Magnetic Field-Induced Transition in Co-Doped Ni41Co9Mn31.5Ga18.5 Heusler Alloy

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Thermal strain, magnetostriction and magnetization measurements of Ni41Co9Mn31.5Ga18.5 polycrystalline ferromagnetic shape memory alloy (FSMA) were performed across the martensitic transition temperature, $T_M$, and the reverse martensitic transition temperature, $T_R$, at atmospheric pressure. When cooling from the austenitic phase, a steep decrease in thermal expansion due to the martensitic transition at $T_M$ was observed. When heating from the martensitic phase, a steep increase in the thermal expansion due to the reverse martensitic transition at $T_R$ was observed. These transition temperatures decreased gradually with increasing magnetic field. The field dependence of the martensitic transition temperature, $dT_M/dB$, is $-4.2$ K/T and that of the reverse martensitic transition temperature, $dT_R/dB$, is $-7.9$ K/T. The metamagnetic transition appeared between 330 and 390 K. The results of thermal strain and magnetization measurements indicate that a magneto-structural transition occurred at $T_M$. The region above $T_M$ or $T_R$ is the ferromagnetic austenite phase and that below $T_M$ or $T_R$ is the paramagnetic or weak ferromagnetic martensitic phase. At constant temperature, a magnetic field-induced strain was observed with a value of $1.0 \times 10^{-3}$, which indicates that this alloy is sensitive to magnetic fields. Strong magneto-structural coupling was revealed by the magnetic properties and phase transitions. [doi:10.2320/matertrans.M2012289]

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1. Introduction

Ferromagnetic shape memory alloys (FSMA) have been extensively studied as potential candidates for smart materials. Among FSMA, Ni$_2$MnGa is the most familiar alloy.\(^1\) It has a cubic $L_2_1$ Heusler structure (space group $Fm\bar{3}m$) with a lattice parameter of $a = 0.5825$ nm at room temperature, and it orders ferromagnetically at the Curie temperature, $T_C \approx 365$ K.\(^2,3\) Upon cooling from room temperature, a martensitic transition occurs at the martensitic transition temperature, $T_M \approx 200$ K. Below $T_M$, a superstructure forms as a result of lattice modulation.\(^4,5\) For Ni–Mn–Ga Heusler alloys, $T_M$ can be varied from 200 to 330 K by nonstoichiometrically changing the concentration of the alloy’s constituent elements.

Giant magnetic field-induced strains (MFIS) have been observed in Heusler alloys. Heusler alloys based on Ni$_2$MnGa have been explained by the rearrangement of martensitic structural variants caused by an external field.\(^1,6,7\) Disordered Fe–31.2%Pd (at%) alloy (A1-type cubic)\(^8,9\) and ordered Fe$_2$Pt (L1$_2$ type cubic)\(^10,11\) ferromagnetic alloys have also attracted much interest because of their giant MFIS. These materials, Ni–Mn–Ga, Fe–Pd and Fe–Pt alloys, have attracted much attention as potential materials for magnetic actuators.

Recently, new alloys in the Ni–Mn–In, Ni–Mn–Sn and Ni–Mn–Sb Heusler alloy systems that are expected to be ferromagnetic shape memory alloys have been studied by the Tohoku University Group.\(^12\) These alloys show very small magnetization in the martensitic phase in comparison to that of the parent phase. Oikawa et al. studied the magnetic and martensitic transition behaviours of Ni$_2$Co$_2$Mn$_{36.3}$In$_{13.3}$ alloy by differential scanning calorimetry (DSC) and vibrating sample magnetometry.\(^13\) A metamagnetic transition from the paramagnetic martensitic phase to ferromagnetic austenite phase was detected, and a magnetic field-induced reverse transition was confirmed in a high magnetic field.\(^14,15\) This alloy is promising as a metamagnetic shape memory alloy with a magnetic field-induced shape memory effect and as a magnetocaloric material. Ni–Co–Mn–In alloys, in which Co is added to Ni–Mn–In alloys to increase the Curie temperature, shows basic shape memory behaviour in compressive stress–strain measurements. Large MFIS has been observed for Ni$_2$Co$_3$Mn$_{36.3}$In$_{13.3}$ (In13.3).\(^16,17\) After a compressive pre-strain of approximately 3% was applied to In13.3, a steady magnetic field was applied parallel to the compression axis of the sample. The MFIS was measured using the three-terminal capacitance method. An expansion of 3.0% was observed at approximately 3.5 T, which indicates that the magnetic field induced almost full shape recovery. Using this expansion, a stress of approximately 100 MPa can be generated in the material under a magnetic field. This stress level is approximately 50 times larger than that of other shape memory alloys.

