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Ferromagnetic and magnetostrictive properties of $Tb_{0.3}Dy_{0.7}(Co_{1-x}Fe_x)_2$ alloys

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Morphotropic phase boundary (MPB) have aroused wide interests due to the exotic properties exhibited by the compositions around MPB [$Tb_{1-x}Dy_xCo_2$, PRL 104, 197201 (2010); $Tb_{1-x}Dy_xFe_2$, PRL 111, 017203 (2013)]. By combining the two MPB compositions $Tb_{0.3}Dy_{0.7}Co_2$ and $Tb_{0.3}Dy_{0.7}Fe_2$, we designed a pseudo-binary system $Tb_{0.3}Dy_{0.7}(Co_{1-x}Fe_x)_2$. The phase diagram is determined from the temperature spectra of magnetic susceptibility and magnetization. A Griffiths-like phase appears above the Curie temperature and gradually vanishes as the Fe content increases to $x = 0.8$. Magnetic hysteresis and magnetoelastic behavior are also investigated. Compared with the Terfenol-D composition $x = 1.0$, $x = 0.8$ exhibits higher Curie temperature (707 K) and comparable magnetostriction (818 ppm), which may be used in the sensors or transducers at high temperature. © 2019 The Japan Society of Applied Physics

The physical basis of ferroic functional materials is the phase transition that involves the symmetry breaking of ferroic order parameters, e.g., the spontaneous polarization, spontaneous magnetization, and lattice strain.[1)] Thus, tuning the material properties via tailoring phase transitions is one effective method to design ferroic functional materials, which has been well exemplified by the morphotropic phase boundary (MPB) that was first discovered in ferroelectrics.[2)] The ferroelectric MPB refers to a multiple-phase-point derived exotic phase regime, and can be obtained from a specific phase diagram: the two end-member compounds possess a common parent phase and different ferroic phases.[3,4)] Many high-performance piezoelectric materials have been designed following the MPB idea.[2,5–10)]

In recent years, MPB phenomena were also discovered in magnetostrictive alloys ($Tb_{1-x}Dy_xCo_2$, $Tb_{1-x}Dy_xFe_2$, $Tb_{1-x}Gd_xCo_2$, $Tb_{1-x}Gd_xFe_2$),[11–15)] which are widely used in sensors, transducers and actuators due to their capability of energy conversion between mechanical energy and magnetic energy.[16,17)] So far, the previous research mainly focuses on how to construct an MPB-involved system with different end-member compounds, but rare attention is paid to the new material systems formed by MPB compositions, i.e., the system $(1-x)Tb_{0.3}Dy_{0.7}Co_2$-$xTb_{0.3}Dy_{0.7}Fe_2$, with the end-members being the MPB compositions of $Tb_{1-x}Dy_xCo_2$ and $Tb_{1-x}Dy_xFe_2$, respectively. Both $Tb_{0.3}Dy_{0.7}Co_2$ and $Tb_{0.3}Dy_{0.7}Fe_2$ exhibit excellent magnetostrictive properties, and undergo paramagnetic to ferromagnetic (M_S//[111]) and then to ferromagnetic (M_S//[001]) transitions.[11,12,18)] Therefore, it is interesting to investigate the ferromagnetic and magnetoelastic properties of the pseudo-binary system $(1-x)Tb_{0.3}Dy_{0.7}Co_2$-$xTb_{0.3}Dy_{0.7}Fe_2$ system [abbreviated as $Tb_{0.3}Dy_{0.7}(Co_{1-x}Fe_x)_2$ hereinafter]. In this work, we report the phase diagram of the $Tb_{0.3}Dy_{0.7}(Co_{1-x}Fe_x)_2$ system, and the temperature spectra of magnetic susceptibility and magnetization, as well as the magnetization (M)–magnetic field (H) hysteresis behavior and magnetostriction, hoping to provide guidance for designing high-performance magnetostrictive materials.

