Kinetic Arrest of Martensitic Transformation
in NiCoMnAl Metamagnetic Shape Memory Alloy

Xiao Xu¹, Wataru Ito¹, Masashi Tokunaga², Rie Y. Umetsu¹, Ryosuke Kainuma¹,* and Kiyohito Ishida³

¹Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
²International MegaGauss Science Laboratory, Institute for Solid State Physics, The University of Tokyo, Kashiwa 277-8581, Japan
³Department of Materials Science, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan

Magnetic properties and martensitic transformation behaviors of NiCoMnAl metamagnetic shape memory alloys were investigated. The kinetic arrest phenomenon was observed at about 40 K during thermomagnetization measurements. At temperatures ranging from 4.2 to 200 K, magnetic field-induced reverse transformation was confirmed by a pulse magnetometer with a magnetic field up to 45 T. By plotting the equilibrium magnetic fields against the measured temperature, the transformation entropy change was calculated by using the Clausius-Clapeyron equation. The transformation entropy change was found to become zero below 40 K, which can explain the appearance of the kinetic arrest phenomenon.

(Received March 18, 2010; Accepted April 26, 2010; Published June 16, 2010)

Keywords: NiCoMnAl, metamagnetic shape memory alloy, kinetic arrest

An unusual type of ferromagnetic shape memory (SM) alloy has been recently found in Ni–Mn–X (X = In, Sn, and Sb) Heusler alloys,¹ for which the parent phase shows much stronger magnetism than that of the martensite phase.²⁻⁵ As a result, during martensitic transformation a drastic change in magnetization can be observed in thermomagnetization measurement. In these alloys, the martensitic transformation temperatures drastically decrease with increasing magnetic field if the specimen is subjected to field cooling. Furthermore, a magnetic field-induced transformation, namely, metamagnetic phase transformation (MMPT), has also been reported in NiCoMnIn,⁶ NiCoMnSn,⁷ NiCoMnGa,⁸ NiCoMnSi⁹ and NiCoMnAl¹⁰ alloys, and an almost perfect magnetic field-induced SM effect, that is, the metamagnetic SM effect, at room temperature has been confirmed in single crystalline Ni₄₅Co₅Mn₃₆.₇In₃₃.₆¹⁻¹¹ and polycrystalline Ni₃₃Co₇Mn₁₀Sn₁₁⁷ alloys. For NiCoMnAl alloys, it has also been reported that the grain boundaries have relatively high strength and that even polycrystalline samples can be subjected to compression and deformation. Additionally, due to its low cost, the potential for practical application has also been pointed out.

Very recently, for Ni₄₅Co₅Mn₃₆.₇In₁₃.₃,¹²,¹³ Ni₃₉Mn₃₄-In₁₆.₄,¹⁴,¹⁵ and Ni₃₃Co₁₃Mn₃₉Sn₇Ga₁₄.₉,¹⁶ alloys, the kinetic arrest (KA) phenomenon has been reported. In this phenomenon, martensitic transformation is interrupted at certain temperatures during field cooling and does not proceed with further cooling. Here the corresponding temperature is noted as KA temperature (T_{KA}). Since the KA phenomenon affects the transformation properties of metamagnetic SM alloys, it is very important to clarify the behavior of the KA phenomenon at low temperatures. In NiCoMnAl alloys, however, huge magnetic fields are required to obtain a complete MMPT, because the transformation hysteresis and interval in the MMPT are over five tesla at least.¹⁰ In this study, an investigation of the kinetic arrest phenomenon on a NiCoMnAl alloy was performed by magnetization measurements at low temperatures using a pulse magnetometer with magnetic field up to 45 T.

Polycrystalline samples with a composition of Ni₄₄.₃-Co₅.₁Mn₃₁.₄Al₁₉.₂ (19Al alloy) and Ni₄₄.₄Co₅.₁Mn₃₀.₅Al₂₀.₀ (20Al alloy) were prepared by induction melting under an argon atmosphere. For homogenization, small pieces of samples were cut from the ingot and sealed in quartz tubes for a 24-h heat treatment at 1373 K. Composition analysis was subsequently carried out by EPMA by using wavelength dispersive spectrometry. Thermomagnetization (MT) measurements were performed by a superconducting quantum interference device (SQUID) magnetometer ranging from 6 to 350 K (300 K for 7 T). Isothermal magnetization up to 45 T was measured by induction using coaxial pickup coils¹⁷ at the Institute for Solid State Physics, the University of Tokyo.

