Relation between martensitic transformation temperature range and lattice distortion ratio of NiMnGaCoCu Heusler alloys*

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In order to study the relation between martensitic transformation temperature range ΔT (where ΔT is the difference between martensitic transformation start and finish temperature) and lattice distortion ratio (c/a) of martensitic transformation, a series of $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 2$–5) Heusler alloys is prepared by arc melting method. The vibration sample magnetometer (VSM) experiment results show that ΔT increases when $x > 4$ and decreases when $x < 4$ with x increasing, and the minimal ΔT (about 1 K) is found at $x = 4$. Ambient X-ray diffraction (XRD) results show that ΔT is proportional to c/a for non-modulated $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 2$–5) martensites. The relation between ΔT and c/a is in agreement with the analysis result obtained from crystal lattice mismatch model. About 1000-ppm strain is found for the sample at $x = 4$ when heating temperature increases from 323 K to 324 K. These properties, which allow a modulation of ΔT and temperature-induced strain during martensitic transformation, suggest $Ni_{46}Mn_{24}Ga_{22}Co_4Cu_4$ can be a promising actuator and sensor.

Keywords: martensitic transformation temperature range, lattice distortion ratio, martensitic transformation

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1. Introduction

Heusler ferromagnetic shape memory alloys (for example, NiMnGa) undergo martensitic transformation from high symmetric L21 cubic structures to pseudo-tetragonal or pseudo-orthorhombic martensites. Low symmetric martensites show different lattice distortion ratios for pseudo-tetragonal five-layered modulated (5M) ($c/a = 0.941$), pseudo-orthorhombic seven-layered modulated (7M) ($c/a = 0.893$), and pseudo-tetragonal non-modulated (NM) ($c/a = 1.205$) martensites.[1] Theoretical maximal magnetic field induced strain (MFIS) is expressed as $1 - c/a$ for these alloys.

Ni–Mn base alloys have attracted considerable attention since NiMnGa alloys have shown quite large MFISs in 5M (about 6%) and 7M (about 9.5%) martensites.[2,3] Although NiMnGa NM martensites show excellent stabilities,[4] it is difficult to achieve MFIS due to the large blocking stress (about 20 MPa).[5] Recently, Sozinov *et al.*[6] have obtained about 12% MFIS for NiMnGaCoCu NM martensite alloys with low twinning stress(1.2 MPa) by adjusting lattice distortion ratio c/a. The research results expand the study and applications of Ni–Mn base Heusler ferromagnetic shape memory alloys. For example, NiMnGaCoCu alloys may show different values of martensitic transformation temperature range (ΔT) when non-modulated martensites have various values of lattice distortion ratio (c/a).

Heusler alloy undergoes the martensitic transformation which is accompanied with the change of structure symmetry. Anisotropy and elastic modulus determine transformation path and result. Magnetic field and stress have a prominent effect on transformation.[7–10] Martensitic transformation temperatures of ferromagnetic shape memory alloys mainly depend on chemical composition.[11–15] Moreover, the grain sizes show significant effect on martensitic transformation temperature.[16] Applying an external magnetic field can shift martensite transformation temperature from high to low temperature.[17–19] The small martensitic transformation temperature range may be useful for magnetocaloric effect or magnetic field induced transformation.[20–22] However, to our knowledge, the martensitic transformation temperature range has been little investigated.

During martensitic transformation, there are different values of ΔT when NiMnGaCoCu alloy transforms from cubic parent phase to non-modulated martensite with various values of c/a. There may exist a close relation between martensitic transformation temperature range (ΔT) and lattice distortion ratio (c/a) for NiMnGaCoCu alloy, which is verified by vibration sample magnetometer (VSM) and X-ray diffraction (XRD) results and discussed in detail in the present paper. The relation provides an easy way of analyzing ΔT and c/a by VSM or XRD for NiMnGaCoCu alloy.

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In this study, a series of $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 2$–5) Heusler alloys is prepared. Experimental results show that there is a close correspondence between ΔT and c/a. ΔT increases with c/a increasing. A minimal ΔT (about 1 K) is observed for $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 4$) alloy. The decreasing of ΔT may cause the relative increasing of entropy change (ΔS) at a certain temperature with abrupt magnetization jump for magnetocaloric effect.[20–22] The variation may offer the information about magneto-induced or stress-induced martensitic transformation (or reverse transformation) for NiMnGaCoCu alloy.[18,19,23,24]

2. Experiment

High-purity starting elements, nickel, manganese, gallium, cobalt and copper respectively with purities of 99.995%, 99.99%, 99.99%, 99.99%, and 99.995% were used in our experiments. Polycrystalline $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 2$, 3, 4, 5, 3.4, 3.7, 4, 4.3, and 4.6) alloys were prepared by arc melting raw materials under high-purity argon atmosphere. Afterward, the samples were sealed in evacuated quartz tubes and annealed at 1173 K for 48 h, then cooled with a furnace. The martensitic structures of the samples were verified by powder X-ray diffraction (XRD) using CuKα radiation at room temperature. The magnetization measurements were carried out using a vibration sample magnetometer (VSM, 7400 Lakeshore). The strain measurements were conducted by metal strain gauge using the physical property measurement system (PPMS, Quantum Design).

