Structure and magnetic properties of $RCo_{7-x}Zr_x$ (R=Pr or Er, $x=0-0.8$)

M. Q. Huang,[a] M. Drennan, W. E. Wallace, and M. E. McHenry
Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213

Qun Chen and B. M. Ma
Rhodia Inc./Chem Dist. Center, CN7500, Cranbury, New Jersey 08512

Alloys of composition $RCo_{7-x}Zr_x$ (R=Pr or Er and $x=0-0.8$) were synthesized and characterized in the temperature range of 10–1273 K in fields up to 5 T. As with the $SmCo_{7-x}Zr_x$ system studied earlier in our laboratory, the effects of Zr doping on the stability of the $TbCu_7$ phase and the increase in the anisotropy field H_A are also observed in the systems of $PrCo_{7-x}Zr_x$ and $ErCo_{7-x}Zr_x$. Nearly single phase $TbCu_7$ materials were formed in as-cast alloys when $x=0.1-0.2$. In the case of R=Pr, H_A changes from almost planar for $x=0$ to uniaxial with $H_a \sim 100$ kOe for $x \geqslant 0.2$ at room temperature (RT). In the case of R=Er, H_A for the $x=0.1$ composition is almost two times larger than that of the Zr-free alloys, which shows strong uniaxial anisotropy at both RT and 10 K. Spin reorientation behavior (when R=Pr) and R–M antiparallel coupling (when R=Er) were also observed. [S0021-8979(99)44208-2]

I. INTRODUCTION

Currently, there is a vigorous effort to find new magnets or to improve existing magnets particularly for high temperature applications. A systematic study of the structure and magnetic properties of $SmCo_7$-based alloys has been carried out with this goal in mind by several groups.[1–4] Our previous work[4] on the $SmCo_{7-x}Zr_x$ system reported that partly replacing Co dumbbells by Zr atoms plays an important role in stabilizing the $TbCu_7$ structure and significantly increases the magnetocrystalline anisotropy. The earlier work has been extended in the present study to include the ternaries $RCo_{7-x}Zr_x$, in which R=Pr or Er. Alloys with the composition $RCo_{7-x}Zr_x$ (R=Pr or Er and $x=0-0.8$) were synthesized and characterized in the temperature range of 10–1273 K and at fields up to 5 T. The structure and magnetic properties are reported.

II. EXPERIMENTS

Alloys were prepared by arc melting under argon atmosphere. X-ray diffraction (XRD) with Cu radiation and thermomagnetic analysis (TMA) with a thermogravimetric analysis unit (TGA) were used to determine the crystal structure, phases present, and their ordering temperatures. Magnetic properties were measured in the temperature range of 10–1273 K in fields up to 5 T using a vibrating sample magnetometer (VSM) and a superconducting quantum interference device (SQUID) magnetometer. The measured samples were in the forms of chunks, loose powder, or aligned powder (⩽38 μm). The anisotropy field H_A was determined by measuring the easy and the hard axis magnetization on powder aligned in a field of 1.6 T and immobilized in epoxy.

III. RESULTS AND DISCUSSION

A. Structure and phases present in as-cast alloys

Information concerning the structure and the phases present, obtained by XRD and TMA measurements, is shown in Figs. 1 and 2 and summarized in Table I. The XRD patterns of the random and aligned powder samples show that the crystal structures of the as-cast alloys $RCo_{7-x}Zr_x$

