Enhanced magnetocaloric effect in Ni-Mn-Sn-Co alloys with two successive magnetostructural transformations

Xuexi Zhang, Hehe Zhang, Mingfang Qian & Lin Geng

High magnetocaloric refrigeration performance requires large magnetic entropy change $\Delta S_M$ and broad working temperature span $\Delta T_{FWHM}$. A fourth element doping of Co in ternary Ni-Mn-Sn alloy may significantly enhance the saturation magnetization of the alloy and thus enhance the $\Delta S_M$. Here, the effects of Co-doping on the martensite transformation, magnetic properties and magnetocaloric effects (MCE) of quaternary Ni$_{47-x}$Mn$_{43}$Sn$_{10}$Co$_x$ ($x = 0, 6, 11$) alloys were investigated. The martensite transformation temperatures decrease while austenite Curie point increases with Co content increasing to $x = 6$ and $11$, thus broadening the temperature window for a high magnetization austenite (13.5, 91.7 and 109.1 A·m$^2$/kg for $x = 0, 6$ and $11$, respectively). Two successive magnetostructural transformations ($A \rightarrow 10 M$ and $A \rightarrow 10 M + 6 M$) occur in the alloy $x = 6$, which are responsible for the giant magnetic entropy change $\Delta S_M = 29.5$ J/kg·K, wide working temperature span $\Delta T_{FWHM} = 14$ K and large effective refrigeration capacity $R_{Ceff} = 232$ J/kg under a magnetic field of 5.0 T. These results suggest that Ni$_{40.6}$Mn$_{43.3}$Sn$_{10.0}$Co$_{6.1}$ alloy may act as a potential solid-state magnetic refrigerant working at room temperature.

Over the last decade, Ni-Mn-X (X = Sn, In and Sb) metamagnetic shape memory alloys (MSMAs) have attracted significant interests due to their potential applications as magnetic refrigeration materials near room temperature. These materials, based on magnetocaloric effect (MCE), are considered to be environmentally friendly and cost-effective refrigerants because of their large refrigeration capacity ($R_C$) which is comparable to those of expensive rare-earth-containing MCE compounds$^1$. In Ni-Mn-X-based (X = Sn, In and Sb) alloys, the metamagnetic transition from the weak-magnetic martensite to ferromagnetic austenite under an applied magnetic field leads to an inverse MCE$^2–^4$, whereas the magnetic transition of the austenite phase is responsible for a conventional MCE$^5–^7$. Clearly, the metamagnetic transition is driven by the Zeeman energy $E_{Zeeman} = \mu_0 H \Delta M$, where $\Delta M$ and $\mu_0 H$ represent the magnetization difference between martensite/austenite phases and the applied magnetic field, respectively. So, enhanced $\Delta M$ is in favor of large $E_{Zeeman}$ which is responsible for the high magnetic entropy change ($\Delta S_M$) and wide working temperature span ($\Delta T_{FWHM}$, defined as the full width at half maximum of the magnetic entropy peak)$^8$, where the $\Delta T_{FWHM}$ is crucial for magnetic refrigeration applications in the case of inverse MCE$^9,^{10}$.

In Ni-Mn-X off-stoichiometric MSMAs, the $\Delta M$ can be enhanced by composition tuning$^{11,12}$, heat treatment$^{13,14}$ and doping$^{15,16}$. It has been reported that high-Mn content Ni-Mn-X alloys exhibited enhanced $\Delta M$ because the magnetization of the austenite was mainly attributed to the ferromagnetic interaction between the neighboring Mn-Mn atoms$^{17}$. For instance, the austenite of Mn-rich Ni$_{12}$Mn$_{16}$Sn$_{11}$ alloy$^{18}$ shows a higher magnetization of 68 A·m$^2$/kg under a magnetic field of 5.0 T, compared to that of 39 A·m$^2$/kg for Ni$_{15}$Mn$_{40}$Sn$_{15}$ alloy$^{19}$. Heat treatment is also a useful method to modulate the grain constraint in order to control the microstructure, martensite transformation (MT) temperature and magnetic properties of the ferromagnetic MSMAs (FMSMAs)$^{20,21}$. Doping of non-ferromagnetic elements$^{22–24}$ such as Cu, Al and Ti can enhance $\Delta M$ effectively by tuning the valence electron concentration $\epsilon/a$ or changing the unit cell volume, which mainly changes the MT temperatures. Of note is that the doping of ferromagnetic elements such as Fe and Co can effectively improve the $\Delta M$. For instance, the substitution of Fe for Ni can simultaneously enhance the magnetic-field-induced reverse
Martensitic transformation and mechanical properties of Ni-Mn-Sn alloys. Previous studies suggested that Co substitution for Ni in Ni-Mn-X alloys can effectively improve the austenite saturation magnetization and decrease the martensite magnetization\(^{28-30}\), which was mainly due to the following four aspects: 1) The introduction of Co acted as a “ferromagnetic activator” to induce the magnetic moments of the nearest neighboring Mn-Mn atoms aligning in a ferromagnetic order\(^{31,32}\). 2) Upon substitution of Co for Ni in Ni-Mn-X alloys, the austenite Curie point \((T_{c})\) increased significantly with increasing Co concentration, which broadened the temperature window of the high magnetization austenite\(^{33}\). 3) The doping of Co can increase the Curie point and saturation magnetization of the Ni-Mn-X alloys, which accordingly increases the \(E_{\text{excess}}\)\(^{34}\). 4) Co atoms at Ni site contribute a much larger magnetic moment (~1.0 \(\mu_B\)) compared to that of Ni (~0.3 \(\mu_B\)) in the austenite\(^{35}\).

The enlargement of \(\Delta T_{\text{FWHM}}\) may be realized by two successive magentostructural transformations, which have been found in some ferromagnetic alloys. For example, rare earth containing low temperature magnetic refrigeration compounds, such as TbMn\(_{2}\)Si\(_{2}\) have been found in some ferromagnetic alloys. It has been supposed that the L\(_{2}\) austenite is stabilized because its Fermi surface just touches the Brillouin zone boundary\(^{47}\). With \(E_{\text{excess}}\)\(^{34}\) increasing and thus the Fermi surface overlapping the Brillouin zone, the co-existence of the martensite twins with different widths in the present work implied the existence of different martensite structures possess different morphologies for Ni-Mn-Sn alloys, where the 10 M martensite phase of the Co\(_{6}\) alloy is shown in Fig. 1, where the sample was firstly kept in the ice water for several minutes to reach the martensite state. The microstructure is very similar to those modulated martensite structures reported in some ferromagnetic shape memory alloys\(^{43}\). Many cracks distributed along the grain boundaries were observed, as shown in Fig. 1a, implying the brittleness of the polycrystalline alloy. In addition, the martensite morphology is plate-like, which can be recognized by the straight twin boundaries of each plate. Fine twins with thickness of 2–10 \(\mu\)m exist inside the broad martensite plates, as shown in Fig. 1b. Previous report\(^{44}\) showed that Mc in Table 1. Generally, the change in MT temperatures can be interpreted from the following two aspects. Firstly, the co-existence of the martensite twins with different widths in the present work implied the existence of different martensite structures in Co\(_{6}\) alloy at room temperature (RT). Detailed martensite structure of the present alloy will be analyzed by XRD and discussed in the later sections.

