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Synthesis and magnetic properties of melt-spun high Pr-content magnetostrictive alloys

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ABSTRACT

Pseudobinary high Pr-content $Tb_{1-x}Pr_x(Fe_{0.4}Co_{0.6})_{1.93}$ ($0.70 \le x \le 1.00$) magnetostrictive alloys have been fabricated by a melt-spinning method. The effects of the composition, spinning, and annealing processes on the structure, thermal stability, and magnetic properties are investigated. At a wheel speed of $v \le 30$ m/s, the as-spun ribbons consist of a mixture of $(Tb,Pr)(Fe,Co)_2$ cubic Laves phase and some non-cubic phases. A single $(Tb,Pr)(Fe,Co)_2$ phase with $MgCu_2$-type structure is formed with the process for the speed of $v \ge 35$ m/s and subsequent annealing at 500 °C for 30 min. The lattice parameter of the $Tb_{1-x}Pr_x(Fe_{0.4}Co_{0.6})_{1.93}$ Laves phase increases from 0.7354 nm for $x = 0.70$ to 0.7384 nm for $x = 1.00$ and approximately follows the linear Vegard's law. The Curie temperature decreases, while the saturation magnetization increases as increasing Pr content. The Pr-rich alloys possess the relatively lower coercivity and the faster saturation of magnetostriction as compared with the Tb-rich alloys, which can be understood by their lower magnetic anisotropy.

1. Introduction

The Laves-phase RFe_2 (R = rare earth) giant magnetostrictive compounds are of considerable interest for actuator applications. $TbFe_2$ possesses the largest magnetostriction ($\lambda_{111} = 2460$ ppm) at room temperature (RT) up to date. However, its large magnetocrystalline anisotropy, $K_1 = -7.6 \times 10^6$ J/m^3 at RT, restricts the range of practical applications because then large magnetic fields are required to realize a large magnetostriction [1,2]. Thus, the anisotropy of $TbFe_2$ should be lowered by introduction of other rare earth such as Dy while still maintaining the desired large magnetostriction in applications. As a result, $Tb_xDy_{1-x}Fe_2$ and $Tb_xHo_{1-x}Fe_2$ were found to be accepted alloy systems, and the well-known compound $Tb_{0.27}Dy_{0.73}Fe_{1.92}$ (called Terfenol-D) was discovered. Although Terfenol-D is useful, its main constituting metals, the heavy rare earths Tb and Dy, are expensive. It would be beneficial to applications if relatively low-cost, light rare earths could be greatly substituted for Tb and Dy, while competitive properties could still be maintained. Unlike $HoFe_2$ and $DyFe_2$, $PrFe_2$ should have a larger magnetostriction than that of $TbFe_2$, according to the calculation based on the single ion model [1]. Moreover, $PrFe_2$ has a very small anisotropy, $K_1 = 0.73 \times 10^6$ J/m^3 at 1.5 K, which is even an order smaller than that of $TbFe_2$ (-7.6×10^6 J/m^3) and that of $DyFe_2$ (2.1×10^6 J/m^3) at RT [3]. Together with this, Pr is much cheaper than Tb and Dy, making $PrFe_2$ a potential magnetostrictive candidate material. Unfortunately, a pure $PrFe_2$ Laves-phase compound cannot be synthesized at ambient pressure [4]. Thus, much attention has been paid to the synthesis and the magnetostrictive properties of $(R,Pr)Fe_2$ compounds [5–7]. However, in most of previous work, an unanticipated non-cubic phase appeared when the Pr content exceeds 20–25 at% of the total rare earth content at ambient pressure. Therefore, a key problem for developing the cheaper Pr-based magnetostrictive materials is to synthesize the single Laves-phase compounds with high Pr content. Recently, new progress was made with non-equilibrium techniques [8–11]. As an example, the melt-spinning with post-annealing was shown to be an effective method to synthesize meta-stable phases which cannot be prepared at equilibrium condition. In this article, high Pr-content $Tb_{1-x}Pr_x(Fe_{0.4}Co_{0.6})_{1.93}$ alloys were prepared by a melt-spinning method, and the effects of heat treatment on the structure, phase transformation, and magnetic properties were investigated. Single phase $Tb_{1-x}Pr_x(Fe_{0.4}Co_{0.6})_{1.93}$ compound with cubic $MgCu_2$-type structure forms with proper wheel speed and annealing temperature.

