Influence of Fe and Co on Phase Transitions in Ni-Mn-Ga Alloys

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Differential scanning calorimetry (DSC) and magnetic measurements were performed to study the influence of ferromagnetic 3-d transition elements Fe and Co on structural and magnetic properties of ferromagnetic shape memory alloys Ni2MnGa. Addition of Fe or Co on the Ni sites decreases the temperature of martensitic phase transition $T_m$, whereas addition of Co on the Mn sites results in a considerable increase of $T_m$. Magnetic measurement revealed that Curie temperature $T_C$ increases upon substitution of Fe or Co for Ni. This observation is of importance for design of high temperature ferromagnetic shape memory alloys.

Keywords: quaternary Heusler alloys, martensitic transition, Curie temperature, ferromagnetic shape memory alloys

I. INTRODUCTION

In recent years ferromagnetic shape memory alloys have attracted considerable attention as a new class of actuator materials (see, for a recent review, Ref. 1). Among ferromagnetic shape memory alloys, the largest magnetic-field-induced strains arising from conversion of martensitic variants under action of a magnetic field2–3 or caused by the shift of the martensitic transition temperature4–5 have been observed in the most intensively studied Ni2MnGa alloy system.

Ni2MnGa is a representative of Mn-containing Heusler alloys. For the stoichiometric composition a structural phase transition of martensitic type from the parent cubic to a complex tetragonally based structure occurs at $T_m = 202$ K, whereas long-range ferromagnetic ordering sets at $T_C = 376$ K. The martensitic transition temperature $T_m$ was found to be very sensitive to the composition, ranging from liquid helium temperature up to over 600 K. Contrary to $T_m$, Curie temperature $T_C$ of Ni-Mn-Ga alloys is less composition dependent. Based on the published experimental results6–8 it can be concluded that the highest $T_C \approx 380$ K is observed in the stoichiometric Ni2MnGa. A decrease of $T_C$ in the alloys with deficiency in Mn, which possesses a magnetic moment of $\sim 4 \mu_B$, is due to the dilution of the magnetic subsystem. For the alloys with Mn excess, it was suggested that the decrease in $T_C$ is accounted for by antiferromagnetic coupling of the extra Mn atoms9–11.

Analyzing data collected for a broad compositional range of Ni-Mn-Ga alloys, Chernenko12 pointed out that there exists a correlation between the electron concentration and stability of high-temperature $\beta$-phase in the Ni-Mn-Ga system. Now it is generally acknowledged that a change of electron concentration $e/a$ significantly affects martensitic transition temperature $T_m$ of Ni-Mn-Ga alloys, and, therefore, an empirical relationship between $T_m$ and $e/a$ can be reasonably used for the preparation of alloys with required martensitic transition temperature. Since large magnetic-field-induced strains are observed only in the ferromagnetic state, an efficient control of the ferromagnetic ordering temperature is of importance for realization of this effect in a large temperature interval and development of high temperature ferromagnetic shape memory alloys. Since previous experimental studies13 have shown that any deviation from the stoichiometry results in decrease of $T_C$ in Ni-Mn-Ga alloys, we studied the influence of 3-d ferromagnetic transition elements Fe and Co on Curie temperature $T_C$ and martensitic transition temperature $T_m$ of Ni-Mn-Ga.

II. SAMPLE PREPARATION AND MEASUREMENTS

Co- and Fe-containing Ni-Mn-Ga ingots of various compositions were prepared by arc-melting of high-purity initial elements in argon atmosphere. The ingots were annealed at 1100 K for 9 days in quartz ampoules and quenched in ice water. Samples for the measurements were cut from the middle part of the ingots. The real compositions of the alloys were determined by an Inductively Coupled Plasma Mass Spectrometry (ICPMS) method. Determination of the chemical compositions by ICPMS revealed that the real compositions of the alloys are close to the nominal ones. Characteristic temperatures of the direct (martensite start, $M_s$ and martensite finish, $M_f$) and the reverse (austenite start, $A_s$ and austenite finish, $A_f$) martensitic transformations were determined from differential scanning calorimetry (DSC) measurements. The martensitic transition temperature $T_m$ was calculated as $T_m = (M_s + A_s)/2$. A vibrating sample magnetometer (VSM) was used for low-field magnetic measurements. Curie temperature $T_C$ was determined as a minimum on the temperature derivative of magnetization curve measured upon heating, $dM/dT$. 


