High Pr-content $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ magnetostrictive alloys

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High Pr-content $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ magnetostrictive alloys $(0.05 \leqslant x \leqslant 0.15)$ with a single cubic Laves phase were synthesized by arc-melting and subsequent annealing. The Curie temperature, T_c, and the lattice parameter, a, of the Laves phase in the alloys increase with increasing the boron content up to $x=0.10$, which is ascribed to the preferential occupation of boron in the interstitial sites of the Laves phase. The addition of a small amount of boron to the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93}$ alloy reduces the magnetocrystalline anisotropy constant K_1 and improves the magnetostriction $\lambda_a=\lambda_{\parallel}-\lambda_{\perp}$ at relatively low magnetic fields at room temperature. The composition dependence of the ratio λ_a/K_1 for $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys reaches a maximum value at $x=0.10$, suggesting that the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.83}B_{0.1}$ alloy should be a good candidate material for magnetostriction applications. © *2005 American Institute of Physics*. [DOI: 10.1063/1.2034088]

The C15 cubic Laves phase compounds $(R,R')Fe_2$ ($R,R' \equiv$ rare earths), such as $Tb_{0.27}Dy_{0.73}Fe_2$ (Terfenol-D), have been widely applied as magnetostrictive materials in acoustic transducers, sensors, actuators, etc.[1,2] The single-ion model indicated that the giant magnetostriction of the pseudobinary system was mainly due to the R^{3+} ions, which was originated from the large spin–orbit interaction between the electron spin and spatially anisotropic $4f$ charge, and predicted that at 0 K a larger magnetostriction should be generated by a Pr^{3+} ion than a Tb^{3+} or Dy^{3+} ion.[1,2] Furthermore, a magnetostrictive alloy with high Pr-content should have a good practical prospect because Pr is much cheaper than Tb or Dy. Thus, much attention has been focused on the synthesis and the study of the magnetostrictive properties of $(R,Pr)Fe_2$ compounds.[3–5] However, it is very difficult to synthesize a single phase of Pr-containing magnetostrictive alloy with Laves structure if the Pr content exceeds 25 at. % in the rare-earth sublattice, due to the large radius of Pr^{3+}. It was found that the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.9}$ alloy, with a large spontaneous magnetostriction λ_{111} as high as 2370 ppm, could be a potential candidate for use as a magnetostrictive material.[6] Nevertheless, this alloy contained some amount of $(Tb,Pr)(Fe,Co)_3$ phase with a rhombohedral $PuNi_3$-type structure.[6] It was reported that a small amount of boron can effectively inhibit the appearance of the $PuNi_3$-type phase and help to form the Laves phase with high Pr content.[7–9] In this Letter, structural,magnetic, and magnetostrictive properties of$(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys are reported. High Pr-content $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ $(0.05 \leqslant x \leqslant 0.15)$ alloys with a single Laves phase are synthesized successfully, due to the introduction of boron and the proper annealing process, thanks to the improved Fe-Pr phase diagram.[10] A high Curie temperature, a low magnetocrystalline anisotropy, and a large magnetostriction at relatively low magnetic fields are achieved for $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.83}B_{0.1}$ alloy, which should be a good candidate for practical magnetostrictive material.

All polycrystalline samples of $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys with $x=0$, 0.05, 0.10, 0.15, 0.20, 0.30, and 0.40 were prepared by arc melting the appropriate constituent metals in a high-purity argon atmosphere. The purities of the constituents are 99.9% for Tb, Pr, and B, and 99.8% for Fe and Co. The ingots were homogenized at 700 °C for seven days in a high-purity argon atmosphere, which was carefully chosen based upon the improved Fe-Pr phase diagram.[10] Temperature dependences of AC initial susceptibility χ_{AC} were measured at H=2 Oe to determine Curie temperatures T_c of the compounds in the alloys. X-ray diffraction (XRD) data were recorded at room temperature with Cu K_α radiation in a Riguku D/max-2500pc diffractrometer with a graphite crystal monochromator. High-precision XRD step scanning was performed for the (440) line of the Laves phase and then the effect of the $K_{\alpha 2}$ radiation was removed with a standard method, in order to investigate its spontaneous magnetostriction coefficient λ_{111}. Magnetization curves at room temperature were measured by a quantum design superconducting quantum interference device (SQUID) magnetometer at fields up to 50 kOe. The magnetostriction at room temperature was measured either parallel or perpendicular to the applied field using a standard strain gauge technique.

