Intermetallics 100 (2018) 57–62

Contents lists available at ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

# Large room temperature adiabatic temperature variation in a $Ni_{40}Co_8Mn_{42}Sn_{10}$ polycrystalline alloy

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ARTICLE INFO

*Keywords:*
Ni-Co-Mn-Sn alloys
Martensitic transformation
Magnetostructural coupling
Magnetocaloric effect

ABSTRACT

For the potential applications in magnetic refrigeration, low-cost and high-performance refrigerants with large magnetocaloric effect at relatively lower field change are highly desired. In this work, we report a large adiabatic temperature variation for a low-field change of 1.5 T near room temperature in a $Ni_{40}Co_8Mn_{42}Sn_{10}$ bulk alloy. With the large magnetization difference between weak magnetic martensite and ferromagnetic austenite, this alloy exhibits significant inverse magnetocaloric effect. Under the field change of 5 T, large magnetic entropy change $\Delta S_M$ of 21.6 J kg$^{-1}$K$^{-1}$ and effective refrigeration capacity $RC_{eff}$ of 293 J kg$^{-1}$ were achieved. Moreover, a large $\Delta T_{ad}$ up to −4.4 K was obtained under the low-field change of 1.5 T, which is much higher than previously reported $\Delta T_{ad}$ values in Ni-Mn-Sn based alloys.

## 1. Introduction

Heusler-type Ni-Mn-X (X = In, Sn) based meta-magnetic shape memory alloys have attracted considerable attention in recent years due to their remarkable magnetic field induced functional behaviours [1]. On cooling, these alloys usually undergo a first-order magnetostructural transformation from a ferromagnetic austenite to a weak magnetic (anti-ferromagnetic or paramagnetic) martensite [2]. Such strong magnetostructural coupling enables that the inverse martensitic transformation from martensite to austenite can be induced by application of an external magnetic field [3–7]. As a consequence of that, significant shape change can be recovered through this field induced phase transformation, *i.e.*, magnetic shape memory effect [3,5,7–10]. So far, significant field induced strains up to 1% and 3% have been successfully achieved in a $Ni_{43}Co_7Mn_{39}Sn_{11}$ polycrystalline alloy and a $Ni_{45}Mn_{36.7}In_{13.3}Co_5$ single crystal alloy [3,7], respectively. Thus, these alloys are conceived as promising candidates for magnetically driven sensor and actuator applications.

Besides the magnetic shape memory effect, Ni-Mn-X alloys also exhibit remarkable inverse magnetocaloric effect (MCE) associated with the magnetostructural transformation [2,4,8–17]. In such case, the sample cools down when the field is applied and it warms up when the field is removed, which is in contrast to the conventional MCE. Based on the MCE, the recently developed solid-state magnetic refrigeration offers an energy-efficient and environment-friendly alternative to the conventional gas compression/expansion technique in facing the increasing challenge of ozone depletion and global warming. From the viewpoint of potential applications, high-performance magnetic refrigerants with large MCE are in great need.

In general, the MCE can be characterized in term of the isothermal magnetic entropy change ($\Delta S_M$) or the adiabatic temperature variation ($\Delta T_{ad}$). Considerable, even giant $\Delta S_M$ values [2,11–15], indirectly determined from the isothermal magnetization curves according to the Maxwell relation, have been reported in Ni-Mn-X alloys. Nevertheless, it was pointed out that the $\Delta S_M$ values sometimes were greatly overestimated from magnetization measurements when referring to a first-order magnetostructural transformation [18–21]. In actuality, direct measurement of $\Delta T_{ad}$ is more relevant and straightforward to evaluate the magnetocaloric properties. Recently, giant $\Delta T_{ad}$ up to −5.2 K, −6.2 K and −8 K have been reported respectively in $Ni_{49.8}Mn_{35}In_{15.2}$, $Ni_{45.2}Mn_{36.7}In_{13}Co_{5.1}$ and $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ alloy for a moderate field change of 2 T [4,16], due to the field induced inverse martensitic transformation. Compared to Ni-Mn-In based alloys, Ni-Mn-Sn based alloys exhibit the similar field induced inverse martensitic transformation behavior, but with much lower cost of the raw materials since the less expensive element Sn is involved. In this regard, Ni-Mn-Sn based alloys are quite attractive for practical applications. However, the $\Delta T_{ad}$ values in Ni-Mn-Sn based alloys are relatively smaller with respect to those in Ni-Mn-In based alloys [22–24]. For instance, the $\Delta T_{ad}$ around the inverse martensitic transformation was −1 K in a