Martensite transformation of Ni\(_{40.6}\)Mn\(_{43.3}\)Sn\(_{10.0}\)Co\(_{6.1}\) (Co\(_{6}\)) alloys. Figure 2 shows the DSC curves of Ni\(_{40.6}\)Mn\(_{43.3}\)Sn\(_{10.0}\)Co\(_{x}\) (x = 0, 6, 11) alloys in the temperature range 220–500 K. The strong exothermic and endothermic peaks produced by the forward and reverse MT correspond to the starting and finishing temperatures \(T^f_{\text{DSC}}, T^r_{\text{DSC}}, A^f_{\text{DSC}}\) and \(A^r_{\text{DSC}}\), respectively, determined by the intersection of the base-line and tangent line. These temperatures are summarized in Table 1 together with the values of the valence electrons per atom (e/a). With the addition of Co element, a monotonic decrease in the MT temperatures occurs, as shown in Table 1. Generally, the change in MT temperatures can be interpreted from the following two aspects. Firstly, the e/a dependence of MT temperatures has been found to increase monotonically in Ni-Mn-based Heusler alloys\(^{45,46}\). It has been supposed that the L\(_2\) austenite is stabilized because its Fermi surface just touches the Brillouin zone boundary\(^{47}\). With e/a increasing and thus the Fermi surface overlapping the Brillouin zone, the

Figure 1. Optical microscope (OM) images showing the grains and martensite twin morphology in the Co\(_{6}\) alloy. (a) and (b) are low and high magnification images, respectively.
alloys at heating and cooling rates of 10 K/min. (b) Co0, (c) Co6 and (c) Co11. Insets in (b) and (c) are enlarged images showing the magnetic transitions around the Curie point.

Figure 2. Differential scanning calorimetry (DSC) plots of the annealed Ni_{47-x}Mn_{2}Sn_{10}Co_{x} (x = 0, 6, 11) alloys at heating and cooling rates of 10 K/min. (c) Co11, (b) Co6 and (c) Co11. Insets in (b) and (c) are enlarged images showing the magnetic transitions around the Curie point.

Table 1. Martensite transformation temperatures ($A_{\text{DSC}}$, $A_{\text{M}}$, $M_{d}$, $M_{f}$, $T_{t}$), transformation enthalpy change ($\Delta H_{\text{endo}}$, $\Delta H_{\text{exo}}$) and transformation entropy change ($\Delta S_{\text{endo}}$, $\Delta S_{\text{exo}}$) during heating/cooling process obtained by DSC curves of Ni_{47-x}Mn_{2}Sn_{0.5Co_{x}} (x = 0, 6, 11) alloys. $^{1}$Co0 - Ni_{45.6}Mn_{2}Sn_{0.5Co_{0.1}}; $^{2}$Co6 - Ni_{45.6}Mn_{2}Sn_{0.5Co_{0.2}}; $^{3}$Co11 - Ni_{45.6}Mn_{2}Sn_{0.5Co_{0.3}}. (Data indicate atomic percent, at. %).

| Alloys          | Transformation temperatures, K | $\Delta H_{\text{exo}}$ J/g | $\Delta S_{\text{exo}}$ J/kg·K | $\Delta H_{\text{endo}}$ J/g | $\Delta S_{\text{endo}}$ J/kg·K |
|-----------------|--------------------------------|-----------------------------|--------------------------------|-----------------------------|--------------------------------|
| Co0$^{1}$       | 336                           | 344                         | 334                            | 327                         | 16.5 ± 0.2                    | 48.5 ± 0.5                    | 16.9 ± 0.1                    | 51.1 ± 0.3                    |
| Co6$^{2}$       | 314                           | 326                         | 310                            | 304                         | 10.8 ± 0.06                   | 33.7 ± 0.2                    | 9.9 ± 0.06                    | 32.2 ± 0.2                    |
| Co11$^{3}$      | 307                           | 323                         | 289                            | 271                         | 5.5 ± 0.2                     | 17.7 ± 0.6                    | 4.7 ± 0.2                     | 16.9 ± 0.6                    |

L2$_{1}$ austenite structure becomes instable, which induces the occurrence of the MT$^{47}$. Here, the values of $e/a$ are the concentration-weighed sum of $s$, $d$, and $p$ valence electrons, i.e. 10 ($3d^{8}4s^{2}$) for Ni, 7 ($3d^{3}4s^{2}$) for Mn, 4 ($5s^{2}5p^{2}$) for Sn and 9 ($3d^{5}4s^{2}$) for Co, respectively. The calculated $e/a$ decreases with increasing Co substitution of Ni mainly because the valence electrons of Co is less than Ni, thus decreasing the MT temperatures of the alloy, which is in good agreement with the $e/a$ dependence rule$^{45,46}$. On the other hand, the atom size effect, originating from the unit cell expansion of the austenite, is not favorable to the occurrence of MT due to changes of the relative positions between the Fermi surface and Brillouin zone$^{29}$. The substitution of larger Co atoms (atomic radius $r = 0.126$ nm) for smaller Ni atoms ($r = 0.125$ nm) causes a slight expansion of the austenite unit cell. Both factors stabilize the austenite phase and therefore decrease the MT temperatures.

A further feature of weak shoulder thermal effect ($T_{t}^{\text{A}}$) is also observed for sample Co6 and Co11, as shown in the inset in Fig. 2b,c, respectively, which corresponds to the magnetic transition from ferromagnetism to paramagnetism of the austenite during cooling process. But the $T_{t}^{\text{A}}$ point was not found for Co0 probably because the magnetic transition occurs below MT temperatures leading to the extremely low magnetization of the austenite (as shown in Fig. 3a). Therefore, it can be deduced that the substitution of Co for Ni in Ni-Mn-Sn alloys effectively increases the $T_{t}^{\text{A}}$, which is consistent with refs$^{29,30}$. The comparison of the transformation entropy changes during heating ($\Delta S_{\text{endo}}$) and cooling ($\Delta S_{\text{exo}}$) process are also listed in Table 1 ($\Delta S_{\text{endo}} = \Delta H_{\text{endo}}/T_{t}$, where $T_{t} = (A_{\text{DSC}} - A_{\text{M}})/2$; $\Delta S_{\text{exo}} = \Delta H_{\text{exo}}/T_{t}$, where $T_{t} = (M_{f} + M_{d})/2$; $\Delta H_{\text{endo}}$ and $\Delta H_{\text{exo}}$ denote as the enthalpy changes during the inverse and direct MT, respectively). The substitution of larger Co atoms (atomic radius $r = 0.126$ nm) for smaller Ni atoms ($r = 0.125$ nm) causes a slight expansion of the austenite unit cell. Both factors stabilize the austenite phase and therefore decrease the MT temperatures.

Figure 3 shows the field-heating (FH) and field-cooling (FC) magnetization vs temperature plots ($M$-$T$) of Ni$_{47-x}$Mn$_{2}$Sn$_{0.5}$Co$_{x}$ (x = 0, 6, 11) alloys measured under magnetic fields of 0.02 and 5.0 T. The magnetization change ($\Delta M$) in Co0 between austenite and martensite phases during MT is very small (Fig. 3a) because the phase transformation temperatures are higher than the magnetic transition point ($T_{t} > T_{c}^{A}$) and thus MT occurs in a weak-magnetic state. Furthermore, the metamagnetic transition behavior is also weak in Co0 alloy, i.e. its MT...
temperatures shift little to lower temperatures with increasing magnetic field ($\Delta A_s/\Delta H = -0.2 \text{ K/T}$, as shown in Table 2 based on Fig. 3a), which is unfavorable to MCE2. In contrast, both Co6 and Co11 alloys undergo the transformation between a weak-magnetic martensite and a ferromagnetic austenite (Fig. 3b,c), leading to higher $\Delta M$.

