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Magnetic behavior of rapidly solidified Pr–Co alloys with the $TbCu_7$-type structure

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Rapid solidification has been utilized to produce a series of Pr–Co alloys between the Pr_2Co_{17} and $PrCo_5$ stoichiometries. In this system, $PrCo_5$ has easy axis magnetization while Pr_2Co_{17} has easy-plane magnetization. Alloys of the form $(Pr_xCo_{1-x})_{94}Ti_3C_3$ with x ranging from 0.105 corresponding to the Pr_2Co_{17} compound to $x=0.167$ corresponding to the $PrCo_5$ compound were produced by melt spinning at a tangential wheel speed of 40 m/s. The rapid solidification and alloying additions were found to suppress the formation of the Pr_2Co_{17} ordered phase, leading to the formation of the disordered $TbCu_7$-type structure over a range of Pr/Co ratios. Hysteresis loops were characterized by a smooth demagnetization curve reflective of single-phase demagnetization. Heat treatment at 800 °C led to the formation of the Pr_2Co_{17} and $PrCo_5$ phases, and the presence of the soft magnetic Pr_2Co_{17} phase drastically decreased the coercivity. The soft magnetic behavior was consistent with in-plane magnetization of the Pr_2Co_{17} structure that formed during heat treatment. However, the relatively high coercivity observed in the as-solidified alloys with the disordered $TbCu_7$-type structure suggests that dumbbell disorder may create easy axis magnetization, and changes in saturation magnetization also imply that dumbbell configuration is important to the magnetic properties. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2167349]

INTRODUCTION

Rapidly solidified Pr–Co has attracted little attention, primarily because of difficulties associated with deleterious phase formation in conventionally processed materials. For example, numerous soft magnetic compounds exist compositionally close to the hard magnetic $PrCo_5$ compound, including $Pr_2Co_{17}, Pr_2Co_7, Pr_5Co_{19}$, and $PrCo_3$. However, some studies have shown that rapid solidification, coupled with appropriate alloying, can result in excellent hard magnetic properties, at least in Pr-rich compositions, by suppressing formation of these deleterious phases.[1,2] Specifically, C additions resulted in as-solidified coercivities of approximately 16 kOe,[1] while Ti and C additions lead to good magnetic properties after heat treatment.[2] However, these studies have centered on compositions hyperstoichiometric relative to the $PrCo_5$ compound. Here, we investigate the rapidly solidified structure and properties of hypostoichiometric alloys that extend to the Pr_2Co_{17} stoichiometry. Of particular interest is the role of transition-metal dumbbell disorder on the magnetic behavior. For example, the disordered $SmCo_7$ structure with the $TbCu_7$-type structure was stabilized by rapid solidification between the 2:17 and 1:5 stoichiometries, and a large dependence of coercivity was observed as the Sm/Co ratio changed.[3] In this system the transition from hard $PrCo_5$ to soft Pr_2Co_{17} is the subject of this study.

EXPERIMENTAL PROCEDURES

A series of alloys with nominal compositions of $(Pr_xCo_{1-x})_{94}Ti_3C_3$ with x ranging from 0.105 to 0.167 (corresponding to the region ranging from the Pr_2Co_{17} to the $PrCo_5$ stoichiometries) was made from high-purity (>99.95%) elements by arc melting in a high-purity argon atmosphere. The ingot was then rapidly solidified by melt spinning in high-purity argon at a chamber pressure of 1 atm and a tangential wheel velocity of 40 m/s. Heat treatments were conducted after sealing lightly a ground ribbon wrapped in Ta foil in quartz capsules under high-purity Ar. Samples were heat treated at 800 °C for 10, 20, and 30 min, and quenched in water at the conclusion of the heat treatment.

The magnetic measurements were made by supeconducting quantum interference device (SQUID) magnetometry at 300 K utilizing a Quantum Design magnetic property measurement system (MPMS) magnetometer with a maximum field of 7 T. Magnetic measurements were made on several ribbon pieces mounted so that the magnetic field was applied in the plane of the ribbon. Structural characterization by x-ray diffraction was also conducted using a Philips diffractometer and Cu $K\alpha$ radiation on powdered ribbon. Phase analysis was conducted using Rietveld refinement of the x-ray-diffraction patterns using *SIROQUANT*, a commercial software package.

