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Multifunctional properties related to magnetostructural transitions in ternary and quaternary Heusler alloys

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ABSTRACT

In this report, the results of a study on the effects of compositional variations induced by the small changes in concentrations of the parent components and/or by the substitution of Ni, Mn, or In by an extra element Z, on the phase transitions, and phenomena related to the magnetostructural transitions in off-stoichiometric Ni–Mn–In based Heusler alloys are summarized. The crystal structures, phase transitions temperatures, and magnetic and magnetocaloric properties were analyzed for representative samples of the following systems (all near 15 at% indium concentration): Ni–Mn–In, Ni–Mn–In–Si, Ni–Mn–In–B, Ni–Mn–In–Cu, Ni–Mn–In–Cu–B, Ni–Mn–In–Fe, Ni–Mn–In–Ag, and Ni–Mn–In–Al.

1. Introduction

In spite of the significant progress made in recent years in understanding the multifunctional properties related to magnetostructural transitions (MSTs) in Ni–Mn–In based Heusler alloys, the detailed mechanisms responsible for the MSTs are far from being well understood. A MST is a structural martensitic transition that results in a change of the magnetic state of the material. Magnetic states of high temperature austenitic (AP) and low temperature martensitic (MP) phases in magnetic, off-stoichiometric Heusler alloys can be quite different and inhomogeneous. As a result, MSTs are responsible, not only for large magnetocaloric effects (normal and inverse), but also for a slew of other pronounced physical properties including magnetoelasticity, large Hall effect, giant magnetoresistance, high spin polarization, magnetic shape memory effects, and exchange bias [1–5]. These multiproperties are all a consequence of a magnetostructural phase transition, and are therefore related to each other. Identifying the connections between these properties, and their relationships to the phase transitions, is an important issue in condensed matter physics, as such advances will help in better understanding the origins of MSTs, and to develop new materials for multifunctional applications.

In-based Heusler alloys with nearly 15 at% concentration of In undergo MSTs near room temperature that result in sharp changes in the magnetization and related magnetoresponsive phenomena. Due to the delicate balance between electronic, ionic, vibrational, and magnetic energies in the vicinity of the MST, the properties of these alloys are extremely sensitive to any changes in intrinsic parameters, such as chemical composition, type of crystal structure, as well as on extrinsic parameters, such as fabrication techniques and conditions, annealing temperature, applied magnetic field, pressure, rate of heating and cooling, sequence of measurements, and cycling. It is widely believed (see, for example [6]) that the specific features of electronic band structure of the Heusler alloys are responsible for the MST. Therefore the alloy composition, the concentration of valence electrons per atom (e/a), interatomic distances, and crystal structure homogeneity are interconnected major factors affecting the phase transitions and the related phenomena. Following these consideration, the multicomponent alloys with even a small volume fraction of the extra elements, Z, present an opportunity to search for desirable properties at ambient temperatures and at accessible magnetic fields.

The changes in e/a ratio and in structural parameters (cell parameters and volume) are commonly considered to be the

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factors affecting the electronic structure, and therefore the phase stability and MST temperature in solid solutions based on Heusler alloys. However, in the multi-component Ni–Mn–In–Z systems with a small volume fraction of the extra element Z, these approaches are not always applicable (see [7,8]).

In this report, we summarize the results of our studies on the effects of small changes in concentration of the parent components, and/or by the substitution of Ni, Mn, or In by an extra element Z on the phase transitions and phenomena related to the MSTs in off-stoichiometric Ni–Mn–In based Heusler alloys.

2. Experimental procedure

Polycrystalline samples of $Ni_{50}Mn_{35}In_{12}Si_3$, $Ni_{50.5}Mn_{32.32}Cu_{2.02}In_{14.14}B_{1.01}$, $Ni_{50}Mn_{1-x}Cu_xIn_{14}B$, $Ni_{50.5}Mn_{33.08}Cu_{1.26}In_{14.14}B_{1.01}$, $Ni_{50.51}Mn_{34.34}In_{14.14}B_{1.01}$, $Ni_{50}Mn_{35}In_{13.5}Al_{1.5}$, $Ni_{50}Mn_{33.75}Cu_{1.25}In_{15}$, $Ni_{50}Mn_{35}In_{11}Si_4$, $Ni_{50}Mn_{34}In_{16}$, $Ni_{49.9}Mn_{34.9}In_{15}Ag_{0.2}$, $Ni_{49.8}Mn_{35.26}In_{14.94}$, $Ni_{49.9}Mn_{35.1}In_{15}$, $Ni_{49.8}Mn_{34.9}In_{15.3}$, $Ni_{50}Mn_{34}In_{15}$, $Ni_{49.9}Mn_{34.7}In_{15.4}$, $Ni_{49.6}Mn_{34.8}In_{15.2}$, $Ni_{49.8}Mn_{34.7}In_{15.5}$, $Ni_{49.6}Mn_{34.5}In_{15.9}$,$Ni_{49.7}Mn_{34.8}In_{15.5}$ and, $Ni_{46.7}Fe_3Mn_{34.8}In_{15.5}$, $Ni_{50}Mn_{34.8}In_{15.2}$ have been prepared using 4 N purity metals in an Ar atmosphere by arc-melting methods, and annealed in high vacuum ($\approx 10-5$ Torr) for 24 h at a temperature of 850 °C. The crystal structures were determined by powder X-ray diffraction methods using Cu Kα radiation. Thermomagnetic curves M(H,T) have been acquire using a superconducting quantum interference device magnetometer (Quantum Design) in the temperature interval 5–400 K and in magnetic fields up to 50 kOe. The measurements have been carried out during heating after the samples were cooled from 400 K to the starting temperature at zero magnetic field in the zero-field-cooled (ZFC) measurements. Some of magnetization data were collected during the field cooling cycle (FCC). Magnetotransport measurements have been carried out using the standard four-probe method, in the temperature interval 5–400 K at magnetic fields up to 50 kOe. All magnetotransport measurements have been carried out in ZFC conditions. Direct measurements of the adiabatic change of temperature, ΔT_{AD}, under an applied magnetic field have been done using an adiabatic magnetocalorimeter (MagEq MMS 801) in a temperature range of 250–350 K, and in magnetic fields up to 1.8 T. The external magnetic fields have been ramped at a rate of up to 20 kOe/s during ΔT_{AD} measurements. A differential scanning calorimeter (DSC 8000) has been used to obtain heat flow curves (with a ramp rate of 20 K/min during heating and cooling) in the temperature range of 103–573 K. In the measurements under hydrostatic pressure, Daphne (7373) oil was used as the pressure transmitting medium. The value of the applied pressure was calibrated by measuring the shift of the superconducting transition temperature of Pb used as reference manometer ($T_C \sim 7.2$ K at ambient pressure) [9].

