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Mechanically milled nanostructured $(Sm,Pr)_{12.5}Co_{85.5}Zr_2$ magnets with $TbCu_7$ structure

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Nanostructured (Sm,Pr)(Co,Zr) magnets with the $TbCu_7$-type structure have been synthesized by mechanically milling $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ alloys ($0 \leq x \leq 0.8$) followed by appropriate annealing. Magnetic properties, structure, and microstructure have been investigated. It is found that single-phase $(Sm,Pr)(Co,Zr)_7$ magnets with the $TbCu_7$ structure and with nanoscale grain size (14–19 nm) form in the whole composition range. Intrinsic coercivity H_{ci} decreases from 20.7 to 5.6 kOe with increasing Pr content from 0 to 0.8, while energy products $(BH)_{max}$ shows an optimum value of 12.6 MGOe (H_{ci} of 17.9 kOe) at $x = 0.2$ due to increase in remanent magnetization. Remanence ratio is observed in the range of 0.64–0.69, with an optimum value of ∼0.69 at $x = 0.3$. The high coercivity is ascribed to the formation of nanocrystalline $(Sm,Pr)(Co,Zr)_7$ phase of the $TbCu_7$-type structure with large anisotropy, and the remanence enhancement may result from the exchange-coupling interactions between nanosized $(Sm,Pr)(Co,Zr)_7$ grains. The magnetic properties can be understood in term of the anisotropy of the magnetically hard phase and the interactions between the nanosized grains. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1447509]

I. INTRODUCTION

Co-based permanent rare-earth magnets have attracted much attention[1,2] recently during the process of search for permanent magnets applicable at high temperatures, owing to its high Curie temperature and high magnetic performance. It is well known that the 1:7 phase with $TbCu_7$-type structure plays an important role in the development of cellular-structure Sm(Co,Fe,Cu,Zr) magnets which possess high coercivity.[1] It was also reported two decades ago that $Sm(Co,Fe,Cu,Zr)_z$ magnets with the 1:7 composition exhibited better temperature dependence of coercivity than that of the 2:17 counterpart.[3] Recently, it has been reported that R–Co (R=Sm,Pr, etc.) alloys with the $TbCu_7$ type structure could be achieved by introducing a small amount of stabilizing elements like Zr or Ti.[4–6] These alloys with 1:7 composition and the $TbCu_7$ structure possess high Curie temperature, high magnetization, and exhibit large anisotropy.[4–6] For example, anisotropy field values up to ∼160 and ∼100 kOe at room temperature were reported for the $Sm(Co,Zr)_7$ alloys[4] and $Pr(Co,Zr)_7$ alloys[5] with a small amount of Zr, respectively. Therefore, good high temperature magnetic performance may be expected in the nanostructured R–Co magnets (R=Sm, Pr) with $TbCu_7$ structure.

Mechanical milling or mechanical alloying have been proven to be a powerful technique in the fabrication of nanostructured Co-based magnets.[7,8] Some previous researches[9,10] have shown that high coercivity (H_{ci}) could be obtained in the mechanically milled nanostructured $Sm(Co,Zr)_7$ magnets with the $TbCu_7$-type structure. H_{ci} value as high as 5.3 kOe was also reported in the mechanically milled $Pr(Co,Zr)_7$ magnets[11] (low Zr content) with $TbCu_7$-type structure. Compared with the Sm counterpart, $Pr(Co,Zr)_7$ alloys with

$TbCu_7$ structure possess higher magnetization (above 110 emu/g)[5] than $Sm(Co,Zr)_7$ alloys (∼92 emu/g)[4] with a small amount of Zr, whereas the alloy retains a high anisotropy field value of up to 100 kOe.[5,11] Therefore, high coercivity and optimum energy products [$(BH)_{max}$] could be expected in nanostructured $(Sm,Pr)(Co,Zr)_7$ alloys with a small amount of Zr. Our previous investigations on mechanically milled $Sm_{12.5}Co_{87.5-x}Zr_x$ magnets have indicated that high H_{ci} and optimum $(BH)_{max}$ could be achieved with $x=2$ after appropriate processing.[10,12] In this study, we focus on the nanostructured $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ ($x=0–0.8$) magnets synthesized by means of mechanical milling followed by appropriate annealing. Optimum $(BH)_{max}$ of 12.6 MGOe (with H_{ci} of 17.9 kOe) is obtained with $x=0.2$.

II. EXPERIMENT

$(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ ($x=0.0$, 0.1, 0.2, 0.3, 0.5, 0.8) alloys were prepared by arc melting the constituent elements with at least 99.9% purity. After grinding into powders with particle size of less than 0.1 mm, the alloy powders were mechanically milled in a Spex 8000 Mill for a period of 5 h in an atmosphere of high-purity argon gas. The ball-to-powder mass ratio was fixed at 8:1. The powders were handled in a glove box under protection of high-purity argon gas. The milled powders were then sealed in quartz tubes after being evacuated and then backfilled with high-purity argon gas. The sealed powders were annealed at 650 °C for 20 min then furnace cooled to room temperature. The phase and structure were characterized with x-ray diffraction (XRD) with Cu $K\alpha$ radiation. The microstructure was investigated with transmission electron microscopy (TEM). The magnetic properties were measured at room temperature (295 K) using a superconducting quantum interference device (SQUID) magnetometer with a field range of ±55 kOe.

