Entropy change at the martensitic transformation in ferromagnetic shape memory alloys Ni$_{2+x}$Mn$_{1-x}$Ga

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Abstract

The entropy change $\Delta S$ between the high-temperature cubic phase and the low-temperature tetragonally-based martensitic phase of Ni$_{2+x}$Mn$_{1-x}$Ga ($x = 0 – 0.20$) alloys was studied. The experimental results obtained indicate that $\Delta S$ in the Ni$_{2+x}$Mn$_{1-x}$Ga alloys increases with the Ni excess $x$. The increase of $\Delta S$ is presumably accounted for by an increase of magnetic contribution to the entropy change. It is suggested that the change in modulation of the martensitic phase of Ni$_{2+x}$Mn$_{1-x}$Ga results in discontinuity of the composition dependence of $\Delta S$. 
I. INTRODUCTION

For shape memory alloys, the change of entropy $\Delta S$ between high-temperature austenitic and low-temperature martensitic phase can be obtained either from calorimetry$^{1,2,3}$ or from results of stress-strain measurements at different temperatures above the martensitic start temperature $M_s$ (Ref. 4). Owing to the diffusionless character of martensitic transformations, configuration contributions to the entropy change are absent, which considerably simplify the evaluation of the relative phase stability. In the case of thermoelastic martensitic transformations, which are characterized by a small temperature hysteresis and complete transformation to the austenitic (martensitic) state, the change of entropy $\Delta S$ can be determined experimentally with a good precision.

$\text{Ni}_2\text{MnGa}$, a representative of the family of Heusler alloys, undergoes a thermoelastic martensitic transformation on cooling below $T_m \sim 200$ K. Since ferromagnetic ordering in this compound sets at a considerably higher temperature, $T_C = 376$ K, the martensitic transformation occurs in the ferromagnetic state. Both $T_m$ and $T_C$ are sensitive to stoichiometry. For instance, a partial substitution of Mn for Ni in Ni$_{2+x}$Mn$_{1-x}$Ga alloys results in increase of $T_m$ and decrease of $T_C$ until they couple in a composition range $x = 0.18 - 0.20$ (Ref. 5). Results of x-ray and electron diffraction studies of Ni-Mn-Ga alloys indicate that the crystal structure of the martensitic phase depends on composition. The martensitic phase of the alloys with a low temperature of martensitic transformation ($T_m < 270$ K) has a five-layered modulation whereas the martensitic phase with a moderate temperature of martensitic transformation ($T_m > 270$ K) has a seven-layered modulation. For Cu-based shape memory alloys, which transform to various martensitic structures upon cooling, it has been shown that the entropy change depends on the particular structure of the low-temperature martensitic phase. Hence, similar behavior could be expected in the Ni-Mn-Ga alloys. Contrary to the Cu-based shape memory alloys, which are nonmagnetic, Ni-Mn-Ga alloys possess a long-range ferromagnetic ordering at temperatures below $T_C$. Such distinct magnetic properties could result in peculiar behavior of the entropy change in Ni-Mn-Ga as compared to nonmagnetic shape memory alloys. The purpose of this work is to perform a preliminary calorimetric analysis of the entropy change $\Delta S$ between the high-temperature cubic phase and low-temperature tetragonally based martensitic phases of Ni$_{2+x}$Mn$_{1-x}$Ga ($x = 0 - 0.20$) alloys.
II. EXPERIMENTAL DETAILS

Polycrystalline ingots of Ni$_{2+x}$Mn$_{1-x}$Ga ($x = 0 - 0.20$) alloys were prepared by an arc-melting method. The ingots were annealed in evacuated quartz ampoules at 1050 K for 9 days. Sample for calorimetric measurements were spark cut from the middle part of the ingots. The calorimetric measurements were performed using a Perkin-Elmer differential scanning calorimeter with a heating/cooling rate of 5 K/min. In the experiments we have also used samples with the same thermal treatment from our previous work.

III. EXPERIMENTAL RESULTS AND DISCUSSION

An example of the calorimetric measurements of Ni$_{2+x}$Mn$_{1-x}$Ga alloys is presented in Fig. 1. The direct and reverse martensitic transformations are accompanied by well-defined calorimetric peaks. From these data, it is easy to determine 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 transformation. Results for the alloys studied, together with composition of the samples and the equilibrium temperature $T_0 = (M_s + A_f)/2$, are given in Table I. It is worth noting that transformation temperatures slightly differ for different samples of the same composition and the values of the temperatures presented in Table I are averaged over several specimens.

