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Effect of Fourth Elements on Phase Transformations in Ni - Mn - Ga Heusler Alloys

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Effect of addition of Al, Co, Cu, Ge, or Sn on phase transformation behavior was investigated for Ni-Mn-Ga ferromagnetic shape memory alloys. Dependence of the Curie temperature and martensitic transformation temperature on valence electron density seems to be different from that of ternary alloys, except for the case of an alloy with Co.
Key words: shape memory alloys, twinning magnetostriction, the Heusler alloys, lattice parameters

1. INTRODUCTION

There have been an increasing number of researches on Ni-Mn-Ga Heusler alloys since the alloy exhibits large twinning magnetostriction in martensite phase, and is a good candidate for magnetic actuator materials[1,2]. However, there exist several problems to be overcome for the materials to be practically used, e.g., inherent brittleness and lower martensitic transformation temperatures. To improve the properties we have been investigating the effect of composition, heat treatment and addition of fourth elements on phase transformation behavior.
This paper describes some preliminary results concerning the effect of fourth elements on phase transformation behavior of Ni-Mn-Ga alloys.

2. EXPERIMENTAL

Alloy ingots were prepared by argon arc melting. They were homogenized at 1073 K for 48 - 72 hours in an Ar atmosphere, then quenched into room temperature water. Compositions of the ingots were analyzed by EDX in JEOL JSM – 6300 SEM. List of analyzed composition use is shown in Table 1.

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

composition (at%)	e/a
Ni-23.8Mn-24.9Ga-3.2Co	7.52
Ni-23.7Mn-24.5Ga-3.6Cu	7.61
Ni-22.5Mn-24.1Ga-3.1Al	7.43
Ni-24.0Mn-23.7Ga-2.4Ge	7.48
Ni-27.6Mn-22.4Ga-3.5Sn	7.57

Phase transformation behavior was characterized by DSC in the range between 120 K - 373 K, and magnetic properties by VSM. Details of the experiments are described in an accompanying paper. X-ray powder diffractometry was done on RIGAKU RINT - 2200 (50 kV - 30 mA) using Mo-K_α radiation ($\lambda_{K\alpha 1}$ = 0.7029 Å). Sample powders were obtained by crashing and grinding in an agate mortar. They are sealed in a silica tube and treated at 1073 K for an hour followed by quench into water.

3. RESULTS and DISCUSSION

An example of X-ray diffraction pattern is shown for Ni-Mn-Ga-Cu in Fig. 1. The pattern indicates the sample is a single phase of bcc. Other alloys were also found to be a single bcc phase at room temperature.
Lattice parameters, a, measured for the quaternary alloys are listed in Table 2 along with the value for

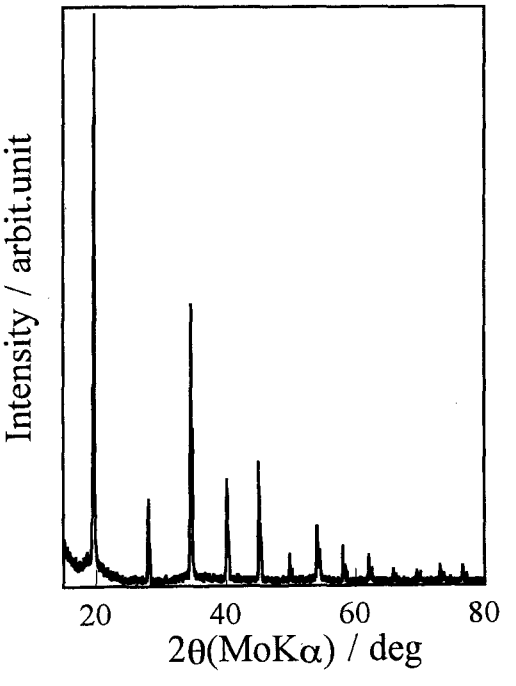

Fig. 1. X-ray diffraction pattern of Ni-Mn-Ga-Cu alloy.

stoichiometric Ni_2MnGa[3]. There seems to be no systematic dependence of lattice parameters on e/a. An alloy with Sn has the largest lattice parameter, reflecting its large atomic radius and those with Cu and Al exhibit smaller lattice parameters. For the present alloys M* was found to be lower than the measurable temperature range for the DSC; only T_c was determined.