XRD patterns of homogenized $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys are shown in Fig. 1. It is seen that the matrix of $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93}$ alloy consists predominantly of the cubic Laves phase with $MgCu_2$-type structure, coexisting with a small amount of impurity phase with $PuNi_3$-type structure. Homogenized B-containing alloys, up to $x=0.15$, are almost single Laves phase. As the boron content further increases, some weak peaks emerge in the XRD patterns, which belong to the excessive rare earth phase. No trace of the noncubic $PuNi_3$-type phase is found in all the boron-containing alloys. This result shows that a small amount of boron can effectively inhibit the appearance of the $PuNi_3$-type phase and that boron is helpful for the formation

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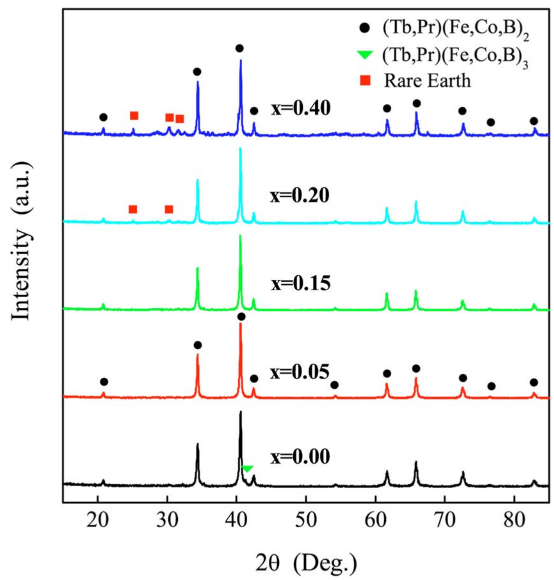

FIG. 1. (Color online) X-ray diffraction patterns of the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys.

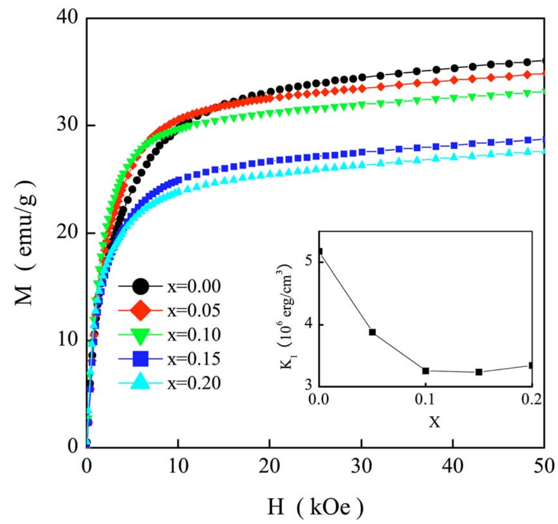

FIG. 3. (Color online) Magnetization curves and the magnetocrystalline anisotropy constant K_1 at room temperature of the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys.

of the (Tb,Pr)Fe_2 Laves phase, in consistent with the previous report.[8]

The concentration dependence of the lattice parameter a of the Laves phases in $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys is shown in Fig. 2(a). The lattice parameter increases with increasing the boron concentration up to $x=0.10$ and then decreases in the range of $0.15 \leqslant x \leqslant 0.40$. This suggests that the boron atoms can occupy either the substitutional or interstitial site. Because of its small size, the boron occupies preferentially the interstitial sites until its concentration reaches the solubility limit $x=0.10$ (about 3.41 at % in this system). Above this value, the boron atom starts to occupy the Fe/Co sites in the lattice, which leads to the lattice contraction.