Albertini et al. investigated the composition dependence of the structural and magnetic properties of the Co-doped Ni–Mn–Ga ferromagnetic shape memory alloy around the Mn-
The Ni41Co9Mn32Ga18 alloy was studied in this paper. When cooling from 500 K, it shows a ferromagnetic transition at $T_C^\lambda = 456$ K in the austenite phase. At the martensitic transition temperature, $T_M = 420$ K, its AC susceptibility drastically decreased. Below 300 K, its AC susceptibility gradually increased and a distinct peak was found at $T_C^M = 257$ K in the martensitic phase. When heating from 200 K, the Curie temperatures $T_C^M$ and $T_C^\lambda$ were same as the temperatures in the cooling process. The reverse martensitic temperature $T_r$ was 436 K. Thus the AC susceptibility indicates re-entrant magnetism, ferromagnetic-paramagnetic, or weak ferromagnetic-ferromagnetic states, which may be related to the crystal structures.

In this paper, we studied the magnetostructural transition in the Co-doped ferromagnetic shape memory alloy, Ni$_{41}$Co$_9$Mn$_{31.5}$Ga$_{18.5}$, by means of thermal strain, magnetization and magnetostriction experiments and discussed the structural and magnetic properties by comparison with other magnetic shape memory alloys.

2. Experimental Procedure

The sample used in this study was synthesized at Yamagata University. The Ni$_{41}$Co$_9$Mn$_{31.5}$Ga$_{18.5}$ alloy was prepared by arc melting 99.99% pure Ni, 99.99% pure Co, 99.99% pure Mn and 99.9999% pure Ga in an argon atmosphere. To obtain a homogenised sample, the reaction product was sealed in double-evacuated silica tubes, and then, annealed at 1123 K for three days and then quenched in cold water. The resulting sample was polycrystalline. From X-ray powder diffraction, the sample was confirmed as a single phase with a tetragonal $D_0_{22}$ structure at 298 K. The lattice parameters of the tetragonal structure were $a = 0.38794$ nm and $c = 0.66247$ nm. The size of the sample was 2.0 mm $\times$ 2.0 mm $\times$ 4.0 mm. The all measurements in this study were performed at atmospheric pressure, $P = 0.10$ MPa. Thermal strain measurements (linear thermal expansion) and magnetostriction measurements were performed using strain gauges (Kyowa Dengyo Co., Ltd., Chofu, Japan) under steady fields.

The electrical resistivity of the strain gauges was measured by the four-probe method. The relationship between strain, $\varepsilon$, and the deviation of electrical resistivity, $\Delta R$, is given by

$$\varepsilon = \frac{1}{K_S} \frac{\Delta R}{R_0} = \frac{1}{K_S} \frac{(R - R_0)}{R_0},$$

where $K_S$ is the gauge factor ($K_S = 1.98$) and $R_0$ is the electrical resistivity above $T_R$. The strain gauge was fixed parallel to the longitudinal axis of the sample.

Thermal strain measurements were performed using a helium-free cryo-cooled superconducting magnet at the High Field Laboratory for Superconducting Materials, Institute for Materials Research, Tohoku University. The magnetic field was applied along the longitudinal axis of the sample. The thermal strain was measured relative to the reference strain at 420 K in the austenite phase.

Magnetization measurements were performed using a Bitter-type water-cooled pulsed magnet (inner bore: 26 mm; total length: 200 mm) in Akita University. The magnetic field was applied along the longitudinal axis of the sample. The pulsed magnetic field applied had a half sine wave shape, with a time constant of 2.6 ms corresponding to a frequency of 192 Hz. The magnetization values were corrected using the values of spontaneous magnetization for 99.99% pure Ni.