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https://doi.org/10.1016/j.intermet.2018.06.005
Received 21 December 2017; Received in revised form 28 April 2018; Accepted 5 June 2018

$Ni_{50}Co_1Mn_{36}Sn_{13}$ alloy for a field change of 1.9 T [22], −2.5 K in a $Ni_{48.6}Mn_{34.9}Sn_{16.5}$ alloy for a field change of 5 T [23], and −2.6 K in a $Ni_{45.7}Mn_{37.9}Sn_{11.5}Co_{4.9}$ alloy under a field change of 1.9 T [24], respectively. These $\Delta T_{ad}$ values are far from those in Ni-Mn-In based alloys [4,16]. For the potential applications, further exploitation of higher $\Delta T_{ad}$ values in Ni-Mn-Sn based alloys is highly desired in order to obtain better cooling effect.

In this work, we reported a large MCE around room temperature in a $Ni_{40}Co_8Mn_{42}Sn_{10}$ bulk polycrystalline alloy. Through the modification of Mn content and the introduction of a fourth element Co, the magnetization difference across the magnetostructural transformation can be greatly enlarged, thus a strong magnetostructural coupling. Consequently, large magnetic entropy change $\Delta S_M$ of 21.6 J kg$^{-1}$K$^{-1}$ and effective refrigeration capacity $RC_{eff}$ up to 293 J kg$^{-1}$ were achieved under the field change of 5 T. Moreover, a large $\Delta T_{ad}$ up to −4.4 K around room temperature for a field change of 1.5 T was obtained. The present $\Delta T_{ad}$ value is not only higher than previous $\Delta T_{ad}$ values obtained in Ni-Mn-Sn based alloys, but also achieved in a much lower field change. In fact, the exploration of low-cost and high-performance magnetocaloric materials that exhibit giant MCE at relatively lower field is of great significance for the magnetic refrigeration applications.

## 2. Experimental

Bulk polycrystalline alloy with the nominal composition of $Ni_{40}Co_8Mn_{42}Sn_{10}$ (at. %) was prepared by arc-melting using the pure elements Ni (99.99 wt%), Co (99.99 wt%), Mn (99.9 wt%), and Sn (99.99 wt%) under the protection of Ar atmosphere. To achieve a good composition homogenization, the alloy was remelted for four times. The as-cast alloy was then sealed in a vacuum quartz tube and homogenized at 1173 K for 24 h, followed by quenching into water.

The actual composition of the alloy was verified to be $Ni_{39.4}Co_{8.0}Mn_{42.1}Sn_{10.5}$ by Energy Dispersive Spectrometer (EDS). The martensitic transformation temperatures were measured by differential scanning calorimetry (DSC), with a heating and cooling rate of 10 Kmin$^{-1}$, respectively. The crystal structure was analyzed by powder X-ray diffraction (XRD) using Cu-$K_\alpha$ radiation in a Rigaku SmartLab diffractometer with a heating/cooling stage. The thermal-magnetic (heating and cooling rate: 3 Kmin$^{-1}$) and isothermal magnetization measurements were performed using the Quantum Design MPMS-3 system, where disc shaped samples with the dimension of φ3 × 1 mm were employed. The magnetic field was applied along circular plane in order to minimize the influence of internal demagnetization field. Direct measurement of adiabatic temperature variation ($\Delta T_{ad}$) under the magnetic field change was performed in a self-designed experimental setup with a maximum field of 1.5 T produced by NdFeB permanent magnet. The temperature change of the sample (rectangular parallelepiped sample: 5 × 5 × 10 mm) was monitored by an attached thermocouple, where the magnetic field was applied along the longer edge of the rectangular parallelepiped sample. The magnetization condition was realized through the insertion of the sample into the magnetic field. Accordingly, the demagnetization was realized through the extraction of the sample from the magnetic field.

## 3. Results and discussions

Fig. 1a shows the DSC curves of the $Ni_{40}Co_8Mn_{42}Sn_{10}$ bulk alloy on cooling and heating. In the figure, the large exothermic and endothermic peaks indicate the forward and inverse martensitic transformation on cooling and heating, respectively. Besides, the small inflection points at relatively higher temperature (~437 K) on cooling and heating paths represent the magnetic transition ($T$), as indicated in the figure. Based on the DSC curves, the forward transformation start and finish temperatures ($M_s$, $M_f$) were determined to be 289 K and 274 K, and the inverse transformation start and finish transformation

