Structural and Magnetic Properties of Magnetic Shape Memory Alloy Ni_{46}Mn_{41}In_{13} under Magnetic Fields

Kenichi Abematsu^{1,*}, Rie Y. Umetsu^{2}, Ryosuke Kainuma^{3}, Takeshi Kanomata^{3,4}, Kazuo Watanabe^{2} and Keiichi Koyama^{1}

^{1}Graduate School of Science and Engineering, Kagoshima University, Kagoshima 890-0065, Japan
^{2}Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
^{3}Graduate School of Engineering, Tohoku University, Sendai 980-8571, Japan
^{4}Research Institute for Engineering and Technology, Tohoku Gakuin University, Tagajo 980-8537, Japan

The structural and magnetic properties of Heusler alloy Ni_{46}Mn_{41}In_{13} were studied by magnetization and X-ray powder diffraction measurements in the 4.5–350 K temperature range and in magnetic fields up to 5 T. The alloy undergoes martensitic transformation from an L2_{1}-type cubic structure with a = 0.600 nm at 293 K to a six-layered monoclinic (6M) structure in the transition temperature of 160–230 K. The lattice parameters for the 6M structure were estimated to be a_{6M} = 0.441 nm, b_{6M} = 0.357 nm, c_{6M} = 1.30 nm, α_{6M} = 90.0°, β_{6M} = 94.0°, and γ_{6M} = 90.0° at 75 K. In this transformation from the L2_{1} to 6M structures, the cell volume contracts by 0.34% at 8 K. In addition, we observed the magnetic field-induced reverse transformation of this alloy. [doi:10.2320/matertrans.M2013372]

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1. Introduction

Ferromagnetic shape memory alloys (FSMAs) have attracted considerable attention as magnetic field-controlled materials.\(^{1}\) Among the various FSMAs, the Ni–Mn–Ga alloy system has been extensively studied. Ni–Mn–Ga shows a martensitic transformation from a high temperature phase (HTP) with a cubic structure to a low temperature phase (LTP) with another structure below room temperature (RT).\(^{1–8}\) The magnetic anisotropy of LTP is larger than that of HTP. When a magnetic field was applied, Ni–Mn–Ga showed a magnetic field-induced strain over 5%\(^{3}\).

In 2004, Sutou et al. reported that ferromagnetic Heusler alloys Ni_{50}Mn_{50−x}X_{x} (X = In, Sn and Sb) showed a martensitic transformation from a L2_{1} cubic structure to an orthorhombic four-layered (4O) structure.\(^{9}\) Previous results indicated that the Ni_{50}Mn_{50−x}X_{x} alloy exhibited field-induced magnetic and structural transitions.\(^{10–13}\) The magnetic moment of LTP is much smaller than that of HTP in Ni–Mn–X Heusler alloys.\(^{9,14}\) This magnetic property is novel and quite different from that of Ni–Mn–Ga. Especially, the Ni–Co–Mn–In Heusler alloys show the high potential for magnetic field-controlled materials, such as field-induced large stress over 100 MPa, large magnetic entropy change over 28.3 K J kg\(^{-1}\) K\(^{-1}\), etc.\(^{13}\)

It has been known that the crystal structure of LTP in FSMAs is complicated in many cases. For Ni–Mn–X based Heusler alloys, the structural and magnetic properties of LTP are dependent on the X atom and the composition of Ni, Mn and X. Therefore, it is important to reveal these properties of the Ni–Mn–X Heusler alloys under zero and magnetic fields. Previous report suggests that LTP of Ni_{50}Mn_{35}In_{15} has mainly a 4O structure with other structures.\(^{9}\) However, the lattice constant of LTP of Ni_{50}Mn_{35}In_{15} could not be determined because of coexistence with a large number of other structures.\(^{9}\) Recently, we prepared a good quality sample of Ni_{46}Mn_{41}In_{13}. The temperature dependence of the magnetization of the sample showed a sharp phase transition between HTP and LTP at the temperature below 230 K.

In this study, in order to clarify the crystal structure of LTP and its field-induced transformation of magnetic shape memory alloy Ni_{46}Mn_{41}In_{13}, we have carried out X-ray powder diffraction (XRD) and magnetization measurements under magnetic fields up to 5 T in 4.5–350 K temperature range.

2. Experimental

Polycrystalline Ni_{46}Mn_{41}In_{13} was prepared by induction melting under an argon atmosphere. The detailed sample preparation was reported in previous report.\(^{9}\) The obtained sample was confirmed to be a single phase with a L2_{1} structure by XRD measurements at room temperature (RT). The magnetization \(M\) was measured using a Superconducting Quantum Interference Device (SQUID) magnetometer for a bulk sample (21.0 mg) in magnetic fields \(\mu_0H\) up to 5 T and in the temperature \(T\) ranging from 4.5 to 350 K. In this measurement, the sample was fixed with nonmagnetic grease in a sample holder after measuring the mass.

