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Effect of multi-element addition of Alnico alloying elements on structure and magnetic properties of $SmCo_5$-based ribbons

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New $SmCo_5$ + x wt% Alnico composite ribbons melt-spun at 40 m/s are designed by multi-element addition of Alnico alloy into $SmCo_5$ matrix, and their structure and magnetic properties are investigated. The results show that the main phase in $x \leq 2.5$ ribbons is $Sm(Co,M)_5$, whereas the main phase changes into $Sm(Co,M)_7$ at $x = 4.0$–8.5, and simultaneously that the content of Al-rich and amorphous phases increases with increasing x. The hard magnetic properties of the ribbons are found to improve with an increase in Alnico content, and particularly the average magnetic properties reach maximum, i.e., $H_c = 19.6 \pm 1.2$ kOe, $M_r = 47.7 \pm 3.4$ emu/g and $M_{2T} = 59.1 \pm 5.6$ emu/g, at $x = 4.0$. The main reasons for such improvement are that the finer grains divided by three grain boundaries exist in main phase, the dispersed Al-Ni and Al-Co-rich phases distribute in grains and grain boundaries, and the Fe-rich Alnico alloying elements dissolve into $Sm(Co,M)_7$ matrix phase. However, when $x > 4.0$, the gradually increasing Al-Co and amorphous phases lead to the reduction of hard magnetic properties.

1. Introduction

$SmCo_5$ magnet, the first generation rare earth permanent magnet, has been widely used in many industrial fields due to its high magnetocrystalline anisotropy field (H_a), high Curie temperature (T_c), excellent thermal stability and corrosion resistance [1–3]. Alloying is a common method to improve the coercivity and magnetization of $SmCo_5$-type magnets. Tellez-blanco et al. [4] obtained the high coercivity (H_c) of 25 kOe and low remanence (M_r) of 28 emu/g in the $SmCo_{2.5}Cu_{2.5}$ ingot annealed at 1273 K for three weeks. They found that the Cu addition enhanced the coercivity due to the pinning of domain walls at the Cu-rich grain boundary phase, whereas the nonmagnetic Cu addition reduced the magnetization of the magnet. Kündig et al. [5] reported that the magnetic properties of $SmCo_{4.7}Sn_{0.08}$ ribbons melt-spun at a speed of 20 m/s reached H_c = 32 kOe and M_r = 40 emu/g, and found that the Sn-rich non-magnetic grain boundary phase with a thickness of 10–20 nm smoothed the $Sm(Co,Sn)_5$ grain surface, restrained the nucleation of reverse domains, and meanwhile such Sn-rich phase acted as the pinning centers of $SmCo_5$ domain walls to further enhance the coercivity of ribbons. Laslo et al. [6] obtained the coercivity of as high as 50 kOe and the remanence of 47 emu/g at 4.2 K in the $SmCo_4Al$ bonded magnet, and stated that the substitution of Al for Co gave rise to the decrease in exchange constant (A_{ex}) and domain wall energy, and as a result the increased resistance to domain wall movement lead to a high coercivity. However, the addition of nonmagnetic Al caused a decrease in magnetization of the magnet. From the above, a high coercivity magnet could be acquired by adding M metal element (such as Cu, Al, Sn) into $SmCo_5$ alloy to form the M-rich grain boundary phase, which could strongly pin the $SmCo_5$ domain walls. However, the addition of single M element usually reduced the magnetization.

In order to improve the magnetization of $SmCo_5$ alloy, Saito et al. [7] added Fe into the Sm-Co alloy and prepared the $SmCo_2Fe_3$ ribbons by melt spinning at 50 m/s and followed by annealing at 600 °C for 5 min, which were composed of $Sm(Co,Fe)_7$ main phase and soft magnetic Fe phase, and obtained a high remanence of 100 emu/g but a low coercivity of 2.9 kOe, so Fe addition improved the magnetization but reduced the coercivity obviously. In addition, Rai et al. [8] got the remanence of 59.2 emu/g and coercivity of 2.5 kOe in the high energy ball milled $SmCo_5$ powder with 5 wt% FeNi addition. And they found that the FeNi addition was conductive to the magnetization but detrimental to the coercivity of $SmCo_5$/FeNi nanocomposites, which finally consisted of hard $SmCo_5$ and soft Fe-Ni magnetic phases.

