Phase Transformation and Magnetic Properties in $\text{Ni}_{52}\text{Fe}_x\text{Mn}_{21-x}\text{Ga}_{27}$ Alloys

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Effect of chemical composition was investigated on martensitic transformation temperatures, Curie temperature, magnetization for $\text{Ni}_{52}\text{Fe}_x\text{Mn}_{21-x}\text{Ga}_{27}$ alloys. X-ray diffraction patterns revealed that all the samples were in a single Heusler (L_{2_1}) phase state at room temperature. Forward and reverse martensitic transformation temperature, M^* and A^* , decreased with Fe content, x , up to 15 mol% and then turned to increase by further addition of Fe. Composition dependence of the Curie temperature exhibited a reversed tendency compared with M^* . The structure of martensite was 10M for the alloys with $x < 15$ and a mixture of 14M and 10M for $x = 20$. Electron diffraction patterns of L_{2_1} phase exhibited intense diffuse streaks on cooling, which were longer than those observed in ternary Ni–Mn–Ga.

KEY WORDS: martensitic transformation; shape memory alloys; Curie temperature; Heusler alloy.

1. Introduction

Interplay between martensitic transformation and magnetic field had been studied mainly for academic reasons. Kakeshita *et al.* investigated the effect of magnetic field on transformation kinetics in Fe–Ni alloys.¹⁾ They have also found that the magnetic field also influence the morphology of field induced martensite phase.²⁾ Muto *et al.* reported that magnetic field can affect arrangements of martensitic twins during cooling in Fe–Pd shape memory alloys.³⁾

Recently, large magnetic-field induced strain was reported for martensite phase in Ni_2MnGa Heusler alloy.⁴⁾ The observed strain is due to the rearrangements of martensitic twin variants. This discovery ignited extensive investigations on ferromagnetic shape memory alloys (FSMAs). More recently 10% strain has been reported in 14M martensite phase in Ni–Mn–Ga,⁵⁾ and thus FSMA is potential material for a new class of magnetic actuators. Various FSMA systems have been investigated, such as, Ni–Fe–Ga,⁶⁾ Co–Ni–Al,⁷⁾ Fe–Pd⁸⁾ and Fe–Pt.⁹⁾ However the problem with these FSMA is low stability of ferromagnetic martensite. Ni–Mn–Ga alloy is one of a few FSMA systems in which ferromagnetic martensite phase is stable above room temperature.

Present paper reports the results of investigation on the effect of the chemical composition on the stability of ferromagnetic martensite phase and magnetic properties in $\text{Ni}_{52}\text{Fe}_x\text{Mn}_{21-x}\text{Ga}_{27}$.

2. Experimental

Alloy ingots were prepared using tri-arc melting furnace. Ingots were heat-treated at 1073 K for 259.2 ks in a sealed quartz tube for homogenization and then quenched into water. The samples for various measurements were cut from the ingots. Chemical composition of the ingots was measured by energy dispersive X-ray spectroscopy (EDX) on scanning electron microscope (SEM).

Phase transformation temperatures were determined by RIGAKU DSC-8230L differential scanning calorimeter (DSC) with a heating/cooling rate of 0.17 K s^{-1} . Magnetization curves were measured by Tamagawa TM-VSM261843-HGC vibrating sample magnetometer (VSM). The Curie temperature was determined by measuring temperature dependence of magnetization under an applied field of 1 kOe. Crystal structure of parent and martensite phases was characterized by X-ray powder diffraction on RIGAKU RINT-2200X with Cu-K_α radiation. Sample cooling stage was used to characterize the martensite structure at low temperatures. Lattice parameters were calculated using “CellCalc” software.¹⁰⁾

Microstructural observations were made on Hitachi H-800 and JEOL JEM-2010 transmission electron microscope (TEM) both operated at 200 kV. Sample cooling stage was used to observe the changes in crystallographic structures at low temperatures.

3. Results and Discussion

X-ray diffraction patterns measured at room temperature

Fig. 1. X-ray diffraction patterns at room temperature.