3. Results and discussion

The martensitic transformation behaviors of compositions $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 2$, 3, 4, 5) were measured in a magnetic field of 300 Oe (1 Oe = 79.5775 A/m) on heating and cooling in a temperature range between 180 K and 400 K as shown in Fig. 1(a). For the sake of clarity, we use the arbitrary units for magnetization axis.

Figure 1(a) shows that the reversible martensitic transformations are typical ferromagnetic–ferromagnetic transitions for $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 2$, 3, 4, 5) alloys. The martensite start (M_s) and martensite finish (M_f) temperatures during cooling and the austenite start (A_s) and austenite finish (A_f) temperatures during heating increase with x increasing, and the minimal ΔT is found to be about 1 K at $x = 4$.

The martensitic transformation and reverse martensitic transformation have been measured three times for $x = 4$ sample. The experimental results show that the thermal hystereses, which are expressed as $((A_f - A_s)/2 - (M_s - M_f)/2)$, are about 9 K in the three cycles. Moreover, small values of ΔT are observed to be about 1 K in the three cycles. The thermal hystereses show small differences among the three cycles, which may be attributed to the fact that the sample has been annealed at 1173 K for 48 h and cooled with a furnace. Since a long annealing and slow cooling can remove internal stress and defects efficiently in the sample, the annealed sample shows unchanged thermal hysteresis and ΔT.

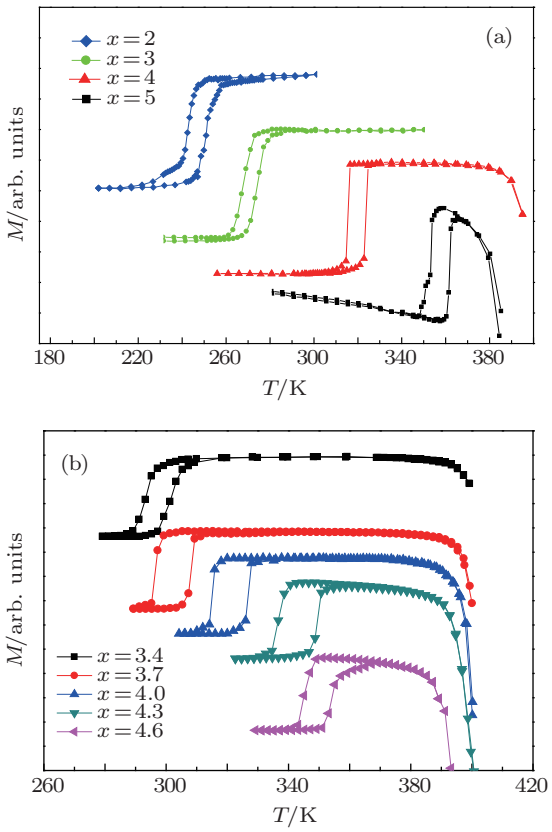


Fig. 1. (color online) Thermo-magnetization curves for $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ alloys at (a) $x = 2$, 3, 4, 5, (b) $x = 3.4$, 3.7, 4, 4.3, 4.6 on heating and cooling.

In NiMnGaX (X = Co, Cu, CoCu) alloys, Co has a strong tendency to occupy the Ni sublattice. Co doping leads to the increase of Curie temperature and the decrease of characteristic temperature ($M_s/M_f/A_s/A_f$).[25,26] $M_s/M_f/A_s/A_f$ is raised by Cu doping.[26–28] In the present paper, Co is fixed at 4%, VSM results show $M_s/M_f/A_s/A_f$ increases with Cu content value increasing. These results are in accordance with other previous analysis results.[25–28]

The small value of ΔT is useful for magneto-induced or stress-induced martensitic transformation (or reverse transformation).[18,19,23] It is obvious that only $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 4$) alloy shows a minimal value of ΔT (about 1 K). In order to obtain more details about the small value of ΔT, a new series of $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 3.4$, 3.7, 4, 4.3, 4.6) alloys is prepared. As in Fig. 1, thermo-magnetic curves show that the value of ΔT increases when $x > 4$ and decreases when $x < 4$ with x increasing, and a minimum value of ΔT (about 1 K) is found at $x = 4$. Curie temperature (T_c) decreases with the value of x increasing.

