$ ($M$ = Cr, V, Ti, Mo, W, 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 R(Fe, $M$)₁₂ compounds having high phase stability by substituting a small amount of elements.

In recent years, Hirayama et al. reported that the SmFe₁₂(Co₀₂)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 NdFe₁₂B compound. Since then, a lot of studies have been performed on Sm(Fe₀₈Co₀₂)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 SmFe₁₂(Co₀₂)₁₂ thin film¹¹. It is thought that additive elements will play an important role for improving the magnetic properties of the Sm(Fe₀₈Co₀₂)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 ThMn₁₂-type main phase or grain boundary phase and it is considered to have a great influence on the structure and magnetic properties of Sm(Fe₀₈Co₀₂)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 has been widely investigated¹². In this study, in order to see the effect of light elements on the structure and magnetic properties for Sm(Fe₀₈Co₀₂)₁₂ thin films, Sm(Fe₀₈Co₀₂)₁₂-X ($X$ = B, C, N, 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 Sm(Fe₀₈Co₀₂)₁₂-X ($X$ = B, C, N, B-C and B-N) layer was deposited. Film thickness of Sm(Fe₀₈Co₀₂)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 N₂ 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 Sm₇.₃Fe₆₇.₆Co₁₆.₀B₉.₁.

![Fig. 1. Effect of film thickness on the XRD patterns for Sm(Fe₀₈Co₀₂)₁₂-B thin films. The film thickness $t_{FeCOB}$ was changed from 5 to 200 nm. Enlarged view of the high-angle (004) peak is also shown.](image-url)
(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 N2 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-Kα radiation from the out-of-plane configuration, the magnetization curves were measured by using a superconducting quantum interference device (SUQID) 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 Sm(Fe0.8Co0.2)12-B thin films, Sm(Fe0.8Co0.2)12 thin films with B content of 9.1 at.% were prepared. XRD patterns of Sm(Fe0.8Co0.2)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 ThMn12-type phase with the strongly texture toward (00) direction were began to observe for the film with rsch 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 nm, but changed to a low angle beyond that.

The magnetization curves for Sm(Fe0.8Co0.2)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 Hc was increased with increasing the film thickness, and high Hc of 9.4 kOe, high Ms of 1230 emu/ cm3 and moderate high uniaxial magnetic anisotropy Ku of 34.7 Merg/ cm3 were obtained for the film with rsch of 100 nm (f). With further increasing of film thickness, Hc was slightly decreased to 8.2 kOe for the film with rsch of 200 nm (h).

Subsequently, the effect of B content to Sm(Fe0.8Co0.2)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 are shown in Fig. 3. The peaks from (002) and (004) of ThMn12-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
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 formed.

The magnetization curves for Sm(Fe0.8Co0.2)12-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 Sm(Fe0.8Co0.2)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/ cm³ and moderate high $K_u$ of 32.2 Merg/ cm³ 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 Sm(Fe0.8Co0.2)12-C (100 nm) thin films with different C content are shown in Fig. 5. The peaks from (002) and (004) of ThMn12-type compound were observed for all the samples. With increasing C content, the intensity of these peaks decreased and shifted to higher angle, indicating that the lattice constant of c-axis slightly shrank. It is also thought that peaks from the SmN (200) and (400) began to observe at 35.6º and 74.8º when N content was reached 0.2 % or higher, and the SmN (220) peak began to observe at 51.2º 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 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 formed.

The magnetization curves for Sm(Fe0.8Co0.2)12-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 Sm(Fe0.8Co0.2)12-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 for Sm(Fe0.8Co0.2)12-N (100 nm) thin films with different N content are shown in Fig. 7. The peaks from (002) and (004) of ThMn12-type compound were observed for the films with N content up to 0.25 %. With increasing N content as in the case of the Sm(Fe0.8Co0.2)12-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 35.6º and 74.8º when N content was reached 0.2 % or higher, and the SmN (220) peak began to observe at 51.2º 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
same width of the (004) peak, this is because the ThMn12-type structure has hardly changed.

The magnetization curves for Sm(Fe0.8Co0.2)12-N (100 nm) thin films with different N content are shown in Fig. 8. It was confirmed that the Hc was increased with increasing N content, and high Hc of 3.9 kOe was obtained for the film with N of 0.2 % (c). However, Hc 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, Hc 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 Sm(Fe0.8Co0.2)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 is 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 Hc was increased by the addition of B, the films were prepared by adding C and N to the B content in which Hc was improved. XRD patterns for Sm(Fe0.8Co0.2)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 Sm(Fe0.8Co0.2)12 thin film was fixed at 11.2 at.% and Hc of 3.9 kOe, high Mf of 1260 emu/ cm³ and moderate high Kc of 32.2 Merg/cm³ were obtained for the film with B content of 11.2 at.% and B:Fe30 of 100 nm. It was found that the B addition was very effective in improving the magnetic properties for Sm(Fe0.8Co0.2)12 compounds. However, no significant improvement in magnetic properties was observed with the addition of C and N to the Sm(Fe0.8Co0.2)12 thin film. Magnetic anisotropy was changed from the out-of-plane to the in-plane and Hc was decreased with the combined addition of C and N to the Sm(Fe0.8Co0.2)12-B thin films. It was confirmed that only the addition of B contributes significantly to the improvement of magnetic properties of Sm(Fe0.8Co0.2)12 alloy. From the results of this study, the addition of C and N is not suitable for further improving Hc in the Sm(Fe0.8Co0.2)12 compound. However, in order to further improve the magnetic properties of Sm(Fe0.8Co0.2)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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