Table 2 collected the MT and magnetic transition temperatures of the Ni$_{47-x}$Mn$_{43}$Sn$_{10}$Co$_x$ ($x = 0, 6, 11)$ alloys. It can be seen that the MT temperatures determined from vibrating sample magnetometer (VSM) under 0.02 T are consistent with those from DSC (Table 1). The thermal hysteresis values $\Delta T_{\text{hys}}$, defined as $[(A_f + A_s) - (M_s + M_f)]/2$, are 6.0 K under both 0.02 and 5.0 T in the Co6 alloy, which are much smaller than those of 27 K (0.02 T) and 38.5 K (5.0 T) in the Co11 alloy. As the phase boundary friction strength during MT is responsible for $\Delta T_{\text{hys}}$, this implies that the friction resistance during MT in Co11 alloy is larger than that in Co6 alloy.

It can also be seen from Table 2 that, during heating, the magnetization of the martensite $M_M$ changes little but that of the austenite $M_A$ increases significantly with increasing Co content. As a result, $\Delta M$ in Co6 and Co11 alloys reaches 85.7 and 96.1 A·m$^2$/kg under a magnetic field 5.0 T, respectively, which is much higher than $\Delta M = 9.2$ A·m$^2$/kg in Co0. The enhancement of $\Delta M$ favors the magnetic entropy change $\Delta S_M$, according to the Maxwell equation and broadens the $\Delta T_{\text{FWHM}}$ due to the increase in Zeeman energy. Furthermore, the percentage of MT caused by field-induced metamagnetic transition mainly relies on $dT_{\text{Ms}}/dH^{\text{SW}}$ ($T_{\text{Ms}}$ denotes the MT equilibrium temperature, as shown in Fig. 3, which can be assessed by the Clausius-Clapeyron magnetic equation $-dT_{\text{Ms}}/dH = \Delta M/\Delta S_p$. Utilizing the values of $\Delta M$ under 5.0 T (Table 2) and $\Delta S_p$ determined by DSC (Table 1), the calculated $\Delta M/\Delta S_p$ is $-2.5$ and $-5.4$ K/T for Co6 and Co11, respectively. By contrast, the

Table 2. Martensite transformation temperatures and magnetic properties obtained by vibrating sample magnetometer (VSM) for Ni$_{47-x}$Mn$_{43}$Sn$_{10}$Co$_x$ ($x = 0, 6, 11$) alloys under magnetic fields of 0.02 and 5.0 T. $M_A$ and $M_M$ are magnetizations of the austenite and martensite, respectively. $1^*\Delta T_{\text{hys}} = [(A_f + A_s) - (M_s + M_f)]/2$. $2^*$Data obtained during heating process. $3^*\Delta M = M_A - M_M$.

![Figure 3. Temperature dependence of the magnetization ($M$-$T$) curves under external magnetic fields of 0.02 and 5.0 T for the alloys of (a) Co0, (b) Co6 and (c) Co11. The inset in (a) shows an enlarged $M$-$T$ curves of Co0 alloy under a magnetic field of 0.02 T.](image-url)
magnetic-field-induced shift of the reverse MT temperature $\Delta T_S/\Delta H$ is $-2.6$ and $-6.6$ K/T for Co6 and Co11 alloys, respectively, as listed in Table 2. So, the applied 5.0 T magnetic field may induce a full metamagnetic transition from weak-magnetic martensite to ferromagnetic austenite in Co6 alloy, but only a partial transition in Co11 alloy, meaning that a 5.0 T magnetic field cannot compensate for the thermal energy loss during MT in Co11 alloy48. Supposing a negligible difference of heat capacity between martensite/austenite phases, a maximum magnetic entropy change $\Delta S_{m}^\text{max} \approx \Delta S_{m}$ should be expected under a high $\Delta AS/\Delta H$49. As a result, a sizable inverse MCE in Co6 alloy is expected when taking the $\Delta M$, $\Delta S_m$, $\Delta A/\Delta H$ and $\Delta T_H$ into account.

In order to investigate the martensite transformation behavior of the Co6 alloy, X-Ray diffraction (XRD) measurements were performed in the temperature range 343–173 K during cooling process. The data were recorded at a temperature interval 10 K (except for 223 K and 173 K), as shown in Fig. 4. The diffraction peaks marked with five-pointed star are associated with the sample platform (Fig. 4). The martensite peaks were indexed as 10 M and 6 M martensite phases according to the theoretical calculation results49 and is displayed in the Supplementary Materials Fig. S2. The alloy exhibits a L21-type austenite structure at high temperatures. With decreasing temperature from 343 to 283 K, the peaks corresponding to the 10 M martensite occur starting at 303 K, as shown in Fig. 4a. As the temperature further decreases, several peaks associated with the 6 M martensite appear at 273 K (much lower than $T_M$ = 304 K from Table 1), as shown in Fig. 4b. It can also be seen that the peak intensity of 6 M martensite becomes stronger with decreasing temperature. On the other hand, the peak intensity of 10 M martensite still keeps increasing with decreasing temperature after the occurrence of the 6 M martensite, implying the co-existence of the A, as shown 6 M transitions and the mixed A $\rightarrow$ 10 M + 6 M phase state during the MT process of the Co6 alloy. Such mixed state of 10 M and 6 M martensite phases has also been found in Ni$_{43}$Co$_7$Mn$_{39}$Sn$_{11}$ alloy and Ni$_{52}$Co$_{11}$Mn$_{43}$Sn$_{9}$ alloys. It is worth noting that the peak (220)$_A$ of the L21-type austenite can still be observed at temperature as low as 173 K (see Fig. 4b), indicating that an incomplete MT with residual austenite even at 173 K. This phenomenon is consistent with some other Ni-Mn-based alloys22,23, implying that the complete MT might be difficult to be achieved supposed that slightly inhomogeneous composition distribution exists in the bulk alloy. Furthermore, the two successive magnetostructural transition processes (A $\rightarrow$ 10 M and A $\rightarrow$ 10 M + 6 M) in the present alloy are essentially different from the two successive martensite (MT) and intermartensite transition (IMT) occur in some other types of FMSMAs such as Ni$_{55.8}$Mn$_{18.1}$Ga$_{26.1}$ alloys.

In addition, the XRD pattern measured at 343 K ($T_M$ = 326 K) is shown in Supplementary Materials Fig. S1b. Single austenite phase is detected without any secondary phases, which is consistent with the back scattered electron (BSE) micrograph observations (Supplementary Materials Fig. S1a). The result is consistent with that in Ni$_{43}$Co$_7$Mn$_{39}$Sn$_{11}$ and Ni$_{52}$Co$_{11}$Mn$_{43}$Sn$_{9}$ after annealing. Secondary phases were observed in Ni$_{49}$Cu$_2$Mn$_{30}$Sn$_{13}$ (0.5 $< x < 2$) alloys in addition, the XRD pattern measured at 326 K ($T_M$ = 326 K) is shown in Supplementary Materials Fig. S1b. Single austenite phase is detected without any secondary phases, which is consistent with the back scattered electron (BSE) micrograph observations (Supplementary Materials Fig. S1a). The result is consistent with that in Ni$_{43}$Co$_7$Mn$_{39}$Sn$_{11}$ and Ni$_{52}$Co$_{11}$Mn$_{43}$Sn$_{9}$ after annealing. Secondary phases were observed in Ni$_{49}$Cu$_2$Mn$_{30}$Sn$_{13}$ (0.5 $< x < 2$) alloys in addition, the XRD pattern measured at 326 K ($T_M$ = 326 K) is shown in Supplementary Materials Fig. S1b. Single austenite phase is detected without any secondary phases, which is consistent with the back scattered electron (BSE) micrograph observations (Supplementary Materials Fig. S1a). The result is consistent with that in Ni$_{43}$Co$_7$Mn$_{39}$Sn$_{11}$ and Ni$_{52}$Co$_{11}$Mn$_{43}$Sn$_{9}$ after annealing. Secondary phases were observed in Ni$_{49}$Cu$_2$Mn$_{30}$Sn$_{13}$ (0.5 $< x < 2$) alloys, respectively.