Figure 1(a) shows the MT curves measured under magnetic fields of 0.05, 3, 5 and 7 T for the 19Al alloy. During the measurement, the specimen was first field-cooled to 6 K followed by field-heating back to 350 K (300 K for 7 T), as indicated by the arrows. The martensitic transformation starting temperature (T_M) and reverse transformation finishing temperature (T_A) are defined as the crossing point at which the extrapolation of the side of the peak and dM/dH = 0 axis line intersect, as shown in inset of Fig. 1(a). As reported by Kainuma et al.,¹⁰ the addition of cobalt to the NiMnAl ternary alloy drastically changes the magnetic property of the parent phase from paramagnetic to ferromagnetic, while the magnetization in martensite phase remains very weak. Moreover, an application of magnetic field greatly lowers the martensitic transformation temperatures during field cooling and heating. At about 284 K, an ordinary ferromagnetic–paramagnetic transformation occurs and this is noted as Curie Temperature (T_C) in the figure. On the

*Corresponding author, E-mail: kainuma@material.tohoku.ac.jp, Present address: Department of Materials Science, Tohoku University, Sendai 980-8579, Japan
other hand, by the addition of less than 1% Al to this alloy, namely, in the 20Al alloy, a unique behavior, i.e., the martensitic transformation is arrested at a low temperature, can be observed, as shown in Fig. 1(b). This indicates the appearance of the KA phenomenon. In the present case, the $T_{KA}$, which is defined as the temperature where the heating and cooling curves coincide, is evaluated as being about 40 K.

Magnetization of 19Al alloy was measured at temperatures ranging from 4.2 to 150 K, where the martensite phase is stable under a low magnetic field of 0.05 T. Additionally, magnetization was also measured at 175 and 200 K, where two phases coexist under a low magnetic field. The results at 4.2, 100 and 200 K are shown in Fig. 2. Magnetic field-induced reverse transformation was clearly observed at all the measured temperatures, while the absolute value of the magnetization obtained by the pulse magnet is arbitrary. For all the temperatures, although the hysteresis is quite small compared to that of NiCoMnGa alloys, the interval of transformation is found to be very large, which is also consistent with the result of MT measurements in Fig. 1(a).

After initiation of the reverse transformation, an extra magnetic field of about 20 to 30 T was required to complete the transformation. It can also be observed that the magnetic field, which is required to initiate the transformation, gradually becomes larger with decreasing measurement temperature.

The martensitic transformation starting magnetic field ($H_{Ms}$) and the reverse transformation finishing magnetic field ($H_{Af}$) are defined by the same method as the $T_{Ms}$ and the $T_{Af}$ in Fig. 1(a) as shown in the inset. $H_{0}$ is defined as $H_{0} = (H_{Ms} + H_{Af})/2$. The martensitic transformation starting temperature ($T_{Ms}$) and the reverse transformation finishing temperature ($T_{Af}$) obtained from thermomagnetization curves are also plotted, and $T_{0}$ is defined as $T_{0} = (T_{Ms} + T_{Af})/2$.
alloys, this refers to the appearance of the KA phenomenon in the NiCoMnAl alloy at about 40 K. However, the difference between \( H_A \) and \( H_M \), which corresponds to the hysteresis of the transformation, does not change so much with decreasing temperature, while becoming slightly enlarged below about 20 K. It is interesting to note that for this alloy, even at 4.2 K, the field-induced parent phase perfectly returns to the martensite phase after removing the magnetic field, as shown in Fig. 2, whereas for the NiCoMnIn alloy, the field-induced parent phase does not transform back to the martensite phase even if the magnetic field is removed.\(^{12} \) This can be simply explained by the fact that the driving force for transformation, which is proportional to the applied magnetic field, is huge for the present case.