The mean values of the heat exchanged upon the reverse ($Q^{L\rightarrow H}$) and direct ($Q^{H\rightarrow L}$) transformation are shown in Table II. The average of the absolute values of ($Q^{L\rightarrow H}$) and ($Q^{H\rightarrow L}$) was taken as the change of enthalpy $\Delta H$. When the Gibbs free energies of martensite and austenite are equal, which takes place at temperature $T_0$, the entropy change $\Delta S$ can be evaluated as $\Delta S = \Delta H/T_0$. Determined in such a way, the entropy change is also shown in Table II.

Figure 2 shows the entropy change $\Delta S$ as a function of Ni excess $x$ in the Ni$_{2+x}$Mn$_{1-x}$Ga alloys. It is evident that $\Delta S$ increases with deviation from the stoichiometry. It can also be inferred that the entropy change has different composition dependencies in concentration intervals $0 \leq x \leq 0.13$ and $0.16 \leq x \leq 0.20$.

Since configuration contributions to the entropy change are absent in the case of martensitic transformations, it is customary to consider that $\Delta S$ has three main contributions:
2.16
Mn
0.84
Ga

FIG. 1: Typical calorimetric curves corresponding to the direct (cooling) and reverse (heating) martensitic transformations, measured in Ni$_{2+x}$Mn$_{1-x}$Ga alloys.

\[ \Delta S = \Delta S_{\text{vib}} + \Delta S_{\text{el}} + \Delta S_{\text{mag}}, \]

where $\Delta S_{\text{vib}}$ is the vibrational contribution, $\Delta S_{\text{el}}$ is the contribution of the conduction electrons, and $\Delta S_{\text{mag}}$ is the contribution from magnetic subsystem. Although specific heat measurements of Ni-Mn-Ga alloys at a low temperature have not been performed, it can be expected, nevertheless, that the electronic contribution $\Delta S_{\text{el}}$ to the entropy change in Ni$_{2+x}$Mn$_{1-x}$Ga alloys is small. This assumption is supported by the measurements of specific heat at low temperatures for several ferromagnetic X$_2$MnSn (X = Co, Ni, Pd, and Cu) Heusler alloys. Thus, the increase in $\Delta S$ with the deviation from the stoichiometry in Ni$_{2+x}$Mn$_{1-x}$Ga is likely due to the $\Delta S_{\text{vib}}$ and $\Delta S_{\text{mag}}$ terms.

An analysis of $\Delta S_{\text{vib}}$ contribution to the entropy change of Cu-based shape memory alloys
TABLE I: Composition of the studied Ni$_{2+x}$Mn$_{1-x}$Ga alloys and the critical temperatures of the martensitic transformation.

| Alloy | $M_s$ (K) | $M_f$ (K) | $A_s$ (K) | $A_f$ (K) | $T_0$ (K) |
|-------|-----------|-----------|-----------|-----------|-----------|
| $x = 0$ | 194       | 187       | 198       | 203       | 199       |
| $x = 0.02$ | 221       | 214       | 224       | 229       | 225       |
| $x = 0.03$ | 229       | 224       | 233       | 237       | 233       |
| $x = 0.04$ | 238       | 233       | 238       | 243       | 240       |
| $x = 0.05$ | 242       | 237       | 244       | 248       | 245       |
| $x = 0.08$ | 266       | 262       | 269       | 272       | 269       |
| $x = 0.10$ | 274       | 269       | 277       | 281       | 277       |
| $x = 0.13$ | 277       | 272       | 280       | 285       | 281       |
| $x = 0.16$ | 308       | 304       | 308       | 312       | 310       |
| $x = 0.18$ | 329       | 324       | 332       | 337       | 333       |
| $x = 0.19$ | 338       | 331       | 342       | 348       | 343       |
| $x = 0.20$ | 338       | 332       | 344       | 349       | 344       |

showed that the vibration contribution depends on the elastic anisotropy at the transformation temperature. The authors found that for a given crystal structure of the martensitic phase, the elastic anisotropy constant $A$ at $M_s$ does not depend on composition, which means that vibration contribution to $\Delta S$ remains constant for all of the composition studied. In the case of Ni$_{2+x}$Mn$_{1-x}$Ga alloys, data on elastic anisotropy are absent. The observed increase of $\Delta S$ in Ni$_{2+x}$Mn$_{1-x}$Ga can indicate that elastic anisotropy depends on composition. However, since Debye temperature did not change significantly with composition, it is more likely, that composition dependence of $\Delta S$ is accounted for by the magnetic contribution $\Delta S_{mag}$.