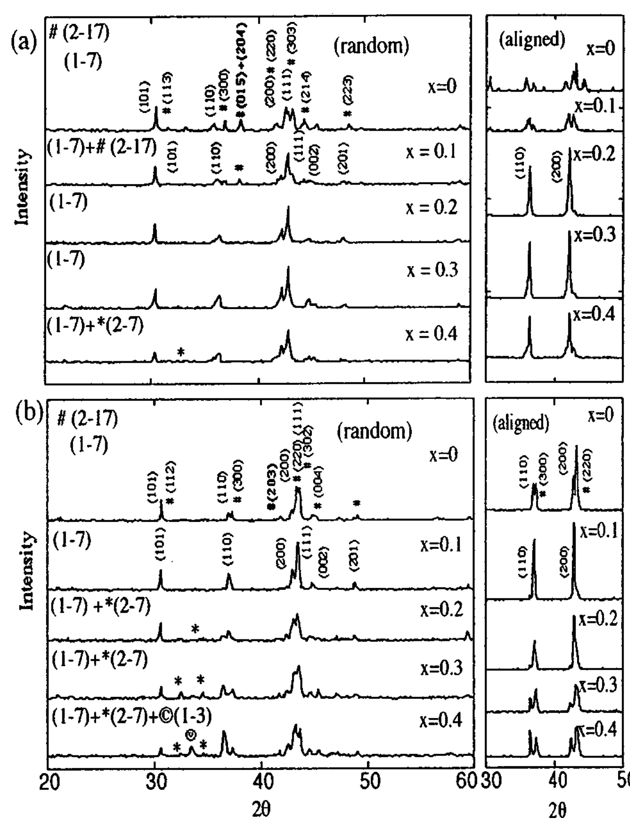

FIG. 1. XRD of $RCo_{7-x}Zr_x$ as-cast alloys ($x=0-0.4$) in random and magnetically aligned powder (a) R=Pr and (b) R=Er.

[a]Electronic mail: mh8f@andrew.cmu.edu

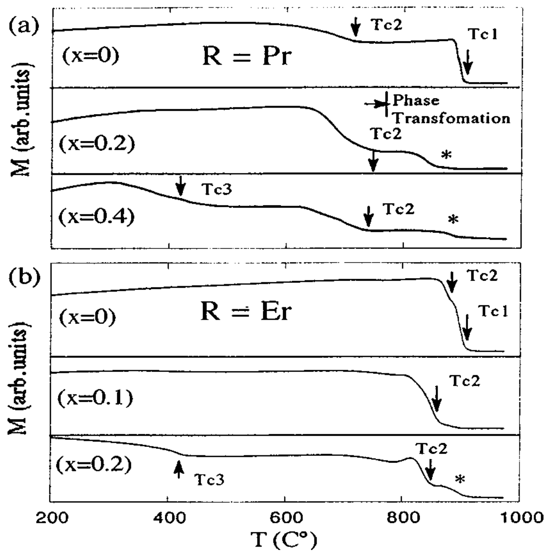

FIG. 2. M vs T of $RCo_{7-x}Zr_x$ as-cast alloys ($H \sim 20$ Oe), (a) R=Pr and (b) R=Er.

varies significantly with the Zr content. For R=Pr, typical superlattice reflections for the Th_2Zn_{17} structure (i.e., 015 and 204) disappear when $x \geqslant 0.2$ [Fig. 1(a)]. This indicates that the structure of the main phase changes from rhombohedral (Th_2Zn_{17} type) ($x=0$) to hexagonal ($TbCu_7$ type) ($x \geqslant 0.2$). This is also evident in the XRD of aligned samples, where only two strong reflections (110 and 200) belonging to the 1–7 phase, remain for $x \geqslant 0.2$. Nearly single phase materials with the $TbCu_7$ structure were formed for Pr alloys with $x=0.2-0.3$.

In the case of R=Er, the structure of the main phase changes from an ordered hexagonal (Th_2Ni_{17} type) ($x=0$) to a disordered hexagonal ($TbCu_7$ type) when $x \geqslant 0.1$. As shown in Fig. 1(b), for the randomly oriented samples, a typical superlattice reflection (203) for the Th_2Ni_{17} structure disappears when $x \geqslant 0.1$. For the aligned samples, two pairs of strong reflections at $x=0$ that belong to the 2–17 and 1–7 phases, became a single pair, belonging to the 1–7 phase when $x \geqslant 0.1$. A nearly single phase material with the $TbCu_7$ structure was formed for R=Er alloys when $x=0.1$. As the Zr content was further increased, some other R-rich phases, such as the 2–7 (Ce_2Ni_7 or Er_2Co_7 types) and the 1–3 ($PuNi_3$ type) phases also were observed.

The above mentioned magnetic phases were also identified by the TMA measurements (Fig. 2 and Table I). The four Curie temperatures (T_{c1}, T_{c2}, T_{c3}, and T_{c4}) correspond to four magnetic phases, i.e., the 2–17, 1–7, 2–7, and 1–3 phases, respectively. Notice that as was observed in the $SmCo_{7-x}Zr_x$ system[4] in an earlier study, a phase transformation from the disordered 1–7 phase to the ordered 2–17 and 1–5 phases also occurs above 750–800 °C in Pr or Er alloys. This was confirmed by XRD measurement in our lab.