TABLE I: Nominal composition, martensitic transition temperature $T_m$ and Curie temperature $T_C$ of the alloys studied.

| Nominal composition | $T_m$ (K) | $T_C$ (K) |
|---------------------|-----------|-----------|
| Ni$_{2.13}$Co$_{0.03}$Mn$_{0.84}$Ga | 318 | 348 |
| Ni$_{2.10}$Co$_{0.06}$Mn$_{0.84}$Ga | 315 | 361 |
| Ni$_{2.07}$Co$_{0.09}$Mn$_{0.84}$Ga | 306 | 367 |
| Ni$_{2.16}$Mn$_{0.80}$Co$_{0.04}$Ga | 345 | 352 |
| Ni$_{2.16}$Mn$_{0.75}$Co$_{0.09}$Ga | 437 | 372 |
| Ni$_{2.16}$Mn$_{0.70}$Co$_{0.14}$Ga | 525 | 350 |
| Ni$_{2.16}$Fe$_{0.04}$Mn$_{0.80}$Ga | 317 | 347 |
| Ni$_{2.12}$Fe$_{0.08}$Mn$_{0.80}$Ga | 289 | 358 |
| Ni$_{2.08}$Fe$_{0.12}$Mn$_{0.80}$Ga | 267 | 377 |
| Ni$_{2.04}$Fe$_{0.16}$Mn$_{0.80}$Ga | 223 | 395 |

Nominal compositions of the alloys studied together with their martensitic and ferromagnetic transition temperatures are given in Table 1.

III. EXPERIMENTAL RESULTS

A. Co-containing alloys

The nominal compositions of the alloys studied are Ni$_{2.16-x}$Co$_x$Mn$_{0.84}$Ga ($x = 0.03$, 0.06 and 0.09) and Ni$_{2.16}$Mn$_{0.84-y}$Co$_y$Ga ($y = 0.04$, 0.09 and 0.14). It was found that the compositional dependencies of $T_m$ strongly depend on the Co position. Thus, the martensitic transition temperature $T_m$ of the Ni$_{2.16-x}$Co$_x$Mn$_{0.84}$Ga alloys slightly decreases with the Co excess, whereas in the Ni$_{2.16}$Mn$_{0.84-y}$Co$_y$Ga alloys the increase in Co content results in a significant increase of $T_m$ (Table 1). A marked increase in the temperature of martensitic transition in the alloys where Co is substituted for Mn makes these materials attractive for use as high-temperature shape memory alloys.

The behavior of Curie temperature $T_C$ in these two series of alloys also depends significantly on the position of Co. In the Ni$_{2.16-x}$Co$_x$Mn$_{0.84}$Ga alloys Curie temperature increases from 348 K to 367 K with increasing Co content from $x = 0.03$ to $x = 0.06$ (Table 1). Contrary to this, $T_C$ in the Ni$_{2.16}$Mn$_{0.84-y}$Co$_y$Ga alloys exhibits a non-monotonic dependence, and initially increases from $T_C = 352$ K ($y = 0.04$) to $T_C = 372$ K ($y = 0.09$) and then decreases to $T_C = 350$ K for $y = 0.14$ (Fig. 1). Moreover, $T_C$ in the Ni$_{2.16}$Mn$_{0.80}$Co$_{0.04}$Ga alloy exhibits hysteretic feature, as evidenced from $M(T)$ measured upon heating and cooling (Fig. 2). Such an unusual behavior of ferromagnetic transition temperature is caused by the coupling of martensitic and ferromagnetic transition temperatures and has been observed in Ni$_{2.18}$Mn$_{0.82}$Ga and Ni$_{2.19}$Mn$_{0.81}$Ga alloys.