The magnetic permeability measurements were performed in AC fields with a frequency, $f = 73$ Hz, and a maximum field, $B_{\text{max}} = 0.0050$ T, using an AC wave generator (WF 1945B; NF Co., Ltd., Yokohama, Japan) and an audio amp (PM17; Marantz Co., Ltd., Kawasaki, Japan) with the same magnet that was used for the magnetization measurement, with a compensating high homogeneity magnetic field. AC fields were applied along the longitudinal axis of the sample.

DSC measurement was carried out at Yamagata University. The heating rate was 5 K/min. The sample for the DSC measurements was taken from the same ingot as that for the thermal strain and magnetization measurements.

3. Results and Discussions

Figure 1 shows the thermal strains of Ni$_{41}$Co$_9$Mn$_{31.5}$Ga$_{18.5}$. When heating from 280 K, gradual expansion was observed at zero magnetic fields. The ratio of the thermal strain increased around 380 K and clear bent was observed at 390 K. Taking other results for Ni$_{41}$Co$_9$Mn$_{32}$Ga$_{18}$ into consideration, the results show that the reverse martensitic transition occurred at approximately $T_R = 380$ K. Above 390 K, in the austenite

![Fig. 1](image-url)
phase, the thermal strain increased linearly. When cooling from 440 K, the thermal strain decreased linearly. Just below 320 K, it decreased abruptly, indicating that a contraction occurred due to the martensitic transition. On the basis of the contraction indicated by the thermal strain result, the martensitic transition temperature, $T_M$, was obtained as 315 K.

As shown in Fig. 1, the large thermal hysteresis, $T_R - T_M = 65$ K, was observed in the strain measurement. The thermal strains measured at constant magnetic field were also shown in Fig. 1. It is noticeable that $T_M$ and $T_R$ gradually decrease with increasing magnetic field. Figure 2 shows the magnetic phase diagram of Ni$_{41}$Co$_9$Mn$_{31.5}$Ga$_{18.5}$ obtained by thermal strain measurements. $T_M$ and $T_R$ decrease almost linearly with increasing magnetic fields. The field dependence of the martensitic transition temperature, $dT_M/dB$, is $-4.2$ K/T, and the reverse martensitic transition temperature, $dT_R/dB$, is $-7.9$ K/T between 4 and 8 T. These values are considerably larger than that for In$_{13.3}$, for which $dT_R/dB = -3.7$ K/T.  

Figure 3 shows the magnetization of Ni$_{41}$Co$_9$Mn$_{31.5}$Ga$_{18.5}$ under a pulsed magnetic field. Before each measurement, the sample was cooled down to 293 K in the martensitic phase. Subsequently, it was heated to the target temperature. Above 316 K, a metamagnetic behaviour was observed. At 338 K, a large $M$–$B$ hysteresis was observed. The $M$–$B$ curve at 361 and 388 K shows an S-like shape, which indicates that a metamagnetic transition occurred in high magnetic fields. Comparing the thermal strain results in Fig. 1 and the phase diagram in Fig. 2, the metamagnetic transition was related to the reverse martensitic transition. Below 300 K, it is assumed that Ni$_{41}$Co$_9$Mn$_{31.5}$Ga$_{18.5}$ is paramagnetic or weakly ferromagnetic, which is considered in terms of the permeability as shown in Fig. 4. Below 300 K, the permeability was approximately 1.2 arbitrary units. This is two-thirds of the permeability at 400 K for the ferromagnetic austenite phase. The spontaneous magnetization at 316 K in Fig. 3 was 14 Am$^2$/kg, which suggests a weak ferromagnetic state was realised in the martenite phase.

Figure 5 shows the DSC curve of Ni$_{41}$Co$_9$Mn$_{31.5}$Ga$_{18.5}$ in the heating process. Comparing the results of thermal strain and the magnetization measurements, the cusp at 378 K corresponds the reverse martensitic transition. The temperature dependence of the magnetization by means of the VSM indicates the Curie temperature for the austenite phase, $T_C^A$, is 460 K. The anomaly of the DSC curve at 460 K indicates the ferromagnetic to paramagnetic transition.