B. Magnetic properties of as-cast alloys

The magnetic properties M, H_A, T_c, and T_{sr} are given in Figs. 2–4 and Table I. The $M-H$ curves of the aligned powder samples with compositions of $RCo_{7-x}Zr_x$ (R=Pr or Er, $x=0-0.2$) show that the anisotropy field H_A at both 300 and 10 K can be significantly increased by a small amount of Zr substitution. The types of the H_A, i.e., the preferred directions of the magnetization (DOM) vector, were identified by XRD measurement in the aligned powder samples (Fig. 1). As listed in Table I, for R=Pr, the anisotropy type changes from basic planar (EBP) for $x=0$ to uniaxial (EA) with $H_A \sim 94$ kOe for $x \geqslant 0.2$ at 300 K and from planar for $x=0$ to conical (EC) for $x \geqslant 0.1$ at 10 K. For R=Er, as x increases from 0 to 0.1, H_A(EA) increases from 50 to 95 kOe at 300 K and from 80 to 168 kOe at 10 K. The strong uniaxial anisotropy was developed by a small amount of Zr substitution for Co in these two RCo_7 systems. Zr plays the same important role as in the $SmCo_{7-x}Zr_x$ system. It replaces the Co dumbbells and restores the anisotropy of the Co (2c sites) sublattice, which were reduced when Co was replaced by R atoms (i.e., as the Th_2Zn_{17} or Th_2Ni_{17}-type structures were formed from the $CaCu_5$-type structure). As noted by Buschow[5] and Wallace,[6] both Pr_2Co_{17} (Th_2Zn_{17} type) and Er_2Co_{17} (Th_2Ni_{17} type) show small anisotropy at room temperature (RT)—

TABLE I. Magnetic properties of $RCo_{7-x}Zr_x$ as-cast alloys (R=Pr or Er, $x=0-0.8$).

		T_c (°C)				M (emu/g)		H_A (kOe)-D_0M	
R	X	T_{c1}	T_{c2}	T_{c3}	T_{c4}	300 K	10 K	300 K	10 K
Pr	0	897	692	⋯	⋯	126.1	139.5	EB	EB
	0.1	877	689	⋯	⋯	116.9	127.6	EB+EA	EC
	0.2	a	683	⋯	⋯	111.0	119.7	94	EC
	0.3	a	670	368	⋯	99.0	109.6	97	EC
	0.4	⋯	660	350	⋯	90.9	100.3	100	EC
	0.8	⋯		312	⋯	49.2	67.4	100	EC
Er	0	893	863	⋯	⋯	77.3	15.1	50	85
	0.1	⋯	849	⋯	⋯	68.7	18.4	95	168
	0.2	a	835	417	⋯	66.9	25.6	92	150
	0.3	a	830	416	⋯	61.0	27.4	73	130
	0.4	a	830	414	207	56.1	33.1	78	140
	0.8	⋯	⋯	⋯	206	48.2	38.7	83	200

[a]Related to (2–17) phase, which was formed after heating up to 750–800 °C due to a phase transformation from 1–7 to 2–17 and 1–5.

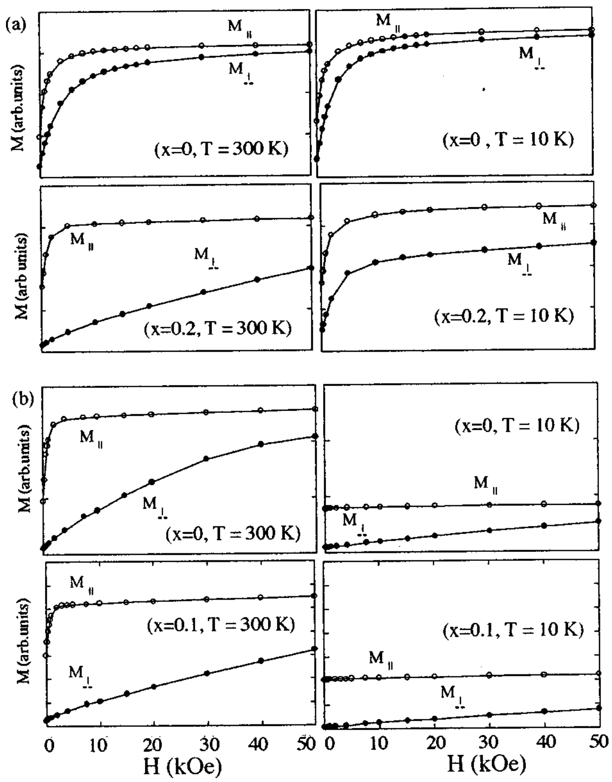

FIG. 3. M vs H (at 300 and 10 K) of $RCo_{7-x}Zr_x$ as-cast alloys (a) R=Pr and (b) R=Er.

