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Published in *Journal of Applied Physics*, Vol. 101 No. 5 (2007) at doi: 10.1063/1.2710779

Recommended Citation
Khan, Mahmud, Ali, Naushad and Stadler, Shane. "Inverse Magnetocaloric Effect in Ferromagnetic Ni50Mn37+xSb13−x Heusler Alloys." (Mar 2007).

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Inverse magnetocaloric effect in ferromagnetic $Ni_{50}Mn_{37+x}Sb_{13-x}$ Heusler alloys

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(Received 26 October 2006; accepted 13 January 2007; published online 15 March 2007)

A study of the magnetocaloric effect (MCE) in the ferromagnetic Heusler alloys $Ni_{50}Mn_{37+x}Sb_{13-x}$ ($x=0,0.5,1$) has been carried out through magnetization measurements. An inverse magnetocaloric effect was observed in the vicinity of the first order martensitic transition. A maximum positive magnetic entropy change of $\Delta S_m \approx 19$ J/kg K at approximately 297 K for a magnetic field change of 5 T was observed. It is demonstrated that the martensitic transformation temperature, and the corresponding ΔS_m, can be tuned through a slight variation in composition. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2710779]

INTRODUCTION

For many decades magnetocaloric cooling techniques have been restricted to low-temperature cryogenic applications. Recent discoveries of magnetic materials exhibiting giant magnetocaloric effects (MCEs) near room temperature[1,2] have opened up the possibility of using the magnetocaloric cooling technology for near room temperature refrigeration applications. The utilization of this solid state cooling technology represents an environment friendly alternative to conventional compressed gas refrigeration.[3,4] The MCE occurs when an applied external magnetic field causes the alignment of magnetic moments in a material under adiabatic conditions. Due to this alignment, a reduction occurs in the magnetic randomness or in the magnetic component of the total entropy. In order to compensate for this reduction, other components of the total entropy increase. In the case of magnetocaloric materials, the increase is channeled into electronic entropy and lattice entropy, or heat. Pecharsky *et al.* have presented a detailed discussion of the thermodynamics of the MCE in Ref. 5. In general, the MCE occurs in all magnetic materials, and the most noticeable MCE occurs at temperatures near magnetic transitions, where the change in magnetic ordering configuration varies rapidly with temperature. The MCE is strongly dependent on the type of magnetic transition and is strongest for first order magnetic transitions. Some of the recently reported materials exhibiting large MCE include $Gd_5(SiGe)_4$,[1] $MnFeP_{1-x}As_x$,[2] $Ni_{2+x}Mn_{1-x}Ga$,[6–10] and $Ni_2Mn_{1-x}Cu_xGa$.[11] The reported phase transitions responsible for the large MCE in these materials are first order magnetostructural transitions (i.e., the magnetic and structural transitions occur at the same temperature). The cooling effect in these materials is generated in two different steps. First, an external magnetic field is applied under adiabatic conditions, resulting in the heating of the material. The excess heat is removed through some convection process, and the material is subsequently demagnetized adiabatically causing its cooling. There are, however, certain materials where the cooling occurs in the first step of adiabatic magnetization (inverse MCE). The inverse MCE is observed in materials where first order magnetic transformations from antiferromagnetic to ferromagnetic (AF/FM) or from antiferromagnetic to ferrimagnetic states (AF/FI) take place. Some examples of such systems are $Fe_{0.49}Rh_{0.51}$ (AF/FM),[12] $Mn_{1.6}Cr_{0.05}Sb$ (AF/FI),[13] and $Mn_{1.82}V_{0.18}S$ (AF/FI).[14] Due to the presence of mixed magnetic exchange interactions, it is suggested that the application of an external magnetic field results in further spin disorder in these systems, causing an increase in the configurational entropy.[13]