**Magnetic properties of the Ni$_{40.6}$Co$_{11}$Mn$_{40.6}$Sn$_{18.0}$Co$_{11}$ (Co6) alloy.** The temperature dependent FH/FC magnetization curves and the $dM/dT$ vs $T$ of the Co6 alloy recorded at magnetic fields 0.02, 1.0, 3.0 and 5.0 T are shown in Fig. 5a,b. It can be observed from Fig. 5a that slope changes in the FH/FC curves exist around MT temperatures at magnetic fields above 1.0 T. To clarify this phase transformation character, the first-derivative of the FC magnetization curves with respect to temperature ($dM/dT$ - $T$) was plotted in Fig. 5b. Upon cooling, two successive maxima occur under magnetic fields of 1.0, 3.0 and 5.0 T, while only one inflection peak emerges at 0.02 T. Additionally, the $dM/dT$ - $T$ curves show that $M_{s}^{\text{max}}$ and $M_{s}^{\text{min}}$ denote as the 10 M and 6 M transformation starting temperatures, respectively, decrease with increasing magnetic field (i.e. the 10 M and 6 M change from 321 and 315 K under $\mu_B H = 1.0$ T to 308 and 301 K under $\mu_B H = 5.0$ T, respectively). This phenomenon probably indicate that the two successive magnetostructural transformations (A $\rightarrow$ 10 M + 6 M and A $\rightarrow$ 10 M) can be induced by an external magnetic field, which is still an open question and will be studied in the near future. Compared to the XRD patterns during cooling from 343 to 173 K (see Fig. 4), the magnetic-field-induced inverse martensite transformation is much easier than the temperature-field-induced one.

![Figure 4. In-situ X-ray diffraction (XRD) patterns for Co6 alloy in the range 35$^\circ$ < 20 < 50$^\circ$ during cooling (a) from 343 K to 283 K and (b) from 273 K to 173 K, respectively. The diffraction peaks marked by five-pointed star corresponds to the sample stage.](image-url)
The isothermal magnetization $M-H$ loops for Co6 alloy at temperatures 290–330 K are shown in Fig. 6a. The plots were recorded under magnetic field up to 5.0 T and at a temperature interval $\Delta T = 2$ K covering the $A_s$ and $A_f$. At a temperature of 295 K, far below $A_s^{VSM}$ (314 K in Table 1), no austenite was induced by magnetic field up to 5.0 T. When test temperatures approach $A_s$, the magnetic-field-induced austenite (MIA) transformation gradually occurs, with MIA critical magnetic field decreasing with increasing temperatures. At 307 K, a large jump in magnetization at about 3.4 T (Fig. 6a), due to the occurrence of MIA, was observed. After removing the magnetic field, the sample transformed back to martensite, but with a small amount of field-induced austenite remaining because the test temperature 307 K was slightly higher than $M_f^{DSC}$ (304 K in Table 1). The $dM/dH$ curve measured at 309 K shows two successive inflection points that indicate the occurrence of two successive magnetostructural transformations. (c) The temperature dependent hysteresis loss ($H_L$) plot during the isothermal magnetization $M-H$ cycling. The fitting line just acts as a guide for the eye. (d) Arrott ($M^2$ vs $H/M$) plots revealing the appearance of the magnetic-field-induced austenite (MIA) at temperatures above 295 K.

Figure 5. Magnetization curves as a function of temperature under magnetic fields of 0.02, 1.0, 3.0 and 5.0 T in the Co6 alloy. (a) Isofield magnetization ($M-T$) curves, (b) First-derivative plots of $M-T$.

Figure 6. Magnetic transition behavior of the Co6 alloy. (a) Representative isothermal magnetization $M-H$ loops under magnetic fields up to 5.0 T. (b) $dM/dH$ curve measured at a temperature of 309 K showing two inflection points that indicate the occurrence of two successive magnetostructural transformations. (c) The temperature dependent hysteresis loss ($H_L$) plot during the isothermal magnetization $M-H$ cycling. The fitting line just acts as a guide for the eye. (d) Arrott ($M^2$ vs $H/M$) plots revealing the appearance of the magnetic-field-induced austenite (MIA) at temperatures above 295 K.
peak at $H_{M2} = 4.5$ T to the 10 M → A. The fact that $dM/dH$ under 4.0 T is larger than that under 4.5 T implies that the phase transition resistance of the former is smaller than the latter one.

During isothermal magnetization $M$-$H$ cycling, the hysteresis loss ($HL$) was determined by integrating the areas between magnetization and demagnetization branches (purple shaded area in Fig. 6a). The temperature dependence of $HL$ is plotted in Fig. 6c. The average hysteresis loss ($AHL$), calculated by averaging the integral area under the temperature range of the full width at half maximum of the hysteresis peak $AHL = \int_{T1}^{T2} H/(HL_{MT})$ (where $T1 = 306$ K, $T2 = 318$ K, as shown in Fig. 6c), was determined to be 99 J/kg under 5.0 T. This is comparable with those of the Ni-Mn-Sn-based alloys, i.e. $AHL = 138$ J/kg under 5.0 T in Ni$_{43}$Mn$_{46}$Sn$_{11}$ and $AHL = 78$ J/kg under 3.0 T in Ni$_{45}$Co$_{5}$Mn$_{39}$In$_{12.5}$ alloys. In order to reveal the first-order martensite transformation (FOMT) temperature, Arrott plots ($M^2$ vs $\mu_0H/M$) were derived as shown in Fig. 6d. The negative slopes can be detected at temperatures ≥ 295 K, suggesting the occurrence of the magnetic-field-induced austenite (MIA) formation. Furthermore, the large degree of negative slope indicates that MIA is fast, which is consistent with the $M$-$H$ curves displayed in Fig. 6a.

**Magnetocaloric effects (MCE) of the Ni$_{40.6}$Mn$_{43.3}$Sn$_{10.6}$Co$_{6.1}$ (Co6) alloy.** The MCE can be evaluated via $\Delta S_M$ calculated using thermodynamic Maxwell equation:

$$\Delta S_M(T, H) = S(T, H) - S(T, 0) = \int_0^{H_{max}} (\partial M/\partial T) dH.$$ 

Based on isothermal magnetization data with a field interval of $\Delta H = 0.05$ T at various temperatures (shown in Fig. 6a), the above partial derivative and integration may be numerically approximated to the equation:

$$\Delta S_M(T, H) = \sum_i^N (M(T_{i+1}, H) - M(T_i, H)) (T_{i+1} - T_i).$$

The $\Delta S_M$ related to the FOMT for the Co6 alloy under $\Delta H = 0.5$—5.0 T is plotted as a function of temperature displayed in Fig. 7a. The positive $\Delta S_M$ is attributed to inverse MCE originating from a magnetic-field-induced metamagnetic transition from the weak-magnetic martensite to the ferromagnetic austenite phase. Additionally, the $\Delta S_M$ peak temperature exhibits a field-dependent behavior, i.e. shifting to lower temperatures with increasing magnetic fields.

