Research Article

Amorphization, Crystallization, and Magnetic Properties of Melt-Spun $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ Alloys

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Effects of Cr_3C_2 content and wheel surface speed on the amorphous formation ability and magnetic properties have been investigated for melt-spun $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ ($x = 0.10\text{--}0.25$) alloys. Ribbon melt-spun at lower wheel speed (30 m/s) has composite structure composed of mostly SmCo_7 , a small amount of $\text{Sm}_2\text{Co}_{17}$, and residual amorphous phases. The grain size of SmCo_7 phase decreases with the increase of Cr_3C_2 content x . When melt spinning at 40 m/s, $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ alloys can be obtained in the amorphous state for $0.15 \leq x \leq 0.25$ with intrinsic coercive H_{ci} of the order of 40–70 Oe. DSC analysis reveals that SmCo_7 phase first precipitates from the amorphous matrix at 650°C, followed by the crystallization of $\text{Sm}_2\text{Co}_{17}$ phase at 770°C. Optimal coercivity H_{ci} of 7.98 kOe and remanent magnetization M_r of 55.05 emu/g have been realized in $\text{SmCo}_{6.8}(\text{Cr}_3\text{C}_2)_{0.20}$ magnet subjected to melt spinning at 40 m/s and annealing at 650°C for 5 min. The domain structure of the annealed ribbon is composed of interaction domains typically 100–400 nm in size, which indicates the presence of a strong exchange coupling between the grains.

1. Introduction

Permanent magnet materials capable of operating at elevated temperatures are needed for advanced power systems [1]. Most attention has been paid to the Sm–Co 1:7 magnets because of their large coercivity and high Curie temperature [2]. Powder metallurgy method has been used successfully to fabricate $\text{Sm}(\text{Co}, \text{Fe}, \text{Cu}, \text{Zr})_7$ bulk magnets with a coercivity of 10 kOe at 500°C [3]. The microstructure of sintered Sm–Co 1:7 magnets consists of 2:17R phase as cells are surrounded by 1:5H boundary with Zr-rich platelet phases running across cells and cell boundaries. 1:5H phase is responsible for enhancement of coercivity by domain wall pinning mechanism.

An alternative route to fabricate nanostructure, high-temperature magnets is mechanical alloying [4, 5]. Sm–Co 1:7 nanophase hard magnets with high coercivity and enhanced remanent magnetization are synthesized using mechanically induced amorphization and the crystallization

of nanoscale grains during the subsequent annealing processes. Optimal coercivity of 21 kOe and remanent magnetization of 73.4 emu/g have been obtained in $\text{Sm}_{12.5}\text{Co}_{85.5}\text{Zr}_2$ magnet [6].

Besides mechanical alloying, melt spinning has been proved to be another effective route to fabricate nanocomposite permanent magnets, especially in the Nd–Fe–B systems. To obtain nanocrystalline microstructure and high coercivity, it is necessary to make amorphous ribbons first and then crystallize it by annealing. Unfortunately, the amorphous formation ability of Sm–Co alloys is very poor [7]. Thus, the fine microstructure for high coercivity is difficult to realize in melt-spun ribbons. However, it has been shown that a small amount of carbon addition is helpful for the grain refinement in the system of Sm–Co–Hf–C [8], Sm–Co–Nb–C [9], and Sm–Co–Fe–C [7]. Recently, we focus our investigation on the effect of the addition of Cr_3C_2 on the magnetic properties and microstructure of SmCo_7 magnets. It has been found that, even melt-spun at a low wheel surface

speed of 20 m/s, the grain size of Cr_3C_2 -doped SmCo_7 alloys is significantly reduced from 300–600 nm to below 80 nm [10]. Therefore, in this work, the effect of Cr_3C_2 content and wheel speed on the amorphization behavior of the melt-spun $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ alloys has been further investigated.

2. Experimental Procedure

Alloys with nominal compositions of $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ ($x = 0.10\text{--}0.25$) were prepared by arc melting under argon. The ingots were melted four times for homogeneity and an excess of 7 wt.% Sm was added to compensate for the Sm loss during processing. The arc-melted ingots were cut into small pieces and then were melt-spun at 30 and 40 m/s. Thickness of this two types of ribbons was about 30 and 25 micrometer, respectively. The as-spun ribbons were sealed in quartz tube under vacuum and then annealed at 650–800°C for 5 min to crystallize and develop a fine microstructure. The crystal structure of the ribbons was identified by Bruker D8 Advance/Discover X-ray diffraction (XRD) with the Phillips diffractometer using the Co K_α radiation. The phase transformation temperatures were determined by differential scanning calorimeter (DSC) at a heating rate of 40 K/min. Hard magnetic properties at room temperature were measured by a Lake Shore 7410 vibrating sample magnetometer (VSM) with a maximum field of 23 kOe. The magnetization of the ribbons could not be saturated using VSM; therefore the maximum magnetization M^{2T} under 20 kOe is used to represent the saturation magnetization M_s . The magnetic domain structure and corresponding atomic force microscopy (AFM) image were studied using a Digital Instruments NanoScope IIIA D-3000 magnetic force microscope (MFM) at RT.