Table. 2. Lattice parameters determined by X-ray diffraction.

Composition (at%)	lattice parameter, a (Å)
Ni-23.8Mn-24.9Ga-3.2Co	5.821 ± 0.005
Ni-23.7Mn-24.5Ga-3.6Cu	5.796 ± 0.044
Ni-22.5Mn-24.1Ga-3.1Al	5.799 ± 0.018
Ni-24.0Mn-23.7Ga-2.4Ge	5.855 ± 0.005
Ni-27.6Mn-22.4Ga-3.5Sn	5.877 ± 0.014
Ni-25.0Mn-25.0Ga	5.825 [3]

Results of magnetization measurements are shown in Fig. 2 for the case of Ni-Mn-Ga-Cu alloy. Slope of the initial part of the magnetization curve decreases with decreasing temperature. This tendency can be seen more clearly in Fig. 3 in which the magnetization at fixed values of applied field are plotted as a function of temperature. This can be attributed to an increase in magnetic anisotropy and to a decrease in a volume for which the axis of easy magnetization is close to the direction of the applied field, both caused by the lowering of crystallographic symmetry by martensitic transformation.

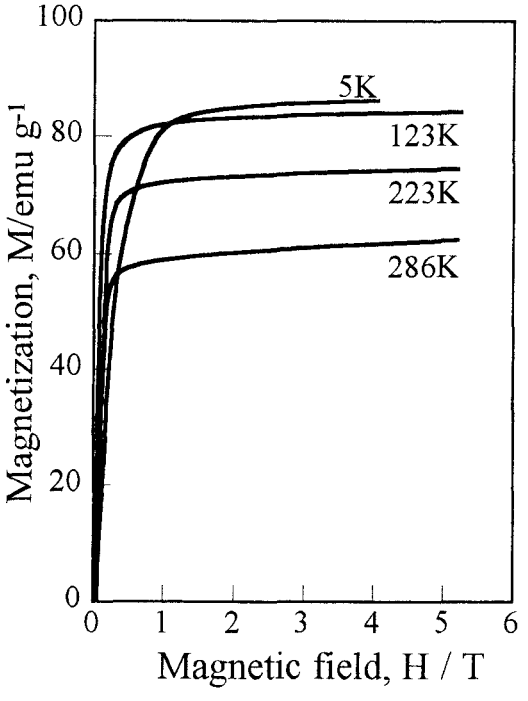

Fig. 2. Magnetization curves obtained at various temperatures for Ni-Mn-Ga-Cu alloy.

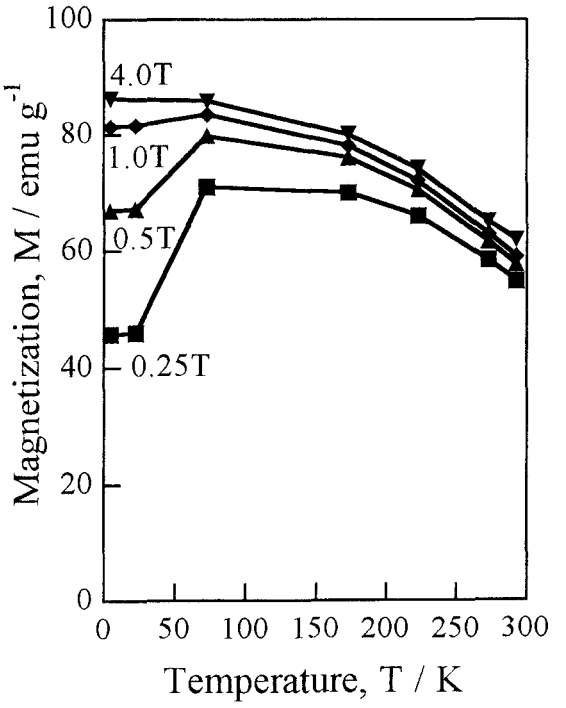

Fig. 3. Saturation magnetization as a function of temperatures for Ni-Mn-Ga-Cu alloy.