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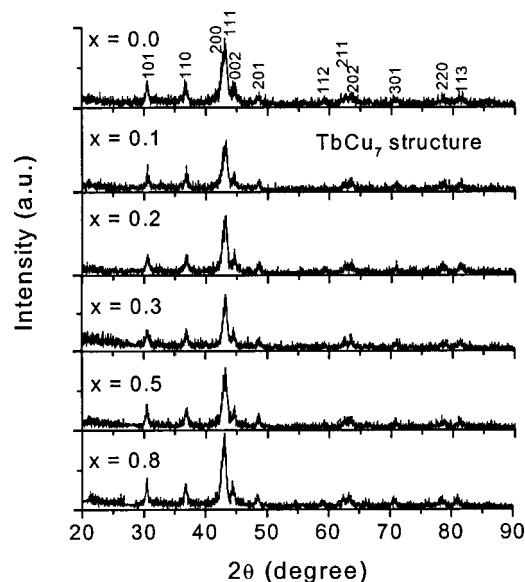
FIG. 1. XRD patterns for the mechanically milled and annealed $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ magnets.

FIG. 2. TEM image for mechanically milled $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ ($x=0.0$) magnets.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for the milled $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ magnets after annealing at 650 °C for 20 min. It shows that all the milled and annealed powder samples are basically of single phase with $TbCu_7$-type structure, although the corresponding as-cast alloys are not of single phase (mixture of $TbCu_7$ phase and Th_2Zn_{17} phase) for $x>0.3$. The lattice parameters of the $TbCu_7$-type phase obtained by fitting the XRD patterns are listed in Table I. The lattice parameters are consistent with the reports[4,5] for $Sm(Co,Zr)_7$ and $Pr(Co,Zr)_7$ as-cast alloys with appropriate Zr content. With variation of Pr, parameters a, c and the ratio c/a vary slightly.

The broadening of the diffraction peaks results from nanosized grains. The grain sizes d estimated using the Scherrer formula are listed in Table I. It is seen that the grain size is in the range of 14–19 nm. The nanostructure developed after milling and annealing is supported by the TEM investigations. Figure 2 shows the TEM image for the milled and annealed $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ magnet powders with $x=0.0$. The inset is the selected-area electron diffraction rings, which exhibits the nature of single phase with

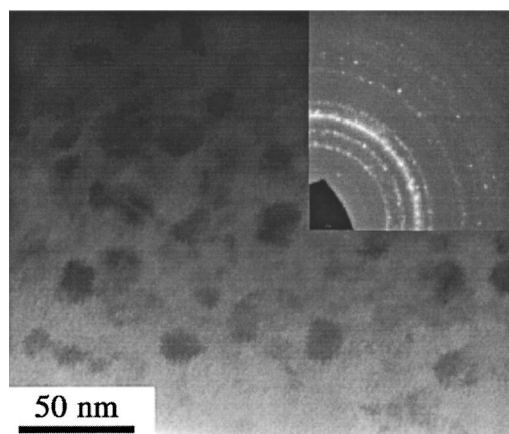$TbCu_7$-type structure. From TEM image, the nanostructure with grain size of ~15 nm is obvious, which is in good agreement with the XRD estimate.

Figure 3 shows the magnetization curves and magnetic hysteresis loops at room temperature for the milled and annealed $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ magnet powders. It is clear that high H_{ci} values are realized in these nanostructured magnet powders. Hard magnetic property parameters [H_{ci}, M_r, M_r/M_s and $(BH)_{max}$] are listed in Table I. The saturation magnetization values (M_s) are obtained by fitting the high-field portion of the initial magnetization curves in terms of an approach-to-saturation law containing a term proportional to H^{-2}. The M_s values for the two end compositions are in good agreement with the reported values[4,5] for as-cast alloys ($TbCu_7$ type phase) with suitable Zr content. The dependence of hard magnetic property parameters is replotted against Pr content, as shown in Fig. 4. It is obvious that H_{ci} decreases from 20.7 to 5.6 kOe as the Pr content varies from $x=0.0$ to $x=0.8$, and correspondingly M_r increases. $(BH)_{max}$ exhibits an optimum value of 12.6 MGOe at $x=0.2$. The H_{ci} value for the end composition with $x=0.8$ is still higher than the reported for nanostructured $Pr(Co,Zr)_7$ magnets with $TbCu_7$ structure.[11] The M_r/M_s ratio, being in the range of 0.64–0.69, is much higher than that of ideally isotropic hard-magnetic particles (0.5).

The high coercivity is ascribed to the nanostructure of the $(Sm,Pr)(Co,Zr)_7$ phase with high anisotropy.[2] Generally,

TABLE I. Hard magnetic properties [H_{ci}, M_r, M_s and $(BH)_{max}$], lattice parameters (a, c, and c/a ratio) and grain size (d) for the $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ magnets.

