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Development of High-temperature Shape Memory Alloys in the $Ni_{2+x}Mn_{1-x}Ga$ System

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We present results of experimental study of $Ni_{2+x}Mn_{1-x}Ga$ alloys in a composition interval $0.16 \leq x \leq 0.39$. Calorimetric measurements evidenced that in a range of compositions $0.16 \leq x \leq 0.27$ the martensitic transformation temperature T_m changes from 310 K ($x = 0.16$) to 370 K ($x = 0.27$). With the further increase in the Ni excess x, T_m rapidly increases and is above 600 K in the alloys with $x \geq 0.33$. The occurrence of martensitic transformation at such high temperatures indicates that these materials have the potential for application as high-temperature shape memory alloys. Temperature dependencies of a low-field magnetization were used for determination of ferromagnetic transition temperature T_C in these alloys. The measurements revealed that the martensitic and ferromagnetic transitions are coupled in a composition interval $0.18 \leq x \leq 0.27$. In the alloys with $x \geq 0.30$, T_C decreases with Ni excess and, therefore, ferromagnetic ordering in these alloys sets at a temperature considerably lower than the martensitic transformation temperature.

Key words: high-temperature shape memory alloys, Ni-Mn-Ga, phase diagram

1. INTRODUCTION

Ni_2MnGa-based alloys are interesting from both fundamental and practical points of view (see, for a recent review, Ref. [1]). These alloys have been the subject of numerous studies by reason of their rich phase diagram. In particular, stoichiometric or near-stoichiometric alloys undergo a weak-order premartensitic phase transition, resulting in a modulation of the parent cubic structure [2]. Beside the premartensitic transition, off-stoichiometric Ni-Mn-Ga alloys exhibit several phase transitions between different crystallographic modifications of martensite, induced by a change of composition, temperature, or stress, or by the combination of these parameters [3]. From practical point of view, the interest in the study of Ni-Mn-Ga alloys is due to the fact that they exhibit large magnetic-field-induced strains which can be obtained either by reorientation of martensitic variants [4, 5] or by shifting the martensitic transformation temperature [6, 7].

Recent experimental results have shown that, along with the phenomenon of large magnetic-field-induced strains, Ni-Mn-Ga alloys exhibit other properties of practical importance. They are the large magnetocaloric effect [8-14] and the occurrence of martensitic transformation at high temperatures. Early studies of Ni-Mn-Ga have already indicated that the martensitic transformation temperature is sensitive to composition and can be observed in a wide temperature range [15]. Systematic studies of composition dependencies of the martensitic transformation temperature T_m showed that there is a relation between T_m and electron concentration, e/a, and that T_m increases with increasing e/a [16-18]. Furthermore, alloying of Ni-Mn-Ga with a $3d$ transition element can also considerably increase the martensitic transformation temperature [19,20]. These observations provoke studies of Ni-Mn-Ga aimed at the development of a new high-temperature shape memory alloys system [19,21-23].

Very recent experimental investigations [21-23] were devoted to the study of Ni-Mn-Ga alloys with deficiency in Ga, $Ni_{2.048}Mn_{1.244}Ga_{0.708}$ and $Ni_{2.16}MnGa_{0.84}$, which undergo a martensitic transformation at $M_s = 423$ K and $M_s = 533$ K, respectively. On the other hand, Vasil'ev *et. al.* have shown [24] that in the alloys with deficiency in Mn, $Ni_{2+x}Mn_{1-x}Ga$, martensitic transformation temperature increases from $T_m = 202$ K to $T_m = 332$ K as the Ni excess changes from $x = 0$ to $x = 0.20$. Contrary to T_m, the Curie temperature T_C was found to decrease with increasing Ni excess. As the result of these tendencies of T_m and T_C, the phase diagram of $Ni_{2+x}Mn_{1-x}Ga$ exhibits an interesting feature, namely, the martensitic and ferromagnetic transitions are merged in a compositional interval $0.18 \leq x \leq 0.20$.

Studies of $Ni_{2+x}Mn_{1-x}Ga$ alloys with a higher Ni excess are motivated by several reasons. Firstly,

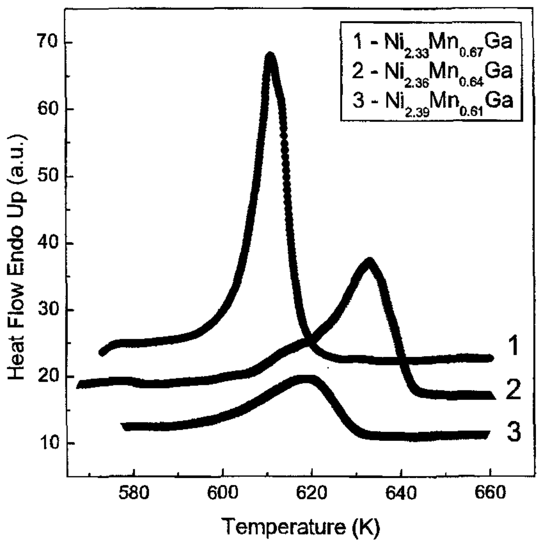

Figure 1: Examples of DSC scans measured upon heating for the studies $Ni_{2+x}Mn_{1-x}Ga$ alloys.