The polycrystalline $Tb_{0.3}Dy_{0.7}(Co_{1-x}Fe_x)_2$ alloy samples were prepared by arc melting method with the raw materials of Tb (99.9%), Dy (99.9%), Co (99.9%) and Fe (99.9%) in argon atmosphere, and the compositions of the samples in this work are nominal stoichiometric compositions. In order to guarantee the homogeneity of the samples, the magnetic stirring was employed during the arc melting process and all ingots were melted six times. The arc-melted samples are directly used for the present study and without no further treatment, thus remaining polycrystalline state. The temperature spectrum of magnetic susceptibility (2–400 K) was measured using the superconducting quantum interference device (SQUID-MPMS3, Quantum Design) with the applied magnetic field of 50 Oe, the frequency of 133 Hz and the temperature rate of 3 K min^{-1}. The magnetization (M) versus magnetic field (H) hysteresis loops at room temperature and temperature spectrum of magnetization (300–800 K) were measured using vibrating sample magnetometer (Lakeshore), and the latter one was measured with the applied magnetic field of 300 Oe and the temperature rate of 3 K min^{-1}. The magnetostriction was measured with strain gauges.

The ferromagnetic transitions are usually determined from the temperature spectra of magnetic susceptibility and magnetization, as shown in Fig. 1. Figures 1(a1) –1(a8) exhibit the magnetic susceptibility versus temperature curves of some selected compositions ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0). For the composition $x = 0$ ($Tb_{0.3}Dy_{0.7}Co_2$), it undergoes two phase transitions from 2 to 400 K [Fig. 1(a1)]: the one around 167 K is the Curie transition from paramagnetic to ferromagnetic phase (M_S//[111]), and the other one around 116 K corresponds to the transition from the ferromagnetic phase (M_S//[111]) to another ferromagnetic phase (M_S//[001]), which has been identified as the "morphotropic phase transition" in the $Tb_{1-x}Dy_xCo_2$ system.[11)] The temperatures for the above two transitions are denoted as T_C and T_M, respectively. While the Fe content increases to $x = 0.1$, both T_C and T_M increase [Fig. 1(a2)]; while the Fe content increases to $x = 0.2$, T_C is beyond the measurement temperature range, and T_M increases up to 212 K; from $x = 0.2$ to $x = 1.0$, T_M gradually increases from 212 to 320 K at $x = 0.6$, and then slowly decreases to 245 K at $x = 1.0$.

Figures 1(b1)–1(b8) show the magnetization versus temperature curves of the selected compositions ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0) for the temperature range from 300 to 800 K, which is seldomly studied for the rare earth alloys. For $x = 0$ [Fig. 1(b1)], an unknown phase transition appears, which is observed above the Curie transition temperature that has been

