Magnetic Properties of Sm-Co-Cu and Sm-Co-Cu/Co Exchange-Spring Films with High Coercivity

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The magnetic properties of Sm-Co-Cu films and Sm-Co-Cu/Co multilayered films prepared by rf-sputtering were investigated. The addition of Cu to Sm-Co film had the effect of decrement of crystallization temperature. The Sm₂₈Co₅₉Cu₁₃ film annealed for 1 h at 623 K showed a reversible demagnetization curve with 82% springback ratio of $[Mr' - M(H)]/[Mr - M(H)]$ and a high coercivity of 2480 kA·m⁻¹. This film was found to be an exchange-spring magnet film composed of the hard magnetic phase such as SmCo₅ and Sm₂Co₇ phases and a soft magnetic phase of Co. Sm₂₈Co₅₉Cu₁₃/Co(x nm) multilayered film whose Co thickness was from 0 to 15 nm was also found to be an exchange-spring magnet film.

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I. Introduction

The maximum energy products $(BH)_{\max}$ of anisotropic Nd-Fe-B sintered magnets are 430 kJ·m⁻³, which are the highest value among all magnets. It nearly approaches the theoretical limited value of 530 kJ·m⁻³, and a new idea of enhancement of $(BH)_{\max}$ is required to overcome the limit.

Recently, nanocomposite magnets called as exchange-spring magnets consisted of soft and hard magnetic phases have been reported⁽¹⁾⁽²⁾. The magnets consisted of the mixture of hard and soft phases whose sizes are larger than domain wall thickness show a constricted loop, and have low value of $(BH)_{\max}$. But the magnets consisted of the mixture of hard and soft phases whose sizes are smaller than domain wall thickness show a hysteresis loop like a single hard magnetic phase. Latter is called as the exchange-spring magnet. This magnet has an exchange coupling between a hard magnetic phase and a soft magnetic phase whose size is smaller than domain wall thickness. Exchange-spring magnets have the reversible magnetization process where the value of magnetization nearly returned to residual magnetization Mr as a mechanical spring, when applied magnetic field H is removed at the demagnetization curve. It is reported that theoretical maximum energy products of anisotropic exchange-spring film magnets would exceed 1000 kJ·m⁻³⁽³⁾. But few papers about exchange-spring film magnets have been reported⁽⁴⁾⁽⁵⁾.

The researcher of film magnets focus on mainly

Sm-Co system⁽⁶⁾ and Nd-Fe-B system⁽⁶⁾⁽⁷⁾ which have SmCo₅⁽⁸⁾ and Nd₂Fe₁₄B compounds⁽⁹⁾. Table 1 shows intrinsic magnetic properties of the compounds. Comparing SmCo₅ with Nd₂Fe₁₄B compounds, Nd₂Fe₁₄B compound has larger saturation magnetization, but SmCo₅ compound has larger anisotropy field. In our study, Sm-Co system has been chosen since SmCo₅ compounds have high anisotropy field, and it may be easier to observe the exchange-spring behaviors. In fact, Sm-Co film has been reported to show a high coercivity⁽⁶⁾. It is known that SmCo₅ phase decomposes eutectoidally into Sm₂Co₇ and Sm₂Co₁₇ phases at 1078 K⁽¹⁰⁾. It is reported that Cu addition to SmCo₅ alloy is effective for lowering the eutectoid temperature⁽¹⁰⁾. It is expected that annealing temperature of Sm-Co-Cu film at which SmCo₅ is formed would become lower than that of Sm-Co film.

Then the purpose of the present study is to investigate the magnetic properties of Sm-Co-Cu films and Sm-Co-Cu/Co films and is possibly to obtain exchange-spring magnet film.

II. Experimental Procedures

Film samples are prepared by rf sputtering from Sm-Co targets, which are made by induction-melting in an argon atmosphere. Detail conditions of film deposition are presented in Table 2. Two types of film samples are pre-

Table 1 Magnetic properties of SmCo₅ and Nd₂Fe₁₄B compounds.

Compound	Ms/T	$H_A/MA \cdot m^{-1}$
SmCo ₅	1.14	35
Nd ₂ Fe ₁₄ B	1.61	7.2

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Table 2 Conditions of rf-sputtering for film deposition.

Background pressure	2.7×10^{-4} Pa
RF input power	30–200 W
Ar gas pressure	0.5–0.8 Pa
Substrate	Quartz
Film thickness	3.5–5.5 μm

Table 3 Composition of Sm-Co films and Sm-Co-Cu films.