In the previous investigations for ternary alloys a good linear correlation was found between M*, T_c, and valence electron density e/a[4,5]. Thus the transformation temperatures for the quaternary alloys are also plotted against e/a in Fig. 4. Here the M* was shown as a temperature range over which the magnetization decrease was observed. The solid line and broken line in Fig. 4 indicate the e/a dependence of M* and T_c for ternary alloys, respectively. Electron configuration are assumed to be, Ni: $3d^84s^2$, Mn: $3d^54s^2$, Ga: $4s^24p^1$, Co: $3d^74s^2$, Cu: $3d^{10}4s^1$, Al: $3s^23p^1$, Ge: $4s^24p^2$ and Sn: $5s^25p^2$. They are consistent with those used in electronic calculations for the Heusler alloys. In Fig. 4, T_c increases slightly with e/a, while M* seems to decrease except for a Co containing alloy. This is different from the case of ternary Ni-Mn-Ga alloys. It should be noted that for the alloy with Co, M* seems to agree with the ternary data and lattice parameter also agree with that of the Ni_2MnGa.

It is well known that the interatomic distance is also an important factor controlling the magnetic and electronic interaction in several compounds. In the case of the Heulser alloys an effect of hydrostatic pressure was investigated for several Ni-base Heusler alloys including Ni_2MnGa by Kanomata et al. [6]. They have found that hydrostatic pressure of 5.7 GPa increases the Curie temperature from 355 K to about 360 K, while it decreases martensitic transformation temperature from 168 K to 162 K. Thus, in addition to e/a, the lattice parameter could be also a pertinent parameter to describe the

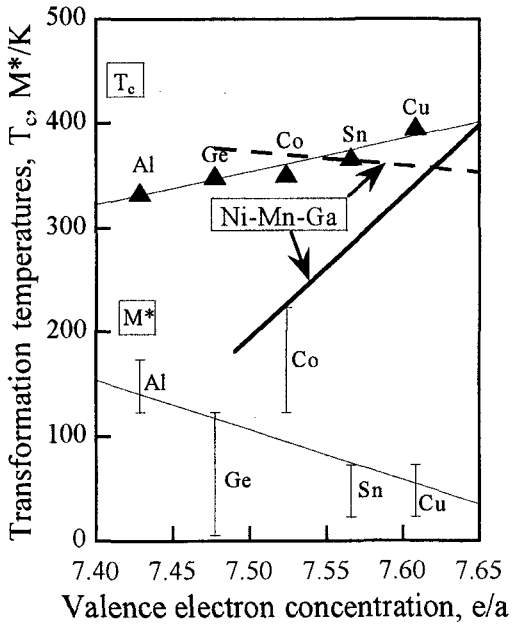

Fig. 4. M* and T_c as a function of e/a.

transformation behavior in the quaternary system. In the present results, the alloys with Ge or Sn has the largest lattice parameter but they appear to have a lower M* than the ternary alloys. Thus it does not agree with the previous results. This difference might be due to a change in the ordered structures by the addition of fourth elements. In ternary Ni-Mn-Ga alloys, an increase in a degree of $L2_1$ order raises M* and T_c as described in an accompanying paper [7]. Thus both M* and T_c are sensitive to the ordered structures. If the effect of forth elements are so that they decreases the B2 or $L2_1$ ordering temperature, they would suppress the ordering reaction, which could affect M* and T_c.

More detailed investigations are in progress to clarify the effect of fourth elements on phase transformation behavior in Ni-Mn-Ga alloys.

References

1) K. Ullakko, J. k. Huang, C. Kantner, C. O'Handley and V. V. Kokorin, J. Appl. Phys. Lett., **69** (1996) 1966.
2) K. Ullakko, J. K. Huang, V. V. Kokorin and R. C. O'Handley, Scrip. Metall., **36** (1997) 1133.
3) P. J. Webster, K. R. A. Ziebeck, S. L. Town and M. S. Peak, Philos. Mag., **49B** (1984) 295.
4) V. A. Chernenko, Scripta Mater., **40** (1999) 523.
5) K. Tsuchiya, A. Ohashi, D. Ohtoyo, H. Nakayama and P. G. McCormick, manuscript in preparation.
6) T. Kanomata, K. Shirakawa and T. Kaneko, J. Magn. Magn. Mater., **65** (1987) 76.
7) K. Tsuchiya, D. Ohtoyo, M. Umemoto and H. Ohtsuka, J. Mater. Res. Soc. Japan, to be published.

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