The fact that entropy change in Ni-Mn-Ga alloys depends on composition has already been mentioned in Ref. 10, where Ni-Mn-Ga alloys were divided into three groups according to their transformation behavior. The authors found that alloys with a low martensitic transformation temperature $M_s$ have low values of $\Delta S$, whereas alloys with a high $M_s$ are characterized by higher values of the entropy change. Their observations agree with the results of our study.
FIG. 2: The entropy change at the martensitic transformation in Ni\textsubscript{2+x}Mn\textsubscript{1-x}Ga alloys as a function of Ni excess \(x\). The solid lines are linear fits to the data.

Since the crystal structure of the martensitic phase of Ni-Mn-Ga depends on composition, an analysis of \(\Delta S\) as a function of Ni excess \(x\) is worth performing. From the data shown in Fig. 2, it is difficult to draw an unambiguous conclusion because the composition dependence of \(\Delta S\) can be approximated in the whole studied interval of \(x\) as shown by the dashed line. However, we suggest that the entropy change has different composition dependencies in concentration intervals \(0 \leq x \leq 0.13\) and \(0.16 \leq x \leq 0.20\) as shown in Fig. 2 by the solid lines. The alloys with \(x \geq 0.16\) (\(M_s > 300\) K) are expected to have seven-layered martensitic structure, as evident from their high martensitic transformation temperatures and unusual behavior of resistivity, whereas the \(0 \leq x < 0.16\) alloys undergo structural transformation to the five-layered martensitic structure. Since different martensitic phases have different densities of vibrational states, this should lead to discontinuity of
TABLE II: Heat exchanged upon reverse ($Q^{L\rightarrow H}$) and direct ($Q^{H\rightarrow L}$) martensitic transformation, enthalpy ($\Delta H$) and entropy ($\Delta S$) changes for Ni$_{2+x}$Mn$_{1-x}$Ga alloys.

| Alloy | $Q^{L\rightarrow H}$ (J/g) | $Q^{H\rightarrow L}$ (J/g) | $\Delta H$ (J/g) | $\Delta S$ (mJ/gK) |
|-------|----------------|----------------|-----------------|------------------|
| $x = 0$ | 1.39 | - 1.34 | 1.365 | 6.8 |
| $x = 0.02$ | 1.7 | - 1.87 | 1.785 | 7.9 |
| $x = 0.03$ | 2.38 | - 2.3 | 2.34 | 10 |
| $x = 0.04$ | 2.6 | - 2.57 | 2.585 | 10.8 |
| $x = 0.05$ | 2.72 | - 2.72 | 2.72 | 11.1 |
| $x = 0.08$ | 3.65 | - 3.8 | 3.725 | 13.8 |
| $x = 0.10$ | 4.69 | - 5.09 | 4.89 | 17.6 |
| $x = 0.13$ | 5.71 | - 5.57 | 5.64 | 20.1 |
| $x = 0.16$ | 7.96 | - 7.74 | 7.85 | 25.3 |
| $x = 0.18$ | 8.65 | - 8.57 | 8.61 | 25.9 |
| $x = 0.19$ | 9.41 | - 9.59 | 9.5 | 27.7 |
| $x = 0.20$ | 9.08 | - 8.86 | 8.97 | 26.1 |

the composition dependence of $\Delta S$ as the martensite of the Ni$_{2+x}$Mn$_{1-x}$Ga alloys changes its modulation. If this is the case, the alloys with seven-layered modulation of the martensitic phase are characterized by a higher $\Delta S$ as compared to the alloys with five-layered modulation (Fig. 2).

In this article we have studied the entropy change at the martensitic transformation in Ni$_{2+x}$Mn$_{1-x}$Ga ($x = 0 - 0.20$) alloys. The lowest value of the entropy change, $\Delta S = 6.8$ mJ/gK, was found for the stoichiometric Ni$_2$MnGa. Upon substitution of Mn for Ni, $\Delta S$ significantly increases up to $\sim 26$ mJ/gK in alloys with $x > 0.16$. The increase in $\Delta S$ is presumably due to the magnetic contribution. It is suggested that the change in modulation of the martensitic phase results in discontinuity of the composition dependence of $\Delta S$. This assumption, however, requires further systematic studies of thermodynamic properties of Ni-Mn-Ga alloys.
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