Characterization of preferential orientation of martensitic variants in a single crystal of NiMnGa

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Received 19 December 2003; received in revised form 6 March 2004; accepted 11 March 2004 by C.E.T. Gonçalves da Silva

Abstract

We report the detailed observation of martensitic variants in NiMnGa single crystals. The variants that are twinned with each other in different ways can be clearly identified in our single crystals by optical observation. We also investigated the preferential orientation of the martensitic variants in NiMnGa single crystals. We observed the motion of the variant boundary in response to application of a magnetic field. This observation can be used to explain phenomenologically the magnetic-field-induced strain. In the single crystal with composition Ni52Mn24Ga24, martensite with seven modulated layers (7M) shows preferentially oriented variants. A completely recoverable two-way shape-memory behavior was also observed by measuring the free sample in three different directions during a complete temperature cycle. It was found that the largest strains in the [001] and [010] directions occur in different temperature ranges.

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PACS: 81.30Kf; 71.20.Lp; 75.50C
Keywords: A. Magnetic materials; B. Crystal growth; D. Martensitic transitions

1. Introduction

The Heusler alloy NiMnGa has been systematically investigated for years in relation to its structure, martensitic transformation and magnetic properties. Webster et al. [1] have shown that the alloy is ferromagnetic and has a highly ordered L21 type of structure. The two-way shape-memory effect [2,3] and the magnetic-field-induced strain (MFIS) [2–5] associated with the martensitic transformation from a cubic structure to a complex tetragonal structure in NiMnGa have been reported in recent years. This alloy is a promising shape-memory actuator material because it can overcome the disadvantage of traditional shape-memory alloy actuators as it exhibits a rapidly induced shape-memory effect in a magnetic field [6]. This material exhibits a shape-memory effect associated with the martensitic transformation, superelasticity, and MFIS in the martensitic state. Various micromagnetic models [7,8] have been established based on the experimental observations, all indicating that the preferential orientation of martensitic variants plays an important role in the magnetic-field-induced macroscopic strain. In this paper, we report on the detailed optical observation of the variant orientation in single-crystalline NiMnGa, and confirm that the preferential reorientation greatly contributes to the large strain in the NiMnGa alloys.

2. Experimental procedures

Single crystals of Ni52Mn24Ga24 with a diameter of 6–10 mm and a length of 20–80 mm were grown at a rate of 5–30 mm/h and a rotation rate of 30 rpm by the Czochralski
method with a cold crucible system. The starting material was prepared from Ni, Mn, and Ga with a purity of 99.95%. The crystals were annealed at 1123 K for four days and subsequently quenched in ice water. It is believed that the annealing and quenching are important to achieve a high degree of L2₁ structural order [16]. The single crystals were oriented by Laue diffraction in back-reflection geometry and cut into $1 \times 3 \times 3$ mm$^3$ pieces for metallographical observation by optical microscopy to reveal the forms of the martensitic varieties, and into $2 \times 9 \times 12$ mm$^3$ pieces with the length direction parallel to the [001] direction for strain measurements. The deformation of the samples was determined from the spontaneous length change in the [001] (growth) and the [010] directions by the standard strain-gauge technique. Metal strain gauges with a maximum measurement range up to 5% and highly elastic epoxy resin were utilized to ensure measurement reliability and to avoid gauge debonding.

3. Results and discussion

The high-temperature austenite phase of the NiMnGa alloy adopts the cubic L2₁ structure. It undergoes a tetragonal distortion on the transformation to the martensite phase. For practical applications, one may need the martensitic transformation to occur around room temperature. It has been reported that substitution of Ni atoms for Mn atoms at constant Ga content results in alloys with higher transformation temperature (Ms) [9–11]. We have chosen for the composition Ni$_{52}$Mn$_{24}$Ga$_{24}$ to prepare the single-crystalline samples in this work, in order to investigate the preferential orientation of the variants near room temperature. It was found that our single-crystal sample has a Ms of 286 K and a reversed transformation temperature, As of 292 K, and thus shows a thermal hysteresis of 6 K. For minimizing the free energy of the system, the accommodation effect will generate different martensitic variants that are separated by a twin interface of {110} as habit planes. The different kinds of release are usually visible on the polished sample surface, and indicate the twinned relationship.

The optical micrograph in Fig. 1 clearly shows the martensitic variants on the polished (001) wafer surface of a single crystal with different twinned styles. Based on the specific (001) orientation of the studied surface, twinned variants on (101), (101), (011), and (011) planes show structures with a size of about 0.1 mm in the photograph (Fig. 1(a)). The bright or the dark variants imply that they belong to a different twinning system. On the other hand, the variants twinned on (110) and (110) show up with apparent twin boundaries in the photograph with heights contrast (Fig. 1(b)). The ‘roof’ configuration has been observed in detail with magnetic force microscopy, confirming the different character of these variants [12].

Such martensite is structured with 8 or 10 modulated layers (defined as 8M, 10M) [13,15]. Usually no large thermoelastic strain or MFIS can be obtained from the free samples with 8M or 10M structure because of the non-preferential orientation of the variants. By an appropriate prestress loaded on the sample, one can create a so called ‘single-variant’ configuration to improve the strain situation [13].