B. Fe-containing alloys

In the Fe-containing series of Ni-Mn-Ga alloys Fe was added instead of Ni to the host Ni$_{2.20}$Mn$_{0.80}$Ga composition. The nominal compositions of Ni$_{2.20-z}$Fe$_z$Mn$_{0.80}$Ga alloys are characterized by the Fe content $z = 0.04$, 0.08, 0.12 and 0.16. DSC measurements revealed that the martensitic transition temperature continuously decreases from $T_m = 317$ K to $T_m = 223$ K as Fe content increases from $z = 0.04$ to $z = 0.16$ (Table 1).
The low-field magnetization measurements showed that Curie temperature $T_C$ of the Ni$_{2.20}$Fe$_x$Mn$_{0.80}$Ga alloys increases with the increase in Fe content (Table 1). In the sample with the highest Fe content, Ni$_{2.04}$Fe$_{0.16}$Mn$_{0.80}$Ga, $T_C = 395$ K is higher than that of the stoichiometric Ni$_2$MnGa.

IV. DISCUSSION

It was suggested that the electron concentration plays an important role not only in stabilizing the Heusler structure but that it is also a driving force for the structural phase transition in Ni$_2$MnGa, which takes place when the contact between the Fermi surface and Brillouin zone boundary occurs. The change in a number of valence electrons results in alteration of the density of states curve, which is a basis for the correlation of the extent of phase stability and electron concentration $e/a$.

Our study of Co- and Fe-containing Ni-Mn-Ga alloys revealed that increasing/decreasing in the number of conduction electron results in increase/decrease of the martensitic transformation temperature. Data presented in Fig. 3 clearly demonstrate this tendency. Resulting in decrease of the electron concentration $e/a$, substitution of Co for Ni as well as Fe for Ni leads to the decrease of martensitic transition temperature. In the case of substitution of Co for Mn, the increase in the electron concentration brings to the increase of $T_m$ from 345 K for Ni$_{2.16}$Mn$_{0.80}$Co$_{0.04}$Ga to 518 K for Ni$_{2.16}$Mn$_{0.70}$Co$_{0.14}$Ga. This result is in agreement with an earlier experimental study of Co-containing Ni-Mn-Ga alloys.

Therefore, these results indicate that the approach used for the description of martensitic transition temperature as a function of electron concentration in ternary Ni-Mn-Ga can also be applied for the case of quaternary Heusler alloys. Obviously, such an approach can be used only in a limited range of concentration of the forth element, where phase separation does not take place. It is worth noting, however, that new ferromagnetic shape memory alloys were found recently in Ni-Co-Ga and Ni-Fe-Ga systems, which formally can be considered as the case of complete substitution of Mn for Co and Fe, respectively.

Magnetization measurements of two series of samples where Ni was substituted by Co or Fe showed that Curie temperature increases with increasing Co (or Fe) content (Table 1). The most pronounced increase of $T_C$ is observed in the Fe-containing alloys, where Curie temperature increases from 347 K ($z = 0.04$) to 395 K ($z = 0.16$). Note that a considerable increase in $T_C$ was also observed in alloys where Fe was added instead of Mn, Ni$_2$Mn$_{1-x}$Fe$_x$Ga. The highest Curie temperature, $T_C = 433$ K, reported in those studies, was observed in the Ni$_{2.01}$Mn$_{0.40}$Fe$_{0.72}$Ga$_{0.86}$ composition.