Fig. 2. Lattice parameter as a function of Fe content.

are shown in **Fig. 1**. It was revealed that all the samples are in a single phase state with the $L2_1$ structure. Lattice parameter, a , of the $L2_1$ phase was calculated and plotted in **Fig. 2**. The a value monotonically decreases with Fe content. Similar tendency has been observed for $\text{Ni}_{50}\text{--Mn}_{25-x}\text{--Fe}_x\text{--Ga}_{25}$ alloys with $x \leq 17.5$.¹¹⁾ A reported value (0.579 nm) for $\text{Ni}_{52}\text{Mn}_{16}\text{Fe}_8\text{Ga}_{24}$ single crystal¹²⁾ also agrees well with the present results. The lattice parameters are close to the line connecting the lattice parameters of a stoichiometric Ni_2MnGa (0.5826 nm¹³⁾ and Ni_2FeGa (0.57405 nm¹⁴⁾). This tendency cannot be explained by the difference in atomic size since Fe and Mn has almost identical atomic radii of 0.17 nm. It can be explained by their electronic structure. Fe has the closer 3d electronic structures to Ni atom at the nearest neighbor sites. Thus stronger hybridization of 3d electrons of Fe and Ni can be expected than with Mn and Ni, which makes the structure more compact.

Effects of replacement of Mn by Fe in $\text{Ni}_{52}\text{Fe}_x\text{Mn}_{21-x}\text{Ga}_{27}$ on martensitic transformation temperature and the Curie temperature are shown in **Fig. 3**. It can be seen that the peak temperatures corresponding to forward and reverse martensitic transformation, M^* and A^* , decrease and the Curie temperature, T_C , increase with Fe content up to 15 mol%. But this tendency is reversed by further addition of Fe. Observed increase in T_C and decrease in martensitic

 Fig. 3. M^* and T_C as a function of Fe content.

Fig. 4. Saturation magnetization at room temperature as a function of Fe content.

transformation temperature by addition of Fe agrees with those reported by Kikuchi *et al.*¹¹⁾ More detailed comparison will be made later.

Saturation magnetization at room temperature slightly decreases with an Fe content up to 15 mol% and become significantly lower for $x=20$ alloy as shown in **Fig. 4**. A slightly higher value of 61.9 emu/g was reported for $\text{Ni}_{52}\text{Mn}_{16}\text{Fe}_8\text{Ga}_{24}$ single crystal¹²⁾ under a magnetic field applied for [100]. Taking into account the difference between a single crystal and polycrystalline sample, the agreement is fair. Magnetization of the martensite phase measured at 4.2 K in $\text{Ni}_{50}\text{--Mn}_{25-x}\text{--Fe}_x\text{--Ga}_{25}$ alloys ($x \leq 17.5$) exhibits similar tendency.¹¹⁾

Figure 5 is the X-ray diffraction pattern obtained at 83 K for $\text{Ni}_{52}\text{Fe}_2\text{Mn}_{19}\text{Ga}_{27}$. The observed main peaks can be indexed as the 10M structure.¹⁵⁾ The lattice parameters were determined to be $a=0.432$ nm, $b=0.548$ nm, $c=2.962$ nm, $\beta=90.1$ degree. However, there are several unidentified minor peaks, which can be due to small deviation of atomic positions (shuffling) in the monoclinic unit cell. Similar patterns were obtained for alloys with Fe content up to $x=15$.

Results of *in situ* cooling TEM observations for $\text{Ni}_{52}\text{Fe}_{20}\text{Mn}_1\text{Ga}_{27}$ alloy are shown in **Fig. 6**. Figures 6(a) and 6(c) are the TEM bright field (BF) images and selected area diffraction (SAD) patterns obtained at room temperature, respectively. The SAD (Fig. 6(c)) indicates diffuse streaks

along the six $\langle 110 \rangle$ directions around the main 220 type spots of the $L2_1$ phase. The diffuse streaks intensify on cooling as seen in Fig. 6(d). The diffuse streaks can be attributed to the phonon softening observed by inelastic neutron scattering.¹⁶⁾ The present authors reported that the formation of satellite spots at $1/6\langle 220 \rangle$ positions at the intermediate transformation temperature, T_1 for the Ni–23.0Mn–25.6Ga.¹⁷⁾ In the present alloy, the satellite spots were not observed and the sample transformed directly to martensite phase without intermediate phase transformation as shown in Figs. 6(b), 6(e) and 6(f). In addition, the length of the streaks are about $1/4$ of the g_{220} , which is significantly longer than the $1/6 g_{220}$ streaks observed in Ni–Mn–Ga, suggesting that phonon softening behavior is different from the one in Ni–Mn–Ga. Figure 6(b) is a BF image of martensite phase at 110 K. Numerous striations seen in the image are high density of stacking faults, corresponding to the streaks in the SADP (Fig. 6(e)). The satellite spots in Fig. 6(e) indicate that the structure of martensite is $14M$. There often exists the area, which exhibits irregular spaced satellite as shown in Fig. 6(f).