The Curie temperature of all the alloys was detected from the measurements of AC initial susceptibility χ_{AC}. Two peaks were observed at 418 and 621 K, in the $\chi_{AC}-T$ curves for the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93}$ alloy. The former corresponds to the Curie temperature of the Laves phase, while the latter is for the $PuNi_3$-type phase. As the boron is introduced into the lattice, only does one peak appear in the χ_{AC}-T curve, which is attributed to the Curie temperature of the Laves phase. It is in consistence with the XRD result that the single phase with the Laves structure forms, free of the $PuNi_3$-type phase. The concentration dependence of the Curie temperature T_c for the Laves phases in $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys is represented in Fig. 2(b). The Curie temperature T_c increases with increasing the boron concentration in the alloys when $0 \leqslant x \leqslant 0.10$, indicating that the exchange interaction in the Laves phase enhances since the boron atoms occupy the interstitial sites.[8,11] Then the Curie temperature T_c decreases when $0.15 \leqslant x \leqslant 0.40$, because of the weakening of the exchange interaction in the Laves phase when the boron atoms substitute the Fe/Co atoms.

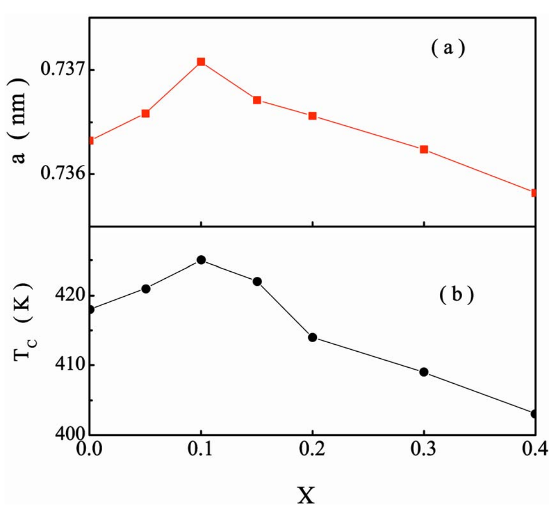

FIG. 2. (Color online) Concentration dependence of (a) lattice parameter a and (b) Curie temperature T_c of the Laves phases in the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys.

The magnetic field dependence of the magnetization at room temperature for the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ $(0 \leqslant x \leqslant 0.20)$ alloys is shown in Fig. 3. The magnetization at the maximum available magnetic field of 50 kOe decreases with increasing the boron content x. It is well-known that in the rare-earth–transition-metal compounds there are parallel (or antiparallel) alignments between the magnetic moments of praseodymium (or terbium) and iron/cobalt atoms. The magnetic moment μ of the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ Laves phase can be described as

$$\mu = 0.8\mu_{Pr} - 0.2\mu_{Tb} + (1.93 - x)\mu_{Fe/Co}. \quad (1)$$

From this formula it would be not difficult to understand why the magnetization decreases with increasing x, if the influence of the small amount of impurities phase on the magnetization were neglected.

The magnetocrystalline anisotropy constant K_1 of the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ Laves phase was determined by simulating the M-H curves using the approximate law of the saturation as follows:[12]

$$M = M_s\left(1 - \frac{a}{H} - \frac{b}{H^2}\right) + \chi_p \cdot H, \quad (2)$$

and the relation[12]

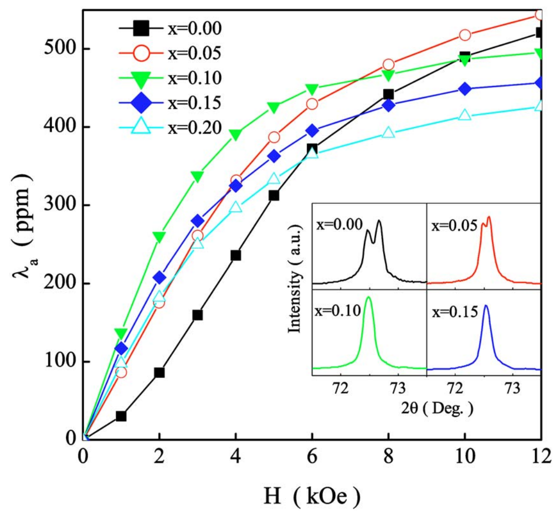

FIG. 4. (Color online) Magnetic field dependence of magnetostriction λa ($=\lambda\| - \lambda\perp$) forthe $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys. The insets show the step-scanned (440) XRD line profiles of the Laves phase of the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys.