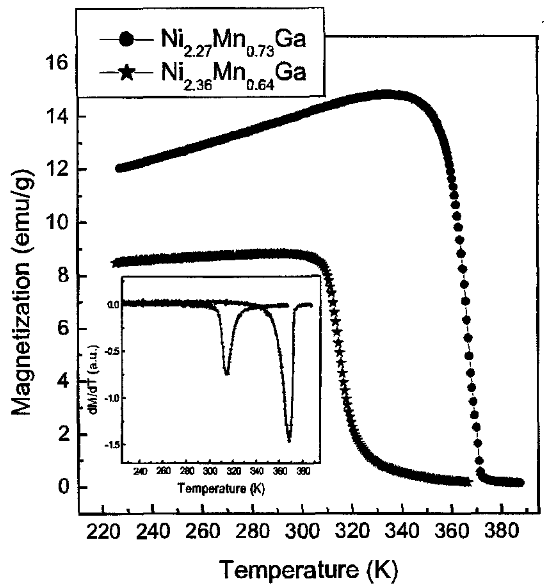

Figure 2: $M(T)$ measured upon heating for $Ni_{2.27}Mn_{0.73}Ga$ and $Ni_{2.36}Mn_{0.64}Ga$ alloys.

it could be expected that stronger deviation from the stoichiometry would result in further increase of the martensitic transformation temperature, and, therefore, high-temperature shape memory alloys can be developed in the $Ni_{2+x}Mn_{1-x}Ga$ system. Secondly, it is very likely that T_m and T_C are still merged in $x \geq 0.20$ alloys and since such alloys with a coupled magnetostructural transition show attractive magnetocaloric properties [13,14], it is interesting to determine the interval of compositions, where $T_m \approx T_C$. For this aim we studied $Ni_{2+x}Mn_{1-x}Ga$ alloys, characterizing by the Ni excess $0.16 \leq x \leq 0.39$.

2. EXPERIMENTAL DETAILS

Ingots with nominal compositions in the mentioned above range of x were prepared by a conventional arc-melting method. Since weight loss during arc-melting was small (0.2%) we assume that the real compositions correspond to the nominal ones. The ingots were annealed at 1100 K for 9 days and quenched in water. Samples for calorimetric and magnetic measurements were cut from the middle part of the ingots. Characteristic temperatures of direct and reverse martensitic transformations were determined from the results of differential scanning calorimetry (DSC) measurements, performed with a heating/coling rate 5 K/min. Curie temperature was determined from temperature dependencies of magnetization, $M(T)$, measured by a vibrating sample magnetometer in a magnetic field $H = 40$ kA/m with a heating rate 2 K/min.

3. RESULTS AND DISCUSSION

The results of DSC measurements upon heating for several alloys from the studied compositional interval are shown in Fig. 1. Describing martensitic transformation, we will use characteristic temperature T_m, determined as $T_m = (M_s + A_f)/2$, where M_s is the martensite start temperature and A_f is the austenite finish temperature.

Our DSC measurements revealed that T_m shows a non-monotonous dependence on the Ni excess x in the studied alloys. In a compositional interval $0.16 \leq x \leq 0.22$ martensitic transformation temperature increases from $T_m = 310$ K ($x = 0.16$) to $T_m = 370$ K ($x = 0.22$). Further increase in x from $x = 0.22$ to $x = 0.27$ does not affect T_m significantly, which remains essentially constant, $T_m \approx 370$ K, in this compositional interval. A drastic increase in T_m is observed, however, as the composition changes from $x = 0.27$ to $x = 0.30$. In the $Ni_{2.30}Mn_{0.70}Ga$ alloy, martensitic transformation temperature is equal to 528 K. In the compositional interval $0.30 \leq x \leq 0.36$ the martensitic transformation temperature increases for 100 K, from $T_m = 528$ K ($x = 0.30$) to $T_m = 626$ K ($x = 0.36$), and, therefore, this increase is more pronounced than that observed in the $0.16 \leq x \leq 0.22$ compositions. Finally, in the composition with the highest Ni excess, $Ni_{2.39}Mn_{0.61}Ga$, martensitic transformation occurs at $T_m = 611$ K, which is slightly lower than that observed in $Ni_{2.36}Mn_{0.64}Ga$.

Since previous studies of the $Ni_{2+x}Mn_{1-x}Ga$ ($0 \leq x \leq 0.20$) alloys [24] have shown that martensitic and ferromagnetic transition temperatures merge in alloys with $x = 0.18$, the non-monotonous behavior of T_m in the $0.16 \leq x \leq 0.39$ alloys could be related to the coupling of T_m and T_C. In order to check this, we measured temperature dependencies of magnetization, which exhibits a drastic drop upon transition from ferromagnetic to paramagnetic state (Fig. 2). Curie temperature T_C was determined as a minimum on the temperature derivative of the magnetization curve, dM/dT (inset in Fig. 2). Results of these measurements revealed that $T_C \approx T_m$ in the interval of compositions $0.18 \le x \le 0.27$. In the alloys with $x \ge 0.30$, Curie temperature is lower than the martensitic transformation temperature.