Fig. 2 shows the preferentially oriented variants on the polished (001) wafer of a single crystal. The type of the martensite at this composition is 7M [13,15]. The variants are of similar size and show a quite developed relief. In the case of free sample, without any external loading, such as prestress and magnetic field, the orientation of the variants is perfectly arranged relative to the [001] (growth) direction (Fig. 2(a)).

Three kinds of tetragonal martensitic variants in this system belong to the six twin systems. Based on the crystallographic theory of martensite in a cubic structure, each twin system can form four different habit planes, leading to 24 possible martensites. Without external loading, there must be a driving force playing a prominent role in determining which of these 24 are adopted. The orientation configuration of the variants, shown in Fig. 2(a) (lamellar layers preferentially arranged perpendicular to the growth direction), is always observed in the crystals with this composition [14]. It does not matter in which shape or size the sample is cut, which rules out a shape-related effect.
Therefore, this clearly indicates a growth process related mechanism for the preferentially orientation of the variants. As pointed out by our earlier work, internal stress governs the orientation of the variants, which could favor one or a subset of those habit planes due to the accommodation of these stresses during the phase transition [13]. Thus the directional internal stress remaining in the grown crystal determines the preferential orientation of the variants.

On applying a magnetic field along the [001] direction of the sample, the variants are rearranged by motion of the twin boundaries. Fig. 2(b) and (c) show the variant configuration in a field of 500 and 2000 Oe, respectively. It can be seen that some fine substructure (dark stripes) is imposed on the wide variants already in the lower field, as shown in Fig. 2(b). When the external field is increased from 500 to 2000 Oe, the dark variants increase their width and increase their volume fraction. This indicates that, for the given direction of the applied field, the dark variants are more favorable to the field than the bright ones, in other words, the material shows an easy magnetization behavior. The driving force for motion of the twin boundaries is a magnetic anisotropy across the twin planes. It should be noted that the whole variant group moves forward to the left, while the dark variant increases its fraction. These observations clearly reveal a directional magnetoelastic coupling in our single-crystalline samples, which generates a macroscopic MFIS as shown below.

Fig. 3 shows the MFIS of the single crystal of Ni_{52}Mn_{24}Ga_{24} measured at 290 K during heating procedure (below the austenite finish temperature A_f point of 292 K). The MFIS is negative in the direction of the field, showing a strain up to 1.2% in this sample. In the direction perpendicular to the field, the strain is positive with the same magnitude. The MFIS increases with increasing field and saturates in a field of about 1.2 T, in which the magnetization also tends to saturation. This indicates that the MFIS is driven by the Zeeman energy provided by the magnetic field.

We note that such large MFIS can only be observed in a sample with preferentially oriented variants. A very low MFIS was observed in a sample with variants arranged as shown in Fig. 1(a). When applying a field on such sample, the MFIS is suppressed by the self-accommodation of the stresses in the variants oriented in random directions.

Fig. 4 shows the transformation strains in three different directions of the single crystal of Ni_{52}Mn_{24}Ga_{24} upon the martensitic transformation. The sample displays a perfect two-way shape-memory behavior with totally reversible shape deformation of 1.2% in a very narrow temperature range of about 6 K. It should be mentioned here that this two-way shape memory is completely spontaneous without any external prestress.

As shown in Fig. 4, the strain in the [001] direction is negative, but both in the [010] and the [011] direction the strains are positive. They start and end at approximately the same temperature. Investigating the strain curves precisely,

Fig. 2. Preferentially oriented variants in Ni_{52}Mn_{24}Ga_{24}: the preferentially oriented variants in the free sample (a), the variant reconfiguration in a field of 500 Oe (b), the variant reconfiguration in a field of 2000 Oe (c) in the [001] direction.

Fig. 3. MFIS measured at 290 K during heating procedure in the [001] (growth) direction (a) and in the direction perpendicular to the growth direction (b) in a magnetic field applied along the growth direction of the Ni_{52}Mn_{24}Ga_{24} single crystal.
however, one can see that the largest strains in the [001] and [010] direction occur in different temperature ranges, while the strain in the [011] direction shows a relative lower slope. This observation implies that, during the martensitic transformation, the orientation of the variants may undergo a complicated two-step process, by which the strains in different directions jump sequentially.

4. Conclusions

The preferential orientation of the martensitic variants in NiMnGa single crystals has been investigated in this work. The variants that are twinned in different ways can be clearly identified by optical observation. In the single crystal with composition Ni_{52}Mn_{24}Ga_{24}, 7M martensite shows preferentially oriented variants. We found that the variants are perfectly oriented in the growth direction. Motion of the variant boundary has been observed when a magnetic field is applied on the sample, which can be used to explain phenomenologically the MFIS. A completely recoverable two-way shape-memory behavior was observed by measuring the sample in three directions during a complete temperature cycle. The results indicate that the preferential orientation of the variants may undergo a two-step orientation process.

Acknowledgements

This work is supported by National High Technology Develop Program funding of AA327021 and the scientific exchange program between The Netherlands and China.

References