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Ni–Mn–Sn: novel ferromagnetic shape memory alloys

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Two series of novel ferromagnetic shape memory alloys, $Ni_{50+x}Mn_{37-x}Sn_{13}$ and $Ni_{50+y}Mn_{39-y}Sn_{11}$ were characterized by differential scanning calorimetry and magnetization measurements. The results obtained showed that the substitution of Mn for Ni results in an increase of martensitic transformation temperature T_m. The trend to T_m increase is not observed in the alloys with x, $y > 2$ at.%. The results of magnetization measurements evidence complex magnetic properties of these compounds.

Две серии новых ферромагнитных сплавов $Ni_{50+x}Mn_{37-x}Sn_{13}$ и $Ni_{50+y}Mn_{39-y}Sn_{11}$ с памятью формы охарактеризованы калориметрическими и магнитными измерениями. Полученные результаты показали, что замещение Mn на Ni приводит к повышению температуры мартенситного превращения T_m. Тенденция к повышению T_m не наблюдается в сплавах с x, $y > 2$ ат.%. Результаты магнитных измерений указывают на комплексные магнитные свойства этих соединений.

Recently, it was found that for ferromagnetic Heusler alloys Ni_2MnSn, Ni_2MnIn, and Ni_2MnSb, a deviation from stoichiometry results in martensitic transformation [1]. For these systems, the martensitic transformation temperature decreases upon substitution of Mn for Sn, In or Sb; an especially drastic decrease was observed in the NiMnIn system. As in the case of a "classical" ferromagnetic shape memory system, Ni–Mn–Ga (see for review [2] and references therein), the crystal structure of the Ni–Mn–Sn martensitic phase was found to depend on composition [3]. It is worth noting that interpretation of the martensite crystallographic structure seems to be a subject of controversy. For instance, basing on X-ray diffraction results for the $Ni_{49.9}Mn_{37.1}Sn_{13}$ alloy, Krenke et al. [3] reported a five-layered modulated (10M) martensitic structure at room temperature, whereas for the alloy of a slightly different composition, $Ni_{50}Mn_{37.5}Sn_{12.5}$, Sutou et al. [1] found from the results of X-ray diffraction and transmission electron microscopy that the martensite has a four-layered (4O) structure. This contradiction can point, in principle, to a strong compositional dependence of the martensitic crystal structure. Note also that a multi-step martensitic transformation has been observed in $Ni_{50}Mn_{37.5}Sn_{12.5}$ while a single-step one has been reported for the $Ni_{49.9}Mn_{37.1}Sn_{13}$ composition.

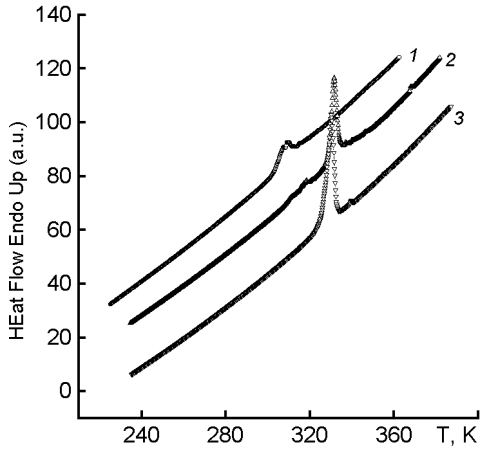

Fig. 1. DSC heating scans for $Ni_{50+x}Mn_{37-x}Sn_{13}$ alloys (*1* – x=1 *2* – x=2; *3* – x=3).

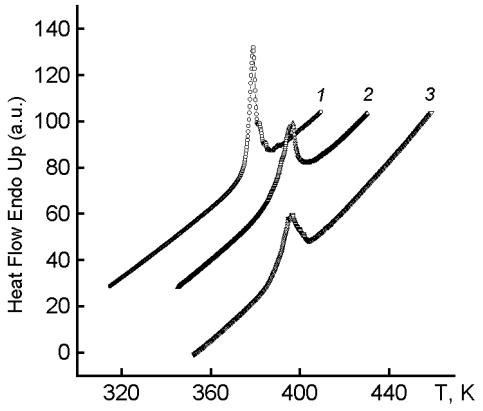

Fig. 2. DSC heating scans for $Ni_{50+y}Mn_{39-y}Sn_{11}$ alloys (*1* – y=1, *2* – y=2, *3* – y=3).