planar for R=Pr and weak uniaxial anisotropy for R=Er. However, in the present study, the RCo_7 alloys (R=Pr or Er) with a small amount of Zr doping exhibit a strong anisotropy at RT. This is potentially beneficial for the fabrication of new magnets for high temperature applications, since the $PrCo_7$ and $ErCo_7$-type alloys also show higher T_c than their 1–5 alloy counterparts.

As the Zr content further increases, in the Pr alloys, the H_A increases at 300 K and the estimated angles of the easy direction from c axis decrease from ~48° for $x \sim 0.1$ to ~31° for $x=0.8$ at 10 K. In the Er alloys, with the increases of Zr content x, the H_A first decreases slightly when $x \leqslant 0.3$, and then increases again at 10 K. The above behavior can be attributed to the formation of the 2–7 and 1–3 phases when the Zr content is higher. H_A at 10 K increases up to ~200 kOe for the Er alloy of $x=0.8$, where the 1–3 phase is predominant in the alloy.

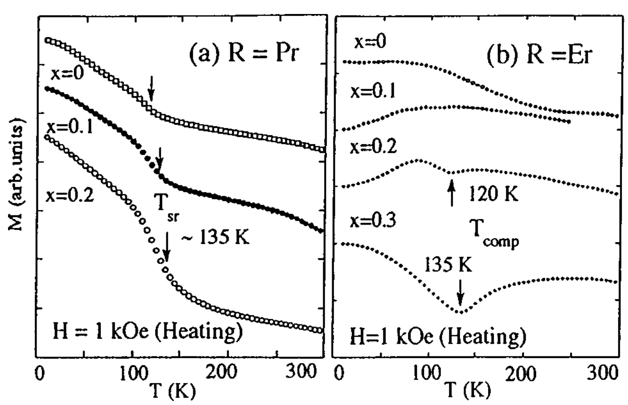

FIG. 4. $M(T)(10-300\,\mathrm{K})$ curves at $H \sim 1000$ Oe (chunk sample). (a) Spin reorientation (T_{sr}) of $PrCo_{7-x}Zr_x$ as cast alloys. (b) Moment compensation (T_{comp}) of $ErCo_{7-x}Zr_x$ as-cast alloys.

As shown in Fig. 4, in the Pr alloys spin reorientation behavior from EC to EA has been observed during heating from 10 to 300 K. This behavior is similar to that observed in $PrCo_5$ alloy ($T_{sr} \sim 105\,\mathrm{K}$).[7] The spin reorientation temperature T_{sr} for the $PrCo_{6.8}Zr_{0.2}$ alloy is apparent around 135 K and shifts slightly to lower temperature as the Zr content decreases. This can be ascribed to the effects of Zr doping on the Pr sublattice anisotropy at low temperature.

In the Er alloys, the partial moment cancellation resulting from the antiparallel coupling between the R (heavy rare-earth element Er) and $3d$ sublattice leads to the observed compensation points in the range of 120–135 K when $x = 0.2-0.4$. This is ascribed to the formation of the 2–7 phase. Buschow[7] has also reported a similar compensation temperature for Er_2Co_7, 140 K. As shown in Table I, with an increase in x, a decrease in M and T_c for both Pr and Er alloys is observed due to an increase in the amount of the nonmagnetic element Zr.

The investigation into the effects of the Zr doping on the stability of the $TbCu_7$ phase and increase in H_A in the RCo_7 system is being continued with other rare-earth elements. We have estimated the moment for Co, M_{Co}, in the $RCo_{7-x}Zr_x$ compounds from the experimental moment of the $YCo_{7-x}Zr_x$ ($x=0-0.1$). M_{Co} decreases slightly from 1.60 to $1.53\mu_B$ as x increases from 0 to 0.1. The Co moment is nearly the same as that in YCo_5 and $Y_2Co_{17}(1.6\mu_B)$.

ACKNOWLEDGMENTS

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