

Microstructural evolution associated with martensitic transformation in Ni-Mn-Ga alloy

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Abstract. Based on the spatially resolved electron backscatter diffraction technique, the microstructural evolution accompanying the martensitic transformation (austenite to 7M martensite) and the intermartensitic transformation (7M martensite to NM martensite) was studied on a polycrystalline Ni₅₃Mn₂₂Ga₂₅ alloy. Results show that the 7M martensite plate groups transformed from initial austenite have a diamond-shape with four twin-related variants. The 7M to NM intermartensitic transformation was accompanied by the thickening of martensite plates. With the experimental results, the characteristics of microstructural evolution during the phase transformations were further analyzed.

1. Introduction

In recent years, Ni-Mn-Ga ferromagnetic shape memory alloys have aroused great attention due to their excellent magnetic shape memory effects in martensite state. This effect, namely the magnetic-field-induced strain, is originated from the magnetic-field-driven rearrangement of martensitic variants through the variant interface movement [1]. So far, giant strains up to 10% can be achieved upon the application of a moderate magnetic field [2]. It is established that on cooling, Ni-Mn-Ga alloys undergo a first-order diffusionless thermoelastic martensitic transformation from the cubic L2₁ ordered austenite to a low-symmetry martensite. Depending on the alloy composition, three types of martensite, i.e. five-layered modulated (5M), seven-layered modulated (7M), and non-modulated (NM) martensite, are frequently observed [3]. In addition to the martensitic transformation, there may also exist in some alloys a first-order intermartensitic transformation from one type of martensite to another [4].

To date, many efforts have been devoted to understanding the phase transformation behaviors by taking into account the physical properties of different phases in Ni-Mn-Ga alloys [5-6]. However, there are still open issues concerning the microstructural evolutions and crystallographic correlations involved in the structural transformation. In this work, based on spatially resolved electron backscatter diffraction (EBSD) measurements, the characteristics of microstructural evolution accompanying the martensitic transformation (austenite-7M) and the intermartensitic transformation (7M-NM) were analyzed

2. Experimental

The off-stoichiometric Ni-Mn-Ga alloy with nominal composition of Ni₅₃Mn₂₂Ga₂₅ (at.%) was prepared by arc-melting of pure elements Ni (99.97 wt.%), Mn (99.9 wt.%) and Ga (99.99 wt.%). The as-cast ingot was sealed in a vacuum quartz tube and homogenized at 1173 K for 24h, followed by quenching in water. A part of the homogenized ingot was grinded into fine powder and annealed at 873 K for 5 h in a vacuum quartz tube. The powder X-ray diffraction (XRD) measurements were conducted on a PANalytical X'Pert diffractometer equipped with a heating and cooling stage, where the Cu K α radiation was used. The martensitic transformation temperatures were measured by differential scanning calorimetry (DSC, TA Q100). The microstructural analyses were performed on a field emission gun scanning electron microscope (SEM, Jeol JSM 6500 F) with electron backscatter diffraction (EBSD) acquisition camera. The “beam control” mode was applied for auto-orientation mapping.



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3. Results and discussion

According to the DSC measurements, the martensitic transformation start and finish temperatures of the present $\text{Ni}_{53}\text{Mn}_{22}\text{Ga}_{25}$ alloy were determined to be 286.5 K (M_s), 277.9 K (M_f), 289.3 K (A_s), and 303.1 K (A_f), respectively. Some minor peaks were also detected at lower temperatures in the DSC curves, suggesting the occurrence of an intermartensitic transformation. Powder XRD measurements at 298 K, 243 K, and 153 K confirmed that three different phases, i.e. austenite ($a_A = 5.811 \text{ \AA}$), 7M martensite ($a_{7M} = 4.222 \text{ \AA}$, $b_{7M} = 5.537 \text{ \AA}$, $c_{7M} = 41.982 \text{ \AA}$, and $\beta = 92.5^\circ$) and NM martensite ($a_{NM} = b_{NM} = 3.879 \text{ \AA}$, and $c_{NM} = 6.511 \text{ \AA}$), may exist at certain temperatures, as displayed in Fig. 1. This clearly demonstrates the existence of a two-step structural transformation with the transformation sequence of austenite $\rightarrow$ 7M $\rightarrow$ NM on cooling.

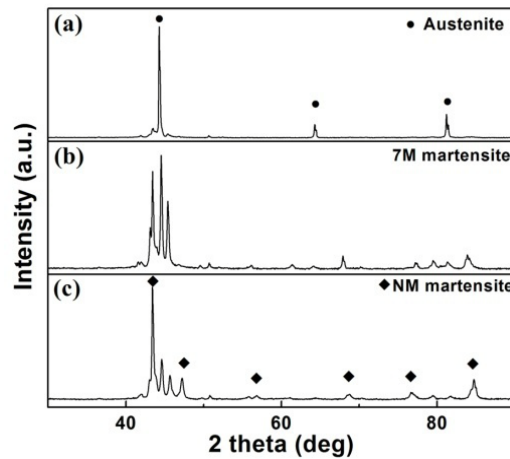


Fig. 1. Powder XRD patterns measured on cooling at (a) 298 K, (b) 243 K, and (c) 153 K.

