Rearrangement of variants in Ni$_2$MnGa under magnetic field

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Abstract

Magnetic field-induced strain which appears in association with rearrangement of variants in a stoichiometric Ni$_2$MnGa single crystal exhibiting a martensitic transformation at 202 K has been investigated. The tetragonality of the martensite phase decreases slightly as temperature decreases and its value at 77 K is about 0.940. When the field is applied along the [001]$_p$ ("P" stands for the parent phase) direction after cooling down to 77 K under zero magnetic field, the specimen contracts along this direction. In association with this contraction, the fraction of the variant whose $c$ axis (easy axis of magnetization) lies along the field direction increases and reaches about 100%. When the specimen is cooled under magnetic field of 3.2 MA/m applied along [001]$_p$, this fraction reaches 100% at the martensitic transformation temperature of 202 K. The energy dissipated due to rearrangement of variants by magnetic field is nearly the same as that obtained from its Stress–strain curve. The maximum shear stress by the magnetic field acting on the twinning plane is evaluated to be about 2.5 MPa from its uniaxial magnetostrictive anisotropy constant (310 kJ/m$^3$ at 77 K). This is an adequate value because it is larger than the shear stress required for the rearrangement of variants (1.2–2.2 MPa) obtained by compressive tests.

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1. Introduction

Since the first discovery of a giant magnetic field-induced strain (MFIS) due to rearrangement of martensite variants in Ni–Mn–Ga alloys by Ullakko et al. [1,2], this system has been intensively studied because its induced strain is more than one order in magnitude larger than that of conventional magnetostrictive materials. So far, most works concerning the MFIS of this system have been made by using alloys with non-stoichiometric compositions, and MFIS of 6% and more have been reported [3,4]. Although those non-stoichiometric alloys exhibit a giant MFIS at room temperature, they are not suitable for a theoretical approach explaining the mechanism of MFIS from microscopic point of view. One difficulty, for example, is the unclearness of site occupancy of atoms for non-stoichiometric alloys. On the other hand, for an ordered stoichiometric Ni$_2$MnGa, the site occupancy is unity for all site [5], so we can make reliable calculation of electronic structure including information of magnetostrictive anisotropy, phase stability, etc. In fact, some electronic structure calculations have already been made for the stoichiometric Ni$_2$MnGa [6,7]. Thus it is desirable to investigate the alloy with stoichiometric composition for clarifying the mechanism of rearrangement of variants from microscopic point of view. However, as far as the authors are aware, there are few experimental results of MFIS of the stoichiometric Ni$_2$MnGa, so it is unclear whether or not the same MFIS behavior reported so far in non-stoichiometric alloys actually appears in stoichiometric Ni$_2$MnGa.

In the present study, therefore, we have examined some basic property of stoichiometric Ni$_2$MnGa which is closely related to the rearrangement of martensite variants under magnetic field such as MFIS, magnetization curve and stress–strain curve. In addition, considering the results obtained, we will discuss the mechanism of rearrangement of variants.
2. Experimental procedure

A single crystal of the stoichiometric Ni$_2$MnGa was grown in a floating zone furnace by using an ingot of the alloy prepared by arc melting, where the crystal was grown with a constant rate of about 4.0 mm/h under a flow of highly purified argon gas. The chemical composition of the top and the bottom parts of the single crystal was analyzed by using an inductively coupled plasma emission spectrometry, and the deviation from the stoichiometric composition was within 0.5 at.% for both parts. After cutting into a suitable shape and an orientation for each measurement described below, every specimen was subjected to homogenization heat treatment at 1073 K for 100 h followed by ordering heat treatment at 923 K for 3 h. Before each measurement, the surface layer was electro-polished.