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2. Experiments

All ingots having $Tb_{1-x}Pr_x(Fe_{0.4}Co_{0.6})_{1.93}$ stoichiometry with $x = 0.70, 0.75, 0.80, 0.85, 0.90, 0.95$, and 1.00 were prepared by arc melting of the appropriate constituent metals in a high purity argon atmosphere. The purities of the constituents are 99.9% for Tb and Pr, and 99.8% for Fe and Co. The ingot was cut into small pieces of about 3 g, and then homogenized at temperature from 500 to 800 °C for 30 min and 7 days in an argon atmosphere, respectively. As for melt-spinning samples, an excess (4 wt%) of Pr and Tb over the stoichiometric amount was added to compensate for the mass loss during arc melting and melt spinning. The ingots were then cut into small pieces of about 10 g, from which the ribbons were fabricated by melt spinning with a wheel speed over a range from 20 to 40 m/s, followed by annealing at temperature from 500 to 800 °C for 30 min under high purity argon atmosphere.

X-ray diffraction (XRD) data were recorded at RT with Cu K_α radiation in a D/max-γA diffractrometer with a graphite crystal monochromator. Temperature dependence of ac initial susceptibility, χ_{ac}, at $H = 160$ A/m, was measured to determine Curie temperatures of the compounds in the alloys. The quasi-static magnetic properties of the alloys were measured at RT by using an automated measurement system [12]. Measurements of the magnetic hysteresis loops were conducted by energizing an electromagnet to provide a cyclic magnetic field H at 0.1 Hz and then measuring the corresponding magnetic flux density B by a search coil wrapped around the samples. The associated magnetization M was calculated using

$$M = \frac{B}{\mu_0} - H \quad (1)$$

where $\mu_0 = 4\pi \times 10^7$ H/m is the permeability of free space. The ribbons, spun at 40 m/s and following annealed at 500 °C, were crushed into powders to the size less than 78 μm. Then, the powders were mixed with epoxy resin at a proper ratio chosen based on the previous work [9], and the volume fraction was determined to be 0.71. The composites were produced by a cold isostatic pressing at a pressure of 100 MPa, and then solidified at freedom state at RT. The magnetostriction at RT was measured either parallel or perpendicular to a cyclic magnetic field using a standard strain gauge technique.

3. Results and discussion

All the as-cast $Tb_{1-x}Pr_x(Fe_{0.4}Co_{0.6})_{1.93}$ samples appear multi-phase and contain a small amount of impurity with non-cubic phase. As an example, the XRD patterns for the as-cast $Tb_{0.1}Pr_{0.9}(Fe_{0.4}Co_{0.6})_{1.93}$ alloy are shown in Fig. 1. It is found that the sample shows three subspectra, corresponding to three-phase structure in the alloy. The main phase is the $(Tb,Pr)(Fe,Co)_2$ Laves phase with a $MgCu_2$-type (1:2) cubic structure, and the secondary phase is the $(Tb,Pr)(Fe,Co)_3$ phase with a $PuNi_3$-type (1:3) structure, coexisting with a small amount of rare earth phases. They are also indicated with symbols indexed in Fig. 1. Upon heat treatment at different temperatures, the phase characteristics are almost the same as the as-cast samples, indicating they are of the three-phase structure. As an example, the as-cast $Tb_{0.1}Pr_{0.9}(Fe_{0.4}Co_{0.6})_{1.93}$ sample was annealed at the temperatures varied from 500 to 800 °C for 30 min, and the XRD patterns do not change except for the diffraction intensity, which shows the three phases still coexisting. To study the annealing time effect on the phases, the as-cast samples were annealed with the prolonged time of 1–7 d, and the impurity phases with 1:3 type and RE cannot be eliminated. These results are in good agreement with the report by Guo [6], indicating that the high Pr-content $(Tb,Pr)(Fe,Co)_2$ single Laves phase cannot be formed by annealing as-cast samples.