In a recent study, it was reported that a Ni–Mn–Sn based Heusler alloy type system undergoes a first order martensitic transition from a low symmetry tetragonal or orthorhombic phase (martensitie) to a high symmetry cubic phase (austenite) upon heating.[15] In the vicinity of this martensitic structural phase transformation, a large inverse MCE (i.e., a positive entropy change) of $\Delta S_m = 19$ J/kg K was reported in Ref. 16. A similar martensitic transformation is also observed in the Heusler alloy Ni–Mn–Sb.[15] In this paper we present the large MCE effect of $Ni_{50}Mn_{37+x}Sb_{13-x}$ ($x=0,0.5,1$) that results from a first order magnetostructural martensitic transformation.

EXPERIMENTAL TECHNIQUE

The fabrication of approximately 5 g of polycrystalline buttons of $Ni_{50}Mn_{37+x}Sb_{13-x}$ ($x=0,0.5,1$) was carried out using conventional arc melting in an argon atmosphere using Ni, Mn, and Sb of 4*N* purity. The combinations of elements were repeatedly melted four times, and the weight loss after melting was found to be less than 0.2%. For homogenization, the samples were wrapped in Ta foil and annealed in vacuum for 24 h at 850 °C, and slowly cooled down to room temperature.

In order to evaluate the phases and lattice constants, x-ray diffraction measurements were conducted at room temperature using a minimaterials analyzer (MMA) x-ray diffractometer made by GBC Scientific Equipment, Inc. The diffractometer employed Cu *K* alpha radiation and Bragg-Brentano geometry.

The magnetization measurements were performed on a superconducting quantum interference device (SQUID) mag-

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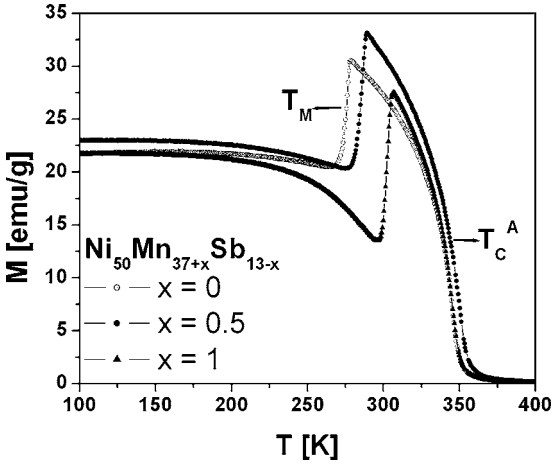

FIG. 1. Magnetization as a function of temperature of $Ni_{50}Mn_{37+x}Sb_{13-x}$ ($x=0,0.5,1$) obtained at a field of 1 kOe.

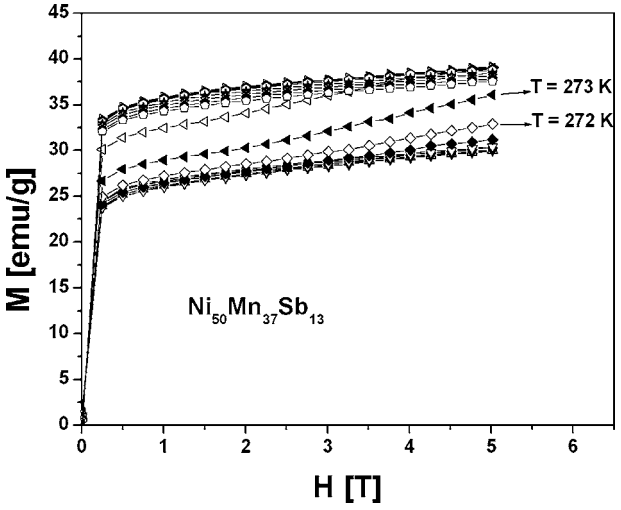

FIG. 2. (a) Isothermal magnetization curves of $Ni_{50}Mn_{37}Sb_{13}$ at temperatures 260–286 K in increments of 2 and 1 K.