The Mn content remains constant in the Fe- and Co-containing alloys (Mn content $y = 0.84$ for the Co-containing samples and Mn content $z = 0.80$ for the Fe-containing samples) and, therefore, the Mn magnetic subsystem is supposed to be not influenced by these substitutions. The observed increase of $T_C$ in the Co- and Fe-containing samples implies that the magnetic properties of Ni-Mn-Ga should be considered taking into account small magnetic moments located on Ni atoms and their coupling with magnetic moments of Mn atoms. For example, the increase in $T_C$ in these alloys can be accounted for by a stronger Co-Mn (Fe-Mn) exchange interaction as compared to the Ni-Mn one. Our experimental data, however, are not sufficient to make an unambiguous conclusion about the mechanism responsible for the increase of $T_C$ and therefore this effect needs further investigation. The experimentally observed increase of $T_C$ in Ni$_{2.16-x}$Co$_x$Mn$_{0.84}$Ga and Ni$_{2.20-x}$Fe$_x$Mn$_{0.80}$Ga is in accordance with a recent theoretical consideration of magnetic properties of Ni$_2$MnGa and Ni$_2$MnAl.

In Ref. [25] a suggestion was made that Ni significantly affects $T_C$ in these alloys and, therefore, Curie temperature in Ni$_2$MnGa could be increased by a substitution of the Ni sites. Note also that this suggestion is in accordance with empirical observation that Curie temperature of Co$_2$MnZ or Cu$_2$MnZ (Z is a non-transition element) alloys is higher than $T_C$ in corresponding Ni$_2$MnZ alloys.

In the Ni$_{2.16}$Mn$_{0.84}$Co$_y$Ga alloys Curie temperature $T_C$ exhibits a non-monotonous dependence as the Co content increases (Fig. 1). This is rather unusual, because in the Mn-containing Heusler alloys the dilution of the Mn magnetic subsystem generally results in decrease of $T_C$. In Ni$_{2.16}$Mn$_{1-x}$Ga alloys, however, merging of $T_m$
and $T_C$ is accompanied by the increase of $T_C$ in a limited composition interval $x = 0.18 - 0.20$. By analogy with the Ni$_{2+y}$Mn$_{1-x}$Ga alloys it could be suggested that the increase of $T_C$ from 352 K to 372 K as the Co content changes from $y = 0.04$ to $y = 0.09$ is accounted for by the coupling of martensitic and ferromagnetic transitions, occurring in the Ni$_{2.10}$Mn$_{0.75}$Co$_{0.09}$Ga alloy. This is not the case, as evident from the DSC measurements, which revealed that for this composition $T_m = 437$ K is considerably higher than $T_C$. Therefore, it is necessary to look for another mechanism responsible for the non-monotonous compositional dependence of $T_C$ in the Ni$_{2.16}$Mn$_{0.84-y}$Co$_y$Ga alloys. It is worth noting that similar behavior of $T_C$ has been observed in a Fe$_2$Mn$_{1-x}$V$_x$ system, where Curie temperature was found to increase from 219 K to 315 K with increasing $x$ from $x = 0$ to $x = 0.5$, followed by a rapid decrease at a higher V content. It was suggested that this unusual behavior of the ferromagnetic ordering temperature in Fe$_2$Mn$_{1-x}$V$_x$Ga could be related to the band structure of the system.

In future it would be interesting to perform similar band calculation for the Ni$_{2.16}$Mn$_{0.84-y}$Co$_y$Ga system. Further experimental studies of Ni$_{2.16}$Mn$_{0.84-y}$Co$_y$Ga alloys are also necessary in order to determine the critical Co content at which Curie temperature has a maximal value.

V. CONCLUSION

In conclusion, our experimental results have revealed that in the studied Fe- and Co-containing Ni-Mn-Ga alloys the behavior of the martensitic transition temperature can be satisfactory described as a function of the electron concentration $e/a$. The magnetic measurements have shown that addition of Fe or Co instead of Ni results in increase of Curie temperature $T_C$. This observation together with the theoretical suggestion gives a basic ground for the development of high temperature ferromagnetic shape memory alloys in the Ni-Mn-Ga system.

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