IOP Conf. Series: Materials Science and Engineering **103** (2015) 012006 doi:10.1088/1757-899X/103/1/012006

Structural and magnetic properties of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ Ribbons

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Abstract. The structural and magnetic properties of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons have been investigated using X-ray diffraction, vibrating sample magnetometry and the standard strain gauge technique. According to the XRD spectra, all ribbons of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$demonstratea pure Laves phase, which benefits from the melt-spun technology. The Curie temperature of the $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ alloys decreases gradually from 366°C for x=0.1 to 328°C for x=0.3. Meanwhile, magnetostriction at room temperature demonstrates a maximum at x=0.1.

1. Introduction

Magnetostrictive materials have been the topic of much recent research for their potential applications on sensors and micro-drivers. According to the single-ion model [1], $CeFe_2$ and $PrFe_2$ compounds demonstrate greater magnetostriction than $TbFe_2$ and $DyFe_2$ at 0K; therefore, Ce-based and Pr-based RFe_2 ("R" refers to rare earth elements) compounds may have great potential as giant magnetostrictive materials. Moreover, the light rare earth elements Pr and Ce are much more cost effective than the heavy rare earth elements Tb and Dy. As a result, considerable studies have focused on Pr-based or Ce-basedcompounds [2-6]. However, the large radius of the Pr^{3+} ion presents difficulties for the synthesis of $PrFe_2$ with a pure Laves phase at ambient pressure [7, 8]. Only a small portion of Pr content is possible in stable RFe_2 compounds. When Pr content exceeds 20-25%, a single Laves phase material cannot be obtained in $(R,Pr)Fe_2$ compounds. Recently, great effort has been exerted to enhance Pr content in $(R,Pr)Fe_2$ compounds [9]. For instance, researchers have used a melt-spinning technique, or introduced substitute/interstitial atoms such as B, Co, etc., into the $(R,Pr)Fe_2$ system [10-12].

In this paper, Mn atoms were introduced into $(Tb,Pr)Fe_2$ compounds to substitute for Fe, and melt-spun technology was applied in the synthesis of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons to obtain potential magnetostrictive materials. The structural and magnetic properties of the obtained $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons were then investigated.

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2. Experimental procedure

The $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ (x=0.1, 0.2, 0.3) alloys were prepared by arcmelting constituent elements in a highly purified argon atmosphere using nonconsumable tungsten electrodes and a water-cooled copper bottom.The purities of rare earth elements are 99.9% and the metals of Fe and Mn have a the purities of 99.99%. The alloy buttons were melted four times to ensure homogenization. Next, ingots of approximately 3 g were annealed at 850°C for 72 hours; ingots of approximately 5 g portions were conducted in an atmosphere of pure argon by ejection of the molten metal onto a rotating copper roll moving at a speed of 50 m/s, which was then cooled by water. Thus, ribbons of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ were obtained, and the ribbons were then annealed in an argon atmosphere at 500°C for 30 minutes. Phase identification was conducted by X-ray powder diffraction methods (Philips X'Pert MPD). The magnetization at room temperature and the Curie temperature of annealed ribbons were determined by a vibrating sample magnetometer (Lake Shore 7407 model). The magnetostriction was measured at room temperature using a standard strain gauge in directions parallel ($\lambda_{//}$) and perpendicular ($\lambda_{\perp}$) to the magnetic field.

3. Results and discussion

The X-ray diffraction spectra for the annealed $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ alloys are shown in figure 1. All arc-melt alloys were composed of a matrix of cubic-structured RFe_2 compound, with a small amount of the R-rich phase and RFe_3 phase. In the formula of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$, the rare earth rich stoichiometry was often chosen to offset the volatilization of rare earth metals in the melting process and to inhibit the formation of the RFe_3 phase. Generally, the Pr content in an $(R,Pr)Fe_2$ system cannot exceed 20-25% for rare earth materials, without the appearance of the second phases (R-rich phase and RFe_3 phase) [8]. In order to fabricate a single Laves phase with Pr content greater than 20%, we employed melt-spun technology and investigated the XRD spectrato confirm the Laves phase and the second phases.

