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# Giant low-field magnetocaloric effect in a textured $Ni_{45.3}Co_{5.1}Mn_{36.1}In_{13.5}$ alloy

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ABSTRACT

We demonstrate a remarkable magnetocaloric effect in a directionally solidified $Ni_{45.3}Co_{5.1}Mn_{36.1}In_{13.5}$ alloy with coarse-grained microstructure and strong $\langle 001 \rangle_A$ texture. Due to this optimized microstructure and the strong magnetostructural coupling, a giant $\Delta T_{ad}$ up to −5.1 K is achieved under low field change of 1.5 T, which is even superior to that of polycrystalline bulk alloys under the field change of 2 T. Furthermore, it is presented that the reversible $\Delta T_{ad}$ can be improved after certain predeformation, which should be attributed to the introduction of certain internal stress by predeformation.



The magnetic refrigeration, based on the magnetocaloric effect (MCE) [1], is conceived to be an energy-efficient and environmental-friendly alternative to the conventional gas compression/expansion technique. For potential applications, the availability of magnetic materials with large MCE is of great importance. Recently, considerable attention is paid to the materials with a coupled first-order magnetostructural transformation [2–9], where an enhanced MCE can be expected due to the involvement of transformation latent heat. Among the most promising candidates, Heusler-type Ni-Mn-In alloys are of particular interest for both fundamental research and practical applications [7,8].

Previous investigations have demonstrated that the magnetocaloric properties in Ni-Mn-In based alloys are strongly dependent on the composition [5,7,8,10,11], since the magnetostructural transformation can be effectively tuned through constituent adjusting or atomic substitution [12–14]. On the other hand, the magnetocaloric properties are also strongly influenced by microstructural features [15,16]. Enlarged grain size [15] as well as enhanced preferred orientation [16] can contribute a lot to the improvement on the magnetocaloric properties, suggesting that microstructure optimization is a practicable strategy to tune magnetocaloric properties in polycrystalline alloys.

Generally, the MCE can be characterized by the isothermal magnetic entropy change ($\Delta S_M$) or the adiabatic temperature variation ($\Delta T_{ad}$). So far, most magnetocaloric studies in Ni-Mn-In based alloys have been implemented through calculating the $\Delta S_M$ from isothermal magnetization curves according to the Maxwell relation. However, such indirect method sometimes may result in overestimations on $\Delta S_M$ values for first-order transformations [17]. Direct measurements on $\Delta T_{ad}$ can not only give more relevant and straightforward evaluations on magnetocaloric properties, but also be close to the conditions in practical applications. To date, giant $\Delta T_{ad}$ up to −5.2 K ($\mu_0\Delta H = 2$ T), −6.2 K ($\mu_0\Delta H = 2$ T), -8 K ($\mu_0\Delta H = 2$ T) and -11 K ($\mu_0\Delta H = 14$ T) have been reported respectively in $Ni_{49.8}Mn_{35}In_{15.2}$ [7], $Ni_{45.2}Mn_{36.7}In_{13}Co_{5.1}$ [7], $Ni_{45.7}Mn_{36.6}In_{13.5}Co_{4.2}$ [8] and $Ni_{50}Mn_{35}In_{15}$ [18] alloy, due to the field induced inverse martensitic transformation [7]. From the point of practical applications, achieving considerable $\Delta T_{ad}$ under low field change is of great significance.

It should be noted that the intrinsic hysteresis behavior associated with first-order transformation in Ni-Mn-In alloys directly impair the efficiency of MCE. Large $\Delta T_{ad}$ can only be observed for the first field application and it is significantly weakened for the subsequent runs of field application [7]. It has been proposed that the hysteresis can be greatly reduced by applying certain hydrostatic pressure during demagnetization process [7], since the martensite is more favorable under stress. Analogously, if certain internal stress is introduced, it may provide additional driving force to assist the field induced austenite to transform back to martensite on demagnetization. On this ground, introduction of certain internal stress could be a practical method to enhance the reversibility of $\Delta T_{ad}$.