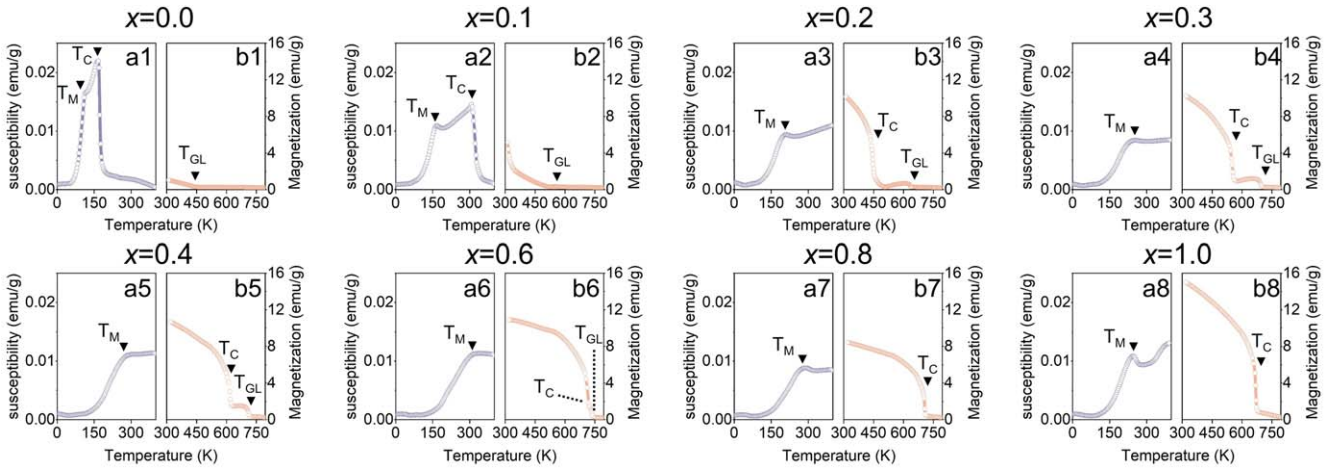

Fig. 1. (Color online) The temperature spectra of magnetic susceptibility from 2 to 400 K (a), and magnetization from 300 to 800 K (b) of the selected compositions ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0). T_M, T_C and T_{GL} denote the transition temperatures of Curie transition, morphotropic phase transition and Griffiths-like transition, respectively.

detected from the temperature spectrum of magnetic susceptibility [Fig. 1(a1)]. This transition has not been reported for Laves-phase rare earth alloys RT_2 (R = rare earth, T = Fe, Co, Mn, Ni) and is quite like the previously reported "Griffiths phase transition".[19–21] For the time being, because of the lack of other experimental evidence to meet the criteria for "Griffiths phase", this transition is called "Griffiths-like transition" in the present study and the transition temperature is denoted by T_{GL}. With the increase of Fe content, the temperature gap between T_C and T_{GL} gradually decreases, and this transition disappears until x increases up to 0.8 [Figs. 1(b2)–1(b8)].

Based on the transition temperature detected from Fig. 1, the phase diagram of the system $Tb_{0.3}Dy_{0.7}(Co_{1-x}Fe_x)_2$ is determined as illustrated in Fig. 2. There are four phase regimes for this system. The compositions $x = 0$–0.7 undergo three phase transitions: Griffiths-like transition, Curie transition and ferromagnetic (M_S//[111]) to ferromagnetic (M_S//[001]) transition, and the compositions of $x > 0.7$ undergo two phase transitions: Curie transition and ferromagnetic (M_S//[111]) to ferromagnetic (M_S//[001]) transition. One should note that the Griffiths-like phase discovered in the present work has not been reported in Laves-phase RT_2 (R = rare earth, T = Fe, Co, Mn, Ni) alloys.

From the phase diagram, it is clearly seen that the changing trend of T_C coincides well with that of T_M. As the content of Fe increases, the gap between T_C and T_M expands and the gap between T_C and T_{GL} shrinks. It is natural to speculate that the extinction of the Griffiths-like phase is due to the interaction effect between Fe and Co.[22] As for the emergence of the Griffiths-like phase in Laves-phase RT_2 alloys, detailed experimental and theoretical work will be followed to clarify its physical nature.

Figure 3(a) shows the magnetization (M)–magnetic field (H) hysteresis loops, and Fig. 3(b) shows the composition dependence of maximum magnetization M_{max} and coercive field H_C. For the composition $x = 0$, its Curie temperature is below the measurement temperature 300 K, so its M–H loop exhibits a liner relationship with the coercive field H_C equals to zero. With the increase of Fe content, T_C increases to above 300 K, and the samples are in ferromagnetic phase and exhibit hysteretic behaviors in M–H loops. In brief, as the content of Fe increases, both M_{max} and H_C increase.

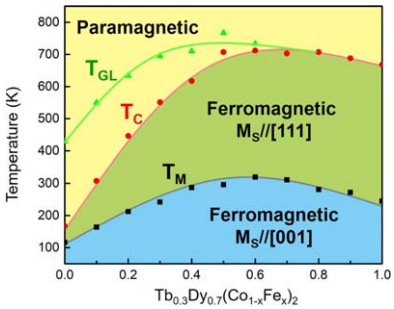

Fig. 2. (Color online) The phase diagram of $Tb_{0.3}Dy_{0.7}(Co_{1-x}Fe_x)_2$.