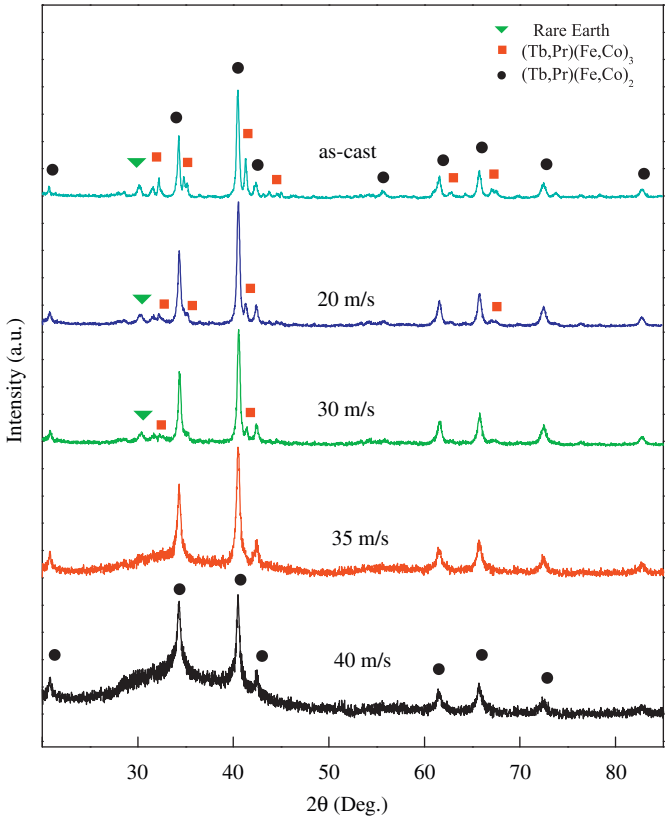

Fig. 1. X-ray diffraction patterns of the $Tb_{0.1}Pr_{0.9}(Fe_{0.4}Co_{0.6})_{1.93}$ alloys as-cast and as-spun at different speeds (20, 30, 35, and 40 m/s, respectively).

The broad crystalline peaks of the Laves phase and the broad amorphous hump are found in all the as-spun $Tb_{1-x}Pr_x(Fe_{0.4}Co_{0.6})_{1.93}$ ribbons, indicating a mixture of ultra-fine $(Tb,Pr)(Fe,Co)_2$ grains and an amorphous phase. As an example, Fig. 1 shows the typical XRD patterns for the as-spun $Tb_{0.1}Pr_{0.9}(Fe_{0.4}Co_{0.6})_{1.93}$ ribbons quenched at various wheel speeds. It can be found that the main phase is the cubic Laves phase for all the ribbons. There is a small amount of impurity with 1:3 type and RE phase for the samples fabricated at relatively low wheel speed of 30 m/s, and especially obvious at the lower speed of 20 m/s. But, the peaks corresponding to the $(Tb,Pr)(Fe,Co)_3$ impurity cannot be observed and the broad amorphous hump becomes more obvious at high wheel speeds ($\geq$35 m/s), indicating that rapid solidification can improve some element solid solubility in certain phase and the high wheel speed is beneficial to eliminate the $(Tb,Pr)(Fe,Co)_3$ impurity and to form the amorphous phase.

The $Tb_{0.1}Pr_{0.9}(Fe_{0.4}Co_{0.6})_{1.93}$ ribbons, quenched at the wheel speed of 40 m/s, were annealed at different temperatures for 30 min, and Fig. 2 shows their XRD patterns for the annealing temperature 800, 700, and 500 °C, respectively. As for the sample annealed at 500 °C, the melt-spun sample crystallizes into the $(Tb,Pr)(Fe,Co)_2$ structure with little or no evidence of any secondary phases (within the accuracy of XRD), like $(Tb,Pr)(Fe,Co)_3$ or RE. All lines in the diffraction patterns can be indexed to the characteristics of the cubic $MgCu_2$-type crystal structure, indicating the formation of the single $(Tb,Pr)(Fe,Co)_2$ Laves phase. This result also suggests that the formation for Laves phase occurs prior to that for $(Tb,Pr)(Fe,Co)_3$ phase during the process of