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Large magnetic entropy change with small thermal hysteresis near room temperature in metamagnetic alloys $Ni_{51}Mn_{49-x}In_x$

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Magnetic properties and magnetic entropy change ΔS have been investigated in Heusler alloys $Ni_{51}Mn_{49-x}In_x$ ($x=15.6$, 16.0, and 16.2). By tuning Ni, Mn, and In contents around composition $Ni_{50}Mn_{34}In_{16}$, large ΔS with small thermal hysteresis near room temperature can be achieved. Martensitic temperature T_m shifts from 308 K to 253 K with x varying from 15.6 to 16.2. The thermal hysteresis around T_m is small, <2 K, for all samples. Because of the fundamental difference in magnetization around T_m, an external magnetic field induces a metamagnetic transition from the martensitic to the austenitic state. As a result, a large magnetic entropy change with positive sign appears in a wide temperature range. The size of ΔS reaches 19, 20, and 33 J/kg K under 5 T magnetic field at 253, 262, and 308 K for samples $x=15.6$, 16.0, and 16.2, respectively. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3073951]

Many materials with first-order magnetic phase transition, such as $Gd_5(Si,Ge)_4$,[1] $La(Fe,Si)_{13}$,[2,3] $MnFeP_{1-x}As_x$,[4] and Ni–Mn–Ga,[5–11] have been discovered to exhibit great magnetocaloric effect (MCE). Among those materials, an attractive candidate is the Mn-based Heusler alloys. Since the first report of a large positive magnetic entropy change associated with structure transformation in a polycrystalline NiMnGa sample,[5] a number of investigations on the magnetic properties and MCE in various ferromagnetic shape memory Heusler alloys (FSMAs) have been carried out.[5–10] For the traditional FSMAs, such as Ni–Mn–Ga, shape memory effect is realized through the field-induced rearrangement of martensite variants. The MCE comes from the magnetization jump caused by the change in magnetic anisotropy upon martensitic structure transition. The achieved magnetic entropy change ΔS can be as high as -86 J/kg K;[9] however, the extremely high ΔS usually concentrates in a very narrow temperature range, 1–2 K, accompanied with a large thermal hysteresis, 10–20 K or higher. One knows that a real magnetic refrigerator requires not only a large MCE but also a wide temperature span of the MCE. A recent discovery of metamagnetic shape memory alloys (MSMAs) has stirred intense interest because of their huge shape memory effect and different mechanism from the traditional FSMAs.[11] In these Ga-free Ni–Mn–Z Heusler alloys (where Z can be a group III or a group IV element, such as In, Sn, or Sb), the strong change in magnetization across the martensitic transformation results in a large Zeeman energy $\mu_0\Delta M\cdot H$, which drives the structural transformation and causes a field-induced metamagnetic behavior. Indeed, inverse MCE with a relatively wide temperature span has been observed.[10,12–14]

$Ni_{50}Mn_{34}In_{16}$ belongs to the so-called MSMAs, which is the only one that exhibits a field-induced transition in $Ni_{50}Mn_{50-y}In_y$ alloys.[15] Several groups investigated its shape memory effect and MCE. The reported ΔS with a considerable large temperature span reaches 12 J/kg K under a magnetic field of 5 T,[16] which is larger than that of Gd. However, the large ΔS takes place around 180 K, which is still far away from room temperature. Furthermore, a large hysteresis is accompanied even for the MSMAs. The reported thermal hysteresis can be as large as ~20 K for Ni–Mn–Sn (Ref. 13) and ~10 K for Ni–Co–Mn–In (Ref. 11) alloys. For $Ni_{50}Mn_{34}In_{16}$, the hysteresis even reaches 20 K, and more seriously it becomes further wider with external field.[16] Recently, we focused on the MCE effect of the so-called MSMAs. Our studies reveal that a little more increase in Ni content not only increases T_m but also enhances the magnetic entropy change. More importantly, it can remarkably improve the thermal hysteresis.

$Ni_{51}Mn_{49-x}In_x$ ($x=15.6$, 16.0, and 16.2) alloys were prepared by arc-melting technique. The obtained ingots were homogenized at 1173 K for 24 hours, then quenched in ice water. X-ray diffraction analysis confirmed that all the samples are with $L2_1$ Heusler-type ordered structure. All magnetic measurements were performed using a superconducting quantum interference device (SQUID) magnetometer.