RESULTS AND DISCUSSION

The $(Pr_xCo_{1-x})_{94}Ti_3C_3$ alloys of $TbCu_7$-type structure where x varied from $x=0.105$ to 0.167 in 0.016 increments were obtained by rapid solidification. Figure 1 presents the x-ray data of the as-solidified $(Pr_xCo_{1-x})_{94}Ti_3C_3$ alloys. Rietveld analysis showed the presence of the disordered $TbCu_7$-type $PrCo_7$ structure in all alloys. No evidence of the ordered Th_2Zn_{17}-type Pr_2Co_{17} structure was observed, even

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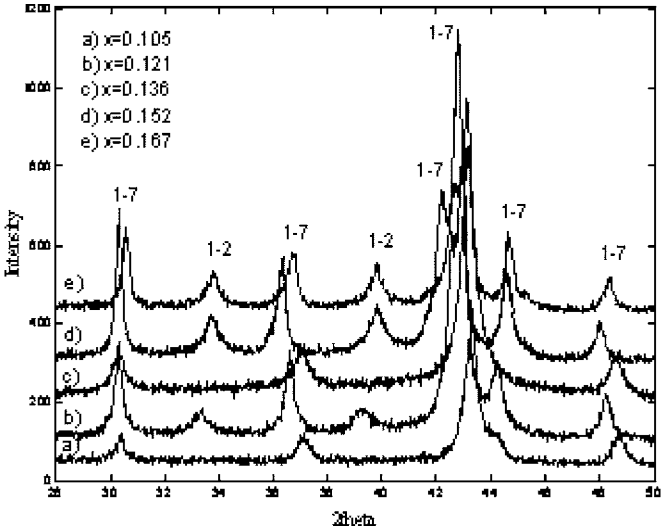

FIG. 1. X-ray-diffraction data of the as-solidified $(Pr_xCo_{1-x})_{94}Ti_3C_3$ alloys.

in Co-rich compositions. It should also be noted that the difference in the $TbCu_7$-type $PrCo_7$ and $CaCu_5$-type $PrCo_5$ structures is only the presence of excess Co, which substitute randomly for the Pr atoms as dumbbells in the $PrCo_7$ structure. No attempt was made to distinguish the two here, though we recognize that the Pr-rich composition at $x=0.167$ is stoichiometric $PrCo_5$ and thus lacks dumbbells. What is important to note is that the disordered, metastable $TbCu_7$-type structure was formed at high Co concentrations. A second phase, the Cu_2Mg-type $PrCo_2$ structure was also observed in alloys with $x=0.105$, 0.121, and 0.152. Due to the peritectic solidification characteristics of the binary Pr–Co alloy, its presence might be expected. However, its absence was not systematic with x, and repeated experiments resulted in similar phase formation. No evidence of other Pr–Co compounds that exist with stoichiometries between $PrCo_5$ and $PrCo_2$, such as $PrCo_3$ or Pr_5Co_{19}, was observed in the x-ray-diffraction scans. These phases are structurally more complicated and can more easily be suppressed during rapid solidification than can the $PrCo_2$ structure.

The hysteresis loops of the as-solidified alloys were

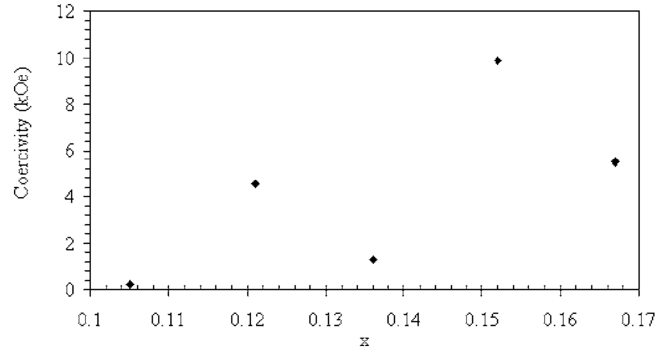

FIG. 3. Coercivity of $(Pr_xCo_{1-x})_{94}Ti_3C_3$ vs Pr fraction.

measured to determine the compositional effects on the magnetic properties. Figure 2 shows the demagnetization curves for the as-solidified alloys. The coercivity was largely dependent on the composition (Fig. 3), as the largest coercivity was observed for $x=0.152$ and the lowest for $x=0.105$. The intrinsic coercivity at $x=0.152$, 9.85 kOe, is relatively high for as-solidified Pr–Co-based alloys, and the intrinsic coercivity of 4.5 kOe at $x=0.121$ is extremely high for this Co-rich composition, given the fact that the Pr_2Co_{17} phase has easy-plane anisotropy and thus is magnetically soft.

Heat treating the $(Pr_xCo_{1-x})_{94}Ti_3C_3$ alloys lead to dramatic decreases in the coercivity for all values of x, decreasing below 1 kOe in all alloys (Fig. 4). The decrease in coercivity was related to phase evolution that occurred during heat treatment. The as-solidified $TbCu_7$-type structure transforms to the equilibrium soft magnetic phase Pr_2Co_{17} and Pr_5Co_{19} for all alloys (Fig. 5). Previous work showed that TiC-modified alloys resisted this decomposition,[2] but under the heat treatments here the transformation occurs. The presence of the soft magnetic phases, particularly the Pr_2Co_{17}, results in the dramatic loss of coercivity.