Martensitic transformation temperature and Curie temperature were determined by three methods: direct current four-probe electrical resistivity measurement, different scanning calorimetry (DSC) with a cooling-and-heating rate of 10 K/min, and magnetic susceptibility measurement using a superconducting quantum interference devise (SQUID) magnetometer, and their results are shown in Fig. 1. The Curie temperature $T_C$ is determined to be 376 K, at which the resistivity curve bends, the heat flow curve shows a shoulder, and the temperature derivative of susceptibility exhibits the minimum. The martensitic transformation start temperature $T_M$ is determined to be 202 K, at which resistivity increases abruptly, heat flow starts to increase, and magnetic susceptibility decreases abruptly. We also notice another characteristic temperature near 250 K corresponding to intermediate transformation temperature $T_I$. The latent heat of martensitic transformation obtained from DSC curves is 380 J/mol (1.57 J/g). Above characteristic temperatures ($T_C$, $T_M$, $T_I$) of the present single crystal are in good agreement with those previously reported [8–10].

Temperature dependence of lattice parameters was determined by powder X-ray diffractometer equipped with cooling and heating stage. Rearrangement of martensite variants by magnetic field was examined by MFIS measurements and optical microscope observation.

The MFIS was measured by a three terminal capacitance method, where a parallelepiped specimen with a dimension of 2.0 mm along [001]p, 2.1 mm along [110]p and 2.2 mm along [110]p was used. Optical microscope observation was made with Nomarski-type differential interference optics, where the same specimen was mounted on the cooling-and-heating stage. Magnetization curve accompanying rearrangement of variants was measured by using the specimen of MFIS measurement. Compressive test was made with a constant strain rate of $1 \times 10^{-2}$ mm/s, where the specimen was a parallelepiped one with a dimension of 3.2 mm along [110]p, 2.6 mm along [110]p, and 1.6 mm along [001]p, and the direction of compression was [110]p.

3. Results

3.1. Temperature dependence of lattice parameters

For the purpose of a quantitative evaluation of the rearrangement of martensite variants, we need lattice parameters of both the parent and martensite phases. Fig. 2 shows temperature dependence of lattice parameters and the tetragonality obtained by X-ray diffraction. Here, the intermediate phase was treated as pseudo-cubic structure, and the martensite phase was treated as a pseudo-tetragonal
structure because their precise structure is not clarified yet [11–13]. As seen in Fig. 2, the lattice parameter does not change significantly in association with the intermediate phase transformation. The lattice parameter changes abruptly at $T_M$ and $a$ of martensite phase increases and $c$ decreases slightly with decreasing temperature.

3.2. Rearrangement of martensite variants by magnetic field

Rearrangement of variants by magnetic field was examined in the following process. First, the specimen was cooled below $T_M$ under zero magnetic field. Then a magnetic field was applied and removed. Subsequently, the specimen was heated up to room temperature.

The curve ‘ZFC’ in Fig. 3 shows the thermal expansion in the zero-field-cooling (ZFC) process from room temperature down to 77 K. The fraction of the variant whose $c$ axis (easy axis of magnetization) lies along [001]$_P$ direction, $f_c$, was calculated to be about 30% at 77 K by using the equation

$$f_c = \frac{a_P(1 + \Delta l/l) - a_M}{c_M - a_M},$$

where $a_P$, $a_M$, $c_M$ are lattice parameters of parent and martensite phases (Fig. 2), and $\Delta l/l$ is the strain. This fraction $f_c$ is reasonable considering three variants are naturally introduced thermally. Incidentally, during this cooling process, magnetostriction of the parent and the intermediate phases were measured, and their results are shown in Fig. 4. From this figure, $\lambda_{001}$ of the parent phase at 286 K is obtained to be $7.3 \times 10^{-5}$ and that of the intermediate phase at 240 K is obtained to be $3.0 \times 10^{-5}$.

After the ZFC, the MFIS was measured at 77 K and the result is shown in Fig. 5. As known from the figure, the specimen starts to contract when the field exceeds about 0.3 MA/m, and the strain saturates to the value of $-3.8\%$. The fraction $f_c$ at this strain is calculated to be about 100% by using the above equation. This means that nearly single variant state is obtained by the field application in the martensite phase. This field-induced strain does not recover when the field is removed. This behavior is different from stoichiometric Fe$_3$Pt [14], although Fe$_3$Pt is also a ferromagnetic shape memory alloy exhibiting a giant MFIS with $c$ axis as the easy axis [14]. The MFIS shown in Fig. 5 recovers in association with reverse transformation.

