Phase Transformations and Magnetostriction in Ni–Mn–Ga Ferromagnetic Shape Memory Alloys

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Composition dependence of martensitic transformation and ferromagnetic transformation behavior has been investigated for Ni–Mn–Ga ferromagnetic shape memory alloys in a polycrystalline state. DSC measurements were performed to determine the transformation temperatures. Magnetic properties were studied by VSM. It was revealed that martensitic transformation temperature depends strongly on valence electron concentration, e/a , of the alloys, while ferromagnetic transformation temperature exhibits only mild dependence. Room temperature magnetization was found to decrease with increasing e/a . Magnetostriction was measured for Ni–23.1Mn–24.6Ga alloy as a function of magnetic field and temperature. The largest magnetostriction was observed near the martensitic transformation temperatures.

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1. Introduction

There have been a growing number of investigations on martensitic transformations in ferromagnetic alloy since it enables to obtain further insights regarding unsettled fundamental issues on martensitic transformation, such as nucleation and kinetics of transformation.¹⁾ In addition, ferromagnetic shape memory alloys are excellent candidates for magnetic actuator materials since one can invoke large strain either through martensitic transformation or rearrangements of martensite variants induced by an external magnetic field. The latter mechanism is, in essence, magnetically induced twinning/detwinning in martensite phase. Thus, it is appropriate to call this kind of magnetostriction as “twinning magnetostriction” to distinguish it from a conventional one, which is the distortion of crystal lattice caused by the rotation of magnetic moment. Among several ferromagnetic shape memory alloys, the present study focuses on Ni–Mn–Ga alloy, the first alloy in which large twinning magnetostriction was found. Martensitic transformation in Ni₂MnGa alloy and its thermoelastic nature were discovered by Webster *et al.*²⁾ They have reported an apparent decrease of low field magnetization at martensitic transformation temperature due to low crystallographic symmetry of martensite phase and, as a result, a high magnetocrystalline anisotropy. Since then, there have been a number of studies regarding various aspects of phase transformations in this alloy. Twinning magnetostriction of 0.15% was discovered by Ullakko *et al.*^{3,4)} for a single crystal of Ni–Mn–Ga; this value is comparable to so-called giant magnetostriction in certain class of 3d/rare-earth intermetallic compounds, such as Tb_{0.3}Dy_{0.7}Fe₂ (commercially known as Terfenol-D). More recently, James *et al.* have shown that

one-way strain of up to 5% can be magnetically induced in a single crystal of martensite phase.⁵⁾

Chernenko *et al.*^{6,7)} investigated composition dependence of phase transformation behavior in Ni–Mn–Ga alloy, but there exists a large scatter in the data, which will be discussed later. Vasilev *et al.*⁸⁾ also studied the phase transformation of Ni–Mn–Ga alloys for a limited range of compositions with a constant Ga concentration of 25 at%. The present investigation was undertaken to further clarify the composition dependence of phase transformation characteristics and to elucidate the temperature dependence of magnetostriction of Ni–Mn–Ga alloy.

2. Experimental

Alloy ingots were prepared by a tri-arc melting furnace under an argon atmosphere. Ingots with 12 different compositions were prepared; their compositions as determined by EDX are plotted in a ternary phase diagram in Fig. 1. The ingots were homogenized at 1073 K for 48–72 hours in an argon atmosphere. They were then cut for various measurements and analysis. Each sample was given a final heat treatment of 1 hour at 1073 K in an argon atmosphere, followed by quenching into water or furnace cooling. Grain size of the samples was a few millimeters.

Martensitic transformation temperature was measured using Rigaku DSC 8230L at a heating/cooling rate of 10 K/min. Magnetic field-magnetization curves were obtained by RIKEN BHV-55 vibrating sample magnetometer (VSM) with an applied field up to 1.19 MA m⁻¹ (1.5 T) at room temperature.

Temperature and field dependence of magnetostriction was determined by measurements of length change of a 5 mm × ϕ 5 mm cylindrical sample under an applied magnetic field up to 9.55 MA m⁻¹ (12 T). Resolution for the measurements is

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Fig. 1 Compositions of alloys used in the present study.

15 μm , equivalent to 2×10^{-5} strain. Details of the equipment for magnetostriction measurements are described elsewhere.⁹⁾