In previous studies [4–8], only one or two alloying elements were considered to add into the $SmCo_5$ matrix for improving the coercivity or the magnetization. Recently, Fukuzaki et al. [9] added three elements, i.e., Cu, Fe, Ta, into the $SmCo_5$ matrix and obtained the coercivity of

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24.5 kOe and remanence of 34 emu/g in $Sm(Co_{0.7}Cu_{0.3})_5Fe_{0.24}Ta_{0.3}$ ribbons annealed at 700 °C. They found that Ta element failed to enter the $SmCo_5$ phase because of its small diffusion coefficient, while the precipitation of Ta-rich phase (Co_3Ta and Co_2Ta) at the grain boundaries enhanced the coercivity by pinning the domain walls of $SmCo_5$ matrix. Additionally, the Fe addition improved the magnetization of ribbons. So the simultaneous addition of multiple elements, such as Cu, Ta and Fe, into the Sm-Co alloys could not only improve the coercivity but also suppress the reduction of magnetization.

Alnico5 alloy is a spinodal decomposition type permanent magnetic alloy with a high T_c, big remanence and large saturation induction density [10], and its typical composition is $Fe_{48.00}Al_{15.58}Ni_{12.54}$-$Co_{21.40}Cu_{2.48}$. According to Refs. [4,6,7,11,12], Cu, Al and Ni addition can improve the coercivity of $SmCo_5$ alloy, Fe and Ni addition can improve its magnetization. In addition, a single α phase with body-centered cubic (BCC) structure can form when the as-cast Alnico5 alloy undergoes solution treatment at 1250 °C, and then the α phase decompose to Fe-Co-rich ferromagnetic α_1 and Al-Ni-rich weak magnetic or nonmagnetic α_2 phases with the same BCC structure after the solution treated Alnico5 alloy is aged at 835 °C [13,14]. It is worth emphasizing that these phases are thermodynamically stable after heat treatment. According to the Slater-Pauling curve, Fe_7Co_3 is the best soft magnetic phase with the largest magnetic moment ($2.5\mu_B$), while the Al-Ni is a weak magnetic phase. Therefore, it is expected that the $SmCo_5$ ribbons have a high coercivity and large magnetization in the case of adding Alnico5 alloy into the $SmCo_5$ matrix on the basis of the optimized composition of Alnico5 alloy. In this paper, the new composite $SmCo_5$-based ribbons with different contents of Alnico5 alloy have been prepared by melt spinning method, and their structure and magnetic properties have been investigated in detail.

2. Experimental

The Alnico5 alloy was prepared by arc melting according to the nominal composition Fe51-Al8-Ni14-Co24-Cu3 (wt%), then, $SmCo_5 + x$ wt% Alnico5 ($x = 0$, 2.5, 4.0, 6.0, 8.5) were re-melted by arc melting using pure Sm, Co and Alnico5 alloy to produce the alloy ingots. The ingots were subsequently melt-spun at a wheel speed of 40 m/s under pure Ar atmosphere to get the as-spun ribbons with a thickness of about 50 μm.

The phases were examined by Rigaku D/max 2500 P_C X-ray diffraction (XRD) using Cu Kα radiation and Beijing Synchrotron Radiation Facility (BSRF). The microstructure was observed by means of FEI Tecnai G^2 F20 transmission electron microscopy (TEM) and high resolution TEM (HRTEM), and the ingredient was analyzed by energy dispersive spectroscopy (EDS) attached in TEM. The hysteresis loops were measured on a LakeShore 7407 vibrating sample magnetometer (VSM). All ribbons were magnetized on the 60 kOe pulse magnetic field before the VSM measurement, and the magnetization direction was consistent with the measurement one of VSM.

