Effect of Fe, Cu, Zr, and Ti on the Magnetic Properties of SmCo-1 : 7 Magnets

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***Abstract*—The effect of Fe, Cu, Zr, and Ti substitution on magnetic properties of SmCo 1 : 7 magnets at temperatures up to 500 °C were studied. As-milled amorphous Sm(Co,Fe,Cu,Ti–Zr)$_7$ magnets crystallized in the TbCu$_7$-type structure after annealing at 750 °C for 2 h. A room-temperature intrinsic coercivity of around 2.5 T is obtained for compositions $SmCo_{6.4}Zr_{0.2}Ti_{0.4}$ and $SmCo_{6.4}Fe_{0.1}Zr_{0.1}Ti_{0.4}$. The high coercivity of the ball-milled $SmCo_{7-x}Ti_x$ magnets is attributed to the strong pinning of the walls of the "interaction domains" by the network of grain boundaries between the nanocrystalline grains. The virgin curve of the ball-milled samples is suggestive of strong domain wall pinning.**

***Index Terms*—Coercivity, Curie temperature, magnetization, X-ray diffraction.**

I. Introduction

NANOCRYSTALLINE SmCo-1 : 7-type alloys have attracted a lot of interest recently because the Sm–Co–Cu–Ti magnets prepared by mechanical milling and subsequent annealing were reported to exhibit excellent room temperature coercivity [1]. In addition, depending on heat treatment and composition, some of the bulk Sm–Co–Cu–Ti magnets exhibit a positive temperature coefficient of coercivity [2], quite promising for high-temperature applications. On the other hand, the temperature coefficient of intrinsic coercivity (β) is too high ($\approx -0.3\%$ °C^{-1}) in the commercial Sm–Co–Fe–Cu–Zr 2 : 17 magnets [3] for high-temperature applications. It was found [2], [4], [5] that Sm–Co 1 : 7 magnets show a low-temperature coefficient of intrinsic coercivity. To search for permanent magnets with operating temperatures above 400 °C, we have investigated the effects of Fe, Cu, Zr, and Ti substitution on the magnetic properties of 1 : 7 magnets at temperatures up to 500 °C.

II. Experimental Methods

The alloys with nominal compositions $SmCo_{6.6-x}$(Fe–Zr)$_x$Ti$_{0.4}$ (x = 0.0, 0.1, and 0.2) and $SmCo_{6.8-x}Ti_xCu_{0.1}Fe_{0.1}$ (x = 0.2, 0.3, 0.4) were prepared by arc melting in a high-purity argon atmosphere. The alloy ingots were then crushed and milled for 12 h using a high-energy ball mill. The as-milled powders were annealed at 750 °C for 2 h. The room-temperature magnetic properties were measured using a SQUID magnetometer with a maximum applied field of 5 T. High-temperature magnetic properties were investigated using a high-temperature VSM with a maximum applied field of 1.5 T. For magnetization measurements, all the samples were magnetized first using a pulsed field of 7 T.

Manuscript received February 9, 2002; revised May 21, 2002.

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Digital Object Identifier 10.1109/TMAG.2002.803235.

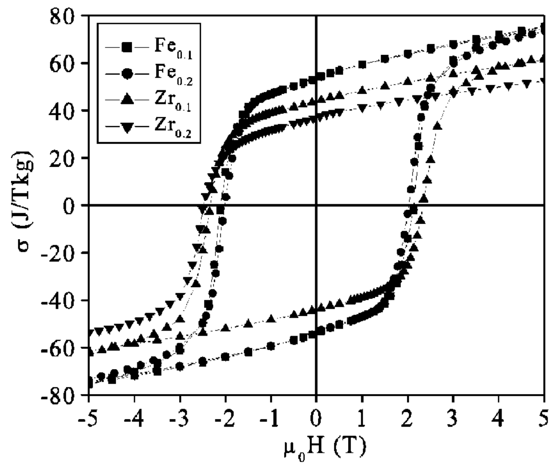

Fig. 1. Room temperature hysteresis loops of ball-milled $SmCo_{6.6-x}$(Fe/Zr)$_x$Ti$_{0.4}$.

III. Results

Ball milling of the as-cast alloys was carried out in order to develop a fine grained microstructure and high coercivity. X-ray diffraction on as-milled powders shows an amorphous structure suggesting that milling for 12 h is enough to destroy the crystallinity. Longer milling time will lead to contamination and Sm loss. After annealing at 750 °C for 2 h, the amorphous powders crystallize into the TbCu$_7$-type disordered phase. The X-ray diffraction patterns of all samples were indexed on the basis of the hexagonal TbCu$_7$-type structure. The broadening of the peaks indicates a very fine 1 : 7 grain size which is estimated from the Scherrer formula to be about 50 nm.

