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# Effect of coherent nanoprecipitates on martensitic transformation in Tb-doped NiMnGa melt-spun ribbons

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ABSTRACT

Martensitic transformation (MT) behavior is compactly related with multiple effects in shape memory alloys. Here we report a special effect of broadening the MT temperature span with keeping the hysteresis stable via introducing coherent nanoprecipitates. The MT temperature span stabilize in the single-phase region and significantly expands with the formation of coherent nanoprecipitates in the matrix. This effect disappears after the growing up of precipitates during annealing treatment. Microstructural analysis indicates a heterogeneous distortion in matrix lattices with the largest distortion up to 10% in the matrix induced by the perfect coherent relationship between matrix and nanoprecipitates. A qualitative thermodynamic model based on Landau theory is employed to understand the effect on heterogeneous local stress field leads on MT temperature span. This work may promote the understanding of MT behavior in ferromagnetic shape memory alloys.

## 1. Introduction

Ferromagnetic shape memory alloys (FSMAs), such as Ni-Mn-Ga, Ni-Mn-In and Ni-Mn-Sn, have attracted considerable interests as advanced smart materials potentially used in sensors, actuators, refrigerators, information recording, etc [1–7]. Magnetic functionalities including large magnetostrain, giant magnetoresistance and large magnetocaloric effect can be triggered by the magnetic field [8–11]. The shape memory effect, superelasticity and elastocaloric effect, as well known in traditional shape memory alloys, are also available in the FSMAs via the stress [12–15]. All the effects above are compactly related with martensitic transformation (MT) behaviors. Therefore, tuning the MT is of crucial importance for FSMAs. At present, studies on the MT of FSMAs still keep active [16–18].

Previously, the MT in FSMAs was mainly studied in single-phase systems, and it has been well revealed that the martensitic transformation is intensively dependent on the chemical composition [19,20], and significant effect of grain size on the MT is also confirmed [21,22]. However, limited studies on MT behavior have been carried out on the dual-phase FSMA systems which are developed to overcome the severe brittleness in single phase FSMAs. For example $\gamma$ phase, a disordered phase with a face-centered cubic structure, was introduced in Ni-excess Ni-Mn-Ga alloys [23–25]. In Ni-Fe-Ga alloys, the $\gamma'$ phase with the ordered $L1_2$ structure was precipitated by aging [26,27]. By alloying the rare earth (RE) elements, such as Tb [28–30], Dy [31,32], Sm [33], Gd [34,35], and Y [33,36], RE-rich precipitates generally possessing the hexagonal structure are introduced [37]. The mechanical properties of FSMAs were well improved by the micron-sized precipitates. Simultaneously the typical thermo-elastic martensitic transformation was still observed in the dual-phase FSMAs, even when the volume fraction of the precipitates was quite high [31–33,36]. It should be noted that in the previous dual-phase FSMAs the average size of precipitates was limited at the micrometer level. Due to the incoherent interfaces between the matrix and the micron-sized precipitates, the thermo-elastic feature of the martensitic transformation as characterized quite narrow temperature span (*TS* is defined as $(A_f\text{-}A_s + M_s\text{-}M_f)/2$ in this paper, where $A_s$ and $A_f$ mean reverse martensitic transformation starting and finishing temperatures, $M_s$ and $M_f$ mean the martensitic transformation starting and finishing temperatures) was not affected by the precipitates so much. The simple effect of the micron-sized precipitates on the MT was featured as shifting of the transformation temperatures due to variations of the matrix compositions caused precipitation reaction [28,29,33]. Therefore, realizing the interaction between coherent nanoprecipitates and MT behavior can promote the understanding of MT in FSMAs.

As is well known, MT temperature can be significantly migrated by the external fields including magnetic field and stress field [38–43]. Therefore, if a heterogeneous stress field is introduced into the Heusler

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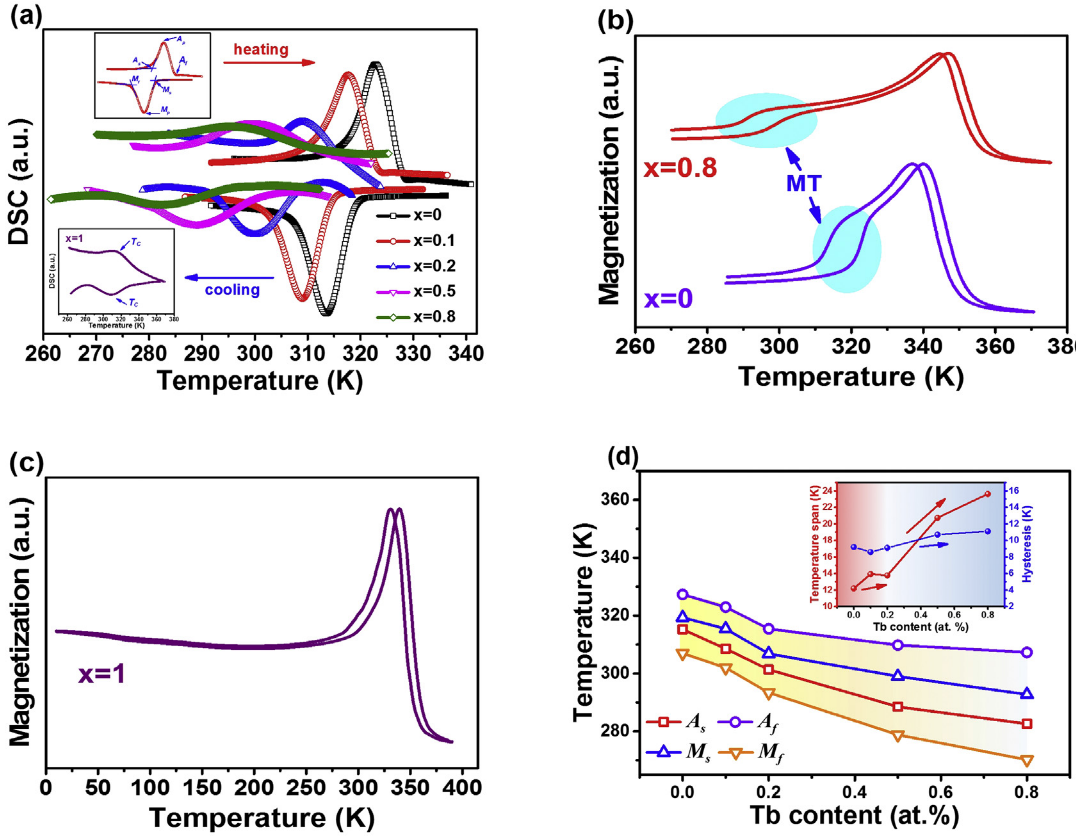