High field XRD experiments\(^{15,16}\) were carried out using Cu Kα radiation at 8 ≤ \(T\) ≤ 320 K for \(\mu_0H\) ≤ 5 T. The powder sample was fixed with vacuum grease on a copper sample holder. The diffraction data were taken at 20° ≤ 2θ ≤ 85° with a step size of 0.01°. We confirmed that the powder sample was not removed by magnetic force until the measurement under magnetic fields was completed. For determining the X-ray reflection indices and the crystal structure, the observed diffraction patterns were analyzed by comparison with calculated patterns using a Rietveld program (RIETAN-FP\(^{17}\)).
3. Results and Discussions

Figure 1 shows the temperature dependence of the magnetization at $\mu_0H = 0.01$ T (a), 1 T and 5 T (b). From the data for $\mu_0H = 0.01$ T, the Curie temperature $T_C$ was determined to be 310 K, and the martensitic transformation starting temperature $T_{MS}$, the martensitic transformation finishing temperature $T_{MF}$, the reverse transformation starting temperature $T_{AS}$ and the reverse transformation finishing temperature $T_{AF}$ were determined to be 220, 160, 180 and 230 K, respectively. It is confirmed that $M$ of LTP is much smaller than that of HTP in Ni$_{46}$Mn$_{41}$In$_{13}$. With increasing $H$, $T_{MS}$, $T_{MF}$, $T_{AS}$ and $T_{AF}$ shift to the low temperature side, and the width of the thermal hysteresis increases slightly. The decrease of the transformation temperatures is due to gain of Zeeman energy by applying magnetic fields.

Figure 2 shows the magnetization ($M$–$H$) curves at 150, 190 and 250 K. Here, the data were measured after zero-field heating from 100 K. For the data of 150 K (LTP) and 250 K (HTP), any anomaly on the $M$–$H$ curves did not observed for $\mu_0H \leq 5$ T. At 190 K ($T_{AS} < T < T_{AF}$), a magnetic field-induced phase transition (metamagnetic transition) between LTP and HTP was observed with a large magnetic hysteresis.

Figure 3 shows the experimental XRD patterns of Ni$_{46}$Mn$_{41}$In$_{13}$ for 20° $\leq \theta \leq 80°$ at 293 K (HTP) and 75 K (LTP) in a zero magnetic field. The XRD patterns of Ni$_{46}$Mn$_{41}$In$_{13}$ for 39.5° $\leq \theta \leq 45°$ at several temperatures for cooling (a) and heating (b) processes in a zero field are shown in Fig. 4. In Figs. 3 and 4, $hkl_c$ denotes the Miller indices for the L2$_1$ cubic structure. Because superlattice peaks (111$_c$ and 200$_c$) were observed for 20° $\leq \theta \leq 30°$ at 293 K, we confirmed that HTP has the L2$_1$ structure. The lattice parameter $a_c$ was estimated to be 0.600 nm at 293 K. The XRD pattern of LTP was complicated and quite different from that of Ni$_{50}$Mn$_{36}$Sn$_{14}$ with 4O structure. The obtained XRD patterns of LTP of Ni$_{46}$Mn$_{41}$In$_{13}$ cannot be represented using any orthorhombic structural models. On the other hand, some monoclinic models (2M, 6M, 10M and 14M) have been proposed to a LTP phase of Heusler alloys. Among them, the monoclinic six-layered (6M) structure represented well the obtained XRD patterns of LTP. In Figs. 3 and 4, $hkl_m$ denotes the Miller indices for the cubic L2$_1$-type and monoclinic 6M structures, respectively. The inset shows the enlarge view of the XRD pattern for 40° $\leq \theta \leq 46°$ at 75 K.
ferromagnetic component was negligibly small in the $M-H$ curves at $T \leq 190$ K. That is, the residual $L2_1$ phase was negligibly small for the bulk sample at low temperature. Therefore, the observed residual phase for the XRD pattern is probably due to partial distortion in the used powder at low temperature. The lattice parameters for the 6M structure at 75 K were estimated to be $a_m = 0.441$ nm, $b_m = 0.557$ nm, $c_m = 1.30$ nm, $\alpha_m = 90.0^\circ$, $\beta_m = 94.0^\circ$ and $\gamma_m = 90.0^\circ$.

The Bragg peaks of the $L2_1$ structure are only seen at temperatures above 230 K for cooling, as shown in Fig. 4(a). With decreasing $T$ from 220 K, the peaks of the 6M structure appear and develop, and the intensity of the peaks of the $L2_1$ structure becomes smaller. As shown in Fig. 4(b), with increasing $T$, the peak intensity of the 6M structure becomes small at temperatures above 220 K and cannot be detected at temperatures above 240 K. That is, the martensitic transformation occurs in this temperature range. This result is consistent with the magnetic data (Fig. 1).