3. Results and discussion

3.1. Phase analysis

Fig. 1 shows the XRD patterns of $SmCo_5 + x$ wt% Alnico5 ribbons. The weak diffuse scattering peaks indicate the existence of a little amorphous phase, which is induced by a disordered periodic arrangement of partially localized atoms owing to the rapid cooling rate (up to 10^6 °C/s). From Fig. 1a, it can be seen that $x = 0$ ribbons are composed of $SmCo_5$ and Sm_2Co_7. Although the nominal composition of $x = 0$ ribbons is $SmCo_5$, the liquid alloy enters the two-phase region of $SmCo_5 + Sm_2Co_7$ during unbalanced cooling and forms the two-phase mixed microstructure due to the narrow composition range of $SmCo_5$ single phase in Sm-Co phase diagram [15] and the rapid cooling rate. The $x = 2.5$ ribbons are also mainly composed of $SmCo_5$ and Sm_2Co_7, as shown in Fig. 1b, where no obvious shift of 002 and 205 peaks is observed from the amplified diffraction peaks at $2\theta = 44°$-$46°$ in Fig. 1B. This illustrates that the M elements in Alnico5 alloy are seldom dissolved into $Sm(Co,M)_5$ and $Sm_2(Co,M)_7$, and the added elements mainly form a small amount of Fe-Co phase.

When x increases to 4.0, not only the Sm_2Co_7 disappears, but also the main phase changes from $Sm(Co,M)_5$ to $Sm(Co,M)_7$. Fe-Co phase is still present, but its content almost does not change. And the BCC-type Al_4Ni_3

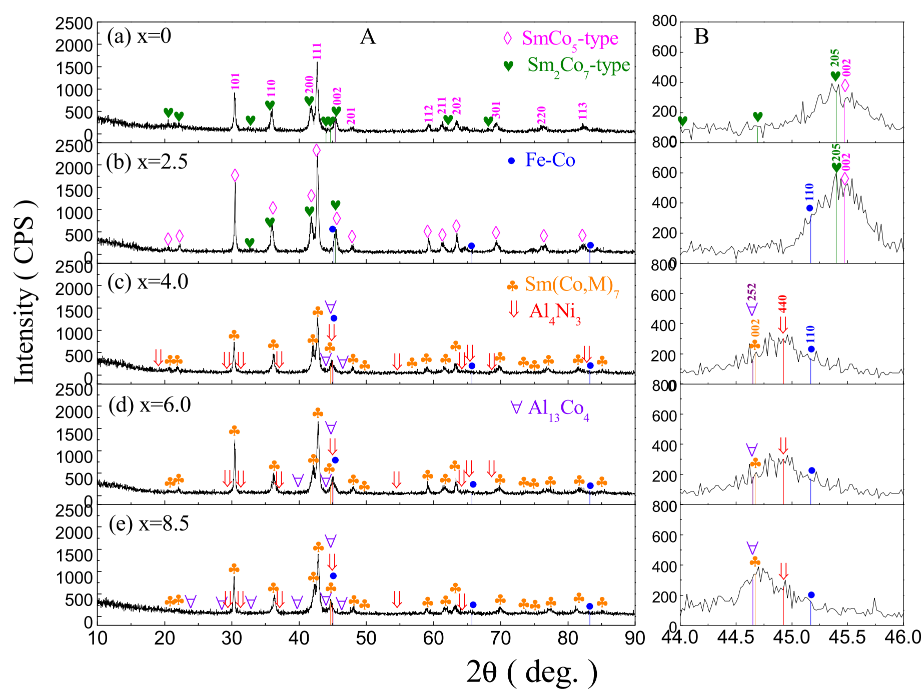

Fig. 1. XRD patterns of $SmCo_5$+x wt% Alnico5 as-spun ribbons.