Fig. 1 shows the room-temperature hysteresis loops of ball-milled $SmCo_{6.6-x}$(Fe–Zr)$_x$Ti$_{0.4}$ compositions. The hysteresis loop exhibits a good squareness. The smooth demagnetization curve suggests a very fine and uniform grain size of the 1 : 7 phase. All these compounds exhibit room-temperature coercivity of more than 2 T. Substitution of Fe in the optimized Ti-substituted composition $SmCo_{6.6}Ti_{0.4}$ leads to an increase of the magnetization but a decrease of the coercivity. A room temperature intrinsic coercivity of around 2.5 T is obtained for compositions $SmCo_{6.4}Zr_{0.2}Ti_{0.4}$ and $SmCo_{6.4}Fe_{0.1}Zr_{0.1}Ti_{0.4}$. An intrinsic coercivity of no more than 0.1 T was observed in any of the as-cast magnets and the coercivity of annealed samples are also quite low, about 0.2–0.3 T at room temperature.

TABLE I
MAGNETIC PROPERTIES OF BALL-MILLED SmCo-1 : 7 COMPOUNDS

Composition	σ_r (J/Tkg)	σ_s (J/Tkg)	σ_r/σ_s	H_c (T)
$SmCo_{6.6}Ti_{0.4}$	49.6	74.0	0.67	2.45
$SmCo_{6.5}Fe_{0.1}Ti_{0.4}$	54.1	80.0	0.67	2.10
$SmCo_{6.4}Fe_{0.2}Ti_{0.4}$	54.0	80.0	0.67	2.00
$SmCo_{6.5}Zr_{0.1}Ti_{0.4}$	44.5	65.0	0.68	2.30
$SmCo_{6.4}Zr_{0.2}Ti_{0.4}$	37.0	56.0	0.66	2.50
$SmCo_{6.4}Zr_{0.1}Fe_{0.1}Ti_{0.4}$	46.0	68.0	0.67	2.46
$SmCo_{6.6}Cu_{0.1}Fe_{0.1}Ti_{0.2}$	53.0	84.0	0.63	1.40
$SmCo_{6.5}Cu_{0.1}Fe_{0.1}Ti_{0.3}$	48.0	71.0	0.67	1.80
$SmCo_{6.4}Cu_{0.1}Fe_{0.1}Ti_{0.4}$	40.7	62.0	0.65	2.20

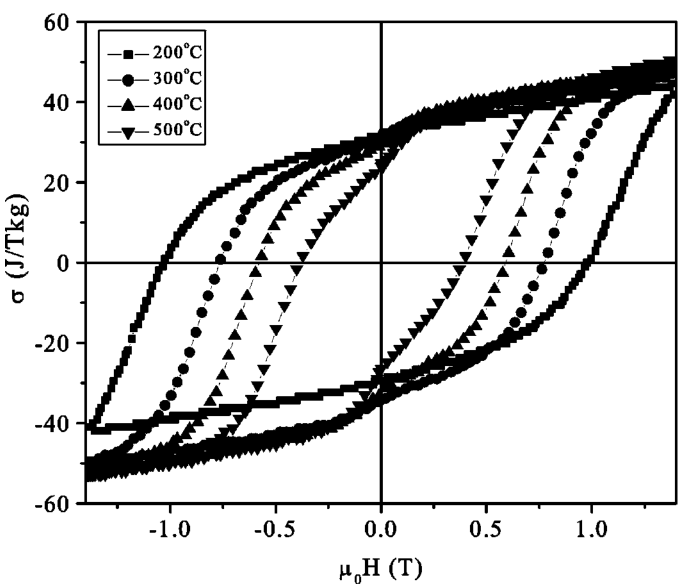

Fig. 2. Variation of coercivity with temperature in $SmCo_{6.6}Fe_{0.1}Zr_{0.1}Ti_{0.4}$.

Table I shows the magnetic properties of all the compounds under investigation. The saturation magnetization (σ_s) was determined from the law of approach to saturation. It can be seen that all the compounds exhibit a coercivity >1 T and an enhanced remanence ($\sigma_r/\sigma_s > 0.5$) indicating the existence of intergrain exchange coupling.

Fig. 2 shows the high-temperature behavior of the ball-milled $SmCo_{6.6}Fe_{0.1}Zr_{0.1}Ti_{0.4}$ and the temperature variation of coercivity of all the compounds is illustrated in Fig. 3.