In order to investigate the relation between ΔT and c/a, ambient X-ray diffraction results are used to study $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 3.4$, 3.7, 4, 4.3, 4.6) alloys. The powder samples are first cooled to 273 K to achieve pure martensitic phase and then measured by XRD at room temperature (about 290 K). As shown in Fig. 2, XRD results show the main diffraction peaks of the five samples, which belong to NM martensite phase. Beside NM martensite, the $x = 3.7$ and 4 samples each contain a small amount of 5-M martensite (the mixed 5-M peaks are marked with arrows in Fig. 2).

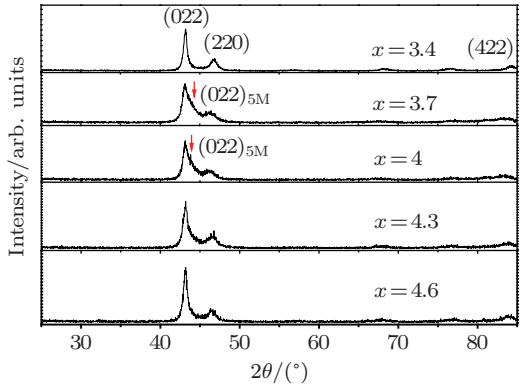


Fig. 2. (color online) Ambient XRD for $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 3.4$, 3.7, 4, 4.3, 4.6) alloys.

The lattice parameters (a, c) and c/a ratios are calculated and summarized in Table 1. The maximal c/a ratio (1.1789) and minimal ratio (1.1445) are found for $x = 3.4$ and $x = 4$ samples. The c/a ratio first decreases and then increases with the increase of Cu content. Figure 3 shows the variation of the c/a with Cu content value for $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 3.4$, 3.7, 4, 4.3, 4.6) alloys.

Table 1. Values of lattice parameters a, c, and lattice distortion ratio c/a for alloys $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 3.4$, 3.7, 4, 4.3, 4.6).

Sample	a/nm	c/nm	c/a
$x = 3.4$	0.5492	0.6475	1.1789
$x = 3.7$	0.5553	0.6382	1.1494
$x = 4.0$	0.5549	0.6352	1.1445
$x = 4.3$	0.5532	0.6411	1.1589
$x = 4.6$	0.5523	0.6438	1.1655

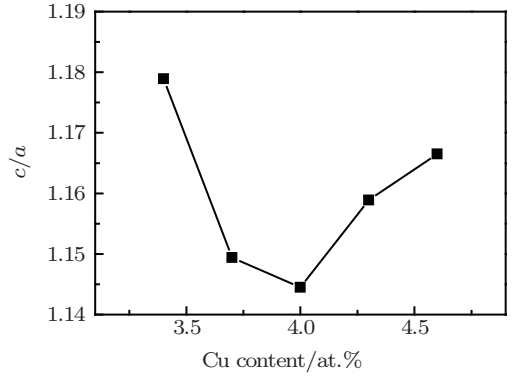


Fig. 3. Variation of c/a with Cu content value for $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 3.4$, 3.7, 4, 4.3, 4.6).

The VSM and X-ray diffraction results show that ΔT and the lattice distortion ratio (c/a) both increase when $x > 4$ and decrease when $x < 4$ with the value of x increasing. $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 4$) alloy shows minimal values of ΔT (about 1 K) and c/a (1.1445). It is observed that ΔT and c/a changes show similar patterns. The patterns can be analyzed with crystal-lattice mismatch mode.[29,30]

Martensitic transformation is a diffusionless structural transformation. For conventional transition, an elastic energy generated by the crystal-lattice mismatch between the parent and martensite phases proves to be equal to or much smaller than the transformation chemical driving force, i.e.,[29,30]

$$\mu\varepsilon_0^2/|\Delta f| \sim 1 \tag{1}$$

or

$$\mu\varepsilon_0^2/|\Delta f| \ll 1, \tag{2}$$

where $\mu\varepsilon_0^2$ is the typical crystal elastic energy, μ is the typical shear modulus, ε_0 is the typical crystal-lattice rearrangement strain characterizing the mismatch between the martensite and parent phases, and Δf is the transformation driving force equal to the difference in specific free energy between the stress-free martensite and parent phases. Equation (1) expresses the phase balance condition between parent and martensite phases.

The Δf arises when the alloy transforms from a high energy state to a self-adaption low energy state, and drives martensitic transformation to overcome crystal elastic energy $(\mu\varepsilon_0^2)$, which determines the martensitic transformation behaviors.