As depicted in Fig. 6a, the magnetization saturates at lower fields with increasing temperature above $A_s$. According to the Maxwell equation, further increase of the magnetic field contributes little contribution to $\Delta S_M$ when the saturation magnetization plots intersect, such as the temperatures of 317, 319 and 321 K in Fig. 6a. Therefore, the maximum $\Delta S_M(\Delta S_M^{max})$ for a field change 5.0 T can be achieved at a specific temperature, i.e. 314 K, reaching 29.5 J/kg·K under a magnetic field 5.0 T, with a working temperature span 306–320 K. The $\Delta S_M$ calculated from the Maxwell relation is compared with those from the Clausius-Clapeyron equation and DSC curves, as shown in Supplementary Materials TABLE S1. The $\Delta S_M^{max}$ is comparable to the value determined by Clausius-Clapeyron (32.9 J/kg·K), and both of them are also similar to the DSC results ($\Delta S_M^{end} = 33.7 \pm 0.2$ J/kg·K and $\Delta S_M^{exo} = 32.2 \pm 0.2$ J/kg·K), implying that $\Delta S_M$ obtained by the Maxwell equation is acceptable in the present work without the occurrence of the so-called “colossal” values around the transition temperature. In addition, the obtained $\Delta S_M^{max}$ in Co6 alloy is slightly higher than those of some other Co-doped Ni-Mn-based compounds whose $\Delta S_M^{max}$ were estimated using the loop-process method as well, such as Ni$_{50}$Co$_{2}$Mn$_{33}$In$_{15}$ (21.5 J/kg·K), Ni$_{45}$Co$_{5}$Mn$_{37.5}$In$_{12.5}$ (20 J/kg·K), Ni$_{44}$Nb$_{5}$Co$_{2}$Mn$_{40}$Sn$_{10}$ (23 J/kg·K) and Ni$_{43}$Co$_{6}$Mn$_{40}$In$_{2}$Sn$_{8}$ (27 J/kg·K). Furthermore, the present $\Delta S_M^{max}$ is also comparable to some rare-earth containing magnetic refrigerants such as Gd$_2$Ge$_{2.3}$Si$_{1.7}$ (35.1 J/kg·K), MnAs$_{0.7}$P$_{0.3}$ (33.4 J/kg·K) and MnFe$_{1.7}$P$_{0.3}$ (34.3 J/kg·K).
T fails to saturate at 5.0 T for the present Co6 alloy and some most studied magnetocaloric materials, such as La(FeSi)13- based72,23, Gd(SiGe)3-based74,75, NiMn-based1,18,45,63,76–84 compounds. These alloys were selected because their magnetocaloric effects (MCE) are all related to the first-order martensite transformation and are tested around the magnetostructural transition temperatures.

On the other hand, MCE related to FOMT usually occurs in a narrow temperature range, for instance 1–5 K. By contrast, a broadened $\Delta T_{\text{FWHM}} \sim 14$ K was obtained in the present Co6 alloy, which may be attributed to two aspects: 1) Two successive magnetostructural transformations ($A \rightarrow 10$ M and $A \rightarrow 10$ M + 6 M), 2) Magnetic-field-induced metamagnetic transition, i.e. the magnetic field dependence of the $\Delta S_{\text{max}}$ position. Here, $A_f^{5.0 T} > A^{0.02 T}$ implies an incomplete reverse MT induced by a magnetic field of 5.0 T. In other words, the field-induced shift of the MT temperature cannot overcome MT width so that $\Delta S_{\text{max}}$ fails to saturate to $\Delta S_{\text{MT}}$.

Whether a maximum of $\Delta S_{\text{max}}$ is reached under a field of 5.0 T needs further investigation in the near future. In Ni45Mn36.7In13.3Co5 alloy, a maximum $\Delta S_{\text{max}}^{\Delta S} = 7$ J/kg K was achieved at a field of 4.0 T using “rectilinear modelization” by Recarte et al.68. While $\Delta S_{\text{max}}^{\text{Str}}$ of the Ni45Co4.5Mn37In13 single crystal does not saturate up to 7.0 T using “curved modelization” adopted by Bourgault et al.69. Both approaches are equally consistent with the experimental data at a low magnetic field range (<4.0 T), whereas the “curved modelization” is better in reflecting $\Delta S_{\text{max}}$ at high fields. The MCE tends to reach a saturation value for fields above 5.0 T in Ni45Mn36.7In13.3Co5 alloy by quasi-directly from isofield calorimetric measurements according to Stern et al.70. Fig. 7b shows $\Delta S_{\text{MT}}$ - $T$ plots at different temperatures in the reverse MT range. At low temperatures (i.e. $T < 316$ K), the field-induced fraction of austenite phase increases with the rise of temperature, which is responsible to a similar increase in $\Delta S_{\text{MT}}$. At higher temperatures, where both martensite and austenite phases coexist at zero field, the field-induced austenite fraction and $\Delta S_{\text{MT}}$ minify as the temperature increases. Furthermore, the negative slope of $\Delta S_{\text{MT}}$ which can be clearly seen in Fig. 7b for high magnetic fields at 320 and 327.5 K, which is due to the contribution of this conventional direct MCE in the vicinity of $T_C$.

The refrigeration capacity ($RC$), which represents the amount of heat transferring between the cold and hot reservoirs in a thermodynamic cycle, is defined as $RC = \int_{T_{\text{cold}}}^{T_{\text{hot}}} |\Delta S_m(T)| dT$, where $T_{\text{cold}}$ and $T_{\text{hot}}$ are the corresponding temperatures at $\Delta T_{\text{FWHM}}$ of $\Delta S_{\text{max}}$. By numerically integrating the area under the $\Delta S_{\text{MT}}$ - $T$ curves between $T_{\text{cold}}$ and $T_{\text{hot}}$ (shaded area in Fig. 7a), the $RC = 322$ J/kg under a magnetic field change of 5.0 T was obtained in Co6 alloy. However, for evaluating the effective magnetic refrigeration capacity, the AHL should be deducted.18,45,71. Therefore, a more reasonable criterion for assessing the cooling efficiency, the effective refrigeration capacity ($RC_{\text{eff}}$) defined as $RC_{\text{eff}} = RC - \text{AHL}$, was adopted here. For comparison, the $RC_{\text{eff}}$ values under a field of 5.0 T for the present work and some most studied magnetocaloric materials1,18,45,63,72–84 are summarized in Fig. 8. Noteworthy, the $RC_{\text{eff}}$ of the present Co6 alloy reaches 223 J/kg, which is significantly larger than those of the stoichiometric Ni-Mn-based alloys1,18,45,63,72–84 and is comparable to those of some Co-doped Mn-rich Ni-Mn-based compounds1,18,45,76–80. Besides, the achieved $RC_{\text{eff}}$ is also comparable to those rare-earth containing La(FeSi)3-based72,73 and Gd(SiGe)3-based74,75 compounds. Of note is that the working temperature of the present alloy is slightly above 300 K, which is very encouraging for room-temperature magnetic refrigeration applications.

**Conclusion**

The effect of Co doping on the martensite transformation, magnetic properties and magnetocaloric effects were investigated in Ni4−xMn3Sn11Co5 (x= 0, 6, 11) alloys. The main conclusions may be drawn as follows:

1) The martensite transformation temperatures decreased and Curie temperature of austenite phase increased significantly with increasing Co concentration, broadening the temperature window for a higher magnetization of austenite: 13.5, 91.7 and 109.1 A·m²/kg for x = 0, 6 and 11, respectively.

![Figure 8](https://example.com/figure8.png)
Two successive magnetostructural transformations, i.e. A → 10 M and A → 10 M + 6 M, existed in the Ni$_{46}$Mn$_{43}$Sn$_{10}$Co$_{6.1}$ alloy whose magnetic-field-induced shift of austenite finishing temperature $\Delta T / \Delta H$ reached $-2.6$ K/T.

A sizable maximum magnetic entropy change $\Delta S_{\text{M}}^{\text{max}} = 29.5$ J/kg·K, a wide working temperature span $\Delta T_{\text{FWHM}}$ 14 K and a high effective refrigeration capacity $RC_{\text{eff}}$ 223 J/kg were obtained in the Ni$_{10}$Mn$_{23}$Sn$_{10}$Co$_{6}$ alloy under a magnetic field of 5.0 T.