3. Experimental Results and Discussion

The progress of the amorphization process by melt spinning can be seen through the measurement of relative intensity of the XRD patterns of SmCo_7 -type phase. The XRD patterns for $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ ($x = 0.10\text{--}0.25$) ribbons melt-spun at 30 m/s are shown in Figures 1(a)–1(d). It is found that only the SmCo_7 phase exists for the ribbon with $x = 0.10$. Two phases, including SmCo_7 and $\text{Sm}_2\text{Co}_{17}$, are detected for a higher Cr_3C_2 substitution. With the increase of Cr_3C_2 content x , the XRD peaks become significantly lower and accompanied with a broad increase in backgrounds, indicating a considerable decrease in the grain size of the SmCo_7 phase. Figures 1(e)–1(h) show the XRD patterns of $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ ribbons melt-spun at 40 m/s as a function of Cr_3C_2 content. It can be seen that the peaks are found to be broadened and the intensities become significantly lower with the increase of wheel surface speed to 40 m/s, indicating that the alloy is driven towards amorphous structure. For the alloys with $x \geq 0.15$, the crystalline structure disappears completely and an amorphous-type phase is developed progressively in the alloys.

In addition, it can be seen from Figure 1 that the intensity of diffraction (002) for the SmCo_7 phase is gradually

FIGURE 1: XRD patterns for $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ ($x = 0.10\text{--}0.25$) ribbons melt-spun at 30 and 40 m/s.

FIGURE 2: Hysteresis loops of $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ ($x = 0.10\text{--}0.25$) melt-spun at 30 m/s.

strengthened when Cr_3C_2 content x increases from 0.10 to 0.25. This is similar to that observed in SmCo_7Ti and SmCo_5 alloys melt-spun at much lower wheel surface speed of 10–15 m/s. In the SmCo_7 - or SmCo_5 -type magnets, the intensity of (002) plane is considered as measure of texture. For the ribbon with $x = 0.20$, the intensity ratio $I_{(002)}/I_{(111)}$ is 4.04 which is much higher than 3.2 for SmCo_7Ti and 2.9 for SmCo_5 magnets [11]. This indicates that the addition of Cr_3C_2 may favor the alignment of SmCo_7 crystalline grains during melt spinning. Further investigations are needed to understand this point.

Hysteresis loops of the alloys melt-spun at 30 m/s are shown in Figure 2. A systematic change in the shape of the loop with the addition of Cr_3C_2 can be seen and the magnetic properties evaluated from these loops are shown in Table 1. With increasing Cr_3C_2 content x , the remanence M_r of the alloys increases up to a maximum value of 56.78 emu/g at $x = 0.20$, beyond which it then decreases to 14.52 emu/g at

FIGURE 3: Hysteresis loops of $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ ($x = 0.10\text{--}0.25$) melt-spun at 40 m/s.

FIGURE 4: DSC curves of melt-spun $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ ($x = 0.20, 0.25$) glassy alloy ribbons.

FIGURE 5: Hysteresis loops of amorphous $\text{SmCo}_{6.8}(\text{Cr}_3\text{C}_2)_{0.2}$ ribbon after annealing at 650°C for 5 min.

TABLE 1: Magnetic properties of $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ ($x = 0.10\text{--}0.25$) melt-spun at 30 m/s.

x (at.%)	H_{ci} (kOe)	M_r (emu/g)	M^{2T} (emu/g)	M_r/M^{2T}
0.10	4.20	27.04	40.23	0.67
0.15	5.04	48.51	68.67	0.71
0.20	1.81	56.78	74.86	0.76
0.25	0.25	14.52	42.55	0.34

$x = 0.25$. Meanwhile, the remanence ratio M_r/M^{2T} of the alloys increases from 0.67 at $x = 0.10$ to 0.76 at $x = 0.20$ and then decreases to 0.34 at $x = 0.25$. The M_r increases with increasing Cr_3C_2 content which is likely attributed to the stronger intergrain exchange coupling between SmCo_7 phase due to the finer grain size as observed in the broadened XRD patterns.

On the other hand, the coercivity H_{ci} initially increases from 4.2 kOe at $x = 0.10$ to 5.04 kOe at $x = 0.15$ and thereafter decreases to 0.25 kOe at $x = 0.25$. This behavior is attributed to size effect of coercivity in fine grain sizes, that is, from multidomain configuration to superparamagnetic state through single domain size [12]. Another reason for the decrease of coercivity may be ascribed to the formation of minor amorphous phase [13]. In magnetization reversal, the amorphous phase can act as reverse domain wall nucleation site and will decrease the coercivity.