Figure 6 shows the magnetostriction at 340 K under steady field by means of the helium-free superconducting magnet. The thermal condition was the same as that for the magnetization measurement. When increasing the magnetic field, distinct magnetostriction was observed. The strain was
The structural transition of Ni41Co9Mn31.5Ga18.5 alloy is sensitive and the thermal strain in Fig. 1 suggest that the magnetostriction at atmospheric pressure is highly sensitive to the magnetic properties and phase transitions of FSMA. In this study, the magnetization M increases with the magnetic field between 338 and 388 K, as shown in Fig. 3. The hysteresis of M at 388 K is smaller than that at 361 K, and no M-B hysteresis is found for high fields above 4 T. The thermal hysteresis of the thermal strain also decreases at high magnetic fields. Another potential application is as a magnetocaloric material. The magnetization shows metamagnetic behaviour as shown in Fig. 3. From the experimental results in this study, dM/dT is determined as −7.9 K/T. Therefore, dB/dT is approximately given by the Clausius–Clapeyron relation in the magnetic phase diagram as

$$\frac{\Delta B}{\Delta T} \approx \frac{dB}{dT} = -\frac{\Delta S}{\Delta M},$$

where $\Delta M$ and $\Delta S$ are the differences in magnetization and entropy change between the austenite and martensitic phases, respectively.\textsuperscript{16,19} From the experimental results in this study, $dT_M/dB$ is determined as −2.8 K/T. The entropy change, $\Delta S$, obtained from the DSC measurement is 7.3 J/kg K. From the magnetization results, $\Delta M = 40 \text{Am}^2$/kg, and then, $\Delta S/\Delta M = dB/dT = -0.18$ K/T, given by eq. (2). However, the measured $dP_k/dB = -0.13$ K/T is 30% smaller than the calculated value. As shown in Fig. 5, the latent heat of the martensitic transition is not small. Therefore, the ambiguity for the value of $\Delta S$ is large, thereby giving rise to the large ambiguity present in this calculation. Albertini et al. studied the structural and magnetic properties of Ni50−ᵋCo₂Mn₆Ga₅₀₋ᵋ.\textsuperscript{18} The field dependence of the martensitic transition temperature, $dT_M/dB$, for the alloy Ni₅₀−ᵋCo₂Mn₆Ga₅₀₋ᵋ (x = 0, y = 0) is +0.57 K/T and that for Ni₄₁Co₃Mn₃₂Ga₁₈ (x = 9, y = 32) is −2.8 K/T.

As mentioned in the introduction, disordered Fe–31.2%Pd (at%) alloy\textsuperscript{8,9} and ordered Fe₃Pt\textsuperscript{10,11} ferromagnetic alloys show giant MFIS under a magnetic field of 1 or 2 T. These alloys show a few % MFIS in single crystals at atmospheric pressure. Under compressive stress above 3 MPa, these alloys do not show MFIS. On the other hand, Ni₄₁Co₃Mn₃₂Ga₁₈ alloy also shows magnetostriction at atmospheric pressure and is highly sensitive to the magnetic field.

Next, we discuss the reason for the magnetic field dependence of the thermal strains in Fig. 1 that decrease with increasing magnetic field. Kataoka et al. performed a theoretical analysis of the phase diagram of FSMA Ni₂Mn₁₋ᵋCuₓGa.\textsuperscript{20} The analyses show that the biquadratic coupling term, together with a higher order coupling term, of the martensitic distortion and the magnetization plays an important role in the interplay between the martensitic and ferromagnetic phases. Their calculation based on the phenomenological free energy is shown as