Film	Sm (at%)	Co (at%)	Cu (at%)
Sm ₁₆ Co ₈₄	15.91	84.00	0.09
Sm ₂₃ Co ₇₇	23.23	76.62	0.14
Sm ₂₀ Co ₆₇ Cu ₁₃	19.60	67.10	13.30
Sm ₂₈ Co ₅₉ Cu ₁₃	28.20	58.80	13.00

pared. The one is Sm-Co-Cu film prepared from Sm-Co and Cu targets. The another is Sm-Co-Cu/Co multilayer films prepared from Sm-Co, Cu and Co targets. Sm-Co-Cu/Co multilayer samples consist of 25 bilayers with Sm-Co-Cu layer of 220 nm thickness and Co layer 5 nm thickness. As-deposited films are annealed at 523–973 K for 1 h in vacuum. Total film thicknesses are 3.5–5.5 μm .

The existed phases of the film are analyzed by X-ray diffractometer using Cu-K α ray. Magnetic properties are measured by a vibrating sample magnetometer and superconducting quantum interference device with maximum applied magnetic field of 1200 kA $\cdot$ m⁻¹ and 5.5 T alternately. All of the magnetic properties presented are measured along the film plane. The film composition was determined by a scanning electron microscope with energy-dispersive X-rays. Table 3 shows the composition of Sm-Co, Sm-Co-Cu films.

III. Results and Discussion

Figure 1 shows that X-ray diffraction patterns of

Sm₁₆Co₈₄ and Sm₂₃Co₇₇ films as deposited and annealed at various temperatures for 1 h. Sm₁₆Co₈₄ films as deposited and annealed at 723 K shows broad peaks, indicating that the as-deposited film is amorphous and stable below 723 K. Sm₁₆Co₈₄ film annealed at 773 and 823 K contains mainly Sm₂Co₁₇ and SmCo₅ phases which are hard magnetic phases, indicating an amorphous phase was crystallized below 773 K. The crystallization temperature of the amorphous Sm₁₆Co₈₄ film is between 723 and 773 K. The diffracted peaks of Sm₂O₃ and Co phases appear for Sm₁₆Co₈₄ films annealed at 923 and 973 K. It is considered that appearance of Co phase is due to the selective oxidation of Sm during annealing. X-ray diffraction patterns of Sm₂₃Co₇₇ film shows the same tendency as those diffraction of Sm₁₆Co₈₄ films as-deposited or after annealing. After deposition and at lower annealing temperature than 623 K, an amorphous phase is stable. On raising annealing temperatures, intermetallic compounds such as Sm₂Co₇ or SmCo₃ phases are formed below 823 K. At higher annealing temperature, Sm₂O₃ and Co phases exist in Sm₂₃Co₇₇ film due to selective oxidation of Sm. The

Fig. 1 X-ray diffraction patterns of Sm₁₆Co₈₄ and Sm₂₃Co₇₇ films annealed at various temperatures.

crystallization temperature of an amorphous $\text{Sm}_{23}\text{Co}_{77}$ film is between 623 and 723 K, and that of $\text{Sm}_{16}\text{Co}_{84}$ film is between 723 and 773 K. This suggests that the crystallization temperature of the amorphous phase becomes lower with increasing Sm content of the film.

Figure 2 shows that X-ray diffraction patterns of $\text{Sm}_{20}\text{Co}_{67}\text{Cu}_{13}$ and $\text{Sm}_{28}\text{Co}_{59}\text{Cu}_{13}$ films as-deposited and annealed at various temperatures for 1 h. Sm-Co-Cu film forms an amorphous phase after deposit and annealing at low temperature. After annealing at intermediate temperature, $\text{Sm}_2\text{Co}_{17}$, SmCo_5 , Sm_2Co_7 and Co phases are crystallized from an amorphous phase. Because the diffracted peaks of Sm_2Co_7 and SmCo_5 phases overlap, it is not sure whether Sm_2Co_7 phase exists or not. It is reported by A. J. Perry that SmCo_5 and Co phases can not coexist in Sm-Co bulk sample but can coexist in Sm-Co-Cu bulk sample⁽¹⁰⁾. Sm_2O_3 and Co phases appear due to selective oxidation of Sm at higher annealing temperature. The crystallization temperatures of $\text{Sm}_{20}\text{Co}_{67}\text{Cu}_{13}$ and $\text{Sm}_{28}\text{Co}_{59}\text{Cu}_{13}$ films are 623–723 K and 523–623 K, respectively. The result indicates that the crystallization temperature of an amorphous phase becomes lower with increasing Sm content of the film and the effect of Cu addition to Sm-Co film is coexistence of SmCo_5 and Co phases and to decrease the crystallization temperature. It is considered that this fact is related to the decrement of eutectoid temperature of SmCo_5 phase by Cu addition⁽¹⁰⁾.

