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Thermal cycling behaviors of the intermartensitic transformation in a polycrystalline $Ni_{52.5}Mn_{23.7}Ga_{23.8}$ alloy

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ABSTRACT

Thermally induced intermartensitic transformation in polycrystalline $Ni_{52.5}Mn_{23.7}Ga_{23.8}$ has been investigated by differential scanning calorimetry (DSC) and X-ray diffraction (XRD). It is found that after annealing at 500 °C for 4 h an intermartensitic transformation, seven-layered orthorhombic martensite (7M) → five-layered tetragonal martensite (5M), appears in polycrystalline $Ni_{52.5}Mn_{23.7}Ga_{23.8}$ alloy quenched from 800 °C, where the sequence of phase transformations is austenite phase (A) → 7M → 5M during cooling and 5M → 7M → A during heating. The intermartensitic transformation is an independent phase transformation, but the critical transition temperatures and the transformation temperature ranges of 7M → 5M are strongly affected by the martensitic transformation.

1. Introduction

NiMnGa based ferromagnetic shape memory alloys (FSMAs) have been attracting considerable interest for their shape memory effect and transition between mechanical energy and magnetic energy [1–4]. In addition to martensitic transformation, intermartensitic transformation (IMT) was observed in some NiMnGa alloys [5,6]. The possible IMT occurs both related to the composition and the action of uniaxial stress [5–8]. A sequence of A → 5M → 7M → 2M (non-modulated tetragonal) was found in single crystalline $Ni_{52.6}Mn_{23.6}Ga_{23.8}$ and controlled by the internal stresses and elastic energy stored in the martensitic state. Wu et al. [7] reported that a perfect thermoelastic IMT, A → 7M → 5M, occurred in single crystalline $Ni_{52}Mn_{24}Ga_{24}$ and it was very sensitive to the internal stress built up during the grinding process. Segui et al. [8] suggested that the IMT shifts towards lower temperatures after quenching from increasing temperatures in single crystalline $Ni_{53.1}Mn_{26.6}Ga_{20.3}$ and such evolution can be related to changes in the $L2_1$ order degree. IMT has been extensively investigated in single crystal NiMnGa, however IMT of the polycrystalline NiMnGa is less studied [5,8,9]. In this article, a thermally induced IMT in polycrystalline $Ni_{52.5}Mn_{23.7}Ga_{23.8}$ has been investigated. The effects of quenching and martensitic transformation on the IMT have been also discussed.

2. Experimental procedure

The $Ni_{52.5}Mn_{23.7}Ga_{23.8}$ (at%) ferromagnetic shape memory alloy ingot was prepared by vacuum arc remelting (VAR). The ingot was cut into two pieces (sample A and sample B) which were sealed into two vacuum quartz ampoules, respectively. Two ampoules were homogenized at 800 °C for 48 h and quenched into cold water. Different from sample A, sample B was further annealed at 500 °C for 4 h, and cooled in furnace to room temperature. The transition temperatures of NiMnGa samples were measured by differential scanning calorimetry (DSC, Perkin Elmer Pyris 1) at a heating/cooling rate of 10 °C/min. The crystal structures of the NiMnGa samples were determined by X-ray diffraction at room temperature (XRD, Dmax-2550 V, Cu K_α, 40 kV, 100 mA).

3. Results and discussion

3.1. Effect of quenching on IMT

Fig. 1 shows the DSC curves of polycrystalline $Ni_{52.5}Mn_{23.7}Ga_{23.8}$ samples after different heat treatments. It was found the peak temperatures of martensitic transformation and its reverse transformation, are T_M = 40.5 °C and T_A = 43.5 °C, respectively, in sample A of the quenched NiMnGa, as shown in Fig. 1(a). After annealing at 500 °C, besides martensitic transformation, the thermally induced IMT appeared as shown in Fig. 1(b). The peak temperatures of phase transformations of sample B are as T_M = 45.8 °C, T_A = 50.2 °C, T_{M1} = 1.1 °C, and T_{A1} = 37.1 °C. Comparing Fig. 1(b) with Fig. 1(a), it is observed that both the martensitic and its reverse transformation temperatures of sample B shifted to higher temperatures, about 5–7 °C higher than that of sample A, and the phase transformation enthalpies also increased from about 5 J/g to 7 J/g. The increase of martensitic transformation temperatures of NiM-