**Methods**

**Sample and heat treatment.** Ni$_{47-x}$Mn$_{10}$Sn$_{10}$Co$_{6}$ (x = 0, 6, 11, atomic percent) ingots, denoted as Co0, Co6 and Co11, respectively, were prepared by induction melting pure Ni (99.99%), Co (99.99%), Mn (99.9%) and Sn (99.99%) in an argon atmosphere and casting in a copper mold. The ingots were sealed in a quartz tube accompanied with Mn powder (to create a Mn vapor atmosphere in the tube) and Ti sheet (acted as oxygen getter), evacuated under vacuum at 10$^{-2}$ Pa, annealed at 1173 K for 24 h and then quenched in iced-water. The composition of the specimens were determined by a Zeiss-SUPRA SEM equipped with an Oxford EDS, using $\alpha$ emission current, 10 mm working distance, 50$\mu$A probe current and ~60 s data acquisition time duration. The composition measurement precision of the EDS was calibrated with chemical analysis results (ICP-OES) to be less than 0.5%.

**Composition and martensite transformation tests.** The actual and nominal compositions of the alloys were shown in Table 1. The microstructure of the specimens was examined by a Zeiss-SUPRA SEM and an Olympus PMG3 optical microscope (OM) with a polarizing filter. The martensite transformation temperatures and Curie points were measured by differential scanning calorimetry (DSC) at heating and cooling rates of 10 K/min. XRD analyses were performed using Cu K$\alpha$ radiation with a low-temperature chamber.

**Magnetic property and magnetocaloric effects (MCE) evaluation.** Magnetization measurements were performed using a vibrating sample magnetometer (VSM) in a commercial Magnetic Property Measurement System (MPMS) of Quantum Design. Magnetization vs temperature (M-T) curves were recorded under magnetic fields 0.02 and 5.0 T with heating/cooling rates of 5 K/min and temperature range 200–400 K. Isothermal magnetization (M-H) curves were measured at different test temperatures ($T_{\text{test}}$) from temperatures 290–330 K under an external magnetic field up to 5.0 T. In order to rule out the temperature and field history effects and thus avoid the spurious spike, the so-called loop process$^{22}$ was performed before each M-H test. The detailed loop process was as follows: 1) The sample was initially zero-field-cooled down to 200 K to ensure a full weak-magnetic martensite state prior to recording each M-H cycle at a constant temperature, 2) Zero-field-heated to ($T_{\text{Hea}}$−10) K at 10 K/min, then heated to $T_{\text{Hea}}$ at 1 K/min and finally maintained at the $T_{\text{Hea}}$ temperature for 2 min before starting the M-H cycle.