The stoichiometric Ni_2MnSn has the Curie temperature T_C about 350 K and the saturation magnetic moment about 4.3 μ_B. The previous studies of $Ni_{3-x}Mn_xSn$ ($0.6 \le x \le 2.2$) have revealed interesting magnetic properties of this system [4]. It was found that the saturation magnetic moment first increases in alloys with $x \le 1$ and then decreases at the further increase in x. In contrast, the Curie temperature T_C was found to increase over the whole x range being studied. The compositional dependence of the magnetic moment can be reasonably explained assuming ferromagnetic coupling between Mn atoms located at 4b (in Wyckhoff notation) positions (i.e. between Mn atoms occupying the Mn-sublattice) and antiferromagnetic coupling between Mn atoms occupying 4b and 4a (or 4c) positions (i.e. between Mn atoms occupying Mn- and Ni-sublattices). Substitution of Mn for Sn in $Ni_{50}Mn_{50-x}Sn_x$ causes a structural instability that has a considerable impact on magnetic properties of these compounds. The compositional dependence of the Curie temperature T_C of the austenitic phase was found to be weak, while T_C of the martensitic phase depends strongly on the composition and decreases drastically with decreasing Sn content. Moreover, different strength of exchange interactions in martensitic and austenitic phases may result in an unusual sequence of magnetic transitions, namely, the material being in ferromagnetic state at low temperatures transforms to a paramagnetic state at intermediate temperatures and then again to ferromagnetic state upon further heating. Due to the unusual sequence of magnetic phase transitions (from paramagnetic martensite to ferromagnetic austenite) observed upon heating, a large inverse magnetocaloric effect has recently been observed in $Ni_{50}Mn_{50-x}Sn_x$ (x = 13, 15) alloys [5]. In order to study further magnetic and structural properties of Ni–Mn–Sn, we have prepared two series of novel ferromagnetic shape memory alloys, $Ni_{50+x}Mn_{37-x}Sn_{13}$ and $Ni_{50+y}Mn_{39-y}Sn_{11}$ (x, y = 1, 2, 3).

The polycrystalline ingots of nominal compositions within the above-mentioned x and y ranges were prepared by a conventional arc-melting method. Since the weight loss during arc-melting was small (<0.2 %), we assume the real compositions to correspond to the nominal ones. The ingots were annealed at 1273 K for 26 h and quenched in ice water. Samples for calorimetric and magnetic measurements were cut from the middle part of the ingots. Characteristic temperatures of the direct and reverse martensitic transformations were determined by differential scanning calorimetry (DSC) measurements performed at the heating/cooling rate 5 K/min. Magnetic properties were studied by a Quantum Design SQUID magnetometer.

The DSC measurements provide a simple and effective tool to detect martensitic transformations. Well-defined peaks seen on cooling and heating DSC curves correspond to direct and reverse martensitic transformation, respectively. The direct martensitic transformation is characterized by the martensite start temperature, M_s, and the martensite finish one, M_f. Accordingly, the reverse martensitic transformation can be characterized by the austenite start temperature, A_s, and the austenite finish one, A_f. As an example of these measurements, DSC heating scans for the alloys from the

studied compositional interval are shown in Figs. 1 and 2. Our DSC measurements have revealed that the martensitic transformation temperature in the alloys studied shows a non-monotonic dependence on the Ni excess x and y. Whereas an increase of martensitic transformation temperature is observed in both the systems as Ni excess increases from 1 at.% to 2 at.%, a further substitution of Mn for Ni does not affect martensitic transformation temperature. In the $Ni_{50+y}Mn_{39-y}Sn_{11}$ system, the martensitic transformation takes place at higher temperatures than in the $Ni_{50+x}Mn_{37-x}Sn_{13}$ alloys, which is in accordance with the results of previous studies [1, 3].

The results obtained from the magnetization measurements point to the complex magnetic properties of these materials. For instance, some of the alloys exhibit several anomalies in the temperature dependence of susceptibility which allows to conclude that, in contrast to NiMnGa alloys [6], the Curie temperature of martensite in the studied Ni–Mn–Sn compositions is lower than that of austenite. An example of these measurements is shown in Fig. 3 for the case of $Ni_{52}Mn_{35}Sn_{13}$ alloy. It is evident that the magnetization of this alloy measured upon cooling in a low magnetic field $H = 100$ Oe exhibits a jump-like increase at ~ 306 K and ~217 K. Since both these anomalies are observed in the martensitic state, the high-temperature anomaly can be attributed to the Curie temperature of martensite. The origin of the low-temperature anomaly remains unclear at present. Most likely, the anomaly at T ~ 217 K corresponds to an intermartensitic transformation between different crystallographic modifications of the low-temperature phase, a phenomenon which has often been observed in the Ni–Mn–Ga system and presumably in the Ni–Mn–Sn alloys [1] as well. The results for the magnetization temperature dependence measured in 3 T field (inset in Fig. 3) suggest that the magnetization saturation of these two martensitic phases is nearly identical. However, a possibility that this anomaly is an evidence that the two martensitic phases have well separated Curie temperatures cannot be excluded, since phase transition temperatures in $Ni_{52}Mn_{35}Sn_{13}$ alloy do not differ significantly from those in $Ni_{50}Mn_{37}Sn_{13}$ [1, 3, 5], and for the latter composition the Curie temperature of martensite $T_C^M = 230$ K has been reported [3, 5].