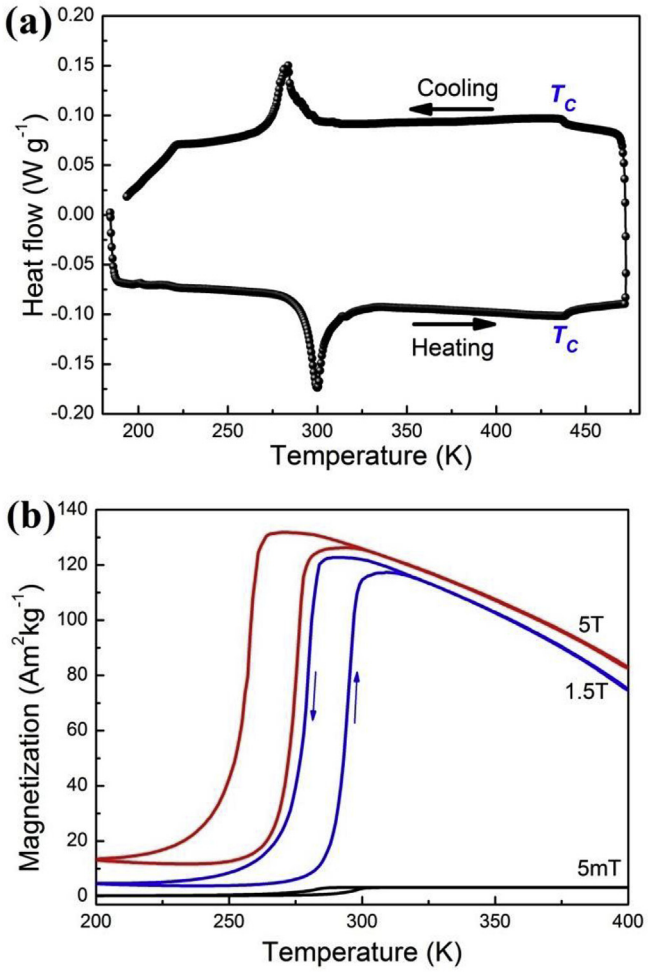


**Fig. 1.** (A) DSC curves of $Ni_{40}Co_8Mn_{42}Sn_{10}$ bulk alloy. (b) Temperature dependence of magnetization ($M$-$T$ curves) measured under the field of 5 mT, 1.5 T and 5 T for $Ni_{40}Co_8Mn_{42}Sn_{10}$ bulk alloy.

temperatures ($A_s$, $A_f$) were determined to be 292 K and 304 K, respectively, suggesting that the martensitic transformation of the present $Ni_{40}Co_8Mn_{42}Sn_{10}$ alloy occurs around room temperature. The thermal hysteresis (determined as ($A_s$ + $A_f$–$M_s$–$M_f$)/2) of the martensitic transformation was 16.5 K. In addition, the entropy change ($\Delta S_M$) associated with the structural transformation was determined to be 21.9 J kg$^{-1}$K$^{-1}$ from the DSC measurements.

Fig. 1b presents the temperature dependence of magnetization ($M$-$T$ curves) measured under the field of 5 mT, 1.5 T and 5 T. According to the $M$-$T$ curves measured under the low field of 5 mT, the martensitic transformation temperatures ($M_s$, $M_f$, $A_s$, $A_f$) were determined to be 287 K, 274 K, 289 K, and 301 K, respectively, which is well consistent with the DSC measurements. With the increase of magnetic field, the martensitic transformation temperatures are found to shift towards lower temperature region, suggesting that the field induced inverse martensitic transformation can be expected. Under the field of 5 T, the $A_s$ is reduced by 27 K, with a rate of 5.4 K/T. In addition, it is confirmed that the martensitic transformation involves simultaneous changes in crystal structure and magnetization, *i.e.*, a magnetostructural transformation from ferromagnetic austenite to weak magnetic martensite. A large magnetization difference associated with phase transformation, *i.e.*, $\Delta M$ = 115Am$^2$kg$^{-1}$, can be identified from the $M$-$T$ curves under the field of 5 T, indicating a strong magnetostructural coupling. Compared with the $\Delta M$ values for ternary alloys, *e.g.*, $Ni_{50}Mn_{35}Sn_{15}$ ($\Delta M \approx$ 30Am$^2$kg$^{-1}$) and $Ni_{50}Mn_{37}Sn_{13}$ ($\Delta M \approx$ 20Am$^2$kg$^{-1}$) [11], the $\Delta M$ value for the present $Ni_{40}Co_8Mn_{42}Sn_{10}$ alloy is greatly enhanced,