Temperature dependent magnetization under different fields has been measured in zero-field-cooled (ZFC) and field-cooled (FC) processes in order to determine the magnetic state, the transition temperature, and the nature of the transitions.[17] Figure 1 presents the ZFC-FC magnetization measured under 0.05, 1, and 5 T for all samples. The austenitic phase at high temperatures shows paramagnetic properties and orders ferromagnetically at Curie temperature T_C (denoted as T_C^A thereafter). The T_C^A is at 316, 304, and 301 K for samples $x=15.6$, 16.0, and 16.2, respectively. A large separation between FC and ZFC magnetization was observed under a low field of 0.05 T, which can be understood by considering magnetic anisotropy in the martensitic state.[15]

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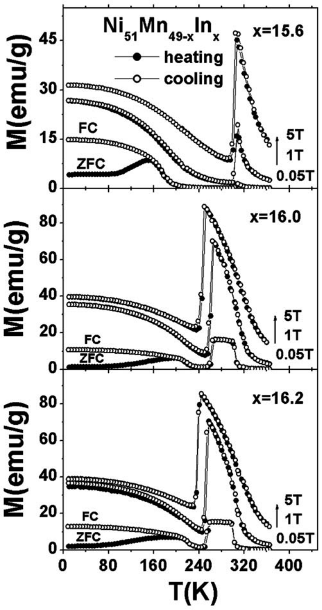

FIG. 1. Temperature dependent ZFC and FC magnetizations measured under different fields 0.05, 1, and 5 T for $\mathrm{Ni_{51}Mn_{49-\mathit{x}}In_{\mathit{x}}}$ (x=15.6, 16.0, and 16.2) alloys.

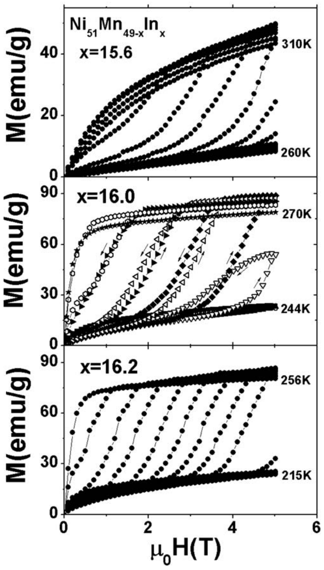

FIG. 2. The magnetization isotherms M-H for all samples. The M-H for x=15.6 and 16.2 is collected on field increase. As a typical display, the M-H for x=16.0 is given on field increase and decrease.

In Fig. 1, one can also find that the present $\mathrm{Ni_{51}Mn_{49-\mathit{x}}In_{\mathit{x}}}$ alloys show a very small thermal hysteresis, <2 K, around T_m. More importantly, an increase in magnetic field does not enlarge the hysteresis for all samples. Previous investigations[18–21] indicated that hysteresis effect is a complicated issue in the thermoelastic martensitic transformation system. The dissipative mechanisms for hysteresis are different at different spatial scales.[20] At a microscopic scale, the hysteresis is related to the nucleation of the new phase and the interaction of interfaces with defects. But at a mesoscopic scale, the hysteresis effect comes from the formation, annihilation, and rearrangement of elastically interacting domains. In this case, heat transfer within the alloy and that between the alloy and the surroundings also affect the hysteresis gap. The average grain size in our samples is about 200 μm. Each specimen we used in the SQUID magnetometer contains about 50–85 grains. Considering the small size, heat transfer should be in a good situation during SQUID measurements. The frictions from domain rearrangements and phase boundary motions are considered to be a main factor affecting the hysteresis gap.[18,19] In other words, the gap of thermal hysteresis may characterize the strength of frictions during the transformation. In present systems, the small hysteresis indicates that the friction to resist the transformation is small. Anyway, the small thermal hysteresis is the aspiration of an engineer in applying MCE materials in a refrigerator. These features guarantee that the MCE is nearly reversible on temperature even if a high magnetic field is applied.

Compared to the stoichiometric $\mathrm{Ni_2Mn}$-based Heusler alloys, the magnetic interaction is quite complex in the off-stoichiometric alloys with an excess of Mn; antiferromagnetic coupling is introduced in the martensitic state, which originates from the change in the Mn–Mn atom distance as the martensitic phase with lower symmetry gains stability.[22] The competition between ferromagnetic and antiferromagnetic coupling leads to the weaker ferromagnetism of the martensitic state, showing a reduction of T_C^M with increasing Mn content. Around T_m, the martensitic phase exhibits paramagnetic, antiferromagnetic, or ferromagnetic properties, but the austenitic phase shows strong ferromagnetism. The fundamental difference in magnetism leads to field-induced metamagnetic transition behaviors. Figure 2 displays the magnetization isotherms M-H for all samples. The M-H for x=15.6 and 16.2 is collected on field increase. As a typical display, the M-H for x=16.0 is given on field increase and decrease. Around T_m, the temperature step is 2 K for samples x=16.0 and 16.2 and 1 K for x=15.6. Above a critical field H_C, a sharp change in magnetization occurs for the three samples, which means that a field-induced metamagnetic transition from a martensitic to an austenitic state takes place. For the temperatures below but close to T_m, a small H_C can induce the metamagnetic transitions. With decreasing temperature, the martensitic structure becomes more stable, and a larger H_C is required to induce the metamagnetic transition. The H_C behaviors govern the characteristics of magnetic entropy change ΔS. In conventional first-order systems with large MCE effect, such as La–Fe–Si systems, the critical transition field H_C increases with increasing temperature, which makes the ΔS peak asymmetrically broaden to higher temperatures.[2] However, the H_C behavior in present systems does the opposite. It becomes smaller with increasing temperature, which predicts that the ΔS peak will broaden to lower temperature.