**Fig. 1.** (a) DSC curves of $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x$ = 0–0.8) ribbons, the inset is the DSC curves of $x$ = 1 ribbon; (b) *M-T* curves of $x$ = 0 and $x$ = 0.8 ribbons measured under the magnetic field of 300 Oe, the inset is the *M-H* curves for both ribbons measured at 280 K; (c) *M-T* curves of $x$ = 1 ribbons measured under the magnetic field of 300 Oe. (d) Tb content dependence of the martensitic transformation temperatures. The inset is the function of Tb content versus MT temperature span and hysteresis.

**Table 1**
Forward and reverse martensitic transformation temperatures of $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x$ = 0–1) melt spun ribbons. $A_s$ and $A_f$ represent reverse martensitic transformation start and finish temperatures, respectively. $M_s$ and $M_f$ represent forward martensitic transformation start and finish temperatures, respectively.

| $x$ | $A_s$ (K) | $A_f$ (K) | $M_s$ (K) | $M_f$ (K) | $A_f$-$A_s$ (K) | $M_s$-$M_f$ (K) |
|---|---|---|---|---|---|---|
| 0 | 315.3 | 327.3 | 319.3 | 307.0 | 12.1 | 12.4 |
| 0.1 | 308.5 | 322.9 | 315.4 | 302.0 | 14.4 | 13.5 |
| 0.2 | 301.3 | 315.4 | 306.8 | 293.4 | 14.1 | 13.5 |
| 0.5 | 288.5 | 309.8 | 299.0 | 278.8 | 21.3 | 20.2 |
| 0.8 | 282.6 | 307.3 | 292.7 | 270.2 | 24.7 | 22.5 |
| 1 | – | – | – | – | – | – |

alloy, the MT temperature span is expected to be effectively expanded. Therefore, coherent nanoprecipitates are considered to produce the heterogeneous stress field. In the previous work, it has been discovered that the combination of doping traces of rare earth element Tb and rapid solidification technology can lead to the formation of nanoprecipitates in the matrix [44,45]. Due to the oversize of the nanoprecipitates, the corresponding interface with the matrix remains a semi-coherent relationship [44]. In this work, the solidification rate is further increased, and coherent nanoprecipitates are successfully introduced into NiMnGa alloys with slight addition of rare earth Tb atoms. MT temperature span can be adjusted from as narrow as ~12 K in single phase ternary alloy to a very large value in the dual-phase of NiMnGa alloys range with the presence of nanoprecipitates. Simultaneously, the transformation hysteresis between the forward and reverse MT keeps stable at around 11 K. High resolution analysis indicates a gradual distortion in matrix lattices with the largest distortion up to 10% in the matrix induced by the coherent nanoprecipitates. A qualitative thermodynamic model based on Landau theory is employed to understand the effect on heterogeneous local stress field leads on MT temperature span.

## 2. Methods

High-purity nickel, manganese, gallium and terbium with a purity level of 99.9%, 99.7%, 99.99% and 99.95%, respectively, were arc-melted four times into ingots for the preparation of $Ni_{50-x}Tb_xMn_{30}Ga_{20}$ ($x$ = 0–1) master alloys. The ingots were encapsulated in a quartz tube filled with argon, heat treated at 1123 K for 48 h for homogenization, and then quenched into cold water. Subsequently, the ingots were induction melted in a quartz tube and melt spinning in vacuum, at copper wheel surface line speed of 60 m/s. The $x$ = 0, 0.8 and 1 ribbons were encapsulated in a quartz tube filled with argon again and heat treated at 1123 K for 12 h for transfer the nanoprecipitates to micron-size precipitates. The phase structures of the ribbons were identified by a Regaku D/Max 2500 PC X-ray diffractometer with Cu $K_\alpha$ radiation at room temperature. The microstructures were examined by JEOL JEM-2100F transmission electron microscope (TEM) equipped with the energy dispersive spectroscopy (EDS). The ribbons for TEM observation were first mechanically ground to about 15–20 μm thick, and dealt by ion milling. The chemical composition analysis is identified by EDS in a scanning transmission electron microscopy mode. The surface morphologies were observed on the free surfaces of the ribbons by JEOL JSM-7500 scanning electron microscope (SEM). METTLER Toledo differential scanning calorimetry (DSC) was used to determine the martensitic transformation temperatures with the heating and cooling rate of 10 K/min. The *M-T* and *M-H* curves are tested by Physical Property