The above process of rearrangement of variants under magnetic field was also observed by optical microscope, and the result is shown in Fig. 6. As seen in (a), the surface of the parent phase at 300 K is flat. When the temperature is lowered below the martensitic transformation temperature under zero-magnetic-field, surface relief due to martensite variants appears, and it remains until the lowest temperature of 80 K as shown in (b). In the field applying process, the surface relief starts to disappear when the field exceeds about 0.4 MA/m as shown in (c), and it completely disappears under the field of 1.2 MA/m as shown in (d). The surface relief does not reappear when the field is removed as shown in (e). These results are in good agreement with the results of MFIS shown in Fig. 5.

When the temperature is raised from 80 K under zero-magnetic-field, the surface relief again appears at the reverse

![Fig. 3. Thermal expansion along [001]$_P$ direction in the zero-field-cooling process (ZFC) and field-cooling process (FC).](image-url)

![Fig. 4. Magnetostriction along [001]$_P$ of parent (286 K) and intermediate (240 K) phases.](image-url)

![Fig. 5. Magnetic field-induced strain (MFIS) along [001]$_P$ direction after cooling down to 77 K under zero magnetic field.](image-url)
transformation temperature as shown in (f), and then disappears completely as shown in (g). The surface relief shown in (f) probably comes from the transformation twinning in order to keep the habit plane as an invariant plane. Form the results of MFIS and optical microscope observation described above, it is apparent that rearrangement of variants actually occurs and \( f_c \) reaches almost 100% under magnetic field.

Fig. 7 shows a magnetization curve at 77 K accompanying rearrangement of martensite variants by magnetic field. Four processes are shown: ZFC process [(a) \( \rightarrow \) (b)]; field applying process [(b) \( \rightarrow \) (d)]; field removing process [(d) \( \rightarrow \) (e)]; and zero-field-heating process [(e) \( \rightarrow \) (g)].

We also examined thermal expansion in the field-cooling process (\( H = 3.2 \) MA/m), and the result is shown by curve ‘FC’ in Fig. 3. The specimen contracts abruptly near \( T_M \) and then gradually with decreasing temperature. The fraction of the variants whose \( c \) axis lies along the field direction, \( f_c \), is almost constant (about 100%) below \( T_M \).

The slight change in strain will be essentially due to the change in lattice parameter \( c \) as shown in Fig. 2.

The rearrangement of martensite variants under the field-cooling process was also observed by an optical microscope and the result is shown in Fig. 8. As seen in (a), the surface of the parent phase (300 K) under the magnetic field of 1.2 MA/m is flat. When the specimen was cooled below \( T_M \), surface relief appears as shown in (b). This surface relief soon disappears on further cooling, and does not reappear until the lowest temperature examined as shown in (c). When the specimen is heated above \( T_M \), the surface relief again appears at the reverse transformation temperature as shown in (d) like the zero-field-heating process (Fig. 6(f)), and then disappears as show in (e). For both cooling-and-heating processes under magnetic field, the twinning appears only when the specimen pass the martensitic transformation temperature.

Results of MFIS, magnetization curve and thermal expansion under magnetic field of the stoichiometric \( \text{Ni}_2\text{MnGa} \) shown in Figs. 5–7 are essentially in good agreement with those of non-stoichiometric alloys reported previously [15–17], although the martensitic transformation temperature is quite different. This agreement suggests that if a theoretical explanation for rearrangement of variants by magnetic field is established in stoichiometric alloy, the explanation will be essentially applicable to alloys with non-stoichiometric composition.
3.3. Rearrangement of variants by external stress

In order to obtain the required stress for the rearrangement of variants, we examined a compressive test at 80 K by applying a compressive stress along [110]P direction, and the result is shown in Fig. 9. In this figure, there is a stage at about 9 MPa, which is the uniaxial flow stress for the rearrangement of variants. The same experiment was repeated several times. As a result, the flow stress was found to lie between 5 and 9 MPa. Its corresponding resolved shear stress on the twinning plane is from 1.2 to 2.2 MPa. These values are discussed later.

