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Structure and magnetic properties of $SmCo_{7-x}Ti_x$ with $TbCu_7$-type structure

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Structure and magnetic properties of $SmCo_{7-x}Ti_x$ with $TbCu_7$-type structure

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The $SmCo_{7-x}Ti_x$, $x=0-0.56$ bulk samples are prepared by arc melting. X-ray diffraction indicates that samples with $0.2<x<0.4$ form a single disordered $TbCu_7$-type structure phase and other minor phases appear for other values of x, which indicates that Ti helps stabilize the 1-7 phase. The lattice parameters ratio (c/a) increases with increasing Ti concentration. Room temperature saturation magnetization and Curie temperature decrease with increasing x. X-ray diffraction and magnetization measurements on aligned samples show that all samples studied have uniaxial anisotropy. The anisotropy field is found to increase with increasing x reaching a maximum of 175 kOe at $x=0.28$ and then decreases for higher values of x. This anisotropy field is 20% higher than that of the same compound with Th_2Zn_{17}-type structure. [S0021-8979(00)21308-X]

I. INTRODUCTION

The rare-earth (RE) transition-metal intermetallic compounds have been widely investigated for many years, among them the Sm–Co series compounds with 1-5 and 2-17 crystal structures. These compounds have been used as sintered and bonded permanent magnets since the 1960s.[1–3] Recently, attention has been focused on the $TbCu_7$-type structure Sm–Co intermetallic compounds because of their potential as high anisotropy magnetic materials.[4–6] Both $SmCo_7$ and Sm_2Co_{17} can have the 1-7 type structure when prepared appropriately. However, $SmCo_7$ is unstable unless a third doping element such as Ti, Zr, Cu, etc. is added to substitute Co.

$TbCu_7$-type crystal structure could be indexed according to the $CaCu_5$-type structure with significant deviations of the lattice constants and the x-ray peaks' intensities. That is because partial of the Ca sites are randomly substituted by a pair of Cu in $CaCu_5$-type structure. In Sm–Co compounds, $SmCo_7$ and Sm_2Co_{17} can form the $TbCu_7$-type structure. Th_2Zn_{17} structure can be formed if the substitution is ordered. Khan[7] found that Sm–Co with composition 1:5.4 has the $TbCu_7$-type structure above 1100 °C. The magnetic properties of these $TbCu_7$-type Sm–Co alloys have been investigated by a few researchers. Saito *et al.*[4] studied $Sm_2(CoMn)_{17}$ with $TbCu_7$-type disordered structure and found that the anisotropy constant (K_{u1}) is about 1.2–1.4 times larger than that for compounds with Th_2Zn_{17}-type structure. Recently, Huang *et al.*[6] studied $SmCo_{7-x}Zr_x$ with $TbCu_7$-type disordered structure and found that at $T=300$ K, these compounds exhibit anisotropy field as high as 180 kOe for $x=0.5$. Lefevre *et al.*[8,9] also reported the existence of $TbCu_7$-type structure in Sm–Co–Zr ternary alloys prepared by arc melting. Disordered $SmCo_7$ compound with $TbCu_7$-type structure plays the role of a bridge between $SmCo_5$ and Sm_2Co_{17} compounds. It is natural to think that the 1:7 composition with 1-7 type structure may keep the merits of $SmCo_5$ such as high anisotropy and of Sm_2Co_{17} such as large magnetization. However, a study of $SmCo_{7-x}Zr_x$ by Huang *et al.*[6] showed that substituting Zr for Co increase the anisotropy field and decrease the magnetization. In this work, we focus our attention on the effects of Ti substituent on the structure and magnetic properties of $SmCo_{7-x}Ti_x$ alloys.

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II. EXPERIMENT

A series of samples based on RE-(Co,Ti) composition 1:7 were prepared by arc melting. $SmCo_{7-x}Ti_x$ with $x=0$, 0.1, 0.2, 0.3, 0.35, 0.42, 0.56, and $SmCo_{6.5}$ (for comparison) with at least 99.9% pure elements were melted in a water-cooled copper boat under flowing argon. An extra amount of Sm (8%–10%) was added to balance the loss of Sm due to evaporation. The alloys were melted several times to insure homogeneity. The same samples were annealed at different temperatures between 650 and 950 °C in a sealed quartz tube under argon pressure. All these samples were wrapped separately in Ta foils to prevent oxidation. The as-cast material was ground in a mortar and the fine powder particles (<38 μm) were subsequently mixed with epoxy and aligned in a magnetic field of 12 kOe for 24 h for magnetic anisotropy measurements.

