Effect of Zr, V, Nb, Mo, and Ta substitutions on magnetic properties and microstructure of melt-spun SmCo_5 magnets

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We have investigated effects of metal substitutions on the magnetic properties and microstructure of melt-spun Sm-Co-Cu-Fe-M ($M = \text{Zr, V, Nb, Mo, Ta}$) magnets. We prepared melt-spun ribbons with compositions of $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5\text{Fe}_{0.54-y}\text{M}_y$ ($x = 0.1-0.5$, $y = 0-0.43$, $M = \text{Zr, V, Nb, Mo, Ta}$). For compositions of $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5\text{Fe}_{0.54}$ ($x = 0.1-0.5$), coercivity increased with increasing of annealing temperature, and a high coercivity of 17.6 kOe was obtained at a Cu content of $x = 0.3$. The coercivity was found to increase with increasing melting point of the substitution element. A high coercivity of 24.5 kOe was obtained for a composition of $\text{Sm}(\text{Co}_{0.7}\text{Cu}_{0.3})_5\text{Fe}_{0.34}\text{Ta}_{0.2}$. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4868501>]

I. INTRODUCTION

Interior permanent magnet (IPM) motors used in hybrid vehicles (HVs) and electric vehicle (EVs) operate in high-temperature environments (up to 200 °C), so the permanent magnets used for these motors must have a high coercivity at 200 °C. The Sm-Co magnet is one candidate for high-performance IPMs used at high temperatures because of the high Curie temperatures (747 °C) of Sm-Co alloys. The coercivity mechanism of Sm-Co is interesting, because it may be possible to achieve much higher coercivity with related materials.

One popular technique to increase the coercivity is to add different metals to Sm-Co compounds. Metal addition to Sm-Co magnets is well known to suppress grain growth and improve coercivity.¹ Another technique to increase the coercivity is to use the melt-spinning method. This method has been effectively used to prepare nanocrystalline magnets, and high coercivity (33 kOe) was reported in $\text{Sm}(\text{Co}_{0.72}\text{Cu}_{0.14}\text{Fe}_{0.14})_5$ melt-spun ribbons.² In the present study, we focus on specific metal-substituted melt-spun SmCo_5 magnets, and the effects of metal substitutions on the magnetic properties and microstructure were investigated by considering melt-spun Sm-Co-Cu-Fe-M ($M = \text{Zr, V, Nb, Mo, Ta}$) magnets.

II. EXPERIMENTAL

Alloy ingots with nominal compositions of $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5\text{Fe}_{0.54-y}\text{M}_y$ ($x = 0.1-0.5$, $y = 0-0.43$, $M = \text{Zr, V, Nb, Mo, Ta}$) were prepared by arc melting. Here, the substitution metals M were selected as elements that do not form compounds with Sm . The alloy ingot was subsequently melt-spun under an Ar atmosphere using a single-roll melt spinner at a wheel speed of 50 m/s. The melt-spun ribbons were crushed into a powder (particle size < 100 μm) and

annealed at 600–800 °C for 10 min in vacuum. The magnetic properties were measured by a vibration sample magnetometer (VSM) with an applied field up to 75 kOe, and the crystal structure and microstructure were determined by X-ray diffraction (XRD) and scanning electron microscopy (SEM).

III. RESULTS AND DISCUSSION

A. Sm-Co-Cu-Fe melt-spun ribbon

Figure 1 shows the XRD patterns of $\text{Sm}(\text{Co}_{0.7}\text{Cu}_{0.3})_5\text{Fe}_{0.54}$ melt-spun samples obtained at different annealing

FIG. 1. XRD patterns of $\text{Sm}(\text{Co}_{0.7}\text{Cu}_{0.3})_5\text{Fe}_{0.54}$ melt-spun samples for different annealing temperatures.