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In this work, a polycrystalline $Ni_{45.3}Co_{5.1}Mn_{36.1}In_{13.5}$ alloy was prepared by directional solidification, where the optimized microstructure with coarse columnar grains and highly preferred orientation is expected to tune the magnetocaloric properties. Consequently, a remarkable $\Delta T_{ad}$ up to −5.1 K under a low field change of 1.5 T was achieved. Furthermore, in order to explore the possible pathways to enhance the reversibility of $\Delta T_{ad}$, the alloy was subject to predeformation. It is shown that the predeformation can result in an enhanced reversibility of $\Delta T_{ad}$. Such effect could be attributed to the introduction of internal stress that is in favor of martensite.

Polycrystalline Ni-*Co*-Mn-In alloy was prepared by directional solidification [19]. The as-solidified alloy was then annealed at 1173 K for 24 h in vacuum for composition homogeneity, followed by quenching into cold water. The alloy composition was verified to be $Ni_{45.3}Co_{5.1}Mn_{36.1}In_{13.5}$ (at. %) by Energy Dispersive Spectrometer (EDS). The martensitic transformation temperatures were measured by differential scanning calorimetry (DSC). The crystal structure was analyzed by powder X-ray diffraction (XRD) in a PANalyical X'Pert Pro diffractometer (Cu-Kα radiation). The $\{220\}_A$ and $\{400\}_A$ incomplete pole figures of austenite were measured up to a maximum polar angle of 70° by the Schulz back-reflection method using Co-Kα radiation in a Rigaku SmartLab X-ray diffractometer. The isofield and isothermal magnetization measurements were performed in a Quantum Design MPMS-3 system. Direct measurement of $\Delta T_{ad}$ was performed in a self-designed experimental setup with a maximum field of 1.5 T produced by NdFeB permanent magnet [19,20]. The temperature change of the sample was monitored by attached thermocouple.

Fig. 1a presents the room temperature powder XRD pattern for the directionally solidified alloy. It is seen that the alloy mainly consists of austenite at room temperature. Moreover, some minor diffraction peaks belonging to martensite can also be identified, suggesting that the martensitic transformation occurs around room temperature. The inset of Fig. 1a shows the DSC curves. The forward ($M_s$, $M_f$) and inverse ($A_s$, $A_f$) transformation start and finish temperatures were determined to be 282.5 K, 274.8 K, 294.4 K and 303.7 K, respectively, with a thermal hysteresis of ~20 K. In addition, the transformation entropy change ($\Delta S$) associated with the structural transformation was determined to be 17.0 J $kg^{-1}$ $K^{-1}$.

Fig. 1b shows the macroscopic microstructure of the longitudinal section for the directionally solidified $Ni_{45.3}Co_{5.1}Mn_{36.1}In_{13.5}$ alloy at room temperature. It can be seen that the initial austenite forms coarse columnar-shape grains along the solidification direction (SD). Fig. 1c displays the $\{220\}_A$ and $\{400\}_A$ incomplete pole figures of austenite measured on the transverse section of the directionally solidified alloy. It is shown that the $\{220\}_A$ poles are almost located at the polar angle of ~40° and the $\{400\}_A$ poles at the center in the corresponding pole figures, suggesting that the austenite develops a strong $\langle 001 \rangle_A$ preferred orientation parallel to SD. Recently, it is shown that the strong textured microstructure in Ni-Mn-In alloys can result in relatively higher magnetization difference between ferromagnetic austenite and weak magnetic martensite than that of the randomly oriented microstructure [21]. Apparently, the enhanced magnetization difference would provide more driving force for the field induced structural transformation, which is quite beneficial to the attainability of magneto-functional behaviors. Therefore, enhanced magnetocaloric properties could be expected in the present strong textured alloy.