$$b = \frac{8}{105}\frac{K_1^2}{\mu_0^2 M_s^2}, \tag{3}$$

where M_s is the saturation magnetization, a and b are constants, χ_p is the susceptibility of the paramagnetic (parallel) magnetization process. μ_0 is the permeability of free space. The dependence of the anisotropy constant K_1 on the nominal boron content x for the Laves phase is shown in the inset of Fig. 3. It can be seen that the anisotropy constant K_1 decreases when x is increased from 0 to 0.15. As the boron content is further increased, the anisotropy constant K_1 increases slightly, which reveals that in the high boron range, the influence of the large amount of the impurities cannot be neglected.

The step-scanned profiles for the (440) XRD line of the Laves phases in $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys with $0 \leqslant x \leqslant 0.15$ are shown as insets in Fig. 4. The split (440) lines are clearly observed for the alloys with $x=0$ and 0.05, and become heavily overlap for the alloys with $x=0.10$ and 0.15. The spontaneous magnetostriction constant λ_{111} was calculated from the distance between the double splitted (440) line.[8,13] λ_{111} decreases from 2370 ppm for $x=0$ to a small value for $x=0.15$, which is too small to be distinguished by XRD method. The magnetic field dependence of the linear anisotropic magnetostriction $\lambda_a = \lambda_\| - \lambda_\perp$ of the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys is shown in Fig. 4. The magnetostriction λ_a for $x=0.05$ is larger than the free B-containing alloy, which can be accounted for by the suppression of the $PuNi_3$-type phase and the decrease of the magnetocrystalline anisotropy by the boron introduction. λ_a at the maximum available magnetic field decreases with increasing x when $0.05 \leqslant x \leqslant 0.20$, due to the decrease of λ_{111}. A large λ_a can be observed for $x=0.10$ at relatively low magnetic fields, indicating that this alloy has a good magnetostrictive property for practical application. It is further proved by the composition dependence of the ratio λ_a/K_1, plotted in Fig. 5, where a peak exhibits at $x=0.10$, at different magnetic fields from 1 to 6 kOe.

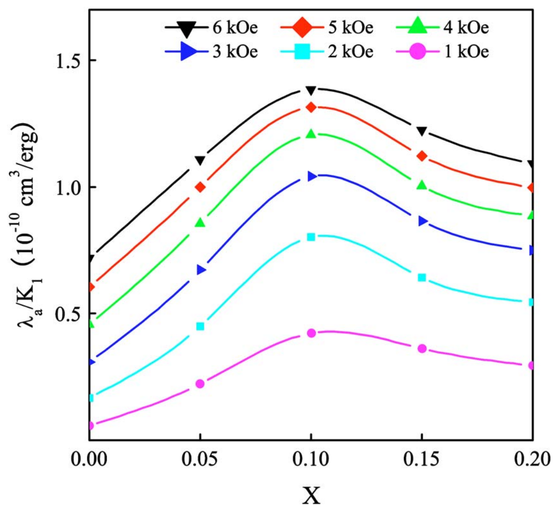

FIG. 5. (Color online) Composition dependence of the ratio λ_a/K_1 for the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys.

In conclusion, the introduction of the small amount of boron to $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93}$ alloys is helpful for the formation of the cubic Laves phase. High Pr-content $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ $(0.05 \leqslant x \leqslant 0.15)$ alloys with a single Laves phase have been synthesized. The addition of the small amount of boron enhances the exchange interaction as well as the Curie temperature T_c of the Laves phase. K_1 and λ_{111} of the Laves phase in the $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.93-x}B_x$ alloys decrease with increasing the boron content. The $(Tb_{0.2}Pr_{0.8})(Fe_{0.4}Co_{0.6})_{1.83}B_{0.1}$ alloy with a single Laves phase has a large λ_a at relatively low magnetic field and a large λ_a/K_1, which should be a potential candidate for use as a magnetostrictive material.

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