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temperatures. As-spun samples consisted of the SmCo_5 and $\alpha\text{-Fe}$ phases, and this structure does not change up to annealing temperatures of 600 and 700 °C. The SmCo_5 phase and a small amount of SmCo_3 and SmFe_9 phases were detected at an annealing temperature of 800 °C. The lattice parameters a and c determined from the XRD patterns indicate that the a parameter of SmCo_5 suddenly increased with annealing temperature, from 4.619 Å for the as-spun sample to 5.034 Å for the sample annealed at 800 °C. The VSM measurement showed that the coercivity increased with increasing annealing temperature from 6.9 kOe to 17.6 kOe. Coercivity enhancement due to Cu substitution has been reported for Sm-Co-Cu alloy,^{3,4} and it was shown that a large coercivity is obtained after optimal annealing is performed in order to replace some of the Co in SmCo_5 with Cu. In melt-spun SmCo_5 ribbon, much Cu and Fe diffuse into the SmCo_5 phase at an annealing temperature of about 800 °C.

Figure 2 shows the coercivity (H_c) and remanence (B_r) of $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5\text{Fe}_{0.54}$ ($x=0.1\text{--}0.5$) melt-spun ribbons annealed at 800 °C as functions of Cu content. The B_r decreases with increasing Cu content because of the increase in the volume fraction of nonmagnetic element Cu. However, H_c is significantly influenced by the Cu content; it increases initially as the Cu content increases, reaching a maximum of 17.6 kOe at $x=0.3$, and then decreases to 2.8 kOe at $x=0.5$. This can be explained by the phase structure, as evidenced by the XRD patterns.

The XRD patterns of the as-spun samples with Cu contents of $x=0.1, 0.2$, and 0.3 show SmCo_5 and $\alpha\text{-Fe}$ phases, and those of the annealed samples show the same structure, as well. Thus, the SmCo_5 phase is stable in a temperature

range of 600–800 °C. The XRD patterns of the as-spun samples and the samples annealed at 600 °C with Cu contents of $x=0.4$ and 0.5 show SmCo_5 and $\alpha\text{-Fe}$ phases. However, multiphase structures consisting of SmCo_5 , SmCo_3 , SmCu_6 , and $\alpha\text{-Fe}$ appear after annealing at 700 °C, and then a SmCo_5 single phase is formed at 800 °C. For Cu contents of $x=0.4$ and 0.5 , the SmCo_5 phase is not stable in the temperature range of 700–800 °C.

In a related study, the effect of the Cu concentration on the magnetic properties was reported for $\text{Ce}(\text{Co,Cu,Fe})_5$ alloy.⁵ According to this report, the coercivity increases with increasing Cu content. However, the coercivity of melt-spun $\text{Sm}(\text{Co,Cu,Fe})_5$ ribbons shows a peak shape when plotted as a function Cu content. This behavior is similar to the observed variation of the coercivity of the 1:5 structure in the $\text{Sm}(\text{Co,Cu,Fe})_7$ system.⁶ Thus, it can be concluded that a Cu concentration of $x=0.3$ can effectively stabilize the 1:5 structure in melt-spun SmCo_5 samples.

B. Effects of Zr, V, Nb, Mo, and Ta substitution

The investigation of metal substitution focused on $\text{Sm}(\text{Co}_{0.7}\text{Cu}_{0.3})_5\text{Fe}_{0.54-y}\text{M}_y$ ($y=0.1\text{--}0.4$) melt-spun ribbon annealed at 700–800 °C. In order to design high-coercivity SmCo_5 magnets, as much as possible we have chosen substitution elements M that do not form alloys or intermetallic compounds with Sm. Here, Zr, V, Nb, Mo, and Ta were chosen as the substitution elements M. Figure 3 shows the XRD patterns of $\text{Sm}(\text{Co}_{0.7}\text{Cu}_{0.3})_5\text{Fe}_{0.54-y}\text{Ta}_y$ ($y=0.1\text{--}0.4$) melt-spun ribbons annealed at 800 °C. A single SmCo_5 phase was formed at $x=0.1$ and 0.2 . The lattice parameters

FIG. 2. Coercivity (H_c) and remanence (B_r) of $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5\text{Fe}_{0.54}$ ($x=0.1\text{--}0.5$) melt-spun ribbons annealed at 800 °C as functions of Cu content.