**Data availability statement.** The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

**References**

1. Huang, L., Cong, D. Y., Sao, H. L. & Wang, Y. D. Giant magnetic refrigeration capacity near room temperature in Ni$_{47}$Co$_{6}$Mn$_{10}$Sn$_{10}$ multiferroic alloy. *Appl. Phys. Lett.* **104**, 132407 (2014).
2. Liu, J., Gottschall, T., Skokov, K. P., Moore, J. D. & Gutfleisch, O. Giant magnetocaloric effect driven by structural transitions. *Nature Mater.* **11**, 620–626 (2012).
3. I. Levov, V. A., Kosogor, A., Barandiaran, J. M. & Chernenko, V. A. Theoretical description of magnetocaloric effect in the shape memory alloy exhibiting metamagnetic behavior. *J. Appl. Phys.* **119**, 013902 (2016).
4. Chen, J. H., et al. Direct measure of giant magnetocaloric entropy contributions in Ni-Mn-In. *Acta Mater.* **105**, (2016).
5. Krautz, M. et al. Systematic investigation of Mn substituted La(Fe,Si)$_{13}$ alloys and their hydrides for room-temperature magnetocaloric application. *J. Alloy. Compd.* **598**, 27–32 (2014).
6. Sarkar, S. K. et al. Giant magnetocaloric effect from reverse martensitic transformation in Ni-Mn-Ga-Cu ferromagnetic shape memory alloys. *J. Alloy. Compd.* **670**, 281–288 (2016).
7. Deng, J. Q., Zhuang, Y. H., Li, J. Q. & Zhou, K. W. Magnetic phase transition and magnetocaloric effect in (Gd$_{1-x}$Tb$_x$)$_{5}$Si$_{1.72}$Ge$_{2.28}$ compounds. *J. Alloy. Compd.* **428**, 28–33 (2007).
8. Hu, F. X., Shen, B.-G. & Sun, J.-R. Magnetic entropy change involving martensitic transformation in NiMn-based Heusler alloys. *Chin. Phys. B.* **22**, 037505 (2013).
9. Dubenko, I. et al. Magnetocaloric effect and multifunctional properties of Ni-Mn based Heusler alloys. *J. Magn. Magn. Mater.* **324**, 3530–3534 (2012).
10. Quetz, A. et al. Giant reversible inverse magnetocaloric effects in Ni$_{100-x}$Mn$_{x}$In$_{2}$ Heusler alloys. *J. Alloy. Compd.* **683**, 139–142 (2016).
11. Dan, N. H. et al. Magnetic properties and magnetocaloric effect in Ni-Mn-Sn alloys. *J. Magn. Magn. Mater.* **374**, 372–375 (2015).
12. Umetu, Y. R. et al. Metamagnetic behaviour under high magnetic fields in Ni$_{100-x}$Mn$_{x}$In$_{2}$ (x = 14.0 and 15.6) shape memory alloys. *J. Phys. D: Appl. Phys.* **42**, 075003 (2009).
13. Wang, X. et al. Influence of annealing temperatures on the magnetostuctural transition and magnetocaloric effect of Ni$_4$Co$_2$Mn$_2$Sn$_2$ powders. *J. Alloy. Compd.* **691**, 215–219 (2017).
14. Pandey, S. et al. Effects of annealing on the magnetic properties and magnetocaloric effects of B doped Ni-Mn-In melt-spin ribbons. *J. Alloy. Compd.* **731**, 678–684 (2018).
15. Liu, J., Scheerbaum, N., Luhbina, J. & Gutfleisch, O. Reversibility of magnetostructural transition and associated magnetocaloric effect in Ni-Mn-In-Co. *Appl. Phys. Lett.* **93**, 102512 (2008).
16. Zhang, Y. et al. Large magnetic entropy change and enhanced mechanical properties of Ni-Mn-Sn-Co alloys. *Scripta Mater.* **75**, 26–29 (2014).
17. Sasooglu, E., Sandratskii, L. M. & Bruno, P. First-principles calculation of the intersublattice exchange interactions and Curie temperatures of the full Heusler alloys Ni$_{100-x}$Mn$_x$X (X $=$ Ga-In,Sn,Sn). *Phys. Rev. B.* **70**, 024427 (2004).
18. Zhang, Y. et al. Enhanced large magnetic entropy change and adiabatic temperature change of Ni$_{100-x}$Mn$_x$Sn$_1$ alloys by a rapid solidification method. *Scripta Mater.* **104**, 41–44 (2015).
19. Das, R., Sarma, S., Perumal, A. & Srinivasan, A. Effect of Co and Cu substitution on the magnetic entropy change in Ni$_{47}$Mn$_{10}$Sn$_{10}$ alloy. *J. Appl. Phys.* **109**, 07A901 (2011).
20. Bruno, N. M. et al. Effect of grain constraint on the field requirements for magnetocaloric effect in Ni$_{55.8}$Mn$_{18.1}$Ga$_{26.1}$ Heusler alloy. J. Appl. Phys. 120, 075101 (2016).
21. Bruno, N. M. et al. The effect of heat treatments on Ni$_{55.5}$Mn$_4$Co$_{20.7}$Sn$_{13.8}$ meta-magnetic shape memory alloys for magnetic refrigeration. Acta Mater. 66, 64–84 (2014).
22. Qu, Y. H. et al. Giant and reversible room-temperature magnetocaloric effect in Ti-doped Ni-Co-Mn-Sn magnetic shape memory alloys. Acta Mater. 134, 236–248 (2017).
23. Cong, D. Y. et al. Low-field-actuated giant magnetocaloric effect and excellent mechanical properties in a NiMn-based multiferroic alloy. Acta Mater. 146, 142–151 (2018).
24. Liu, C. et al. Martensitic transition, inverse magnetocaloric effect and shape memory characteristics in Mn$_{55.8}$Ga$_{26.1}$Co$_{18.1}$Heusler alloys. Phys. Rev. B: Condens. Matter. 508, 118–123 (2017).
25. Tan, C., Tai, Z., Zhang, K., Tian, X. & Cai, W. Simultaneous enhancement of magnetic and mechanical properties in Ni-Mn-Sn alloy by Fe doping. Sci. Rep. 7, 43387 (2017).
26. Liu, C. L. et al. Microstructure, martensitic transformation and mechanical properties of Ni-Mn-Sn alloys by substituting Fe for Ni. Trans. Nonferrous Met. Soc. China. 27, 2234–2238 (2017).
27. Zhang, H. H. et al. Enhanced magnetocaloric effects of Ni-Fe-Mn-Sn alloys involving strong metamagnetic behavior. J. Alloy. Compd. 715, 206–213 (2017).
28. Sharma, J. & Suresh, K. G. Investigation of multifunctional properties of Mn$_{55.8}$Ga$_{26.1}$Co$_{18.1}$Sn$_{13.8}$ (x = 0–6) Heusler alloys. J. Alloy. Compd. 620, 329–336 (2015).
29. Zheng, H., Wang, W., Yu, J., Zhai, Q. & Luo, Z. Martensitic transformation in melt-spun Ni-Mn-Sn-Co ribbons. J. Mater. Res. 29, 880–886 (2014).
30. Cong, D. Y., Roth, S. & Schultz, L. Magnetic properties and structural transformations in Ni-Co-Mn-Sn multifunctional alloys. Acta Mater. 60, 5335–5351 (2012).
31. Guo, Z. G., Pan, L. Q., Qiu, H. M., Zheng, X. F. & Liu, Z. H. Structural and magnetic phase transition in quinary Ni$_{55.8}$Co$_{20.7}$Mn$_{18.1}$Sn$_{13.8}$ Heusler alloy. J. Alloy. Compd. 615, 316–321 (2014).
32. Ito, W. et al. Martensitic and magnetic transformation behaviors in Heusler-type NiMnIn and NiCoMnIn metamagnetic shape memory alloys. Metall. Mater. Trans. A. 38, 759–766 (2007).
33. Wu, Z. G., Liu, Z. H., Yang, H., Liu, Y. N. & Wu, G. H. Effect of Co addition on martensitic phase transformation and magnetic properties of Mn$_{55.8}$In$_{26.1}$Co$_{18.1}$ polycrystalline alloys. Intermetallics. 19, 1839–1848 (2011).
34. Karaca, H. E. et al. Magnetic field-induced phase transformation in NiMnCoIn magnetic shape-memory alloys-A new actuation mechanism with large work output. Adv. Funct. Mater. 19, 983–998 (2009).
35. Wu, Z. G. Development of Ni-Mn-Based Ferromagnetic Shape Memory Alloys. The University of Western Australia. Ph.D. Thesis. 20–21 (2011).
36. Li, G. X. et al. Successive magnetic phase transitions in Tb$_{50}$Mn$_{50}$S$_{5}$ for magnetic refrigeration. Appl. Phys. Lett. 106, 182405 (2015).
37. Chen, J., Shen, B. G., Dong, Q. Y., Hu, F. X. & Sun, J. R. Large reversible magnetocaloric effect caused by two successive magnetic transitions in ErGa$_{3}$ compound. Appl. Phys. Lett. 95, 132504 (2009).
38. Meng, H. et al. Reversible magnetocaloric effect and refrigeration capacity enhanced by two successive magnetic transitions in Dy$_{2}$Ge$_{2}$O$_{7}$ and Dy$_{2}$GeO$_{5}$. J. Magn. Magn. Mater. 358, 277–281 (2014).
39. Guo, Z. G. et al. Investigation of the intermediate phase and magnetocaloric properties in high-pressure annealing Ni-Mn-Co-Sn alloy. Appl. Phys. Lett. 97, 052506 (2010).
40. Zhang, X. X. et al. Enhanced magnetic entropy change and working temperature interval in Ni-Mn-In-Co alloys. J. Alloy. Compd. 656, 154–158 (2016).
41. Krenke, T. et al. Ferromagnetism in the austenitic and martensitic states of Ni-Mn-In alloys. Phys. Rev. B. 73, 174413 (2006).
42. Krenke, T. et al. Martensitic transitions and the nature of ferromagnetism in the austenitic and martensitic states of Ni-Mn-Sn alloys. Phys. Rev. B. 72, 014412 (2005).
43. Zhang, H. H. et al. Magnetocaloric effect of Ni-Mn-Sn-Fe microwires prepared by melt-extraction technique. Mater. Des. 114, 1–7 (2017).