netometer made by Quantum Design, Inc. The measurements were performed in the temperature range of 5–400 K and in magnetic fields up to 5 kOe. The magnetic entropy change, ΔS_m, was evaluated from the isothermal magnetization data using the relation

$$\Delta S_m = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \quad (1)$$

RESULTS AND DISCUSSION

X-ray diffraction (XRD) patterns of $Ni_{50}Mn_{37+x}Sb_{13-x}$ ($x=0,0.5,1$) obtained at room temperature suggest that the samples are of single phase. The samples with $x=0$ and 0.5 possessed the Heusler $L2_1$ structure, and the sample with $x=1$ possessed the $10M$ modified orthorhombic martensitic structure at room temperature. Detailed structural properties of the samples will be published elsewhere. The magnetization curves as a function of temperature $[M(T)]$ of $Ni_{50}Mn_{37+x}Sb_{13-x}$ ($x=0,0.5,1$) are presented in Fig. 1. All the measurements were done in an applied field of 1 kOe. As shown in this figure, for all the alloys a sharp jump of magnetization at T_M is observed with increasing temperature. The $M(T)$ curves also clearly show an increase of T_M with increasing Mn concentration. With further increase of temperature, the austenitic phase undergoes a ferromagnetic transition at the Curie temperature, $T_C{}^A$. For the sample with $x=1$, an additional transition is observed at a slightly lower temperature before T_M. This transition represents the Curie temperature, $T_C{}^M$, of the martensitic state. Initially, an order-disorder magnetic transition begins as the temperature is raised through the Curie temperature of the martensitic phase. However, a magnetostructural transition to a ferromagnetic austenitic phase occurs at about 300 K for the sample with $x=1$.

Using Eq. (1), the MCE properties of $Ni_{50}Mn_{37+x}Sb_{13-x}$ ($x=0,0.5,1$) were evaluated in the vicinity of the first order magnetostructural martensitic transition. Generally, this equation is more suitable for calculating ΔS_m in the vicinity of second order phase transitions. However, this equation is frequently employed to calculate ΔS_m in the vicinity of a first order phase transition which, according to Gschneidner *et al.*,[4] is justified in cases where problematic discontinuities are not present in the phase transition. The majority of the reported ΔS_m values of Ni–Mn–Ga, and other ferromagnetic systems exhibiting first order phase transitions, are calculated using Eq. (1). Based on this common practice, the ΔS_m values of $Ni_{50}Mn_{37+x}Sb_{13-x}$ ($x=0,0.5,1$) were evaluated from the isothermal magnetization measurements. The isothermal magnetization curves as a function of field in the temperature range of 260–285 K are shown in Fig. 2 for $Ni_{50}Mn_{37}Sb_{13}$. The measurements were done in temperature increments of $\Delta T=2$ and 1 K and a magnetic field up to 50 kOe. The magnetic entropy change in $Ni_{50}Mn_{37+x}Sb_{13-x}$ ($x=0,0.5,1$) as a function of temperature is presented in Fig. 3. As show in this figure, the samples with $x=0.0$ and $x=0.5$ possess ΔS_m values of 17.7 and 14.7 J/kg K at 5 T, respectively. The highest values of 8.9 J/kg K at 2 T and 19.1 J/kg K at 5 T were obtained for the sample with $x=1$ at 297 K. These values are similar to those observed in $Ni_{0.50}Mn_{0.50-x}Sn_x$ (20 J/kg K),[15] but much higher than those observed in $Mn_{1.5}Cr_{0.05}Sb$ (7 J/kg K) [Ref. 13] and $Mn_{1.82}V_{0.18}Sb$ (5.5 J/kg K).[14]

