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# Magneto-structural transition and magnetocaloric effect of $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x = 0-1$) alloys

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ABSTRACT

The magneto-structural transition, magnetic properties and magnetocaloric effect of the $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x = 0-1$) alloys were studied. It was found that both the martensitic and magnetic transition temperatures were insensitive to the addition of Tb element. For the alloys with $x = 0$ and $x = 1$, the martensitic transformation and magnetic transition take place independently. For the alloys in the range of $0.1 \le x \le 0.8$, coincidence of martensitic and magnetic transitions was detected, which resulted in a magneto-structural coupling transition from ferromagnetic martensite to paramagnetic austenite. The saturation magnetization of the martensite phase at 300 K marginally decreased with the addition of Tb element. Considerable and stable magnetic entropy change of approximate 6 $JK^{-1}Kg^{-1}$ was obtained in vicinity of the magneto-structural transitions in the dual-phase alloys with $0.1 \le x \le 0.8$.

## 1. Introduction

Ferromagnetic shape memory alloys (FSMAs), e.g. Ni-Mn-based alloys have attracted notable attention with regard to their valuable potential applications in magnetic refrigeration due to the large magnetocaloric effect (MCE) [1–3]. The MCE in FSMAs generally occurs as a result of lattice entropy change during the first-order martensitic transformation and magnetic entropy change during the second-order Curie transition. When the martensitic transformation temperature $T_M$ approaches to Curie temperature $T_C$, the coupled magneto-structural transition has an opportunity to be generated. This may cause simultaneous changes of both the lattice and magnetic entropies, which contribute to an accumulation of both the entropy at a certain temperature. More importantly, this large entropy change can be driven by an external magnetic field, so that this type of alloys become an excellent candidate for green refrigeration materials [1,4–6]. Up to now, the large magnetocaloric effects have been reported in the vicinity of the magneto-structural transition in Ni-Mn-Ga and other Ni-Mn-based alloys such as Ni-Mn-Sn and Ni-Mn-In Refs. [7–11]. However, it is well known that the Ni-Mn-based alloys are too brittle, and introducing the precipitates to form dual-phase microstructure is an effective way to improve the ductility of Ni-Mn-based alloys [12–16]. Recent investigations have confirmed that such dual-phase microstructure can be achieved by doping the rare-earth (RE) elements such as Tb, Dy, Gd, Nd, Sm and Y, etc [17–24]. The mechanical properties of Ni-Mn-based alloys can be significantly improved by the presence of RE-rich precipitates [17–19,21,24]. Previous studies mainly focused on the alloys with substitution of Ga by RE atoms, in which the martensitic transformation temperatures rapidly increase and the Curie temperatures sharply decrease [11,19–21,24,25]. Moreover, the magnetization of the alloys rapidly decreases with the addition of RE atoms. Take $Ni_{50}Mn_{29}Ga_{21-x}Tb_x$ alloys as an example, the magnetization under the magnetic field of 20 kOe decreases from 63.6 emu/g for alloy without Tb to 20.3 emu/g for Tb-1 at.% alloy, indicating the severe reduction in saturation magnetization in the alloys [19]. Since the magnetic entropy change is directly associated with the change of magnetization during the phase transition, the rare low magnetization under such a strong magnetic field limits the rangeability of magnetization, thus large MCE is difficult to access in the alloys with the substitution of Ga by RE atoms. Very recently, we have reported that dual-phase microstructure is also formed in (Ni,Tb)-Mn-Ga alloys where Ni atoms are partially substituted by Tb atoms [26]. It was found that the mechanical properties also improved together with significantly enhanced shape memory effects. More interestingly, the martensitic transformation temperatures were nearly unchanged with the different concentration of Tb atoms. However, the effects of such substitution on the Curie

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temperature and magnetic properties are still unclear. In this work, the magnetic transition behavior and magnetic properties of $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x = 0-1$) alloys are investigated. It is discovered that not only martensitic transformation temperature but also the Curie temperature remains stable with different Tb concentrations. The coupled magneto-structural transition from ferromagnetic martensite to paramagnetic austenite is observed for the alloys with $0.1 \le x \le 0.8$. Sizeable and stable magnetic entropy change is induced by the magnetic field in the vicinity of the coupled magneto-structural transition.

## 2. Experiments

High-purity elements nickel, manganese, gallium and terbium starting materials were arc-melted four times to prepare the $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x = 0-1$) master alloys. The samples were encapsulated in a quartz tube filled with pure argon, heated treated at 1123 K for 48 h for homogenization, and then quenched into cold water. The martensitic transformation and magnetic transition behaviors for the alloys are detected by temperature dependence of the magnetization (*M-T*) curves with the same temperature rate 10 K/min. The isothermal magnetization curves (*M-H*) and the temperature dependent magnetization (*M-T*) curves were measured on the physical properties measurement system (PPMS) produced by Quantum Design. The magnetic entropy change caused by magnetic field was estimated according to the measured isothermal *M-H* curves.