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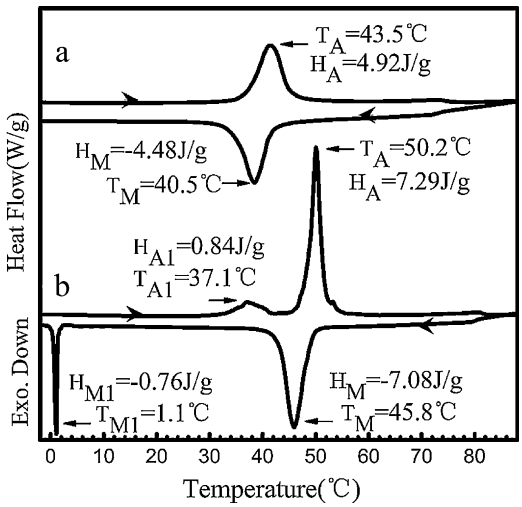

Fig. 1. DSC curves of NiMnGa: (a) sample A, (b) sample B.

nGa after annealing was also observed by other researchers [8,10]. It is suggested that annealing treatment increases the degree of atomic order which is damaged by the internal stress from quenching [8,10].

Wang et al. reported that large internal stress from balling impeded the IMT [7], which reveal that the IMT is sensitive to the internal stress. The present result in Fig. 1 indicates that the large internal stress from quenching suppresses the IMT of NiMnGa. It is noticed that 7M → 5M transformation occurs at a narrow temperature range, while the reverse transformation 5M → 7M occurs at a wide temperature range, as shown in Fig. 1(b). The small enthalpies of IMT of NiMnGa are similar to that in the literatures [11,12].

3.2. Crystal structures

The XRD pattern of Fig. 2(a) was obtained at 20 °C, after the sample B was cooled down to 20 °C from a temperature higher than 70 °C. Fig. 2(b) shows the XRD pattern taken at 20 °C, after the sample B was cooled to −10 °C, and then heated to 20 °C, which is a lower temperature than reverse martensitic transformation temperature As_1. The crystal structures of sample B in Fig. 2(a) and (b) are seven-layer modulation martensite (7M), and five-layer modulation martensite (5M), respectively, as is shown in Fig. 2. Clearly, the thermally induced intermartensitic transformations observed in the sample B are 7M → 5M during cooling and 5M → 7M during heating, while the complete phase transformation sequences are A → 7M → 5M during cooling and 5M → 7M → A during heating, which is similar to the results obtained by Wang et al. [7]. It is noticed that $(2\,2\,0)_{5M}$ peak has an intensity nearly double than $(0\,2\,2)_{5M}$ peak as shown in Fig. 2(b), which is the typical for a tetragonal structure with $c/a > 1$. It is well known that the 5M is tetragonal with $c/a < 1$ [7,13]. It is reasonably concluded that there is a considerable texture in the polycrystalline sample B. Although some compositions of NiMnGa exhibit a non-modulated tetragonal structure with $c/a > 1$ [14,15], the non-modulated martensite was observed usually in NiMnGa with higher e/a value and much higher martensitic transformation temperatures [13,15]. In the present experimental pattern (Fig. 2(b)), the positions (Bragg angle) of the diffracted peaks are more consistent with the lattice parameters of the 5M structure than with the non-modulated phase [7,13–15].

3.3. Effect of martensite transformation on IMT

Fig. 3 shows the DSC curves of sample B during seven thermal cycles. From the first three cycles, it is seen that martensitic

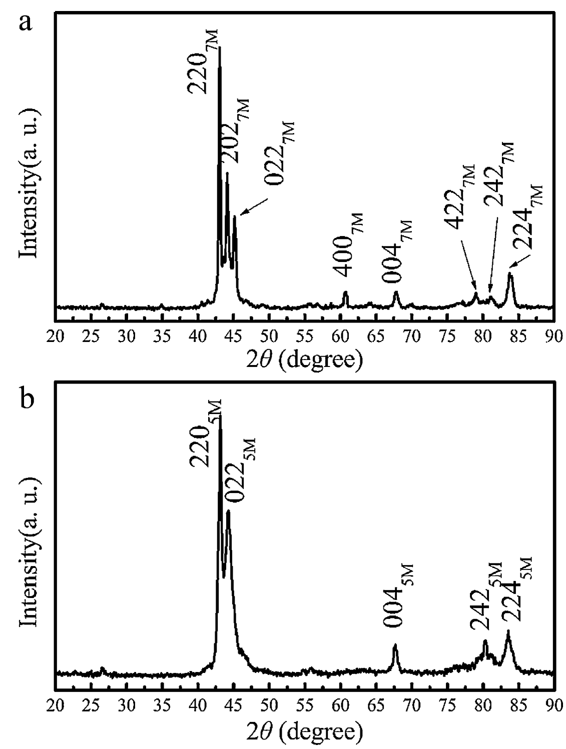

Fig. 2. XRD patterns taken from sample B at 20 °C, (a) after cooling to 20 °C from the temperature higher than 70 °C; (b) cooling to −15 °C and then, heating to 20 °C.