3. Results

The DSC profile of Ni–Mn–Ga alloy vary significantly with composition, indicating that a variety of phase transformations exist in this system. Typical DSC profiles observed in Ni–Mn–Ga alloys are shown in Figs. 2(a)–(c). Figure 2(a) is the profile measured for Ni–23.0Mn–25.6Ga alloy. Step-like features in the DSC profiles denoted by the arrows correspond to ferromagnetic transformation, as confirmed by separated magnetic measurements by SQUID, and can be taken here as the Curie temperature (T_c). For the alloys near the stoichiometric Heusler composition, the transformation temperatures are lower. Also the peaks corresponding to martensitic transformation are relatively small and are comparable to those corresponding to ferromagnetic transformation, suggesting that the martensitic transformation in these alloys is a weak first order transformation. Hysteresis for martensitic and ferromagnetic transformation temperatures is about 15 and 5 K, respectively. Figure 2(b) is a DSC profile for Ni–23.1Mn–24.6Ga alloy ($e/a = 7.59$) with an intermediate transformation temperature of 245 K. In addition to the martensitic transformation peaks and ferromagnetic transformation peaks, minor peaks, denoted by triangles, can be recognized between them. This transformation is reversible and associated with a hysteresis of about 10 K, similar to that for the martensitic transformation. The origin of the minor peaks are still under investigation, but may be related to an intermediate phase reported for near stoichiometric alloys by Kokorin *et al.*,¹⁰⁾ Cesari *et al.*,¹¹⁾ and also by Planes *et al.*¹²⁾ It was reported that for an alloy near the stoichiometric Heusler composition the latent heat associated with intermediate phase transformation is very small and detectable only when a large amount of sample was tested.¹²⁾ The present results suggest that the latent heat becomes large enough to be detected in conventional DSC measurements in off-stoichiometric alloys. Figure 2(c) is a DSC profile for Ni–20.0Mn–25.0Ga alloy associated with a

Fig. 2 Typical DSC profiles of Ni–Mn–Ga alloys.

higher martensitic transformation temperature. In this alloy only the peaks corresponding to martensitic transformation can be seen; other features corresponding to ferromagnetic transformation as well as the minor peaks can not be recognized. Magnetic measurements indicated that this alloy is ferromagnetic at room temperature. However, we were not able to assess the T_c since magnetic measurements at above room temperature were not carried out in the present study.

Peak temperatures corresponding to forward and reverse martensitic transformations (denoted as M^* and A^* , respectively) are plotted as a function of valence electron concentration, e/a , in Fig. 3. For each alloying element, the valence electron configuration was assumed to be $3d^8 4s^2$ for Ni, $3d^5 4s^2$ for Mn and $4s^2 4p^1$ for Ga. These configurations are commonly used in electronic band calculations for the Heusler alloys. Ishida *et al.*¹³⁾ have shown that the lattice parameters of Ni_2MnGa calculated by band theory using the above configuration agree well with experimental results. The single crystal data by Webster *et al.*²⁾ is also indicated for the

Fig. 3 Martensitic transformation temperatures determined by DSC measurements. The solid circles and squares denote M^* and A^* , respectively. The open square indicates the data by Webster *et al.*²⁾

Fig. 4 Ferromagnetic transformation temperatures (T_c , solid circles) and minor peak temperatures (T_l , open circles) as a function of e/a . The open square indicates the T_c measured by Webster *et al.*²⁾

stoichiometric Heusler composition corresponding to e/a of 7.5. As can be seen in Fig. 3, M^* and A^* increase linearly with e/a . This suggests that electron concentration is a key parameter to determine the stability of the parent phase and martensite phase as in the case of Cu–Zn–Al shape memory alloys.¹⁴⁾ Hysteresis is more or less constant for all the alloys except for the alloy with the highest transformation temperatures. The Curie temperatures as well as temperatures corresponding to the minor peaks in DSC profiles, T_l , are also plotted as a function of e/a in Fig. 4. While the M^* depends on e/a rather strongly, the e/a dependence of T_c is insignificant. Also, T_l does not seem to depend on e/a strongly.

Magnetization at 1.19 MA m^{-1} (1.5 T) measured at room temperature for various alloys are plotted as a function of e/a in Fig. 5. In spite of the experimental scatter, the magnetization decreases with increasing e/a . Neutron diffraction measurements by Webster *et al.*²⁾ and more recent ones by Brown *et al.*¹⁵⁾ revealed that Mn atoms carry the most of magnetic moment in Ni_2MnGa , which is also supported by the aforementioned electronic band calculations.^{13,16)} But the present study revealed that the increasing Mn concentration does not always increase the magnetization and e/a seems to be a better parameter to describe the magnetic properties of the Ni–Mn–Ga alloy.

Representatives of magnetostriction curves for Ni–23.1Mn–24.6Ga are shown in Fig. 6. The martensitic transformation start (M_s) and finish (M_f) temperatures for this alloy were 240 and 251 K, respectively, as determined by DSC (Fig. 2(b)). Magnetostriction in the parent phase at 338 K is very small as seen in Fig. 6(a). The largest magnetostriction was obtained at around 250 K (Fig. 6(b)). It can be seen that in the first cycle, the strain appears at a relatively lower field and is larger than the subsequent cycles. The curve is significantly different from those reported by Ullakko *et al.*^{3,4)} and by James *et al.*⁵⁾ The magnetic field required to obtain the maximum strain is far larger than that in the previous studies.

