Kinetic Arrest of Martensitic Transformation in $\text{Ni}_{33.0}\text{Co}_{13.4}\text{Mn}_{39.7}\text{Ga}_{13.9}$ Metamagnetic Shape Memory Alloy

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Martensitic and magnetic properties of $\text{Ni}_{33.0}\text{Co}_{13.4}\text{Mn}_{39.7}\text{Ga}_{13.9}$ metamagnetic shape memory alloy were investigated. The kinetic arrest phenomenon was observed at about 120 K by thermomagnetization measurements, and magnetic field-induced transformation (MFIT) was also detected at various temperatures ranging from 4.2 to 300 K. By evaluation of the equilibrium magnetic fields and temperatures based on the transformation fields and temperatures, it was confirmed that the transformation entropy change below 120 K becomes almost zero, which results in the kinetic arrest phenomenon. [doi:10.2320/matertrans.MBW200915]

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Recently, an unusual type of ferromagnetic shape memory (SM) alloy has been found in Ni–Mn–X ($X = \text{In}$, Sn , and Sb) Heusler alloys,¹⁾ where the parent phase shows considerably stronger magnetism than that of the martensite phase.²⁾ Thus a drastic change in magnetization can be obtained during the martensitic transformation.^{3–5)} In these alloys, an application of magnetic field strongly decreases the martensitic transformation temperatures and a magnetic field-induced transformation, namely, metamagnetic phase transformation, has also been confirmed in NiCoMnIn,⁶⁾ NiCoMnSn⁷⁾ NiCoMnGa⁸⁾ and NiCoMnAl⁹⁾ alloys. Moreover, an almost perfect magnetic field-induced SM effect, that is, a metamagnetic SM effect, has been found in single crystalline $\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.7}\text{In}_{13.3}$, polycrystalline $\text{Ni}_{43}\text{Co}_7\text{Mn}_{39}\text{Sn}_{11}$ ^{6,7,10)} alloys at room temperature.

Very recently, for $\text{Ni}_{45}\text{Co}_5\text{Mn}_{36.7}\text{In}_{13.3}$ ^{11,12)} and $\text{Ni}_{50}\text{Mn}_{34}\text{In}_{16}$ ^{13,14)} alloys, the kinetic arrest phenomenon has been reported. In this phenomenon, martensitic transformation is interrupted at certain temperatures (noted as kinetic arrest temperature, T_{KA}) during field cooling and does not proceed with further cooling. In order to clarify the mechanism of this phenomenon, an alloy with higher Curie temperature is required. We found that in NiCoMnGa alloys, more cobalt can be soluted, the NiCoMnGa alloy system thus having higher Curie temperatures. In this letter, we report the kinetic arrest phenomenon in $\text{Ni}_{33.0}\text{Co}_{13.4}\text{Mn}_{39.7}\text{Ga}_{13.9}$ polycrystalline alloy. Magnetization measurements at low temperatures were mainly used to investigate the process of martensitic transformation.

A polycrystalline $\text{Ni}_{33.0}\text{Co}_{13.4}\text{Mn}_{39.7}\text{Ga}_{13.9}$ alloy was prepared by induction melting under an argon atmosphere. Heat treatment was then conducted at 1273 K for 24 h in an argon atmosphere for homogenization. The composition of the specimen was determined by wavelength dispersive spectrometry. The magnetization was measured by an extraction-

type magnetometer using a superconducting magnet with magnetic field up to 18 T and a superconducting quantum interference device (SQUID) with a magnetic field ranging from 0 to 7 T. Thermomagnetization was measured by SQUID ranging from 6 to 390 K. Moreover, thermal analysis was carried out by differential scanning calorimetry.

Figure 1(a) shows the thermomagnetization (MT) curves measured under magnetic fields of $H = 0.05, 1, 3$ and 5 T, the specimen first being subjected to field cooling (FC) to 6 K, which was followed by field heating back to 390 K, as indicated by the arrows. The inset of Fig. 1(a) shows the differentiation of MT under 5 T. The martensitic transformation starting temperature (T_{Ms}), martensitic transformation finishing temperature (T_{Mf}), reverse transformation starting temperature (T_{As}) and reverse transformation finishing temperature (T_{Af}) are defined as the extrapolation shown in the inset of Fig. 1(a). It is seen that, as reported by Yu *et al.*,⁸⁾ the magnetization of the parent phase is obviously stronger than that of martensite phase and that an increasing magnetic field drastically lowers the T_{Ms} and T_{Af} . For this alloy, however, the parent phase was found to almost reach saturation under a magnetic field of 1 T, while the magnetization of martensitic phase increased with increasing magnetic field. Figure 1(b) shows the magnetization obtained at 6 K by FC in MT under different magnetic fields; a magnetization curve measured at 4.2 K after zero field cooling (ZFC) is also plotted. It can be clearly seen that at low magnetic fields, FC and ZFC show no difference, while the magnetization of FC becomes obviously larger than that of ZFC when the applied magnetic fields are larger than 3 T. This seems to be the result of the appearance of the kinetic arrest phenomenon at around 110–130 K (noted as kinetic arrest temperature T_{KA} in Fig. 1(a)). Therefore, when a magnetic field larger than a critical field of 3 T at least was applied, a part of the martensitic transformation that should have occurred below T_{KA} was interrupted, and thus the remaining parent phase showed stronger magnetization.