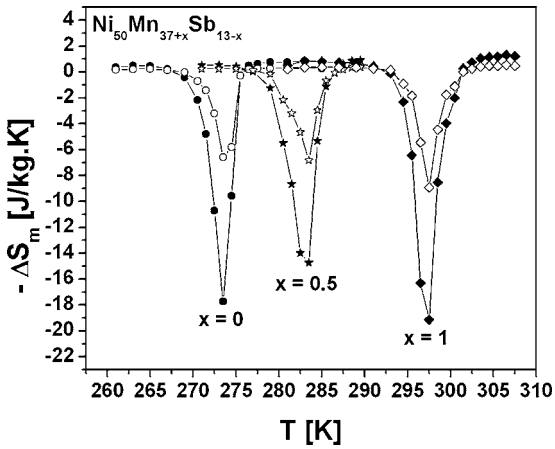

FIG. 3. Magnetic entropy changes (ΔS_m) as a function of temperature of $Ni_{50}Mn_{37+x}Sb_{13-x}$ ($x=0,0.5,1$) for a field change (ΔH) of 5 T (closed symbols) and 2 T (open symbols).

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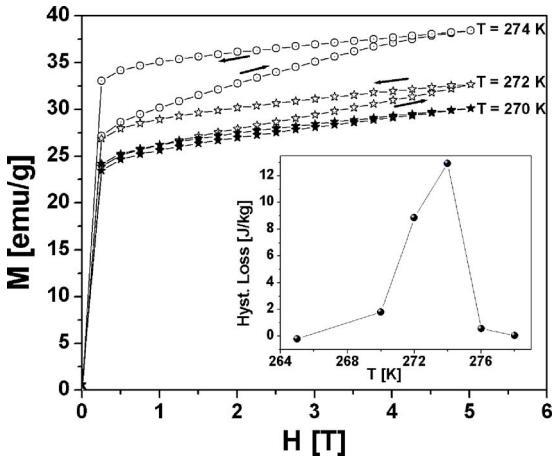

FIG. 4. The hysteresis loops of $Ni_{50}Mn_{37}Sb_{13}$ at temperatures where the maximum magnetic entropy change is observed. The inset shows the hysteresis loss as a function of temperature for the displayed magnetization isotherms.

The evaluation of the magnetocaloric properties of a given material depends strongly on the hysteresis loss at the phase transition, because it directly opposes the refrigeration capacity (RC). One method to estimate RC is to integrate the $\Delta S_m(T)$ curve over the full width at half maximum. The RC calculated for $Ni_{50}Mn_{37}Sb_{13}$ is approximately 32 J/kg. Figure 4 shows the isothermal hysteresis loops of $Ni_{50}Mn_{37}Sb_{13}$ at temperatures where the maximum MCE is observed. The inset shows the hysteresis loss obtained by calculating the area between the increasing and decreasing field segments of the magnetization curves. The hysteresis loss in $Ni_{50}Mn_{37+x}Sb_{13-x}$ system is one of the obstacles for its use as a magnetocaloric material in a real cooling device.

CONCLUSION

An inverse magnetocaloric effect was observed in $Ni_{50}Mn_{37+x}Sb_{13-x}$ $(x=0,0.5,1)$ in the vicinity of the first order martensitic transition. A maximum positive magnetic entropy change of $\Delta S_m \approx 19$ J/kg K at 298 K for a magnetic field change of 5 T was observed. It is shown that the temperature at which the martensitic transformation occurs, and the corresponding ΔS_m, can be tuned through a slight variation in composition. We believe that these results will have significant contribution in understanding the fundamental phenomena of the phase transitions and the related MCE in Ni–Mn–Sb based Heusler alloys, and thus will encourage the study of promising magnetic refrigerants for near room temperature magnetic refrigerators.

ACKNOWLEDGMENTS

This research was supported by the Petroleum Research Fund (Grant No. 42068-GB5), by the Southern Illinois University Materials Technology Center (MTC), and by the Office of Basic Energy Sciences, Material Sciences Division of the U.S. Department of Energy under Contract No. DE-FG02-06ER46291.

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