Detailed microstructural observations revealed that the austenite co-existed with the 7M martensite at room temperature. Fig. 2a presents a typical backscatter electron (BSE) image of the co-existing austenite and 7M martensite in an original austenite grain. Notably, the initially formed 7M martensite plates had an overall diamond-like morphology, and they gradually outstretched into the entire austenite grain. Further EBSD measurements manifested that four distinct martensitic variants (A, B, C, and D) were placed back-to-back in one diamond-like martensite group, as shown in Fig. 2b. Each martensitic variant has a straight interface connecting the parent austenite.

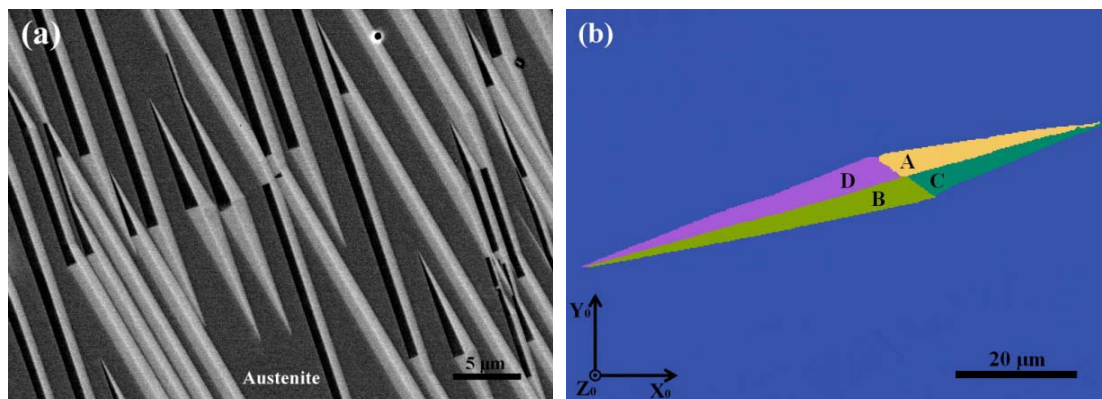


Fig. 2. (a) BSE image of the co-existing austenite and 7M martensite. (b) EBSD micrograph of the diamond-like martensite group having four variants (A, B, C, and D).

Misorientation calculations [7] showed that the four distinct martensitic variants could be twin-related one another, and the possible inter-variant twin relationships can be categorized into three types, i.e. A:C (or B:D) - type I twin, A:B (or C:D) - type II twin, and A:D (or B:C) - compound twin. Actually, only the type I and compound twin relationships exist in the

diamond-like martensite group. More specifically, the long ridge of the martensite diamond represents a type I twin interface and the short ridge a compound twin interface. Using the experimentally measured orientation data, the energetically favorable orientation relationship between the austenite and the 7M martensite was derived to be the Pitsch relation, i.e. $(1\ 0\ 1)_A // (1\ -2\ -10)_{7M}$ and $[1\ 0\ -1]_A // [-10\ -10\ 1]_{7M}$, which is consistent with our previous result determined on a $\text{Ni}_{50}\text{Mn}_{30}\text{Ga}_{20}$ alloy [7].

Through the continuous nucleation and growth, the number and volume of 7M martensite plates increased at the expense of the parent austenite during the martensitic transformation. This transformation process may lead to the formation of different variant groups in the same austenite grain to reduce the transformation strains, as shown in Fig. 3.

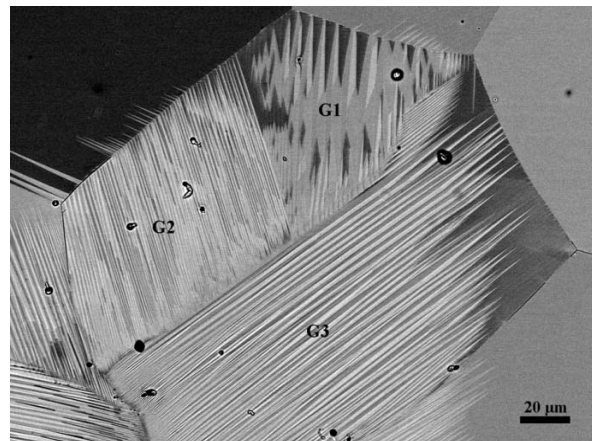


Fig. 3. Formation of different variant groups (G1, G2, and G3) in one austenite grain.