Fig. 2a shows the temperature-dependent magnetization (*M-T*) curves measured under the field of 0.005 T, 1.5 T and 5 T. Under the low-field of 0.005 T, the characteristic transformation temperatures ($M_s$, $M_f$, $A_s$, and $A_f$) were determined to be 282.9 K, 277.2 K, 293.8 K, 299.8 K, respectively, which is in consistent with the DSC measurements. In addition, it is confirmed that the martensitic transformation involves significant magnetization change, *i.e.*, a magnetostructural transformation from ferromagnetic austenite to weak magnetic martensite. A large magnetization difference ($\Delta M$) of 111.2 $Am^2kg^{-1}$ across

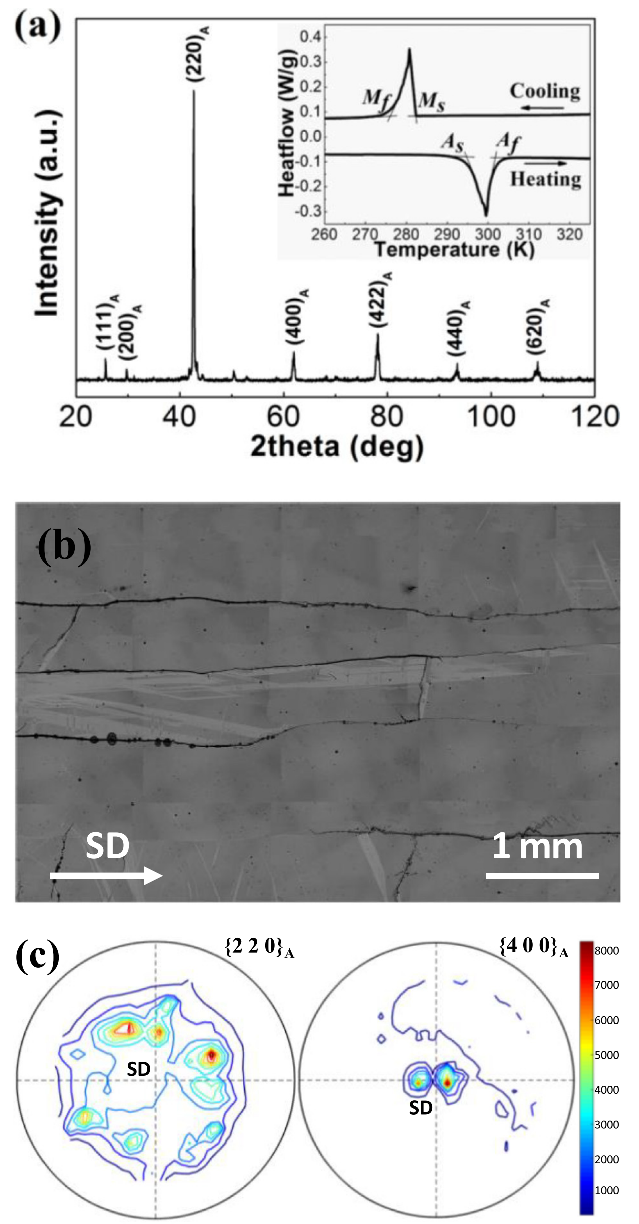


**Fig. 1.** (a) Room temperature powder XRD pattern for the directionally solidified alloy. Inset: DSC curves. (b) Macroscopic microstructure of the longitudinal section for the directionally solidified alloy. (c) $\{2\ 2\ 0\}_A$ and $\{4\ 0\ 0\}_A$ incomplete pole figures (SD: solidification direction).

the transformation can be determined from the *M-T* curves under 5 T, suggesting a strong magnetostructural coupling.

It is noted that the magnetic field can exert a strong influence on the martensitic transformation temperatures. With the increase of magnetic field (*i.e.*, 1.5 T, 5 T), the martensitic transformation temperatures tend to decrease. This phenomenon indicates that the field induced inverse martensitic transformation from weak magnetic martensite to ferromagnetic austenite can occur, even under the relatively lower field of 1.5 T. Under the field of 5 T, the characteristic transformation temperatures (*i.e.*, $M_s$, $M_f$, $A_s$ and $A_f$) were determined to be 244.1 K, 236.3 K, 257.8 K and 268.0 K, respectively. Compared to those under the field of 0.005 T, the $A_s$ can be decreased by ~36.4 K under the field of 5 T, with a reduction rate of 7.3 K/T. The transformation temperature change ($\Delta T$) induced by magnetic field change ($\mu_0 \Delta H$) can be expressed by the Clausius-Clapeyron equation, *i.e.*, $\Delta T = \mu_0 \Delta H\ (\Delta M / \Delta S)$, where $\Delta M$ and $\Delta S$ represent the difference in magnetization and entropy across the