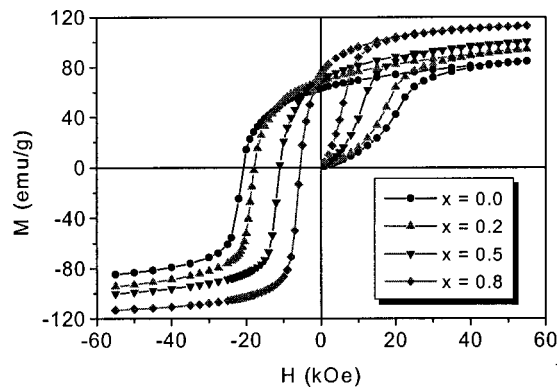|	Hard magnetic property parameters						Lattice parameters		
x	H_{ci} (kOe)	M_r (emu/g)	M_s (emu/g)	M_r/M_s	$(BH)_{max}$ (MGOe)	d (nm)	a (Å)	c (Å)	c/a
0.0	20.7	63.2	97.7	0.647	11.1	14.2	4.878	4.053	0.831
0.1	18.4	62.9	95.9	0.656	10.8	18.2	4.876	4.073	0.835
0.2	17.9	68.7	104.5	0.658	12.6	16.4	4.881	4.078	0.835
0.3	10.5	70.7	103.4	0.683	12.2	15.8	4.865	4.067	0.836
0.5	11.1	69.9	102.6	0.682	11.5	15.2	4.884	4.073	0.834
0.8	5.6	74.9	117.1	0.639	9.4	15.8	4.887	4.079	0.835

FIG. 3. Magnetization curves and magnetic hysteresis loops for mechanically milled $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ magnets.

coercivity of hard magnets can be expressed as

$$H_c = (2K_1/M_s)\alpha_K - N_{eff}M_s,$$

where K_1 and M_s are the anisotropy constant and the saturation magnetization of the material and α_K and N_{eff} are microstructure-dependent factors describing the effect of the microstructure on the crystal field and the local internal dipolar field. With increasing Pr content, the anisotropy of the TbCu$_7$ type phase decreases. Therefore the coercivity variation with Pr content is understandable. The increase of M_r with Pr content is consistent with the fact that Pr(Co,Zr)$_7$ possess higher M_s value than Sm(Co,Zr)$_7$[4,5] since Pr^{3+} has a higher moment.

The remanence enhancement in the nanostructured (Sm,Pr)(Co,Zr)$_7$ magnet powders indicates exchange–coupling interactions between the nanosized grains.[2,7,8] Taking into account this point together with the shape of initial magnetization curve (Fig. 3), it seems that the underlying
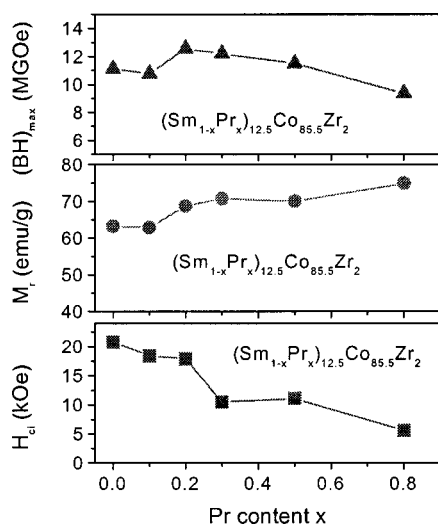
mechanism for the coercivity changes from a pinning type to a mixture of pinning and nucleation.[1,2] However, considering the fact of stronger interactions between the nanosized grains (below 20 nm), the interaction among the domains of the adjacent particles may lead to the formation of "interaction domains." The coercivity in this system is probably controlled by the motion of domain walls in the "interaction domains."[2]

IV. CONCLUSIONS

Nanostructured (Sm,Pr)$_{12.5}$(Co,Zr)$_{87.5}$ magnets with the TbCu$_7$-type structure have been synthesized by mechanically milling $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ alloys $(0 \leq x \leq 0.8)$ followed by appropriate annealing. Single-phase (Sm,Pr)(Co,Zr)$_7$ magnets with the TbCu$_7$ structure and with nanosized grains (14–19 nm) form in the whole composition range. High H_{ci} values are realized in the range of 20.7–5.6 kOe with varying Pr content from 0 to 0.8, while (BH)$_{max}$ shows an optimum value of 12.6 MGOe (H_{ci} remains 17.9 kOe) at $x=0.2$. Remanence ratio in the range of 0.64–0.69 is observed with an optimum value 0.69 at $x=0.3$. The high coercivity is ascribed to the formation of nanostructured (Sm,Pr)(Co,Zr)$_7$ phase of the TbCu$_7$-type structure with large anisotropy, and the remanence enhancement may result from the exchange–coupling interactions between the adjacent nanosized (Sm,Pr)(Co,Zr)$_7$ grains. The magnetic properties can be understood by taking into account the anisotropy of the hard phase and the interactions between the nanosized grains.

FIG. 4. Hard magnetic property dependence on Pr content for the $(Sm_{1-x}Pr_x)_{12.5}Co_{85.5}Zr_2$ magnets.

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