44. Mohd Jani, J., Leary, M., Subic, A. & Gibson, M. A. A review of shape memory alloy research, applications and opportunities. Mater. Des. 56, 1078–1113 (2014).
45. Webster, P. J., Ziebeck, K. R. A., Town, S. L. & Peak, M. S. Thermal hysteresis and friction of phase boundary motion in ferromagnetic Ni$_{50.5}$Mn$_{19.5}$Ga$_{30}$ single crystals. Phys. Rev. B. 65, 014216 (2002).
46. Pecharsky, V. K., Gschneider, K. A., Pecharsky, A. O. & Tishin, A. M. Thermodynamics of the magnetocaloric effect. Phys. Rev. B. 64, 144406 (2001).
47. Umetsu, R. Y. et al. Kinetic arrest behavior in martensitic transformation of NiCoMnSn metamagnetic shape memory alloy. J. Alloy. Compd. 509, 1389–1393 (2011).
48. Kainuma, R. et al. Martensitic shape memory effect in a Heusler-type Ni$_{50.5}$Co$_{20.7}$Mn$_{19.5}$Sn$_{13.8}$ polycrystalline alloy. Appl. Phys. Lett. 88, 192513 (2006).
49. Liu, D. M. et al. In-situ studies of stress- and magnetic-field-induced phase transformation in a polymer-bonded Ni-Co-Mn-In composite. Mater. Sci. Eng., A. 527, 3561–3571 (2010).
50. Chatterjee, S., Giri, S., Majumder, S. & De, S. K. Thermomagnetic irreversibility in Ni$_{50.5}$Mn$_{19.5}$Sn$_{13.8}$ shape-memory alloy. Phys. Rev. B. 77, 224440 (2008).
51. Yu, S. Y. et al. Intermartensitic transformation and magnetic field effect in NiMnInSb ferromagnetic shape memory alloys. J. Magn. Magn. Mater. 322, 2541–2544 (2010).
52. Biskup Muthu, S. et al. Influence of chemical substitution, magnetic field, and hydrostatic pressure effect on martensitic and intermartensitic transition in bulk Ni$_{50.5}$Co$_{20.7}$Mn$_{19.5}$Sn$_{13.8}$ (0.5 ≤ x ≤ 2) Heusler alloys. Appl. Phys. Lett. 104, 092404 (2014).
53. Wu, Z., Liu, Z., Yang, H., Liu, Y. & Wu, G. Martensitic and magnetic transformation behaviours in Mn$_{50.5}$Ni$_{32.5}$Sn$_{15}$Co$_{5}$ polycrystalline alloys. J. Phys. D: Appl. Phys. 44, 385403 (2011).
54. Lázapita, P. et al. Martensitic transformation and magnetic field induced effects in Ni$_{50.5}$Co$_{20.7}$Mn$_{19.5}$Sn$_{13.8}$ metamagnetic shape memory alloy. Acta Mater. 109, 170–176 (2016).
55. Pérez-Sierra, A. M., Pons, J., Santamarta, R., Vermunt, P. & Ochin, P. Solidification process and effect of thermal treatments on Ni-Co-Mn-Sn magnetic shape memory alloys. Acta Mater. 93, 164–174 (2015).
56. Liu, J., Woodcock, T. G., Scheerbaum, N. & Guffuleisch, O. Influence of annealing on magnetic field-induced structural transformation and magnetocaloric effect in Ni-Mn-In-Co ribbons. Acta Mater. 57, 4911–4920 (2009).
57. Guo, Z. G. et al. Magnetic phase transformation and magnetocaloric effect in quinary Ni$_{50.5}$Co$_{20.7}$Mn$_{19.5}$Sn$_{13.8}$-xHeusler alloy. J. Alloy. Compd. 777, 174–178 (2013).
58. Zhao, J. L. et al. Reduction of magnetic hysteresis loss in La$_{5}$Ti$_{5}$Fe$_{7}$Ti$_{2}$Sn$_{13.8}$H$_{2.8}$ hydrides with large magnetocaloric effects. J. Appl. Phys. 107, 113911 (2010).
62. Li, Z., Zhang, Y. L., Xu, K. & Jing, C. Large magnetocaloric effect related to martensitic transformation in Ni$_5$Co$_3$Mn$_9$In$_5$ textured alloy. Phys. Rev. B: Condens. Matter. 476, 179–182 (2015).
63. Bourgault, D., Tillier, J., Courtois, P., Maillard, D. & Chaud, X. Large inverse magnetocaloric effect in Ni$_5$Co$_3$Mn$_{17}$In$_{15+}$ single crystal above 300 K. Appl. Phys. Lett. 96, 132501 (2010).
64. Emre, B., Bruno, N. M., Emre, S. Y. & Karaman, I. Effect of niobium addition on the martensitic transformation and magnetocaloric effect in low hysteresis NiCoMnSn magnetic shape memory alloys. Appl. Phys. Lett. 105, 231910 (2014).
65. Caron, L. et al. On the determination of the magnetic entropy change in materials with first-order transitions. J. Magn. Magn. Mater. 321, 3559–3566 (2009).
66. Sun, N. K. et al. Effect of microstrain on the magnetism and magnetocaloric properties of MnAsO$_{0.97}$PO$_{0.03}$. Appl. Phys. Lett. 100, 112407 (2012).
67. Tibole, H., Guillou, F., Zhang, L., van Dijk, N. H. & Bruck, E. Direct measurement of the magnetocaloric effect in MnFe(PX) (X = As, Sb, S). J. Magn. Magn. Mater. 47, 075002 (2014).
68. Recarte, V., Perez-Landazabala, I. J., Kustov, S. & Cesari, E. Entropy change linked to the magnetic field induced martensitic transformation in a Ni-Mn-In-Co shape memory alloy. J. Appl. Phys. 107, (2010).
69. Bourgault, D., Porcar, L., Rivoirard, S., Courtois, P. & Hardy, V. Entropy change of a Ni$_{51}$Co$_{17}$Mn$_{37.5}$In$_{12.5}$ single crystal studied by scanning calorimetry in high magnetic fields: Field dependence of the magnetocaloric effect. J. Magn. Magn. Mater. 107, 107, 092403 (2015).
70. Stern-Taulats, E. et al. Magnetocaloric effect in the low hysteresis Ni-Mn-In magnetic shape-memory Heusler alloy. J. Appl. Phys. 115, 173907 (2014).
71. Ma, S. C. et al. Wheel speed-dependent martensitic transformation and magnetocaloric effect in Ni-Co-Mn-Sn ferromagnetic shape memory alloy ribbons. Acta Mater. 90, 292–302 (2015).
72. Shamba, P., Zeng, R., Wang, J. L., Campbell, S. J. & Dou, S. X. Enhancement of the refrigerant capacity in low level boron doped La$_x$Ga$_{0.5}$Fe$_{1-x}$Si$_{1.5}$ by the addition of boron. J. Appl. Phys. 109, 07A940 (2011).
73. Provenzano, V., Shapiro, A. J. & Shull, R. D. Reduction of hysteresis losses in the magnetic refrigerator La$_x$Co$_{0.5}$Fe$_{1-x}$Si$_{1.5}$ by the addition of iron. Nature. 430, 810–810 (2004).
74. Min, S. J. et al. Structure, magnetic properties and giant magnetocaloric effect of Th$_x$Gd$_{1-x}$Si$_{1.4}$Fe$_{0.4}$Mn$_{0.3}$, alloy Intermetallics. 57, 68–72 (2015).
75. Varzaneh, A. G. et al. Effect of Cu substitution on magnetocaloric and critical behavior in Ni$_{51}$Mn$_{34}$Sn$_{15}$ alloys. J. Alloy. Compd. 708, 34–42 (2017).
76. Wu, R. et al. Critical dependence of magnetostructural coupling and magnetocaloric effect on particle size in Mn-Fe-Ni-Ge compounds. Sci. Rep. 6, 20993 (2016).
77. Huang, L. et al. Large reversible magnetocaloric effect in a Ni-Co-Mn-In magnetic shape memory alloy. Appl. Phys. Lett. 108, 032405 (2016).
78. Dwivedi, S. & Tiwari, B. Martensitic transformations and magnetocaloric effect in Sn-doped NiMnIn shape memory alloy. J. Alloy. Compd. 540, 16–20 (2012).
79. Chen, L. et al. Magnetoresistive and magnetocaloric properties involving strong metamagnetic behavior in Fe-doped Ni$_x$Co$_{1-x}$Fe$_{1-x}$, alloys. Appl. Phys. Lett. 101, 012401 (2012).
80. Chattopadhyay, M. K., Sharma, V. K. & Roy, S. B. Thermomagnetic history dependence of magnetocaloric effect in Ni$_{51}$Mn$_{34}$In$_{15}$. Appl. Phys. Lett. 92, 022503 (2008).
81. Sharma, V. K. et al. Magnetocaloric effect in Heusler alloys Ni$_{51}$Mn$_{34}$In$_{15}$ and Ni$_{51}$Mn$_{34}$Sn$_{15}$. J. Phys.: Condens. Matter. 19, 496207 (2007).
82. Fabbrici, S. et al. From direct to inverse giant magnetocaloric effect in Co-doped NiMnGa multifunctional alloys. Acta Mater. 59, 412–419 (2011).
83. Zhang, X. X. et al. Magnetostriuctural transformation and magnetocaloric effect in Ni-Mn-Ga-Cu microwires. Appl. Phys. Lett. 108, 052401 (2016).

Acknowledgements
Financial supports from National Key R&D Program of China (grant number 2017YFB0703103), National Natural Science Foundation of China (NSFC) (grant number 51701052) and the Fundamental Research Funds for the Central Universities (grant number HIT.NSRIF.201801) are greatly acknowledged.

Author Contributions
X.X.Z proposed and led the project, analyzed the data and wrote the manuscript. H.H.Z observed the microstructure, carried out the martensite transformation and magnetocaloric effects tests, summarized the data and wrote the manuscript. M.F.Q analyzed the data and revised the manuscript. L.G supervised the project and revised the manuscript. All authors contributed to the discussions of the data and reviewed the manuscript.

Additional Information
Supplementary information accompanies this paper at https://doi.org/10.1038/s41598-018-26564-5.

Competing Interests: The authors declare no competing interests.

Publisher’s note: Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.