Phase diagram of $Ni_{2+x}Mn_{1-x}Ga$ in the studied compositional interval, constructed from the DSC and magnetization measurements, is shown in Fig. 3. Three different regions can be distinguished on this phase diagram. The first region is characterized by the Ni excess $x \le 0.16$. In this region $T_C > T_m$, and martensitic transformation takes place when in the ferromagnetic state. Alloys from the second region with the Ni excess $0.18 \le x \le 0.27$ are characterized by a coupled magnetostructural transition, i.e. $T_m \approx T_C$. Ferromagnetic transition in the alloys from this compositional interval has a characteristic of a first-order phase transition, showing pronounced hysteresis on temperature and field dependencies of magnetization, $M(T)$ and $M(H)$ [25,26]. Such unusual magnetic properties of these alloys have been attributed to simultaneously occurring martensitic and ferromagnetic transitions [1,25]. Finally, the third region is characterized by a high martensitic transformation temperature, $T_m > 550$ K, and a low Curie temperature, $T_C < 350$ K. In this region, with Ni excess $x \ge 0.30$, martensitic transformation takes place in the paramagnetic state. The occurrence of martensitic transformation at high temperatures makes alloys from this region attractive for application as high-temperature shape memory alloys.

The constructed phase diagram evidences that T_m and T_C merge in rather a wide interval of compositions, from $Ni_{2.18}Mn_{0.82}Ga$ to $Ni_{2.27}Mn_{0.73}Ga$. Moreover, T_m and T_C exhibit in this interval a non-monotonous dependence on Ni excess x (Fig. 3). Approaching T_m and T_C results in enhancement of magnetoelastic interaction [24], which reaches its maximum in the $x \ge 0.18$ alloys, when magnetic and structural subsystems couple. Curie temperature, $T_C = 376$ K for Ni_2MnGa, decreases with deviation from the stoichiometry and reaches a local minimum, $T_C = 323$ K, in the $x = 0.18$ composition. The increase of T_C in the $0.18 \le x \le 0.22$ alloys is presumably caused by the coupling of magnetic and structural subsystems and by the tendency of T_m to increase with Ni excess.

Since substitution of Mn for Ni results in dilution of magnetic subsystem [24], the observed increase of T_C in the $0.18 \le x \le 0.22$ alloys manifests a strong interrelation between magnetic and structural subsystems in $Ni_{2+x}Mn_{1-x}Ga$. Almost constant temperature of the magnetostructural transition, $T_m \approx T_C \approx 370$ K, observed in the $0.22 \le x \le 0.27$ alloys, is probably caused by a competition between increasing chemical pressure and further dilution of the magnetic subsystem, occurring in the

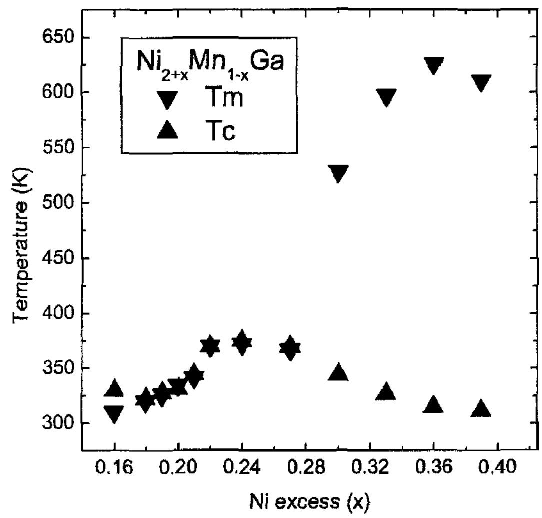

Figure 3: Martensitic (T_m) and ferromagnetic (T_C) transition temperatures as a function of Ni excess x in the studies $Ni_{2+x}Mn_{1-x}Ga$ alloys.

presence of the strong magnetoelastic interaction.

In a critical composition, $x = 0.30$, T_m and T_C are no longer coupled, which results in a drastic increase of the martensitic transformation temperature up to 528 K. In the alloys with higher Ni excess martensitic transformation occurs at temperatures above 600 K. It can be suggested that in the $0.30 \le x \le 0.39$ alloys further increase in the martensitic transformation temperature can be attained by the substitution of Ga for Ni or Mn.

4. CONCLUSION

Experimental study of the $Ni_{2+x}Mn_{1-x}Ga$ ($0.16 \le x \le 0.39$) alloys has shown that the ferromagnetic and martensitic transitions are merged in a wide compositional interval, $0.18 \le x \le 0.27$. It was also found that in the $0.30 \le x \le 0.39$ compositions martensitic transformation occurs at high temperatures. The highest temperature of the martensitic transformation, $T_m = 626$ K, was observed in the $Ni_{2.36}Mn_{0.64}Ga$ alloy.

Future studies of the $Ni_{2+x}Mn_{1-x}Ga$ system, especially the influence of aging on martensitic transformation in the $0.30 \le x \le 0.39$ alloys, are necessary for further development of high-temperature shape memory alloys in this system.

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