It is important to note that significant coercive forces (>4 kOe) were observed in Co-rich compositions close to the 2:17 stoichiometry. The subsequent loss of coercivity upon the formation of the Pr_2Co_{17}-ordered structure suggests that the dumbbell ordering is critical to the magnetic properties, and the intrinsic behavior changes with the amount of

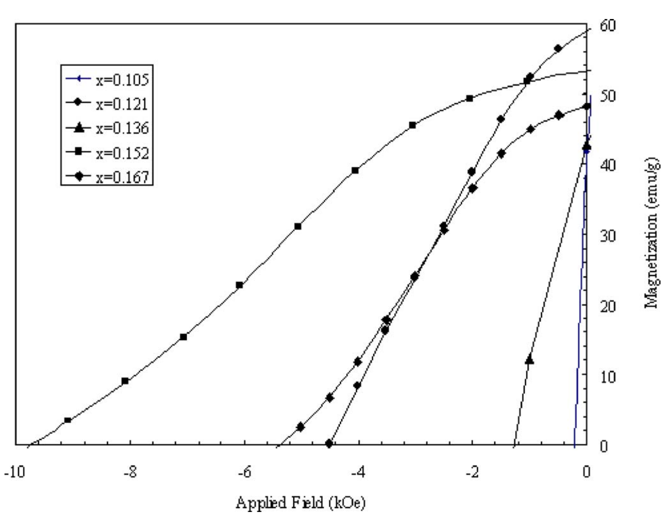

FIG. 2. Demagnetization curves of as-solidified $(Pr_xCo_{1-x})_{94}Ti_3C_3$ alloys.

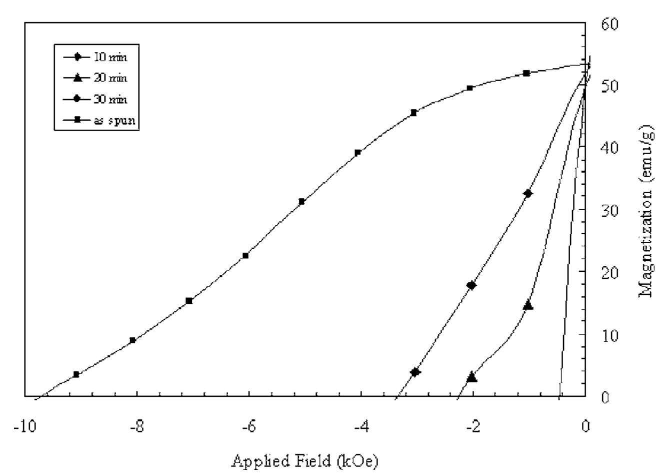

FIG. 4. Demagnetization curves of $(Pr_{0.152}Co_{0.849})_{94}Ti_3C_3$ as-solidified and annealed for 10, 20, and 30 min at 800 °C.

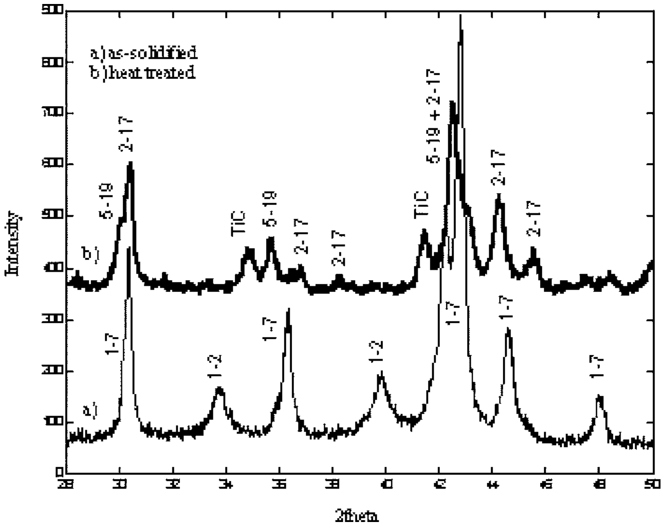

FIG. 5. X-ray-diffraction patterns of the as-solidified $(Pr_{0.152}Co_{0.849})_{94}Ti_3C_3$ and after heat treatment at 800 °C for 30 min. The transformation of the $TbCu_7$-type structure to the Pr_2Co_{17} and Pr_5Co_{19} structures is clearly observed.

order. The relatively high coercivity in the as-solidified material with the $TbCu_7$-type structure indicates that the dumbbell disorder retains a uniaxial easy magnetization direction, while the ordering of the dumbbells leads to easy-plane magnetization. The gradual loss with heat treatment time further suggests that the anisotropy gradually changes with the degree of order. Further work is necessary to further clarify this point.

CONCLUSIONS

High coercivity was obtained in as-solidified Pr–Co alloys modified with Ti and C from the Pr_2Co_{17} to $PrCo_5$ stoichiometries. The as-solidified alloys contained predominantly the disordered $TbCu_7$-type structure, and some alloys also contained the nonmagnetic $PrCo_2$ phase. The coercivity was generally related to Pr/Co ratio and ranged from 9.85 to 1.2 kOe. Heat treatment leads to the formation of the equilibrium Pr_2Co_{17} phase and a dramatic decrease in coercivity, as the Pr_2Co_{17} phase has easy-plane magnetization. The high as-solidified coercivity and the loss upon ordering suggest that the dumbbell ordering significantly influences the intrinsic magnetic properties.

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