According to the thermodynamical theory, magnetic entropy change $\Delta S(T,H)$ is given by the Maxwell relation,[23] $\Delta S(T,H)=S(T,H)-S(T,0)=\int_0^H(\partial M/\partial T)_H dH$. The present samples exhibit inverse MCE effect around the martensitic structural transition point T_m. Figure 3 shows the magnetic entropy change ΔS as a function of temperature and magnetic field. One can note that ΔS is positive, peaks at T_m, and gradually broadens to lower temperature, which is a result of

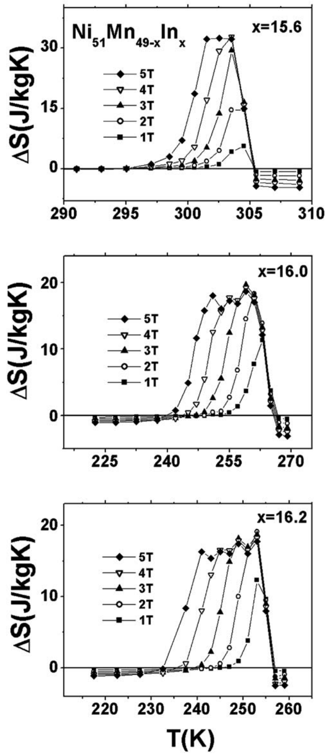

FIG. 3. Magnetic entropy change ΔS as functions of temperature and magnetic field for $Ni_{51}Mn_{49-x}In_x$ ($x=15.6$, 16.0, and 16.2) alloys.

the field-induced metamagnetic transition from the martensitic to the austenitic state at temperatures below T_m. The maximum of ΔS reaches 33, 20, and 19 J/kg K at 308, 262, and 253 K for compositions $x=15.6$, 16.0, and 16.2, respectively. In comparison with ΔS (12 J/kg K, 188 K) observed in $Ni_{50}Mn_{34}In_{16}$ alloys, not only does the T_m, at which ΔS peaks, go much nearer to room temperature, but the size of ΔS is also remarkably enhanced. Actually, the ΔS almost reaches its maximum at 2 T for $x=16.0$ and 16.2 and 4 T for $x=15.6$. Further increasing magnetic field contributes little to the magnitude but remarkably broadens the ΔS to lower temperatures. The ΔS span could reach ~20 K under a field of 5 T.

The ΔS shows a tablelike peak under 5 T for all samples. The flat plateau of ΔS should reflect the intrinsic nature of MCE. In some first-order systems, such as LaFeSi, the ΔS peak usually exhibits a peculiar shape, an extremely high spike followed by a flat plateau. Detailed studies[24] suggested that the extremely high peak does not reflect the intrinsic nature of the entropy change but a spurious signal. The coexistence of two phases at temperatures very close to the transition point makes M-H curves shape in a two-step-like transition, resulting in an overrating of ΔS and the appearance of the ΔS spike. However, careful investigations based on specific heat measurements verified that the flat plateau does reflect the intrinsic nature of ΔS.[24] Because no obvious two-step-like transition shows up in the M-H curves for present samples, ΔS shapes only in a flat plateau without any spikelike peak. Similar to the case of the first-order systems, La–Fe–Si,[24] the broad plateau of ΔS should reflect the intrinsic nature of MCE in present systems. One knows that a plateaulike ΔS is specially desired for Ericsson-type refrigerators.

In summary, great magnetic entropy change near room temperature has been observed in $Ni_{51}Mn_{49-x}In_x$ alloys with In concentration around $x=16.0$. Compared to $Ni_{50}Mn_{50}In_{16}$, a little excess of Ni greatly improves the thermal hysteresis, enhances magnetic entropy change, and makes the structural transition temperature closer to room temperature. The maximum of ΔS takes place at 308, 262, and 253 K, and the magnitude reaches 33, 20, and 19 J/kg K under 5 T for compositions $x=15.6$, 16.0, and 16.2, respectively. The thermal hysteresis is small, <2 K, for all samples, and an application of magnetic field does not enlarge the hysteresis. The great ΔS near room temperature with a relatively wide temperature span, as well as the small thermal hysteresis make the present alloys attractive for real applications.

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