Figure 3(a), (b) and (c) show the hysteresis loop, minor loop and springback ratio of $\text{Sm}_{16}\text{Co}_{84}$ film annealed at

773 K, respectively. The hysteresis loop of this film (Fig. 3(a)) is not constricted, because $\text{Sm}_{16}\text{Co}_{84}$ film annealed at 773 K contains mainly $\text{Sm}_2\text{Co}_{17}$ and SmCo_5 phases which are hard magnetic phases and a small amount of Sm_2O_3 phase. Figure 3(b) shows the minor loop of the film. In this study springback ratio is defined by the following equation,

$$\text{Springback ratio} = [Mr' - Mr(H)] / [Mr - Mr(H)]$$

where Mr is residual magnetization, Mr' is the magnetization at applied magnetic field of $H=0$ after applied magnetic field is removed at H and $Mr(H)$ is the magnetization at removed magnetic field of H . Springback ratio of $[Mr' - Mr(H)] / [Mr - Mr(H)]$ is considered to give the judgement whether the sample is the exchange-spring magnet or not. Figure 3(c) shows the springback ratio at removed H . The springback ratio of this film is approximately below 0.5, which indicates that this film is the conventional hard magnet.

Figure 4(a), (b) and (c) show the hysteresis loop, minor loop and springback ratio of $\text{Sm}_{28}\text{Co}_{59}\text{Cu}_{13}$ film annealed at 623 K, respectively. This film has the magnetization of 0.21 T and the high coercivity of $2480 \text{ kA} \cdot \text{m}^{-1}$. This film is consisted of hard magnetic phases such as SmCo_5 and Sm_2Co_7 phases and a soft magnetic phase such as Co phase (Fig. 2). This film shows a little constricted loop in Fig. 4(a). Figure 4(b) shows the minor loops of this film. After removing the applied magnetic field of -1 T and -2 T , the magnetization nearly returns to the residual

Fig. 2 X-ray diffraction patterns of $\text{Sm}_{20}\text{Co}_{67}\text{Cu}_{13}$ and $\text{Sm}_{28}\text{Co}_{59}\text{Cu}_{13}$ films annealed at various temperatures.

Fig. 3 (a) Hysteresis loop, (b) Minor loop and (c) Springback ratio of Sm₁₆Co₈₄ film annealed at 773 K.

Fig. 4 (a) Hysteresis loop, (b) Minor loop and (c) Springback ratio of Sm₂₈Co₅₉Cu₁₃ film annealed at 623 K.

magnetization. But when applied field is removed at -3 T, the value of the Mr' is smaller than that at -1 T and -2 T. Figure 4(c) shows the applied field dependency of springback ratio. The springback ratio is about 0.8 and nearly constant for $H > -2$ T, but it decreases to 0.5 with $H = -0.3$ T, which indicates that exchange coupling between a hard magnetic phase and a soft magnetic phase exists in $H > -2$ T and becomes weaker with decreasing applied field of H . This suggests that this film is regarded as exchange-spring magnet film. The addition of Cu to Sm-Co film has two effects. The one is possibly to allow to coexist of SmCo₅ and Co phases. The other is the decrement of the crystallization temperature of amorphous Sm-Co alloys, so that the size of Co in the Sm-Co-Cu film restricts within domain wall thickness.