## 3. Results and discussions

Fig. 1 illustrates the *M-T* curves of $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x = 0-1$) alloys measured under a magnetic field of 500 Oe. According to the different shape characteristics of the *M-T* curves, the alloys are divided into two categories. For $x = 0$ and $x = 1$ alloys, as shown in Fig. 1(a), two independent steps of phase transition can be observed. The first step takes place at temperatures around 350 K–355 K with a significant hysteresis in heating and cooling cycles. According to the DSC analysis in Ref. [26], this abrupt change should be attributed to the first-order thermoelastic martensitic transformation. At higher temperature region of 360 K–365 K, there is a second abrupt change of magnetization with narrow hysteresis, which corresponds to the Curie transition of the austenite phase. For the remnant alloys, characteristics of the *M-T* curves are quite different, as shown in Fig. 1(b). During heating process, the magnetizations gradually increase at around 357 K and then suddenly decrease. Similarly, the former increase and the latter decrease are caused by the martensitic transformation and magnetic transition, respectively. Therefore for $x = 0$ and $x = 1$ alloys, the first-order martensitic transformation and the second-order magnetic transition take place separately. While for the alloys with $x = 0.1–0.8$, the magnetic transition is partially coupled with the reverse martensitic transformation.

Based on the measured martensitic and magnetic transition temperatures, the vertical phase diagram of $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x = 0-1$) alloys are plotted in Fig. 2. The relationship between the Tb concentration and the transition temperatures, including the reverse martensitic transformation start and finish temperatures ($A_s$ and $A_f$) and the Curie temperatures ($T_C$), is systematically described in this diagram. Experientially, the martensitc transformation temperature ($T_M$) is sensitive to the valence electron concentration $e/a$ (valence electrons per atom) of the martensite (or austenite phase) in NiMnGa alloys [27–29]. In this work, the alloys are prepared under as-cast conditions. Because of the quite low cooling rate of solidification during the as-cast process, it is rather difficult for Tb atoms to enter the Ni-Mn-Ga lattices. So the role of Tb is to indirectly change the composition of the ternary Ni-Mn-Ga matrix by forming the Tb-rich precipitates, and therefore to affect the martensitic transformation temperatures. It has been confirmed that the precipitates are Tb-rich phases, and the relative concentrations of Ni, Mn and Ga in the precipitates are different to those in the matrix.

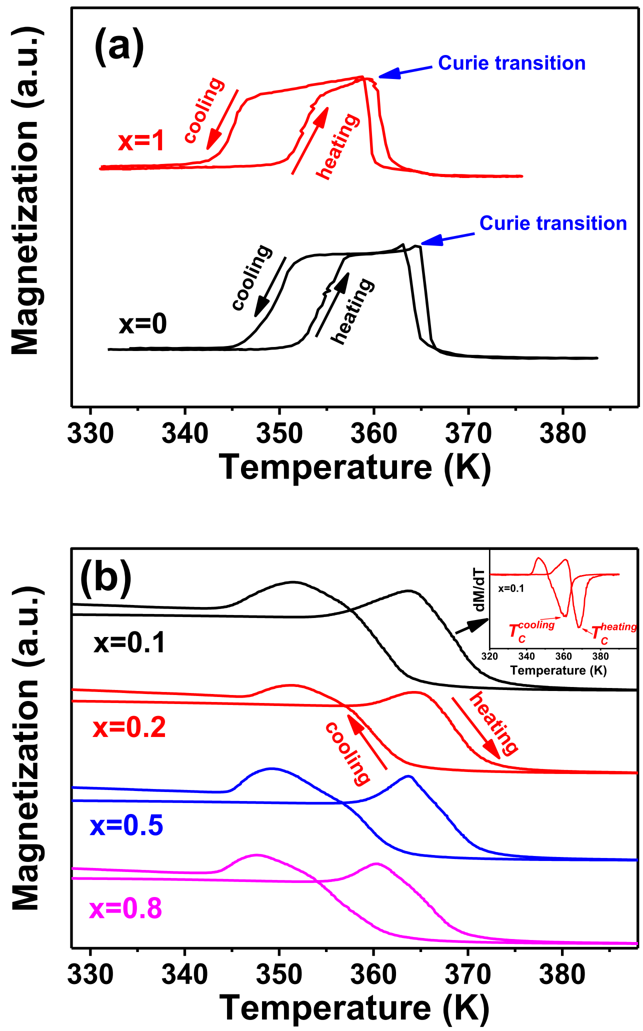


**Fig. 1.** *M-T* curves of $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x = 0-1$) alloys measured under a magnetic field of 500 Oe. (a) $x = 0$ and 1; (b) $x = 0.1–0.8$. The inset in (b) is the differential curve for $x = 0.1$ alloy.

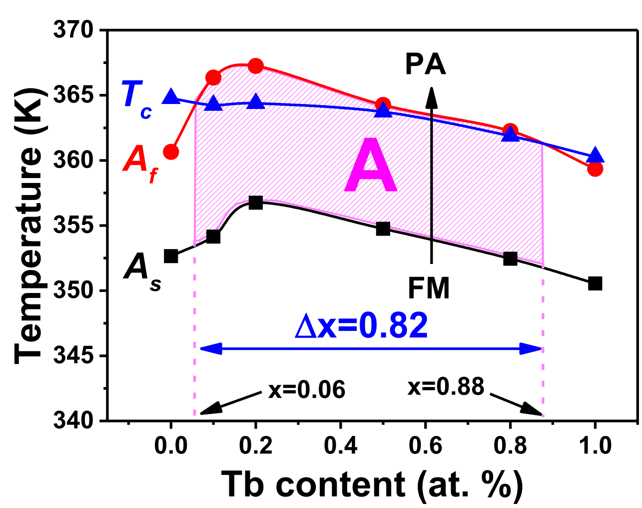


**Fig. 2.** Vertical phase diagram of $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x = 0-1$) alloys. FM and PA in the figure represent ferromagnetic martensite and paramagnetic austenite, respectively.

This results in variations of composition of the ternary Ni-Mn-Ga matrix. With the increase of Tb content, Ni content of the matrix is