The temperature coefficient of intrinsic coercivity (β) of most of the compositions lies in the range -0.15 %/°C to -0.18%/°C in the temperature range 20 °C–500 °C compared to the value of -0.3%/°C for the commercial SmCo 2 : 17 magnets. The hysteresis in some of these nanocrystalline magnets persists to high temperatures with a coercivity of 0.7 T at 400 °C. It should be noted that the intrinsic coercivity of the optimized composition $Sm(Co,Fe,Cu,Zr)_z$ is about 3.5 T at room temperature but only 0.3 T at 500 °C which is too low for applications [4], [13].

It may be seen in Fig. 2 that the hysteresis loop at 500 °C is beginning to develop the characteristic shape of a two-phase system. Prolonged exposure at high temperatures exacerbates this tendency, which is irreversible on cooling. It is likely that this change of loop shape is due to nanocrystallite growth at elevated temperature.

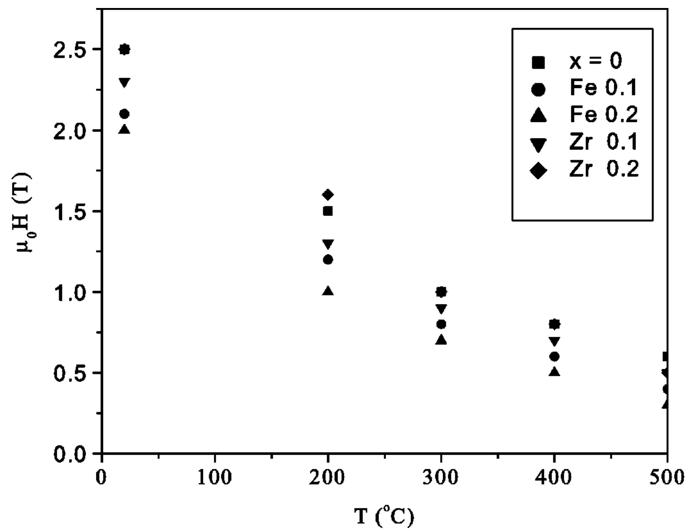

Fig. 3. Temperature dependence of coercivity in ball-milled $SmCo_{6.6-x}(Fe/Zr)_xTi_{0.4}$.

IV. DISCUSSION

Deportes *et al.* [8] pointed out that Co anisotropy in RCo_5 systems comes primarily from the 2c sites. When the Co dumbbells are inserted in place of R, the environment changes in such a way as to reduce the Co anisotropy and also that of the compound. As the doping elements substitute for Co, they preferentially occupy the dumbbell sites, and some of the lost anisotropy is restored which may lead to the coercivity development in these compounds. The anisotropy field for the 1 : 5, 1 : 7 and 2 : 17 Sm–Co phases are 30, 10–18, and 6.5 T, respectively [6], [7], [9], [10]. Good coercivity should be expected in the SmCo 1 : 7 alloys, but the measured values are quite low in both the as-cast and annealed bulk samples, which have the $TbCu_7$ or Th_2Zn_{17} plus $CaCu_5$ structures, respectively. This is attributed to the presence of nucleation centers for magnetization reversal coupled with the absence of dense network pinning sites. However, we obtain excellent coercivities in the ball-milled $Sm(Co,Cu,Fe,Zr–Ti)_7$ magnets, which are found to have the 1 : 7 structure. The behavior of the virgin curves is characteristic of domain wall pinning, similar to that in melt-spun Nd–Fe–B magnets. Single-domain particle behavior [10] is ruled out by the remanence enhancement. The strong intergranular interactions lead to the formation of "interaction domains" or "multigrain domains" [11], [12]. The large high-field susceptibility indicates the random distribution of the interaction domains, which are very difficult to saturate. Magnetization reversal in the fine-grained magnets occurs by flipping the moment of one multigrain domain which then propagates throughout the sample, leading to a square hysteresis loop. Coercivity is related to the pinning of the domain walls between interaction domains along grain boundaries.

V. CONCLUSION

Structural and magnetic properties of ball-milled nanocrystalline SmCo 1 : 7 magnets with Fe, Cu, Zr, and Ti substitution were investigated at temperatures up to 500 °C. In some of these nanocrystalline magnets, coercivity persists to high temperatures with a coercivity of 0.7 T at 400 °C, which gives these magnets potential for high-temperature applications provided it is possible to find a way of stabilizing the nanostructure at the operating temperature.

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