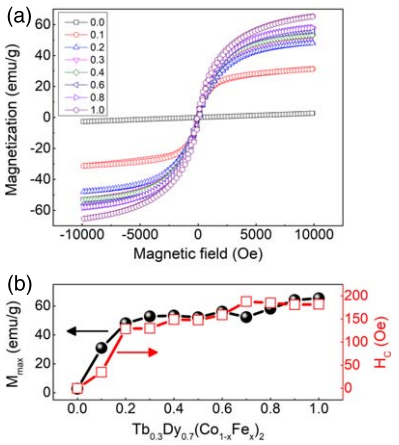

Fig. 3. (Color online) (a) The magnetization (M)–magnetic field (H) hysteresis loops, and (b) the maximum magnetization (M_{max}) and coercive field (H_C) of the selected compositions ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0) at room temperature ~300 K.

Figure 4(a) shows the magnetostriction of the selected compositions ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, 1.0) at room temperature ~300 K. The magnetostriction of the composition $x = 0$ is not zero (144 ppm), implying the existence of nanosized clusters above T_C, which agrees well with that observed for the Griffiths phase.[19–21] By contrast, the ferromagnetic materials at paramagnetic state (without nanosized clusters) usually exhibit zero magnetostriction. The composition dependence of magnetostriction and T_C are depicted in Fig. 4(b). With the increase of Fe content, T_C

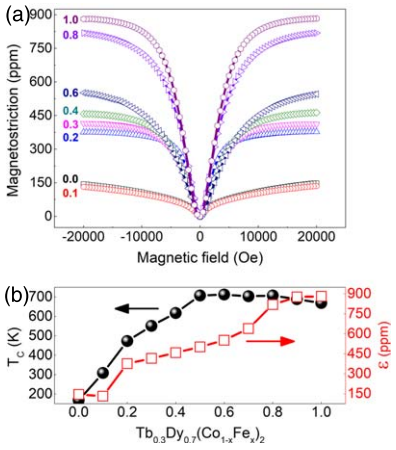

Fig. 4. (Color online) (a) The magnetostriction versus magnetic field curves of $Tb_{0.3}Dy_{0.7}(Co_{1-x}Fe_x)_2$ at room temperature ~300 K; (b) the composition dependence of Curie temperature T_C and saturated magnetostriction ε.

increases up to 712 K at $x = 0.6$, and then decreases slowly to 668 K at $x = 1.0$; the magnetostriction decreases to 131 ppm at $x = 0.1$, and then monotonously increases to 881 ppm at $x = 1.0$. It is interesting to find that, the composition of $x = 0.8$, that is, $Tb_{0.3}Dy_{0.7}Co_{0.4}Fe_{1.6}$, shows large magnetostriction as well as high T_C. Compared with the Terfenol-D composition $Tb_{0.3}Dy_{0.7}Fe_2$ ($x = 1.0$), the composition $Tb_{0.3}Dy_{0.7}Co_{0.4}Fe_{1.6}$ ($x = 0.8$) exhibits higher T_C (from 668 to 707 K) at the cost of magnetostriction of ~60 ppm (from 881 to 818 ppm, under 2 Tesla at room temperature), superior to most magnetostrictive materials.[16] Meanwhile, as mentioned above, $x = 0.8$ corresponds to the composition where the Griffiths-like phase transition vanishes, so it remains an open question that whether the excellent magnetostrictive behavior of $x = 0.8$ is associated with the vanishing of Griffiths-like phase, which will be detailed investigated later.

In conclusion, by combining two ferromagnetic MPB compositions, we designed a new ferromagnetic system $Tb_{0.3}Dy_{0.7}(Co_{1-x}Fe_x)_2$ and determined its phase diagram. Interestingly, except the paramagnetic-ferromagnetic (M_S//[111])-ferromagnetic (M_S//[001]) phase transitions, a new (Griffiths-like) phase transition above T_C is observed for the compositions of $x < 0.8$, and such transition has not been reported for Laves-phase RT_2 (R = rare earth, T = Fe, Co, Mn, Ni) alloys. The vanishing of this transition may originate from the interaction effect between Fe and Co. Moreover, it is discovered that the composition $x = 0.8$ demonstrates excellent magnetostrictive properties (818 ppm) as well as high Curie temperature (707 K), which may be used in the sensors or transducers at high temperature.

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