$$F_{tot} = F_{ela} + F_{mag} + F_{mag-ela}$$

where $F_{tot}$ is the total free energy, $F_{ela}$ the free energy of the elastic strain, $F_{mag}$ the free energy of the magnetic system including the magnetic exchange energy and the magnetic anisotropy energy, and $F_{mag-ela}$ the energy of the interaction between the distortion and the magnetization. The calculated $x$–$T$ phase diagram of Ni₂Mn₁₋ᵋCuₓGa agrees well with the phase diagram, which was obtained from experimental results. In addition, they suggested that the biquadratic term, $e_{ij}^2M^2$, in $F_{mag-ela}$ affects the large magnetostructural coupling. Thus, strong magneto-structural coupling was displayed to play an important role in the magnetic properties and phase transitions of FSMA. In this study, the magnetization $M$ increases with the magnetic field between 338 and 388 K, as shown in Fig. 3. The hysteresis of $M$ at 388 K is smaller than that at 361 K, and no $M$–$B$ hysteresis is found for high fields above 4 T. The thermal hysteresis of the thermal strain also decreases at high magnetic fields. Other Heusler compounds such as Ni₅₀₋ᵋMn₁₂.₅Fe₁₂.₅Ga₂₅₋ᵋ show an $x$–$T$ phase diagram similar to that of Ni₂Mn₁₋ᵋCuₓGa.\textsuperscript{21} Comparing with the experimental results of Ni₄₁Co₃Mn₃₂Ga₁₈ in this study and Ni₂Mn₁₋ᵋCuₓGa, it is considered that the thermal hysteresis of the thermal strain that decreases with increasing magnetic field is an indication of strong magneto-structural coupling in Ni₄₁Co₃Mn₃₂Ga₁₈. The magnetostriction shown in Fig. 6 also suggests strong magneto-structural coupling.

Finally, we comment on the potential applications of this alloy. One of the potential applications is as a material for magnetic actuators. As mentioned above, the magnetostriction of this alloy was 0.10% at 340 K and under atmospheric pressure. This value of magnetostriction is larger than that of Tb₄DyFe single crystal under atmospheric pressure.\textsuperscript{22} Ni₄₁Co₃Mn₃₂Ga₁₈ is polycrystalline, and therefore, it is easy to process and handle. Moreover, the magnetostriction effect occurs at temperatures between room temperature and 380 K, making it useful in high temperature regions, e.g., the engine room of a motorcar.

Another potential application is as a magnetocaloric material. The magnetization shows metamagnetic behaviour and $M$–$B$ hysteresis at temperatures between 330 and 390 K, as shown in Fig. 3. From the $M$–$B$ hysteresis of the magnetization curve at 361 K, the energy of the magnetocaloric effect is obtained as 180 J/kg. This is of the same order as the energy in Ni₄₋ᵋMn₄₁In₁₃.\textsuperscript{13} which shows a reverse magnetocaloric effect due to the magnetic and structural phase transition from the paramagnetic martensitic state to ferromagnetic austenite state.
4. Conclusion

Thermal strain, magnetostriction and magnetization measurements of the polycrystalline ferromagnetic shape memory alloy, Ni$_{41}$Co$_9$Mn$_{31.5}$Ga$_{18.5}$, were performed across the martensitic transition temperature, $T_M$, and the reverse martensitic transition temperature, $T_R$, at atmospheric pressure. Strong magneto-structural coupling was indicated by the magnetic properties and phase transitions.

(1) Thermal strain: When cooling from the austenite phase, a steep decrease in the thermal expansion due to the martensitic transition at $T_M$ was found. When heating from the martensitic phase, a steep increase in the thermal expansion due to the reverse martensitic transition at $T_R$ was observed. These transition temperatures decreased gradually with increasing magnetic field.

(2) Magnetic phase diagram: The field dependence of the martensitic transition temperature, $dT_M/dB$, is $-4.2$ K/T and that of the reverse martensitic transition temperature, $dT_R/dB$, is $-7.9$ K/T. The metamagnetic transition appeared between 330 and 390 K. The results of thermal strain and magnetization indicate that a magneto-structural transition occurred at $T_M$.

(3) Magnetostriction: At constant temperature, a magnetic field induced strain was observed with a value of $1.0 \times 10^{-3}$, which indicates that this alloy is sensitive to magnetic fields.

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