The Clausius-Clapeyron relation between magnetism and temperature can be written as

\[
dH_0 = -\frac{\Delta S}{\Delta M},
\]

where \( dH_0/dT \) is the gradient of \( H_0 \) at temperature \( T \) in Fig. 3, \( \Delta S \) being the transformation entropy change and \( \Delta M \) being the magnetization difference between the parent and martensite phases. Since the martensite phase has very weak magnetism, its magnetization was set to be 6.5 A m\(^2\)/kg (= emu/g) for the whole temperature range. For simplicity, magnetization of the parent phase was set to be the saturation magnetization at temperature \( T \) and is obtained from Figs. 1(a) and 1(b). As a result, \( \Delta M \) was evaluated to vary from 95 to 130 A m\(^2\)/kg. For the present case, eq. (1) is approximated as

\[
dH_0 \approx \frac{-\Delta S}{\Delta M}.
\]

Therefore, \( \Delta S \) can be readily calculated by using eq. (2) and is plotted against temperature in Fig. 4, where the data at 4.2 K was not used for the plot because the field-induced reverse transformation seems not to perfectly complete as shown in Fig. 2. It can be concluded that the transformation entropy change \( \Delta S \) decreases with decreasing temperature and becomes zero at about 40 K. On the other hand, the driving force of transformation can be approximated as

\[
|\Delta G| \approx \Delta S \cdot \Delta T,
\]

where \( \Delta T \) is the supercooling for thermal transformation. Since the decrement of entropy change to zero is shown in Fig. 4, at about 40 K the driving force also becomes zero and this can be used to thermodynamically explain the kinetic arrest phenomenon shown in Fig. 1(b).

Moreover, as pointed out by Ito et al., the decrement of \( \Delta S \) is affected by the magnetism of the parent phase.\(^{19} \) For NiCoMnIn and NiMnIn alloys with a paramagnetic parent phase, \( T_M \), decreases slowly and linearly with increasing In concentration. However, when the Curie temperature appears above the \( T_M \), \( T_M \) begins to abruptly decrease with the addition of In. As a result, by plotting \( \Delta S \) against \( (T_C - T_M) \), it was found that \( \Delta S \) approaches zero when \( (T_C - T_M) \) is larger than 200 K.\(^{19,20} \) In other words, \( (T_C - T_K) \) is expected to be slightly larger than 200 K according to these reports. For NiCoMnIn\(^{12} \) and NiMnIn\(^{15} \) alloys, \( (T_C - T_K) \) was estimated to be about 255 and 225 K, respectively, if one evaluates the \( T_K \) by using the same definition as the present case. For the present NiCoMnAl alloys, \( (T_C - T_K) \) is about 244 K, which shows good agreement. Thus, the magnetism of the parent phase can be considered as a vital factor of the KA phenomenon and a good estimation of \( T_K \) is attainable only by \( T_C \).

Finally, the method of magnetization measurement under a pulse magnetic field should be commented. Compared with normal magnetization measurement under a steady magnetic field, it may be argued that the pulse magnetic field which lasts only several milliseconds should affect the results. Furthermore, it was recently reported by our group that in a NiCoMnIn alloy, the isothermal martensitic behavior was confirmed and the martensitic transformation was observed to proceed when kept in a steady magnetic field for several minutes.\(^{21} \) As a result, in the case of pulse magnetic field, the observed hysteresis of magnetic field may be larger than that measured under steady magnetic field. However, as reported by Sakon et al., for NiCoMnIn alloy at about 300 K, the magnetic field hystereses under pulse fields do not differ observably compared with the previous results under steady fields.\(^{11} \) While for the present NiCoMnAl alloy system, there is still no report of the comparisons up to now, similar to the reports by Sakon et al., the results under pulse magnetic fields may not deviate much from those under steady magnetic fields. Further investigations are still required to experimentally verify this point.

In conclusion, magnetic measurements were performed on NiCoMnAl polycrystalline shape memory alloys and magnetic field induced reverse transformation was confirmed at all the measured temperatures. The kinetic arrest phenomenon was detected by thermomagnetization measurement and confirmed by the \( H_0 - T \) plot. It was verified by magnetic measurements that though the parent phase is partially arrested during thermomagnetization measurement, the magnetic field-induced parent phase transforms back to the martensite phase even at 4.2 K. Transformation entropy change was calculated by using the Clausius-Clapeyron relation. The results showed that the entropy change becomes zero below the kinetic arrest temperature. Moreover, the value of \( (T_C - T_M) \) of this alloy showed general agreement with the reports up to now, which confirms that the magnetism of the parent phase plays an important role on the kinetic arrest phenomenon.
Acknowledgements

This study was supported by a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS) and by the Global COE Program “Materials Integration” (International Center of Education and Research), Tohoku University, MEXT, Japan. This work was also supported in part by a Grant-in-Aid for Scientific Research on priority Areas “High Field Spin Science in 100T” (No. 451) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

REFERENCES