Structure, magnetic and magnetostrictive properties in high-pressure synthesized $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ alloys

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Polycrystalline magnetostrictive alloys $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ (x=0, 0.05, 0.1, 0.15 and 0.2) were synthesized by high-pressure annealing. Measurements of crystal structure, Curie temperature, magnetization and magnetostriction were made on these alloys. X-ray diffraction results show that the alloys exhibit single cubic Laves phase with $MgCu_2$-type structure. The lattice parameter increases with increasing Mn concentration while the Curie temperature decreases. The saturation magnetization decreases with increasing Mn, which could be understood in the frame of the rigid band model. The saturation magnetostriction decreases with increasing Mn concentration while the magnetostriction of the sample with x=0.1 peaks at low magnetic field, which may make $Tb_{0.1}Nd_{0.9}(Fe_{0.9}Mn_{0.1})_{1.9}$ a promising candidate for magnetostrictive application.

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1. Introduction

The C15 cubic Laves phases RFe_2 (R=rare earths) alloys attracted much attention owing to their giant room-temperature magnetostriction. Over the past three decades, many theoretical and experimental investigations have been reported on the binary RFe_2 compounds with large magnetostrictive constants. Terfenol-D ($Tb_{0.27}Dy_{0.73}Fe_2$), as a typical magnetostrictive material, has been widely used in sonar transducer, sensors and actuators etc [1-3]. However, the raw materials Tb and Dy of Terfenol-D are expensive. It is interesting to study magnetostrictive alloys based on cheap light rare earth, such as Sm, Pr or Nd [4-9]. According to the single-ion model, $NdFe_2$ possesses a large magnetostriction 2000 ppm at 0 K [10]. However, only a few investigations about high-Nd content magnetostrictive alloys were reported because RFe_2 cubic Laves phase can only be synthesized under high pressure [11]. As we know, the C15 Laves phases RT_2 (T=transition metals) alloys are interesting system with the striking character of localized 4*f* electrons and itinerant 3*d* electrons [12]. Much attention has been paid to study the magnetic properties of RFe_2 alloys by substituting Fe with other 3*d* transition metals [13-20]. Although the 3*d* atoms have a very small anisotropy due to the quenching of their orbital angular moments, several groups reported that the Mn substitution for Fe can improve the low-field magnetostriction in RFe_2 compounds [16,18]. Recently, Shi *et al.* reported that $Tb_xNd_{1-x}Fe_{1.9}$ cubic Laves alloys could be synthesized by a method of high-pressure annealing and the anisotropy compensation was realized in $Tb_{0.1}Nd_{0.9}Fe_{1.9}$ compound [22]. In the present work, polycrystalline $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ (x=0, 0.05, 0.1, 0.15 and 0.2) alloys with almost single Laves phase were prepared by this method and the effects of substitution of Mn for Fe on the magnetic properties of the alloys were investigated.

2. Experiment

Ingots with stoichiometric composition of $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ (x=0, 0.05,0.1, 0.15 and 0.2) were prepared by melting the constituent metals in an arc furnace under a high-purity argon atmosphere. The as-cast ingots were then high-pressure annealed at 6 GPa and 1173 K for 30 min. The details of the high-pressure annealing apparatus were described before [23]. Conventional x-ray diffraction (XRD) analysis was carried out using Cu kα radiation with a Rigaku D/Max-gA diffractometer. The XRD data were analyzed using the Jade 5.0 XRD analytical software (Materials Data, Inc., Livemore, CA). The Curie temperature T_C was detected by a thermogravimetry analyzer with a vertical gradient magnetic field under the samples. The magnetization of the compounds was measured using a superconducting quantum interference device magnetometer at fields up to 53 kOe. The shape of the sample for magnetostriction measurement was mainly disk-like with a diameter of 10 mm and a height of 2 mm. The linear magnetostriction was measured using standard strain-gauge technique in directions parallel ($\lambda_{\parallel}$) or perpendicular ($\lambda_{\perp}$) to applied magnetic field at room temperature.

3. Results and discussion

The room-temperature powder XRD patterns for $Tb_{0.1}Nd_{0.9}$ $(Fe_{1-x}Mn_x)_{1.9}$ alloys are shown in Fig. 1. It can be found that all the alloys exhibit almost single cubic Laves phase with $MgCu_2$-type structure. However, the cubic Laves phase could not be obtained in the samples using a traditional annealing method without high-pressure. Previous study shows that boron substitution can enhance the Nd content in $Tb_xNd_{1-x}(Fe_{0.9}B_{0.1})_2$ Laves compound [5]. But when the Nd content exceeds 55 at.\% in the rare earth sublattice, the non-cubic phase appears. It is generally believed that the atom radius plays an important role in the formation of RFe_2 cubic Laves alloys and the ideal radius ratio between R and Fe for a cubic Laves phase is $\sqrt{3/2}$ [21]. Owing to the large radius of Nd^{3+}, the cubic Laves phase containing high-Nd content could not be readily obtained under normal pressure [22,24]. So, the method of high-pressure annealing is an effective way that could overcome the difficulties and makes the synthesis of cubic Laves phase possible.