Figure 3 corresponds to the hysteresis loops of the alloys melt-spun at 40 m/s. Those alloys show soft magnetic behavior with narrow hysteresis loops. The coercivity of the as-spun ribbons with $x \geq 0.15$ is found to be very low, ranging from 40 Oe to 70 Oe, and decreases with the increase of x . A reduction of the amount of 1:7 phase and the increase of the amorphous phase are responsible for this low coercivity. Figure 4 presents the DSC curves for crystallization of amorphous $\text{SmCo}_{6.75}(\text{Cr}_3\text{C}_2)_{0.25}$ and $\text{SmCo}_{6.80}(\text{Cr}_3\text{C}_2)_{0.20}$ ribbons. There are two exothermic peaks in both crystallization curves. The first exothermic peak (650°C) can be attributed to the formation of SmCo_7 phase initially from the amorphous phase, and the second one (770°C) is related to the formation of $\text{Sm}_2\text{Co}_{17}$ phase. Therefore, the crystallization behavior of this SmCo_7 alloy doped with Cr_3C_2 is that SmCo_7 phase first precipitates from the amorphous matrix at 650°C , followed by the crystallization of $\text{Sm}_2\text{Co}_{17}$ phase at 770°C . It should also be noticed that the crystallization behavior of the two alloys with different Cr_3C_2 content is distinctly similar.

The crystallization of $\text{SmCo}_{6.80}(\text{Cr}_3\text{C}_2)_{0.20}$ spun at 40 m/s is further studied. Figure 5 shows the typical hysteresis loop of this ribbon heat-treated at 650°C for 5 min. A kink is noted in the demagnetization curve. This indicates that the specimen consists of two magnetic phases with different coercivities. The presence of a small amount of $\text{Sm}_2\text{Co}_{17}$ phase may give rise to the observed kink according to the DSC analysis. However, crystallization of the amorphous ribbon does result in an enhancement of magnetization and coercivity with M_r of 55.05 emu/g, M^{2T} of 70.99 emu/g, M_r/M^{2T} of 0.82, and H_{ci} of 7.98 kOe. It is well known that carbon is one of the most effective elements for getting

FIGURE 6: MFM image of $\text{SmCo}_{6.8}(\text{Cr}_3\text{C}_2)_{0.2}$ ribbon annealed at 650°C for 5 min in the thermally demagnetized state (a) and the corresponding AFM image (b).

amorphous phases. Therefore, carbon addition gives a high amorphous forming ability for this SmCo-based magnet. The enhanced H_{ci} and M_r obtained by crystallization of the amorphous $\text{SmCo}_{6.80}(\text{Cr}_3\text{C}_2)_{0.20}$ alloys may be due to the appropriate inter-grain exchange interaction between high magnetic anisotropy grains with an optimum grain size and optimum size distributions. Figure 6(a) shows an MFM image of the domain structure of this annealed ribbon, while the corresponding AFM topographic data is presented in Figure 6(b). The AFM image reveals a uniform distribution of the grains respectively, and the average grain size is about 50 nm. The magnetic structure consists of irregular domains typically 100–400 nm in size, displayed as dark and bright areas in the MFM image. This magnetic structure is called multigrain domains or interaction domains which are considered as the result of exchange interactions between the spins of adjacent grains [14]. The occurrence of exchange coupling would result in the structure of large interaction domains and a significant enhancement of the reduced remanence [15]. It also can be found that the domain sizes are considerably larger than the grain size of the specimen. Naturally, the interaction domains are clusters composed of many exchange-coupled grains. Therefore, the grain boundaries would act as domain-wall pinning centers. Considering the magnetic behavior, it could be found that the magnetization variation is irreversible (Figure 5). In such cases domain-wall displacement is much difficult and pinning of the domain walls on the grains boundary plays a dominant role. As a consequence, enhanced coercivity is obtained in this annealed ribbon.

4. Conclusions

The amorphous formation ability, crystallization behavior, and magnetic properties of melt-spun and heat-treated

SmCo_7 magnets have been studied using X-ray diffraction (XRD), differential scanning calorimeter (DSC), and magnetic measurements. The ribbons melt-spun at 40 m/s exhibit amorphous structure in the range of $0.15 \leq x \leq 0.25$ for $\text{SmCo}_{7-x}(\text{Cr}_3\text{C}_2)_x$ alloys. In the amorphous state, these alloys are soft magnetic with intrinsic coercive H_{ci} of the order of 40–70 Oe. DSC analysis reveals that SmCo_7 phase first precipitates from the amorphous matrix at 650°C , followed by the crystallization of $\text{Sm}_2\text{Co}_{17}$ phase at 770°C . After optimal thermal treatment, the alloy shows enhanced magnetic properties with H_{ci} of 7.98 kOe, and M_r of 55.05 emu/g. It also can be drawn that the addition of Cr_3C_2 favors the high degree of alignment of SmCo_7 crystalline grains during melt spinning.

Acknowledgments

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