A peculiarity of the studied $Ni_{52}Mn_{35}Sn_{13}$ alloy is the existence of an unusual se-

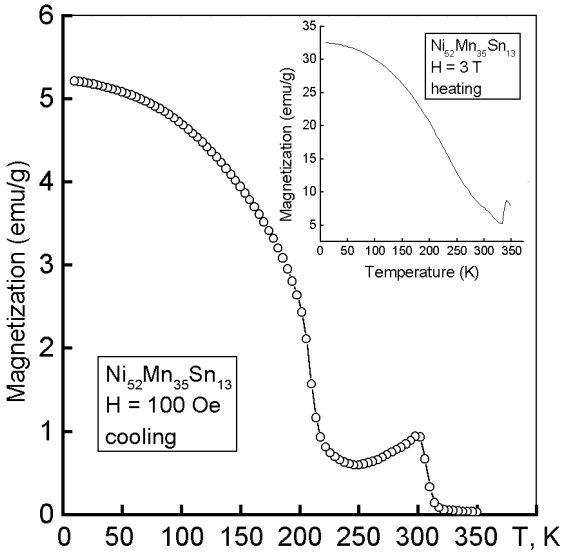

Fig. 3. Temperature dependence of magnetization $M(T)$ for $Ni_{52}Mn_{35}Sn_{13}$ measured upon cooling in a magnetic field $H = 100$ Oe. The inset shows $M(T)$ of this alloy measured upon heating in $H = 3$ T. The anomaly of M seen at ~335 K corresponds to the transition from paramagnetic martensite to ferromagnetic austenite.

quence of magnetic transitions. In this composition, a paramagnetic martensitic phase is sandwiched between ferromagnetic martensitic phases (at low temperatures) and ferromagnetic austenitic phase (at high temperatures). This specific property is essentially due to the difference in the strength of the exchange interactions in martensite and austenite. It is worth noting that the ferromagnetic austenite exists in a narrow temperature interval with Curie temperature of austenite T_C^A roughly coinciding with the austenite finish temperature. For that reason, the magnetization anomaly corresponding to the transition paramagnetic martensite ↔ ferromagnetic austenite is virtually not observed in low magnetic fields and becomes more pronounced in high magnetic fields (Fig. 4). Since such a behaviour of magnetization causes a large inverse magnetocaloric effect [5], our observation implies that a similar phenomenon can be observed in $Ni_{52}Mn_{35}Sn_{13}$.

Thus, our DSC measurements revealed that the martensitic transformation temperature in the alloys studied shows a non-monotonic dependence on the Ni excess x and y. Whereas the martensitic transformation temperature increases in both the systems as Ni excess increases from 1 at.% to

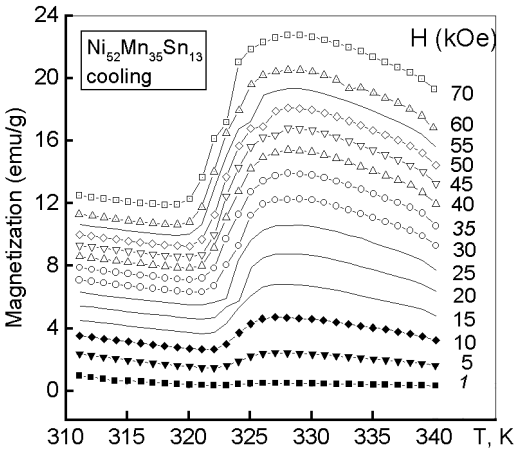

Fig. 4. Features of a transition from ferromagnetic austenite to paramagnetic martensite in $Ni_{52}Mn_{35}Sn_{13}$ measured upon cooling in various magnetic fields.

2 at.%, a further substitution of Mn for Ni does not affect the martensitic transformation temperature. The results of magnetization measurements point to complex magnetic properties of these compounds. The Curie temperature of austenite is higher than that of martensite which results in that the paramagnetic martensitic phase is sandwiched between ferromagnetic martensitic and ferromagnetic austenitic phases.

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Ni–Mn–Sn: нові феромагнітні сплави з пам'яттю форми

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Дві серії нових феромагнітних сплавів $Ni_{50+x}Mn_{37-x}Sn_{13}$ і $Ni_{50+y}Mn_{39-y}Sn_{11}$ з пам'яттю форми охарактеризовано калориметричними і магнітними дослідженнями. Одержані результати показали, що заміщення Mn на Ni приводить до підвищення температури мартенситного перетворення T_m. Тенденція до підвищення T_m не спостерігається у сплавах з x, $y > 2$ ат.%. Результати магнітних досліджень вказують на комплексні магнітні властивості цих сплавів.