To obtain a film with higher magnetic saturation intensity, Sm-Co-Cu/Co multilayered film has been prepared, since Co has a higher saturation magnetization than Sm-Co-Cu alloys. Figure 5 shows the X-ray diffraction patterns of Sm₂₈Co₅₉Cu₁₃/Co(x nm) films where the thickness x of Co layer vary from 0 to 25 nm in deposited state. The as-deposited films with the Co thickness of $x = 0$ and 5 nm are an amorphous phase. The peaks of Co phase increase with increasing Co layer thickness of $x = 10$ –25 nm. Figure 6 shows the X-ray diffraction patterns of Sm₂₈Co₅₉Cu₁₃/Co(x nm) films where the thickness x of Co layer vary from 0 to 25 nm after annealing at 623 K for 1 h. The intermetallic compounds such as

Fig. 5 X-ray diffraction patterns of Sm₂₈Co₅₉Cu₁₃/Co(x nm) films where the thickness x of Co layer vary from 0 to 25 nm in deposited state.

Fig. 6 X-ray diffraction patterns of $\text{Sm}_{28}\text{Co}_{59}\text{Cu}_{13}/\text{Co}(x \text{ nm})$ films where the thickness x of Co layer vary from 0 to 25 nm after annealing at 623 K for 1 h.

SmCo_5 and Sm_2Co_7 phases are formed in Sm-Co-Cu/Co films by annealing at 623 K for 1 h. The $\text{Sm}_{28}\text{Co}_{59}\text{Cu}_{13}/\text{Co}(x \text{ nm})$ films consist of hard magnetic phases such as SmCo_5 and Sm_2Co_7 phases and a soft magnetic phase of Co. The peaks of Co phase of this film approximately increase with increasing Co layer thickness x , which indicates that the content of Co layer becomes larger with increasing Co layer thickness.

Figure 7(a), (b) and (c) show Co thickness dependency of magnetization, coercivity and springback ratio of $\text{Sm}_{28}\text{Co}_{59}\text{Cu}_{13}/\text{Co}$ films annealed at 623 K. All value of coercivity in Fig. 7(b) is measured at the applied field of $1200 \text{ kA} \cdot \text{m}^{-1}$. The increase of saturation magnetization and the decrement of the coercivity with increasing Co layer thickness of x is observed, which will be due to the increment of Co layer thickness x , the high saturation magnetization of Co and the decrement of exchange coupling. The springback ratio of this film is constant for the film thickness of $x=0-15 \text{ nm}$ and decrease with $x>15$. The springback ratio of this film with $x=0-15$ is approximately over 0.73. This fact strongly suggests that this films are regarded as exchange-spring magnet film since the springback ratio of $\text{Sm}_{16}\text{Co}_{84}$ film annealed at 773 K which behaves as a conventional hard magnet is approximately under 0.5. Comparing the exchange-spring Sm-Co-Cu film with the exchange-spring Sm-Co-Cu/Co film, Co layer in Sm-Co-Cu/Co($x \text{ nm}$) films has the effect of having stronger exchange coupling between Co layers and hard magnetic phases as well as increasing the saturation magnetization.

Fig. 7 Co thickness dependency of (a) magnetization, (b) coercivity and (c) springback ratio of $\text{Sm}_{28}\text{Co}_{59}\text{Cu}_{13}/\text{Co}$ films annealed at 773 K.

IV. Summary

The magnetic properties and crystal structures at Sm-Co-Cu films and Sm-Co-Cu/Co multilayers after deposition and annealing at 523–973 K are studied.

The as-deposited Sm-Co and Sm-Co-Cu films are amorphous phases. After annealing, Sm-Co and Sm-Co-Cu films show the tendency that the crystallization temperature of an amorphous phase becomes lower with increasing Sm content of the film. The crystallized temperature of an amorphous phase of Sm-Co-Cu film is lower than one of Sm-Co film. The effect of the addition of Cu to Sm-Co film is decrement of the crystallization temperature.

The $\text{Sm}_{28}\text{Co}_{59}\text{Cu}_{13}$ films annealed at 623 K for 1 h which are composed of a hard magnetic phases and a soft magnetic phase behave as the exchange-spring magnet film with the saturation magnetization of $M_s=0.21 \text{ T}$ and the high coercivity of $H_c=2480 \text{ kA} \cdot \text{m}^{-1}$. This film shows the springback phenomenon that the value of magnetization nearly returned to residual magnetization M_r as a mechanical-spring when applied magnetic field H are removed at the demagnetization curve.

The exchange-spring magnetic behavior are obtained for $\text{Sm}_{28}\text{Co}_{59}\text{Cu}_{13}/\text{Co}$ films where thickness x of Co layer varies from 0 to 15 nm after annealing at 623 K for 1 h. Increment of the saturation magnetization and decrement of the coercive force with increasing Co layer thickness are observed.

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