Figure 5 shows schematic views of the relationship between the $L2_1$ (a) and 6M (b) structures. In this figure, projection on the (010) plane of an ideal $L2_1$ cubic structure is presented.\(^{22,24}\) When the martensitic transformation occurs from the $L2_1$ cubic structure, the crystal takes place diffusional-less shears on successive \{202\} planes and anisotropic distortion along the $a$-axis of the $L2_1$ structure. The 6M-structural model basically consists of the modulated and six-layered [202] sheets of the distorted $L2_1$ structure. It is important to estimate the amount of the distortion of the crystal by the martensitic transformation. However, the number of atoms included in the unit cell of the 6M structure differs from that in the $L2_1$ structure. Therefore, we assume a pseudotetragonal\(^{22,24}\) structure, which denotes a face-centered tetragonal (FCT) structure in Fig. 5(b). The lattice parameters of the FCT and 6M structures are related to $a_{\text{fct}} = b_m$ and $c_{\text{fct}} = \sqrt{4a_m^2 - b_m^2}$. Here, $a_{\text{fct}}$ and $c_{\text{fct}}$ are the lattice parameters of the FCT structure. The unit cell volume $V_{\text{fct}} = a_{\text{fct}}^2 \times c_{\text{fct}}$ of the FCT structure was calculated by using these parameters in order to estimate the volume change between the LTP and HTP transition.

Figure 6 shows the temperature dependence of the lattice parameters ($a$ and $V$) and the cell volume $V$ (b) in a zero magnetic field. Here, the open and closed symbols indicate the data for cooling and heating processes. In this figure, the parameters ($a_c$ and $V_c$) and ($a_{\text{fct}}$, $c_{\text{fct}}$ and $V_{\text{fct}}$) indicate the data for the $L2_1$ cubic structure and a FCT structure, respectively. The dashed lines in this figure indicate thermal hysteresis considering the peak-intensity variation of XRD results between the $L2_1$-HTP and 6M-LTP. From the 202$_m$ diffraction line, $a_{\text{fct}}$ and $c_{\text{fct}}$ of the 6M structure were deduced from 200$_m$, 006$_m$ and 123$_m$ diffraction lines. By the martensitic transformation, the lattice decreases by 5.91% along the $a_{\text{fct}}$ axis (parallel to one of $a_c$), whereas the other lattice increases by 13.1% along the $c_{\text{fct}}$ axis (parallel to another $a_c$). With decreasing $T$ from $T_{\text{Mf}}$, $a_{\text{fct}}$ decreases, whereas $c_{\text{fct}}$ increases. The volume of the FCT structure ($V_{\text{fct}}$) is 3.34% less than that of the $L2_1$ structure ($V_c$).

Figure 7 shows the XRD patterns of Ni$_{46}$Mn$_{41}$In$_{13}$ at 190 K in fields up to 5 T. Here, the data were taken after zero-field heating from 100 K. It is confirmed that the field-induced reverse transformation occurs from the 6M to $L2_1$ structures at 190 K ($T_{\text{AS}} \leq T \leq T_{\text{AF}}$). In $\mu_0 H = 0$ T, the pattern shows...
two-phase coexistence consisting of the 6M and \( L_{21} \) structures. With increasing \( H \), the reflection peak of the 6M structure is suppressed, but the peak of the \( L_{21} \) structure is enhanced. With decreasing \( H \) down to zero, the intensity of the peak of the \( L_{21} \) structure still remains, and the 6M structure did not recover completely as the initial XRD pattern. This irreversible process is also reported in the previous paper for Ni\(_{50}\)Mn\(_{36}\)Sn\(_{14}\).14)

Figure 8 shows the magnetic field dependence of the lattice parameters \( a_c \) for the \( L_{21} \) structure, \( a_{\text{fct}} \) and \( c_{\text{fct}} \) for the FCT structure deduced from the six-layered monoclinic (6M) structure. It is confirmed that the lattice parameters of both structures are almost independent of the magnetic field for \( \mu_0H \leq 5\) T. When a magnetic field is applied, the volume fraction of the \( L_{21} \) and 6M phases is only varied. The difference of the lattice parameters for both the structure is \( -6.06\% \) along the \( a_{\text{fct}} \) axis and \( +13.1\% \) along the \( c_{\text{fct}} \) axis, and \( V_{\text{fct}} \) is \( 0.18\% \) less than \( V_c \) at 190 K under \( \mu_0H = 4\) T.

4. Conclusion

The structural properties of magnetic Heusler alloy Ni\(_{46}\)Mn\(_{41}\)In\(_{13}\) were investigated by magnetization and X-ray powder diffraction measurements in 4.5 \( \leq T \leq 350\) K and in \( 0 \leq \mu_0H \leq 5\) T. The alloy undergoes the martensitic transformation from the \( L_{21} \)-type cubic structure with \( a_c = 0.600\) nm at 293 K to the six-layered monoclinic (6M) structure in the temperature range of 160–230 K. The lattice parameters for the 6M structure were estimated to be \( a_m = 0.441\) nm, \( b_m = 0.557\) nm, \( c_m = 1.30\) nm, \( \alpha_m = 90.0^\circ \), \( \beta_m = 94.0^\circ \) and \( \gamma_m = 90.0^\circ \) at 75 K. In this transformation from the \( L_{21} \) and 6M structures, the cell volume contracts by \( 0.34\% \) at 8 K. The magnetic field induces the reverse transformation in Ni\(_{46}\)Mn\(_{41}\)In\(_{13}\) in the vicinity of the transition temperature.

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