FIG. 3. XRD patterns of $\text{Sm}(\text{Co}_{0.7}\text{Cu}_{0.3})_5\text{Fe}_{0.54-y}\text{Ta}_y$ ($y=0.1\text{--}0.4$) melt-spun ribbons annealed at 800 °C.

FIG. 4. Coercivity H_c of $\text{Sm}(\text{Co}_{0.7}\text{Cu}_{0.3})_5\text{Fe}_{0.54-y}\text{M}_y$ ($y=0.1-0.5$, $\text{M}=\text{Zr}$, Nb, Mo, Ta) melt-spun ribbons annealed at $700-800^\circ\text{C}$ as a function of substitution element content.

a and c determined from the XRD patterns are mostly unchanged from $x=0$ ($a=5.034\text{ \AA}$ and $c=4.036\text{ \AA}$) to $x=0.2$ ($a=5.026\text{ \AA}$ and $c=4.011\text{ \AA}$). Thus, the Ta is located at the boundaries of the SmCo_5 grains. For Ta contents of $y=0.3$ and 0.4 , SmCo_5 , Co_3Ta , and Co_2Ta phases were formed, and it seems that the SmCo_5 peak intensity is lower at $y=0.4$. The crystallinity of the SmCo_5 is decreased by the formation of Co-Ta compounds when there is excess Ta substitution.

Figure 4 shows the coercivity H_c for different contents of each substitution element. The H_c value increases initially with increasing of substitution element content, reaches a maximum value, and then decreases. The highest H_c value was obtained at $y=0.2-0.3$. The changes in H_c for different substitution elements are shown in Figure 5. The x -axis shows each element and its melting point. H_c increased with increasing melting point. A high melting point means that the diffusion constant of the element is low. In this case, the substitution elements at the grain boundaries cannot diffuse into the SmCo_5 phase. Thus, a high coercivity of 24.5 kOe is only obtained for Ta substitution. The inset in Figure 5 gives the demagnetization curve obtained for each substituted element. Samples with Nb, Mo, and Ta show similar demagnetization curves. The squareness ratio of the Zr-substituted sample is larger than those of the other samples. The XRD pattern of the annealed Zr-substituted sample is broad, suggesting that it contains an amorphous phase. This suggests

FIG. 5. Variation in H_c for different substitution elements and demagnetization curves of $\text{Sm}(\text{Co}_{0.7}\text{Cu}_{0.3})_5\text{Fe}_{0.54-y}\text{M}_y$ ($y=0.2$ or 0.3 , $\text{M}=\text{Zr}$, Nb, Mo, Ta) melt-spun ribbons annealed at $700-800^\circ\text{C}$.

that the grain sizes of the Zr-substituted sample are more uniform than those in the other samples.

IV. CONCLUSION

- (1) In melt-spun $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5\text{Fe}_{0.54}$ ($x=0.1-0.5$) ribbon, much Cu and Fe diffuse into the SmCo_5 phase at annealing temperatures of about 800°C . A high coercivity of 17.6 kOe was obtained at an annealing temperature of 800°C .
- (2) A Cu concentration of $x=0.3$ can effectively stabilize the 1:5 structure in melt-spun SmCo_5 samples with compositions of $\text{Sm}(\text{Co}_{1-x}\text{Cu}_x)_5\text{Fe}_{0.54}$.
- (3) A high coercivity of 24.5 kOe has been realized in Ta-substituted melt-spun ribbons. Such high coercivities can be obtained when a high-melting-point element is substituted.

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