3. Results and discussion

The phase composition of the compounds have been identified based on the XRD results mostly as a mixture of austenitic cubic ($L2_1$ or B2) and the martensitic crystal structure modifications at 300 K. The behavior reflects the presence of temperature austenitic/martensitic hysteresis in the vicinity of the room temperature. All samples show ferromagnetic type magnetization curves in high magnetic fields ($H > 1000$ Oe) at 5 K. The phase transitions of the systems were found to be similar to that of “parent” $Ni_{50}Mn_{35}In_{15}$ compound (see Refs. [1] and [2], for example). The samples show three transition temperatures: T_{CM}, T_A/T_M, and T_C, where T_{CM} is the Curie temperature of martensitic phase, T_A/T_M and T_C are the temperatures of the direct/inverse martensitic transition (MST) and Curie temperature of austenitic phase, respectively (see Fig. 1).

The heat flow (HF) and ΔT_{AD} curves with respect to temperature demonstrate endothermic peaks and negative values, in the vicinity of the MST, respectively (see Figs. 2 and 3). The behavior is a signature of first order transitions. The positive reversible changes in ΔT_{AD} are clearly seen in the vicinity of T_C (see Fig. 3). It is necessary to note that several compounds show an irreversibility in the value of ΔT_{AD} for direct and inverse MSTs (see Fig. 3). The sample compositions, transition temperatures T_A/T_M, and T_C (determined from $M(T)$ curves at low magnetic field $H = 100$ Oe), along with maximum values of ΔT_{AD}, are collected in Table 1.

Some of the compounds based on $Ni_{50}Mn_{35}In_{15}$ demonstrate puzzling and interesting behaviors of magnetoresistance (MR) in

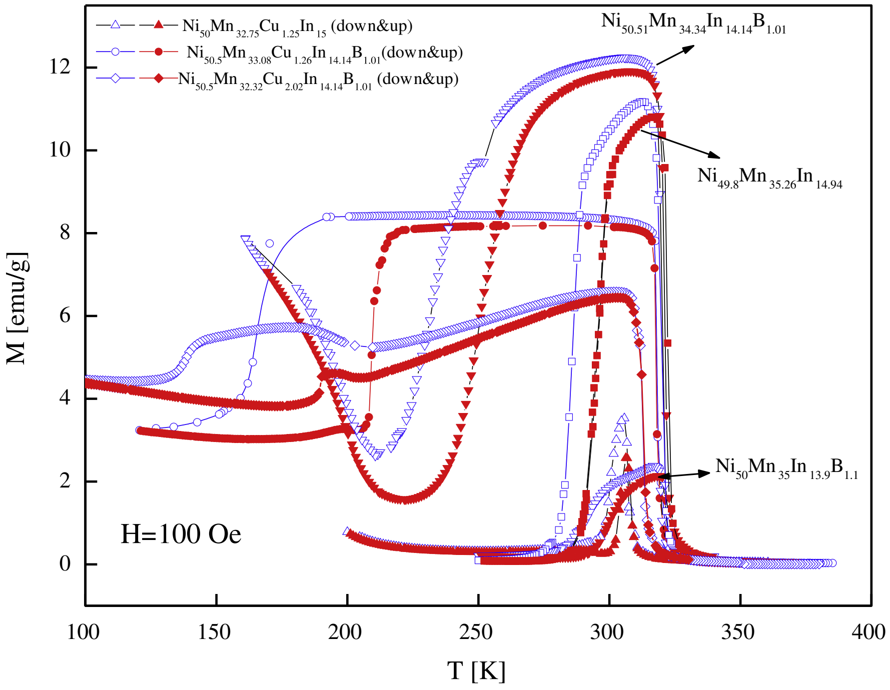

Fig. 1. $M(H)$ curves obtained at $H = 100$ Oe for some compounds based on $Ni_{50}Mn_{35}In_{15}$.

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