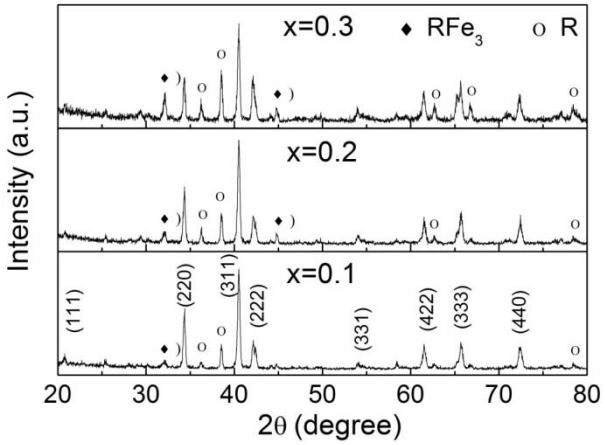

Figure 1. XRD patterns of homogenized $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$alloys at 850°C for 72 hs.

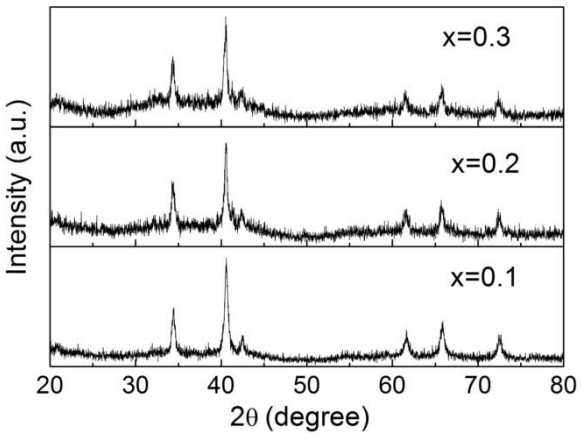

Figure 2. XRD patterns of as-spun $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons.

XRD patterns of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ alloys homogenized at 850°C for 72 hours are shown in figure 1. The X-ray diffraction spectra for the $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons (as-spun and as-annealed) are shown in figures 2 and 3, respectively. In figure 1, the orientation index shows the presence of second phases in the alloys. The peaks of the R-rich phase and the RFe_3 phase are clear in the XRD spectra for the $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ alloys, which were annealed at 850°C for 72 hours. The high temperature and the long annealing time cannot eliminate the second phases in the $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ alloys. However, as shown in figure 2, which represents the as-spun $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons (which were not annealed), the peaks of the R-rich phase and RFe_3 phase disappear. All peaks in the diffraction patterns are indexed to the characteristics of the $MgCu_2$ crystal structure in figure 2. In figure 2, the

broad crystalline peak and the broad hump indicate that a mixture of ultra-fine grains and the amorphous phase exist in the $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons. In order to investigate the effect of the annealing process on the as-spun $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons, the ribbons were annealed at 500°C for 30 minutes. The XRD of the as-annealed $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons are shown in figure 3. Results indicate that all diffraction peaks become sharper in figure 3 than those in figure 2, indicating the formation of the Laves phase in the as-annealed $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons. Thus, the melt-spin technique is determined to be an effective method for the synthesis of Laves phase alloys with high Pr content.

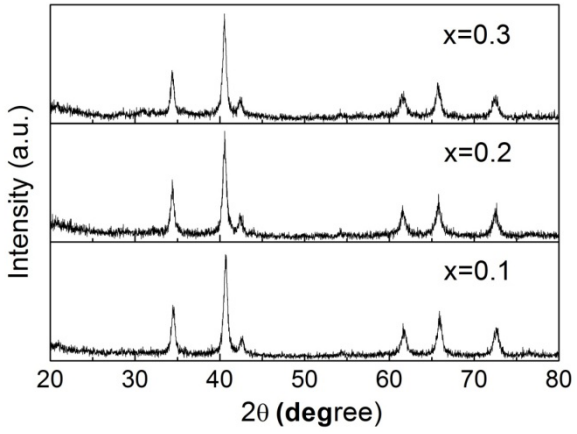

Figure 3. XRD patterns of as-annealed $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ribbons.

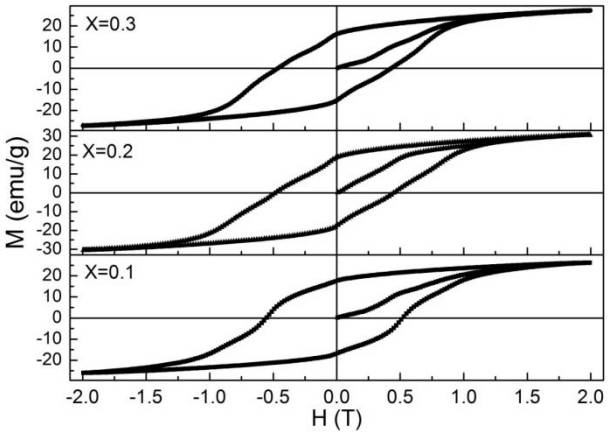

Figure 4. Magnetization of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons (annealed) at room temperature.