The crystal structures of the samples are determined by using x-ray diffraction. Loose powder samples were measured to determine the saturation magnetization at room temperature. Vibrating sample magnetometer (VSM) with a high temperature oven was used to measure the Curie temperature. A SQUID magnetometer with maximum field of 55 kOe was used to measure the magnetization of the aligned samples.

III. RESULTS AND DISCUSSION

Figure 1 shows the x-ray diffraction pattern of the as-cast $SmCo_{7-x}Ti_x$ and $SmCo_{6.5}$. The pattern for $SmCo_7$

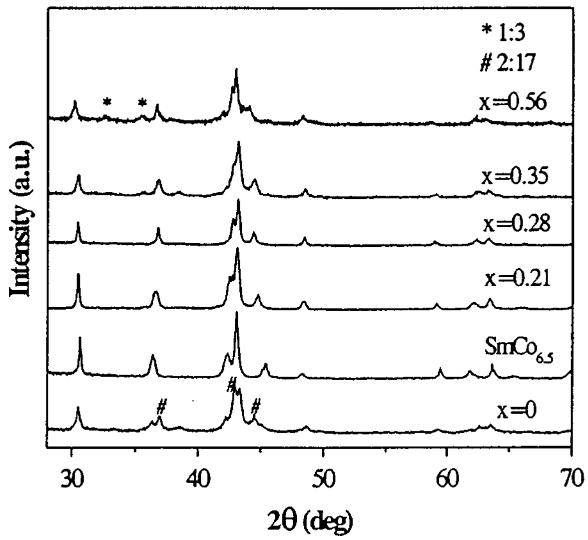

FIG. 1. X-ray diffraction patterns for $SmCo_{7-x}Ti_x$ compounds.

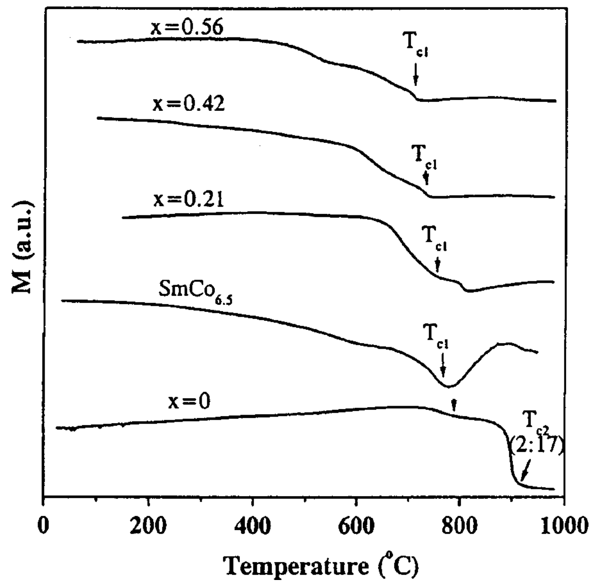

FIG. 2. $M-T$ measurement of $SmCo_{7-x}Ti_x$ compounds under 1000 Oe applied field.

sample shows two phases, $SmCo_7$ with the $TbCu_7$-type structure and Sm_2Co_{17} with $TbCu_7$-type structure. This indicates that the $SmCo_7$ is unstable without the doping element, which is consistent with the results of Huang *et al.*,[6] while Yang *et al.*[5] reported single phase $SmCo_7$ with $TbCu_7$-type structure for samples prepared by mechanical alloying. For comparison, a composition $SmCo_{6.5}$ with 1-7 structure is prepared and presented with the results. X-ray diffraction for samples with $x=0.2-0.35$ show the existence of $TbCu_7$-type structure. This means that Ti can help the formation of the stable structure. For $x>0.4$, other minor phases, mainly $SmCo_3$, appear with the 1-7 type structure. This behavior is similar to that of the $SmCo_{7-x}Zr_x$ series reported by Huang *et al.*[6] Table I shows the changes in the lattice parameters (a) and (c) due to the doping element Ti in $SmCo_{7-x}Ti_x$ compounds. The lattice parameter a decreases with increasing Ti concentration, from 4.935 Å at $x=0$ to 4.900 Å at $x=0.56$, while c increases from 4.013 Å at $x=0$ to 4.134 Å at $x=0.56$ and hence the ratio (c/a) keeps increasing. X-ray diffraction for samples annealed at temperature between 650 and 950 °C shows the Th_2Zn_{17}-type structure. This indicates that annealing does not help the formation of a single $TbCu_7$-type structure.