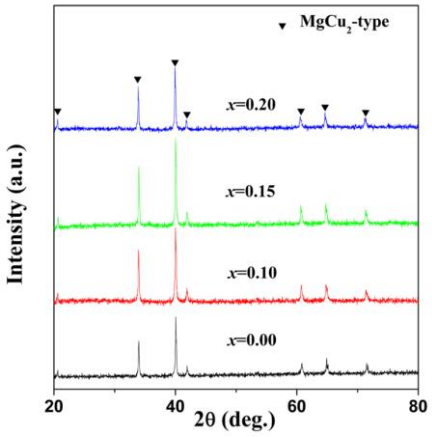

Fig. 1. The room-temperature powder XRD patterns of $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ alloys.

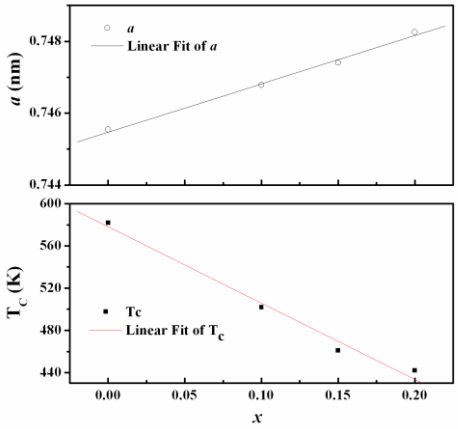

Fig. 2. (a) The lattice parameter a and (b) the Curie temperature T_C of $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ cubic Laves alloys as functions of Mn concentration.

The concentration dependence of lattice parameter (*a*) of the cubic Laves phase in $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ alloys derived from XRD data is shown in Fig. 2(a). The lattice parameter increases slowly from 0.746 nm for $Tb_{0.1}Nd_{0.9}Fe_{1.9}$ to 0.748 nm for $Tb_{0.1}Nd_{0.9}$ $(Fe_{0.8}Mn_{0.2})_{1.9}$, which suggests that Mn with bigger radius takes up the site of Fe in the sublattice.

The Curie temperature (T_C) of the cubic Laves alloys as a function of Mn concentration is shown in Fig. 2(b). We can see that the Curie temperature almost linearly decreases with increasing Mn concentration from 582 K for $Tb_{0.1}Nd_{0.9}Fe_{1.9}$ to 442 K for $Tb_{0.1}Nd_{0.9}(Fe_{0.8}Mn_{0.2})_{1.9}$. The magnetic interaction in the R-T compounds contains three different types: the R-R interactions, the R-T interactions and the T-T interactions [12]. As we know, the T-T interaction is the strongest one due to the direct 3*d*-3*d* exchange while the R-R interaction is the weakest one because of the indirect interaction between the highly localized 4*f* moments of the R. In the present work, the 3*d*-3*d* exchange interactions should become weaker when Fe was partially substituted by Mn, so the Curie temperature decreases with increasing Mn content in the alloys.

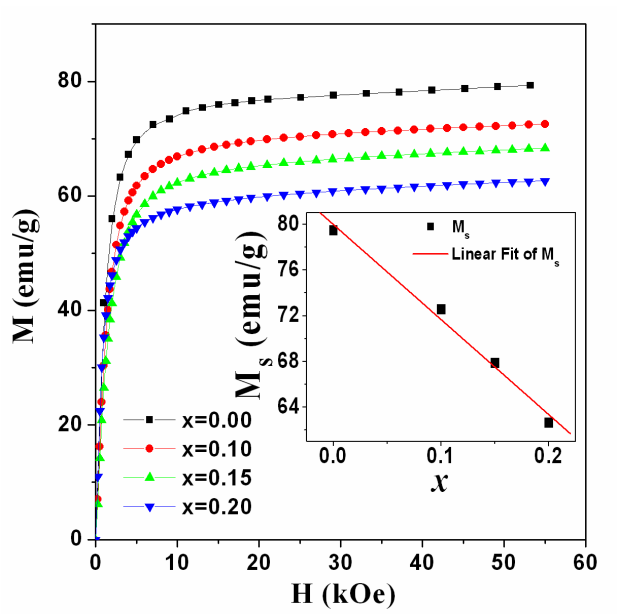

Fig. 3. Magnetization curves for $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ at 300 K. The inset shows the saturation magnetization (M_s) as a function of Mn concentration.