The as-annealed $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons demonstrate a pure Laves phase. The magnetic properties of the as-annealed $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbon powder were then investigated. The magnetization dependence on the external applied magnetic field is shown in figure 4. All samples are soft magnetic materials which easily reach saturation under the external applied magnetic field. The saturated magnetization and the remnant magnetization show a maximum at x=0.2, but the intrinsic coercivity decreases with increasing Mn content. Table 1 lists the values of the saturated magnetization M_s, the remnant magnetization M_r, the intrinsic coercivity H_{ci} and the Curie temperature for the $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons. As summarized in table 1, The Curie temperature of the as-annealed $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbonpowder decreases from 366°C (x=0.1) to 328°C (x=0.3) as the Mn content increases. It is well-known that for R-T compounds (T representing a transition metal element), the Curie temperature is primarily determined by T-T exchange interaction. Thus, the decline of the Curie temperature may be due to the substitution of Mn for Fe in $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons, which disturbs the 3d-3d exchange interaction [13].

Table 1. Saturated magnetization M_s, remnant magnetization M_r, intrinsic coercivity H_{ci} and Curie temperature T_c for $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons (annealed).

x	M_s (Am^2/kg)	M_r (Am^2/kg)	H_{ci} (A/m)	T_c (°C)
0.1	26.099	17.219	5.363	366
0.2	30.553	18.141	4.664	357
0.3	27.316	15.658	4.458	328

The dependence of magnetostriction $\Delta\lambda = \lambda_{//} - \lambda_{\perp}$ on the external applied magnetic field is shown in figure 5. The as-annealed $Pr_{0.3}Tb_{0.7}Fe_{1.9}Mn_x$ ribbons were milled into powder and mixed with a phenol binder, with a weight ratio of powders to binder of 100:6. The composites were compacted at a pressure of 80MPa, and then solidified at room temperature in a free state. The magnetostriction of all samples was far from saturation at the external applied magnetic field of 11 kOe. With the Mn

content increasing from 0.1 to 0.3, the magnetostriction at the largest magnetic field decrease from 400 ppm (x=0.1) to 300 ppm (x=0.3). This interesting magnetostrictive behavior may be ascribed to the complex coupling between R (a rare earth element) and Mn. Because the Mn-Mn interatomic spacing in the R-Fe-Mn alloy is just below the critical value d_c (0.266 nm), the itinerant 3d moment of the Mn atom becomes unstable [14]. Therefore, the substitution of Fe by Mn demonstrates a complex effect on the magnetostrictive behavior of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons.

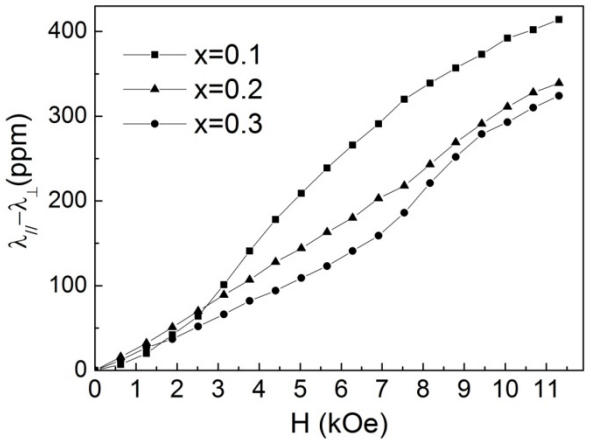

Figure 5. Magnetostriction of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons (annealed) at room temperature.

4. Conclusions

In this work, $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons with a Laves phase structure were fabricated. The melt-spin technique proved to be a good method for the synthesis of alloys with high Pr content in the Laves phase. The substitution of Mn for Fe has a major effect on the magnetic properties and magnetostriction of $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons. The saturated magnetization and the remnant magnetization demonstrate maximum values at x=0.2, but the intrinsic coercivity and Curie temperature decrease with increasing Mn content. The magnetostrictionof $Pr_{0.3}Tb_{0.7}Fe_{1.9-x}Mn_x$ ribbons at a magnetic field of 11 kOe decrease with increasing Mn content, due to the complex coupling between R (rare earth elements) and Mn.

Acknowledgments

This work has been supported by the National Science Foundation of China (grant nos. 11004055 and 50901028), the Fundamental Research Funds for the Central Universities (grant nos. 12MS142, 13ZD23, 2014MS162 and 2014MS168), the Beijing-funded Joint Development Program of the Central Universities in Beijing and the Program for New Century Excellent Talents in University (grant no. NCET-12-0844).

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