Measured phase transformation temperatures are plotted

Fig. 5. X-ray diffraction pattern of $Ni_{52}Fe_5Mn_{16}Ga_{27}$ at 83 K.

Fig. 6. TEM bright field image ((a) and (b)) and electron diffraction patterns ((c)–(f)) for $Ni_{52}Mn_1Fe_{20}Ga_{27}$, (a) and (c): room temperature; (d) 160 K; (b), (e), (f) 110 K. Beam direction/ $[-11-1]_{L2_1}$.

as a function of valence electron concentration, e/a , in Fig. 7. To calculate e/a , the following valence electron configuration was assumed: Ni: $(3d)^8(4s)^2$; Mn: $(3d)^5(4s)^2$; Fe: $(3d)^6(4s)^2$; Ga: $(4s)^2(4p)^1$. Relevant phases in each domains are indicated. The data obtained for similar alloy systems found in the previous investigations are also indicated:

- A) $Ni_{50-x}Mn_{25-x}Fe_xGa_{25}$ ($x \leq 17.5$, Kikuchi *et al.*¹¹⁾): M^* , A^* and T_C determined from temperature dependence of initial magnetic permeability are denoted by solid symbols. The samples were heat-treated at 1 123 K for 259.2 ks and water quenched.
- B) $Ni_{54-x}Fe_xMn_{20}Ga_{25}$ ($x \leq 4$, Khovailo *et al.*^{18,19)}): T_m ($= (M_s + A_s)/2$, M_s and A_s measured by DSC) and T_C measured from permeability are denoted by + and ×, respectively. The samples were heat-treated at 1 050 K for 177.6 ks and quenched in ice water.
- C) Ternary $Ni_{73-x}Fe_xGa_{27}$ ($x \leq 22$, Oikawa *et al.*²⁰⁾): M_s and A_p measured by DSC and T_C measured from per-

Fig. 7. Transformation temperatures as a function of valence electron concentration. Open and gray symbols indicate the data by Kikuchi *et al.*¹¹⁾ and by Oikawa *et al.*²⁰⁾ respectively. Data by Khovailo *et al.*^{18,19)} are denoted by + (T_C) and × (T_m).

meability are denoted by gray solid symbols. The samples were heat-treated at 1473 K for 10.8 ks and quenched into ice water. This data covers the higher e/a range than the present data.

It can be seen that the transformation temperatures measured by Kikuchi *et al.*¹¹⁾ exhibit a similar tendency to the present data but they are less sensitive to e/a than the present data. The T_m data by Khovailo *et al.*^{18,19)} is significantly higher than the present data and those by Kikuchi *et al.* while T_C is lower. The reason for these discrepancies are not clear at this point. Martensitic transformation temperatures and the Curie temperature in these alloys are sensitive to the degree of $L2_1$ order in the parent phase.²¹⁾ Our preliminary investigation indicated that $T_c^{(B2/L21)}$ ($B2$ to $L2_1$ ordering temperature) is in a temperature range between 1000 and 1073 K, very close to the heat treatment temperatures employed in these studies. Thus the discrepancies might be due to a slight difference in the chemical compositions or in the relative position of the heat treatment temperature with respect to the $T_c^{(B2/L21)}$.

It can be also seen in Fig. 8 that for the lower e/a alloy, the M^* decreases with increasing e/a , an opposite tendency to the case of ternary Ni–Mn–Ga.^{22,23)} The e/a dependence of martensitic transformation temperatures changes from negative dependence to positive dependence at around $e/a=7.6$. Structure of martensite also changes from 10M to 14M at this e/a range.

4. Summary

Effects of Fe substitution of Mn on martensitic transformation, the Curie temperature, magnetic properties were investigated in $Ni_{52}Fe_xMn_{21-x}Ga_{27}$. Valence electron density (e/a) dependence of martensitic transformation temperature and the Curie temperature changed its tendency at $e/a \sim 7.6$. The structure of martensite also changed from 10M to 14M although some 10M was also observed. Electron diffraction pattern of indicated the diffuse streaks similar to those observed in ternary Ni–Mn–Ga but they were significantly longer than the ones observed in the Ni–Mn–Ga.

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