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Fig. 1 (a) Thermomagnetization (MT) curves of $\text{Ni}_{33.0}\text{Co}_{13.4}\text{Mn}_{39.7}\text{Ga}_{13.9}$ under magnetic fields of $H = 0.05, 1, 3$ and 5 T and (inset) the differentiation of MT under 5 T. (b) The magnetization obtained from MT plotted together with magnetization curve at 4.2 K.

Fig. 2 Magnetization curves of $\text{Ni}_{33.0}\text{Co}_{13.4}\text{Mn}_{39.7}\text{Ga}_{13.9}$ at 150 K, 200 K and 250 K.

Magnetization was measured from 4.2 K to 350 K, Fig. 2 showing the results at 150 , 200 and 250 K. Magnetic field-induced reverse transformation was observed at all the measured temperatures. The martensitic transformation finishing magnetic field (H_{Mf}) and the reverse transformation starting magnetic field (H_{As}) are defined by the same method as that stated for T_{Mf} and T_{As} . Due to the large hysteresis and interval of the transformation, the reverse transformations

Fig. 3 Martensitic transformation finishing magnetic field (H_{Mf}) and reverse transformation starting magnetic field (H_{As}) measured from magnetization curves plotted against temperature. H'_0 is defined as $H'_0 \equiv (H_{Mf} + H_{As})/2$. Martensitic transformation finishing temperature (T_{Mf}) and reverse transformation starting temperature (T_{As}) obtained from thermomagnetization curves are also plotted, and T'_0 is defined as $T'_0 \equiv (T_{Mf} + T_{As})/2$.

were not finished even by applying a magnetic field up to 18 T. Thus neither the martensitic transformation starting magnetic field (H_{Ms}) nor the reverse transformation finishing magnetic field (H_{Af}) could be determined. H_{Mf} and H_{As} are plotted against temperature in Fig. 3. T_{Mf} and T_{As} obtained from MT measurements are also plotted together. Additionally, $H'_0 \equiv (H_{Mf} + H_{As})/2$ and $T'_0 \equiv (T_{Mf} + T_{As})/2$ are assumed and plotted as the equilibrium magnetic field and temperature where the parent phase and the martensitic phase have an equal Gibbs free energy under the condition that a small amount of parent phase exists in the martensite matrix.¹⁵ Since H_{Mf} below 150 K could not be obtained, the shape of H_{Mf} below about 150 K is deduced from the critical H - T plot reported by Ito *et al.* for NiCoMnIn ,¹¹ as is shown the red broken line in Fig. 3. Therefore, by experimental data, it can be observed that H'_0 increases with decreasing temperature and that its gradient to temperature gradually decreases and is estimated to approach a constant value below about 110 – 130 K.

The Clausius-Clapeyron relation between magnetism and temperature is written as

$$\frac{dH'_0}{dT} \approx -\frac{\Delta S}{\Delta M}, \quad (1)$$

where T is the corresponding temperature, ΔS is the transformation entropy change and ΔM is the magnetization difference between the parent and martensite phases. Since ΔM does not change so much in a relatively small temperature range below Curie temperature, entropy change should be approximately proportional to dH'_0/dT for absolute value. Estimating ΔM to be 95 emu/g and considering H'_0 and T'_0 to be consistent in physical meaning, ΔS was calculated and plotted in Fig. 4. It can be seen that ΔS increases almost linearly with increasing temperature above about 150 K, but inevitably becomes zero below about 120 K. Since the driving force ΔG for the thermal transformation can be estimated by $\Delta G \approx \Delta S \cdot \Delta T$, using supercooling ΔT , the

Fig. 4 Entropy change (ΔS) calculated by using eq. (1) on the basis of the fitting curve for the H_0 - T and T_0 - T plots in Fig. 3, where 95 emu/g is given for the value of ΔM . $\Delta S = \Delta H/T_i$ was also estimated by DSC measurement as demonstrated in the inset.

transformation will stop when the ΔS becomes zero. This is considered to cause the kinetic arrest phenomenon and is shown as T_{KA} in Fig. 4. On the other hand, transformation enthalpy ΔH can be obtained from thermal analysis and ΔS can be calculated as $\Delta S = \Delta H/T_i$, where $T_i \equiv (T_{As}^{DSC} + T_{Af}^{DSC})/2$ in the heating curve (shown by the inset in Fig. 4). This was also plotted in Fig. 4 and it shows good agreement with the calculation by eq. (1).

In conclusion, magnetization measurements were performed on $\text{Ni}_{33.0}\text{Co}_{13.4}\text{Mn}_{39.7}\text{Ga}_{13.9}$ polycrystalline shape memory alloy and magnetic field induced reverse transformation was confirmed at all the measured temperatures. During thermomagnetization measurements, the martensitic transformation was observed to be arrested at about 110–130 K. Data from magnetization measurements enabled us to calculate transformation entropy change using the Clausius-Clapeyron relation. The results showed that the entropy change becomes zero under about 120 K, which is considered to cause the kinetic arrest phenomenon.

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