transformation has the strong effect on the IMT of polycrystalline $Ni_{52.5}Mn_{23.7}Ga_{23.8}$. In the second cycle, only part of the 7M martensite transforms into the parent phase when the heating is stopped at T_A. The remained martensite is called as $7M_{old}$. During cooling, the parent phase transforms back into martensite that is defined as $7M_{new}$. The formation of $7M_{new}$ may be the result of the nucle-

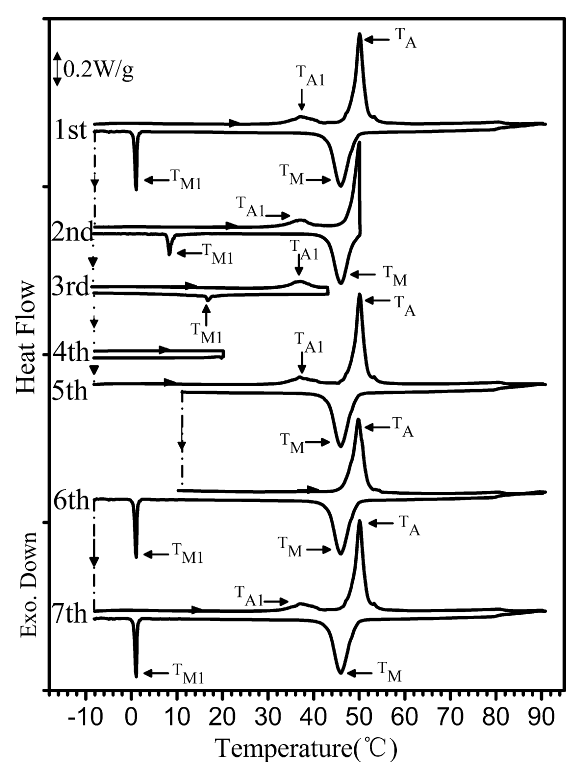

Fig. 3. DSC curves of NiMnGa alloy during seven cycles of heating/cooling.

ation and growth of the martensite nuclei in the parent phase, or the growth of the already existing $7M_{old}$ martensite, which needs to be identified further.

It is noticed that $7M_{new} \rightarrow 5M$ occurs during cooling in the first thermal cycle, while only $7M_{old} \rightarrow 5M$ appears in cooling for the third thermal cycle as different phase transformation. There exists different transformation temperature and transformation temperature range between $7M_{new} \rightarrow 5\,M$ and $7M_{old} \rightarrow 5M$, as is shown in Fig. 3. For the second cycle, the transformation of $7M_{old}$ and $7M_{new}$ into 5M is different from that in Ti–Ni alloys with a kinetic stop [16,17]. The phase transformation of $7M_{old} + 7M_{new} \rightarrow 5M$ in cooling results from the competition of $7M_{new}$ into 5M and $7M_{old}$ into 5M. The mechanism of this phenomenon is not clear and still under investigation using TEM with cooling/heating holder.

No phase transformation is observed for the fourth cycle, where the maximum temperature is less than $A1_s$. In the fifth cycle, the temperature decreases to a temperature higher than $M1_s$ where no appearance of IMT peak during cooling. As a result, no reverse intermartensitic transformation occurs during heating for the sixth cycle, which confirms that T_{A1} peak during heating is a reverse transformation peak corresponding to intermartensitic transformation peak T_{M1}.

The seventh cycle is similar to the first cycle, where all phase transformation restored. IMT is an independent phase transformation, nevertheless the $A \rightarrow 7M$ martensite transformation has the strong effect on it.

4. Conclusions

The martensitic and its reverse transformation temperatures shift higher about 5–7 °C and IMT occurs in polycrystalline $Ni_{52.5}Mn_{23.7}Ga_{23.8}$ after at 500 °C for 4 h. The XRD experiments confirmed a thermally induced intermartensitic transformation between the 7M and 5M, where the sequence of phase transformations is $A \rightarrow 7M \rightarrow 5M$ during cooling and $5M \rightarrow 7M \rightarrow A$ during heating. Martensitic transformation has the strong effect on the thermally induced intermartensitic transformation in polycrystalline NiMnGa.

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