VSM magnetic measurements show that all the samples studied are ferromagnetic. The room temperature saturation magnetization (M_s) values for the different Ti concentrations are listed in Table I. It can be seen that M_s decreases with increasing x, where it drops from 102 emu/g for $x=0-84$ emu/g for $x=0.56$. Figure 2 shows the $M-T$ curves of $SmCo_{7-x}Ti_x$. In this figure, T_{c1} and T_{c2} indicate the Curie temperatures for the 1:7 phase the 2:17 phase. The Curie temperature for the 1:7 phase decreases from 780 °C for $x=0$ to 710 °C for $x=0.56$. For $x>0.42$, measurements show trace of a small amount of $SmCo_3$, which support our x-ray diffraction results. For x values between 0.2 and 0.35, a single 1-7 magnetic phase presents. The decrease in the Curie temperature with increasing x indicates a weakening of the magnetic interactions. The metastable $SmCo_7$ alloy decomposes into $SmCo_5$ and Sm_2Co_{17} above 700 °C.

Field dependence of magnetization is investigated in the directions parallel ($M_{\parallel}$) and perpendicular ($M_{\perp}$) to the aligning magnetic field direction (easy axis direction). Figure 3 shows the magnetization curves for $SmCo_{6.65}Ti_{0.35}$. Other measurements for different values of x showed similar be-

TABLE I. Lattice parameters (a) and (c), (c/a) ratio, phases present, Curie temperature (T_c), saturation magnetization (M_s), and anisotropy field (H_A) of $SmCo_{7-x}Ti_x$ compounds as a function of titanium concentration (x).

x	a (Å)	c (Å)	c/a	Phases	T_{c1} (°C)	M_s (emu/g)	H_A (kOe)
0	4.935	4.013	0.813	1:7+ 2:17	780	102	120
0.21	4.920	4.060	0.825	1:7	756	96	156
0.28	4.897	4.056	0.828	1:7	745	94	175
0.35	4.882	4.076	0.832	1:7	742	92	168
0.42	4.872	4.074	0.835	1:7+ 1:3	733	89	160
0.56	4.900	4.134	0.842	1:7+ 1:3	710	84	

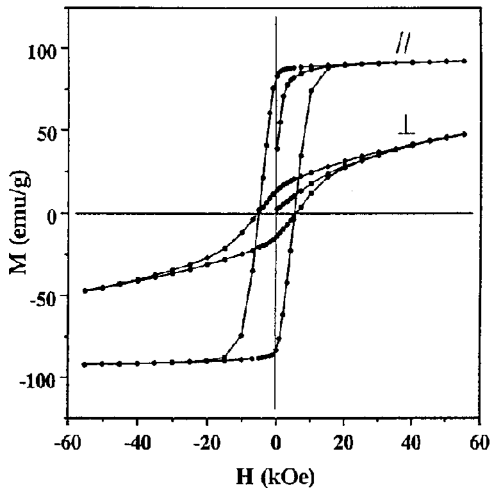

FIG. 3. Typical $M-H$ loops for $SmCo_{6.65}Ti_{0.35}$ aligned sample at a temperature of 300 K.

havior. Extrapolation of $M_{\perp}$ and $M_{\parallel}$ curves were used to estimate the anisotropy field (H_A). Table I shows the H_A values of $TbCu_7$-type $SmCo_{7-x}Ti_x$ as a function of x. H_A increases with increasing Ti concentration reaching a maximum of 175 kOe at $x=0.28$ and then decreases for larger values of x. These results are similar to the results by Huang *et al.*[6] for $SmCo_{7-x}Zr_x$ compounds and comparable to the results of Satyanarayana *et al.*[10] for $Sm_2Co_{17-x}Ti_x$ compounds, where H_A increases from 90 to 125 kOe by increasing x from 0 to 0.5. This effect is important especially in the preparation of commercial $Sm(CoM)_{7+z}$ hard magnetic materials. The H_A value of the 1-7 structure structure $SmCo_{6.79}Ti_{0.21}$ is 20% larger than our H_A value for the same sample with the 2-17 type structure after annealing at 750 °C. The increase in H_A is due to the change in the anisotropy constant K_{u1} which is caused by the preferential occupation of the dumbbell sites by the doping elements as suggested by Deportes *et al.*[11,12]

IV. CONCLUSIONS

Samples of $TbCu_7$-type structure $SmCo_{7-x}Ti_x$ have been prepared and their crystal structures were determined by x-ray diffraction. Doping Ti can help stabilize $TbCu_7$-type structure in these alloys. The doping element is found to decrease T_c and M_s for all values of x, while increasing the anisotropy field for small values of x. An anisotropy field as high as 175 kOe is obtained in these compounds which is about 20% higher than that for the same samples with 2-17 type structure. The basic results in this article help the understanding of the effects of Ti substitution on the structure and magnetic properties of magnetic materials for high temperature applications.

ACKNOWLEDGMENT

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