The strength of mismatch between parent phase and martensite affects strongly the path and result of martensitic transformation. The relation between the maximal crystal-lattice rearrangement strain (ε_m) and lattice distortion ratio (c/a) can be expressed as $\varepsilon_m \propto |1 - c/a|$. The ε_m will increase with the increase of the lattice distortion ratio (c/a). The Landau non-equilibrium free energy of a homogeneous system can always be presented as a functional of the electron density for a fixed homogeneous strain, and decreases with the decrease of temperature. The Δf and lattice distortion ratio (c/a) both show a significant influence on martensitic transformation.

It is especially interesting that the temperature dependence of free energy $\kappa = \partial f/\partial T$ and lattice distortion ratio (c/a) will exert effects on martensitic transformation temperature range (ΔT).

There are several possible effects of Δf, κ, and c/a on ΔT.[31,32]

(i) When samples have the same c/a (from Eq. (1), Δf remains unchanged) and different values of κ, a large value of

κ means that only a small value of ΔT is needed, contrarily, a small value of κ corresponds to a large value of ΔT.

(ii) When samples have the same values of κ and different values of c/a, since κ is a constant, Δf is proportional to ΔT, equation (1) states that the large value of c/a is corresponding to the large value of Δf, noticing that c/a is proportional to ΔT.

(iii) When samples show various values of κ and c/a, there is a complicated relationship between the ΔT and the mixture of Δf, κ, and c/a.

Combining our experimental results with the above analyses, we deem that lattice distortion ratio (c/a) may be the main factor influencing martensitic transformation temperature range (ΔT) for $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 3.4$, 3.7, 4, 4.3, 4.6) alloys. The small value of ΔT (about 1 K) for $x = 4$ sample can be attributed to the low block stress which is associated with small c/a ratio. In addition, a small quantity of mixed 5-M martensites may be helpful for the small value of ΔT as seen in Fig. 2. Moreover, since theoretical maximal crystal-lattice rearrangement strain (ε_m) and lattice distortion ratio (c/a) can be related by $\varepsilon_m \propto |1-c/a|$, and ΔT is proportional to lattice distortion ratio c/a in non-modulated NiMnGaCoCu martensite, it means that a large value of ΔT may be corresponding to large strain in non-modulated NiMnGaCoCu martensite.

The small martensitic transformation temperature range of $Ni_{46}Mn_{24}Ga_{22}Co_4Cu_4$ alloy suggests that it may be a promising thermo-actuator. Due to the small value of ΔT, temperature-induced strain will exhibit abrupt change in martensitic transformation. Figure 4 shows the variation of strain with temperature at zero field for $x = 4$ sample. About 1000-ppm strain is observed for the sample when heating temperature rises from 323 K to 324 K.

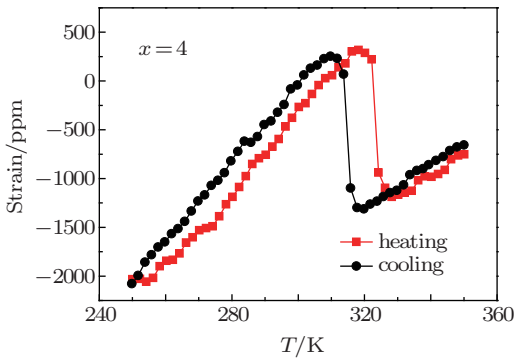


Fig. 4. (color online) Strain–temperature curves for $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ at $x = 4$.

Because of the random crystallographic distribution of $x = 4$ polycrystalline sample, the temperature-induced strain is reduced in comparison with that of the monocrystal (about 3000 ppm for NiMnGa alloys) in the martensitic transformation temperature range.[33] This drop-off in strain for reverse martensitic transformation during heating is strain softening and corresponding to the instability of a multivariant martensitic phase transition.[34,35] $Ni_{46}Mn_{24}Ga_{22}Co_4Cu_4$ alloy shows the characteristics that the strain activity violently changes in a narrow temperature range, which makes this alloy useful in the applications of thermo actuators and sensors.

4. Conclusions

In this paper, the NiMnGaCoCu alloy martensitic transformation between ferromagnetic parent phase and martensite phase is observed. The degree of crystal-lattice mismatch has a prominent effect on martensitic transformation temperature range (ΔT), which is closely related to lattice distortion ratio (c/a). Both ΔT and c/a increase when $x > 4$, and decrease when $x < 4$ with x increasing for $Ni_{46}Mn_{28-x}Ga_{22}Co_4Cu_x$ ($x = 3.4$, 3.7, 4, 4.3, 4.6) alloys. A minimal value of ΔT (about 1 K) and c/a (1.144) are observed at $x = 4$. These changes of ΔT and c/a should be attributed to the influence of mismatch between austenite parent phase and martensite phase. These variations may offer useful information to further search for Ni–Mn-based shape memory alloys.

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