Fig. 5 Magnetization at 1.19 MA m^{-1} (1.5 T) measured at room temperature as a function of e/a . The open square indicates the data by Webster *et al.*²⁾

This can be attributed to that, in the present study, strain was measured in polycrystalline states, while those in the previous ones are for single crystals. In the present samples the martensite variant rearrangements were inhibited by elastic constrain around grain boundaries. A larger magnetic field is required to overcome this constrain. With further decreasing temperature, magnetostriction decreases as shown in Fig. 6(c).

Temperature dependence of the magnetostriction is shown in Fig. 7. Strain obtained at first cycle and those for the subsequent cycles are shown by the solid line and broken lines, respectively. The curves show the maxima at temperatures just below the M^* temperature for both the first cycle and following cycles. This can be attributed to the mobility of boundaries between the martensite variants; at a lower temperature,

Fig. 6 Representatives of magnetostriction curves in Ni–23.1Mn–24.6Ga measured at various temperatures. (a) 338 K ($>M_s$). (b) 251 K ($=M_s$). (c) 208 K ($<M_t$).

the boundaries have a lower mobility and it requires a higher stress to move, as exemplified by the temperature dependence of yield stress in shape memory alloys.¹⁷⁾

4. Discussion

In Fig. 8, the present results of transformation temperature measurements are compared with two previous studies. The present results are in overall agreement with the previous investigations. There are, however, a few remarks to be made. In the investigation by Vasil'ev *et al.*,⁸⁾ both martensitic and magnetic transformation temperatures were determined by electrical resistivity, DSC and low-field magnetic susceptibility measurements for a series of alloys of $\text{Ni}_{2+x}\text{Mn}_{1-x}\text{Ga}$ ($x = 0.0\text{--}0.19$). Their data are reproduced here as a function of e/a in Fig. 8(a). The data has a milder dependence on e/a than the present results, particularly for the high e/a al-

Fig. 7 Magnetostriction as a function of temperature in Ni–23.1Mn–24.6Ga alloy.

loys as shown. Our study indicated that the isothermal aging of the parent phase at 573–673 K increases both M^* and T_c about 30 K.¹⁸⁾ Overholser and Wuttig¹⁹⁾ have measured the order/disorder transformation temperatures and determined the degree of order in Ni–Mn–Ga alloys using high temperature DTA and neutron diffraction. Their results indicate that upon solidification the alloy orders directly to the B2 structure. It was also shown that the B2/L2₁ transition temperature is the highest for the stoichiometric Heusler composition (1071 K), which is very close to our homogenization temperature. The observed M^* increase by aging can be attributed to an increase in the degree of L2₁ order. Difference of e/a dependence between the two studies may be due to a different degree of long range order, caused by a slight difference in homogenization temperatures or in the quenching procedures.

As can be seen in Fig. 8(b) the data obtained by Chernenko *et al.*⁶⁾ exhibit rather large scatter, which could be attributed to compositional inhomogeneity in the alloys. They have pointed out that there exists an inflection on M^* vs. e/a line at $e/a = 7.7$. In the present results, the data with e/a range between 7.6 and 7.7 lie on the line extrapolated from the lower e/a range; we did not find the inflection point at least in the measured e/a range.

The relation between the martensitic transformation and ferromagnetic transformation is also worth to discuss. Vasil'ev *et al.* have shown that martensitic transformation temperatures coincide with ferromagnetic transformation temperatures for the alloys with e/a ranging from 7.63 to 7.65.⁸⁾ For alloys with higher e/a values, martensitic transformation temperatures are higher than that for ferromagnetic transformation as shown by Chernenko *et al.*⁶⁾ Electronic band calculations for the stoichiometric Ni_2MnGa by Fujii *et al.*²⁰⁾ and for a $\text{Ni}_{2.25}\text{Mn}_{0.75}\text{Ga}$ alloy ($e/a = 7.69$) by Ishida *et al.*¹³⁾ have shown that the martensitic transformation is due to the band Jahn-Teller effect, and is possible only in the ferromagnetic state. This is obviously not valid in the case for higher e/a alloys since they transform to martensite state

Fig. 8 Comparison of transformation temperatures in Ni-Mn-Ga alloys. The solid and broken lines indicate the M^* and T_C in the present study, respectively. (a) Data by Vasilev *et al.*⁸⁾ The open square and closed circles denote T_C and M^* , respectively. (b) Data by Chernenko *et al.*⁶⁾ The open and closed symbols denote T_C and M^* , respectively. Different symbols indicate the alloys of different classes (see Ref. 6) for details).

and subsequently to ferromagnetic phase. Thus the martensitic transformation in the alloys with $M^* > T_C$ might have a different origin from that in the alloys with lower e/a .

5. Conclusion

Valence electron concentration e/a has been found to be a useful parameter to describe the composition dependence of phase transformations and magnetic properties of ternary Ni-Mn-Ga ferromagnetic shape memory alloys. Martensitic transformation temperature increases significantly with e/a , while magnetization decreases. Ferromagnetic transformation temperature exhibits only mild e/a dependence. Magnetostriction was measured as a function of magnetic field and temperature. It was revealed that large magnetostriction can be obtained at temperatures just below the martensitic transformation temperature.

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