Magnetic field dependence of magnetization (M-H) at room temperature for $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ alloys is shown in Fig. 3. It can be seen that the magnetization of each sample is close to saturation at the maximum applied field of 53 kOe. The saturation magnetization (M_s) derived from M-H curves is shown in the inset of Fig. 3. One can see that the saturation magnetization M_s linearly decreases as *x* increases. This could be understood on the basis of the

rigid-band model [25]. The 3*d* electrons of Mn and Fe share a common 3*d* band in $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ system. With increasing the concentration of Mn, the electron concentration will decrease and the 3*d* band gradually becomes depleted. It can be assumed that the spin-up and spin-down bands of the 3*d* electrons are unsaturated in $Tb_{0.1}Nd_{0.9}Fe_{1.9}$ alloys. It is known that the Fermi level of the spin-down band resides in a region of a minimum in the density of states. Decreasing the electron concentration with increasing Mn content will deplete the spin-up band and decrease the net 3*d* magnetic moment. Meanwhile, the net 3*d* moment lies parallel to the resultant 4*f* magnetic moment of the (Tb,Nd) sublattice. Therefore, the total magnetic moment in the system will decrease with the substitution of Mn.

The room-temperature magnetostriction $\lambda_{\parallel}$-$\lambda_{\perp}$ for $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ alloys is shown in Fig. 4. It can be seen that the magnetostriction of the sample with x=0.1 peaks at low field, which indicates that $Tb_{0.1}Nd_{0.9}(Fe_{0.9}Mn_{0.1})_{1.9}$ shows a relatively good low-field magnetostrictive property among the present studied compounds. Similar behaviors could also be found in Mn-doped $Dy_{0.6}Tb_{0.3}Pr_{0.1}Fe_2$ [16] or $Tb_{0.28}Dy_{0.57}Ho_{0.15}Fe_2$ alloys [18]. The improvement of the low-field magnetostriction may be associated with the decreased magnetic anisotropy with a small amount of Mn substitution for Fe. We can also note that the magnetostriction of the samples in the maximum available magnetic field decreases with increasing Mn content. According to the single-ion model [26]: the saturation magnetostriction is in proportional to M_{SR}^3, where M_{SR} is the saturation magnetization of the rare-earth sublattice. It is reasonable to assume that the magnetic moment of the rare-earth decreases with decreasing Curie temperature since the long range exchange is determined by 3*d*-3*d* exchange in the RT_2 alloys [15,17]. Thus, the decrease of the saturation magnetostriction with increasing Mn can be understood.

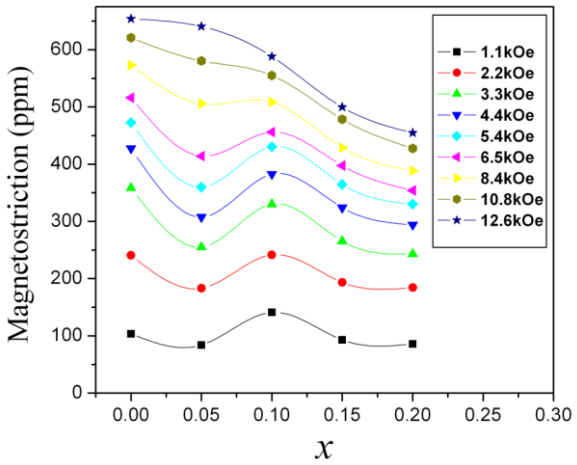

Fig. 4. The room-temperature magnetostriction $\lambda_{||}$-$\lambda_{\perp}$ for $Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ alloys.

4. Conclusion

$Tb_{0.1}Nd_{0.9}(Fe_{1-x}Mn_x)_{1.9}$ alloys which could not be synthesized under normal atmosphere were synthesized by high-pressure annealing. The effects of Mn substitution on the magnetic properties of $Tb_{0.1}Nd_{0.9}Fe_{1.9}$ have been investigated. Both Curie temperature and the saturation magnetization decrease with increasing the Mn concentration. The decrease of the saturation magnetostriction with increasing Mn can be understood on the basis of single-ion model. $Tb_{0.1}Nd_{0.9}(Fe_{0.9}Mn_{0.1})_{1.9}$ shows larger low-field magnetostriction than the sample free of Mn, which may makes it a promising candidate for magnetostrictive application.

Acknowledgements

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