Moreover, the 7M martensite may further transform into the NM martensite in some initial austenite grains. Fig. 4a shows a selected EBSD phase-indexed map covering the co-existing 7M and NM martensite in one initial austenite grain, where the 7M martensite is colored in green and the NM martensite in gray. From Fig. 4a, it is seen that the two kinds of martensite are all in plate-shape and stretch longitudinally almost in the same direction. In general, the plate thickness of the 7M martensite is smaller than that of the NM martensite [9, 10]. When approaching the NM martensite, the 7M martensite has a tendency to thicken. Thus, the 7M to NM intermartensitic transformation is accompanied by a reduction of the specific area of martensite plate interfaces. This tendency implies that the plate interfacial energy of the NM martensite is higher than that of the 7M martensite [9]. By thickening the plates, the total interfacial area could be reduced and thus the interfacial energy is lowered.

Fig. 4b shows the EBSD orientation imaging map corresponding to Fig. 4a, where the martensite plates are colored according to their crystallographic orientations. For the 7M martensite, there exist four distinct orientation variants (A, B, C, and D) constituting one variant group. As for the NM martensite, there appear four differently oriented plates (P1, P2, P3, and P4). Each NM plate is composed of two fine twin-related lamellae alternately distributed [4], with the $\{1\ 1\ 2\}_{NM}$ plane as the twinning plane and the $\langle 1\ 1\ -1 \rangle_{NM}$ direction as the twinning direction. One fine lamella corresponds to one orientation variant of the NM martensite and thus, one NM plate consists of two alternately distributed orientation variants. Further analyses showed that there exist specific orientation relationships between the 7M martensite and the NM martensite, i.e. $(0\ 0\ 1)_{7M} // (1\ 1\ 2)_{NM}$ and $[1\ 0\ 0]_{7M} // [1\ 1\ -1]_{NM}$ as well as $(0\ 0\ 1)_{7M} // (1\ 1\ 2)_{NM}$ and $[-1\ 0\ 0]_{7M} // [1\ 1\ -1]_{NM}$ [4]. Through further atomic reshuffling and lattice distortion, one 7M variant (plate) would finally evolve into one NM plate with two alternately distributed fine twin variants.

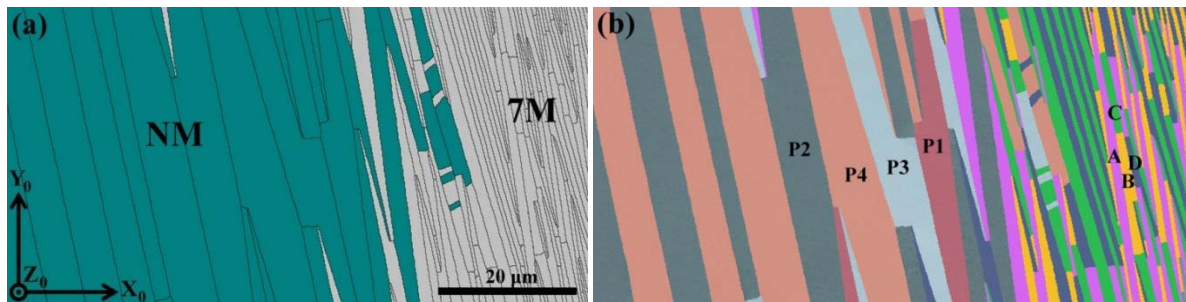


Fig. 4. (a) EBSD phase-indexed map showing the co-existence of 7M martensite and NM martensite in one original austenite grain. (b) Corresponding EBSD orientation imaging map. Four 7M variants are denoted as A, B, C, and D, and four NM plates as P1, P2, P3, and P4. The coordinate frame (X_0 - Y_0 - Z_0) refers to the macroscopic sample coordinate system.

4. Summary

The microstructure evolution accompanying the martensitic transformation (austenite-7M) and the intermartensitic transformation (7M-NM) was studied. The formation of the diamond-shaped 7M martensite with four twin-related variants in initial austenite grains was evidenced. Each diamond-like 7M martensite consists of type I twin (A:C or B:D pair) and compound twin (A:D or B:C pair), the long ridge of which corresponds to type I twin interface and the short ridge to compound twin interface. The 7M-NM transformation was found to be accompanied by the thickening of martensite plates, resulting in a reduction of the specific area of the NM plate interfaces. The orientation relationships between the two martensitic phases refer to $(0\ 0\ 1)_{7M} // (1\ 1\ 2)_{NM}$ and $[1\ 0\ 0]_{7M} // [1\ 1\ -1]_{NM}$ as well as $(0\ 0\ 1)_{7M} // (1\ 1\ 2)_{NM}$ and $[-1\ 0\ 0]_{7M} // [1\ 1\ -1]_{NM}$. One 7M variant (plate) finally evolves into one NM plate with two fine twin variants alternately distributed.

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