4. Discussion

We observed that the rearrangement of variants actually occurs by magnetic field as well as by external stress in stoichiometric Ni₂MnGa. During this rearrangement of variants, we have a hysteresis in magnetization curve or in stress–strain curve, whose area corresponds to the energy dissipation due to the rearrangement of variants. Then we evaluate such energy dissipation because it provides us important information for understanding the path of the rearrangement of variants by magnetic field and external stress.

The area of the hysteresis of the magnetization curve shown in Fig. 7 is about 200 kJ/m³. Considering the increase in \( f \) in this process is 72%, the energy dissipation for 100% change in \( f \) is estimated to be about 280 kJ/m³. Almost the same energy dissipation (about 280 kJ/m³) is obtained from the stress–strain curve shown in Fig. 9. This coincidence in energy dissipation strongly suggests that the path of rearrangement of variants by magnetic field is essentially the same as that by external stress.

Next, we will discuss the rearrangement of variants by considering the shear stress acting across the twinning plane. Since rearrangement of variants occurs under magnetic field, the magnetic field should generate shear stress \( \tau_{\text{mag}} \) across the twinning plane. In evaluating \( \tau_{\text{mag}} \), we must know the magnetic energy difference \( \Delta U_{\text{mag}} \) between the two states, before (multi-variant state) and after the rearrangement of variants. Since the energy evaluation of the multi-variant state is complex, we consider a simple case in which rearrangement of variants occurs from a single variant state to another single variant state although it is a rough approximation. Under this simplification, \( \Delta U_{\text{mag}} \) can be evaluated as the magnetic energy difference between the two variants. Then, the shear stress by magnetic field acting across the twinning plane between the variants will be expressed as \( \tau_{\text{mag}} = \Delta U_{\text{mag}}/s \), where \( s \) is the amount of shear. Since the martensite phase is tetragonal, the magnetocry staline anisotropy energy should be uniaxial one. Therefore magnetic anisotropy energy can be expressed as \( K_u \sin^2 \theta \), where the angle \( \theta \) is the angle between the direction of magnetization and the \( c \) axis (easy axis). Thus the maximum value of \( \Delta U_{\text{mag}} \) is magnetocrystalline anisotropy constant \( |K_u| \), because the magnetic field is applied along [001]P in the present experiments. The value of \( s \) is obtained by using the equation \( s = \left( 1 - (c/a)^2 \right)/4(c/a) \) to be 0.124 at 77 K and \( K_u \) is obtained by using the equation \( K_u = (M_sH_A)/2 \) to be 310 kJ/m³, where \( M_s \) (0.93 T) is the saturated magnetization and \( H_A \) (0.65 MA/m) is the anisotropy field. Using these values, the maximum of \( \tau_{\text{mag}} \)
is obtained to be 2.5 MPa. This is an adequate value because it is larger than the shear stress required for the rearrangement of variants (1.2 ~ 2.2 MPa) obtained by compressive tests.

5. Conclusions

Using a single crystal of the stoichiometric Ni$_2$MnGa prepared by a floating zone method, rearrangement of martensite variants by magnetic field was examined, and the following is obtained: When a magnetic field is applied along [001]$_P$ direction in the martensite state, one variant grows consuming others, as a result almost single variant state is obtained. The grown variant is the one whose $c$ axis (easy axis) lies along the field direction. The energy dissipation due to rearrangement of variants by magnetic field is nearly the same as that by external stress, suggesting that the two processes take essentially the same path. The magnetic field should exert shear stress across the twinning plane, and its maximum value can be estimated from the uniaxial magnetocrystalline anisotropy constant (310 kJ/m$^3$). The value is calculated to be about 2.5 MPa, which is larger than required shear stress evaluated from stress–strain curves.

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