Giant elastocaloric effect in directionally solidified Ni–Mn–In magnetic shape memory alloy

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We have studied the giant elastocaloric effect of directionally solidified Ni–Mn–In magnetic shape memory alloys (MSMAs) near room temperature. The textured microstructure significantly enhances the ductility of Ni–Mn-based MSMAs, which allows obtaining the martensitic transition characteristics of polycrystalline samples in a uniaxial stress field. A significant cooling level of about 4 K is measured when the stress is released. The experimentally measured temperature changes are found to be in good agreement with the theoretically calculated values.

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The recent research on solid-state refrigerant materials for environmentally friendly energy-efficient cooling technologies is fast-growing, with the aim of replacing common gas compression refrigeration technology. The refrigeration parameters defined by the caloric effects mainly depend on the adiabatic temperature change or the isothermal entropy change induced by the application (or removal) of an external field. Concerning energy savings and environmental importance, materials with larger caloric effects are needed to exhibit high energy conversion efficiency. Up to now, much effort has been put into finding new caloric materials with a large refrigeration capacity (RC) [1]. Another potential way of improving the refrigerant performance is by coupling external fields, such as mechanical stress and magnetic field. Thus, it is of particular interest to investigate the multi-caloric effects [2] which include the giant magnetocaloric (GMC) [3], giant elastocaloric (GEC) [4] and giant barocaloric [5] (GBC, driven by hydrostatic pressure) effects in a single material. Here, the material of interest is a magnetic shape memory alloy (MSMA), Ni–Mn–In, which is a representative system to investigate caloric effects [5,6]. We anticipate that a similar magnitude of GEC will occur in many MSMAs which undergo a reversible first-order phase transition.

Currently, one of the largest challenges in using Ni–Mn–In alloys for caloric applications is their poor ductility. The inherent brittleness is a serious problem that must be overcome before these materials are implemented in applications. Tailoring the alloy composition to introduce a second phase may be a powerful way to improve the ductility in Ni–Mn-based alloys [7], but the second phase inevitably hinders the magnetostructural (martensitic) transitions by changing the local composition around the second phase.

In a recent work, we reported that a large reversible superelastic effect, comparable to that in single crystals, was achieved in Ni–Fe–Ga–Co polycrystals with a textured structure [8]. This textured structure obtained by directional solidification technologies promotes strain compatibility between grain boundaries, reducing the stress concentrations and crack initiation at triple junctions. Such textured structures can provide a potential way of reducing brittleness in Ni–Mn-based alloys. This fabrication method allows studying the martensitic transformation characteristics of polycrystalline Ni–Mn-based MSMAs under uniaxial stress fields.

Here, a zone melting directional solidification method is used to promote a textured microstructure in the Ni₄₈Mn₃₅In₁₇ alloy (at.%). The process of the directional
solidification has been described in detail elsewhere [7]. In this work, the directional solidification was conducted with the temperature gradient of \( G_L = 1000 \text{ K/cm} \) and the crystal growth rate of \( 10 \mu \text{m/s} \). Identification of the crystal structure and the preferred orientation was conducted by X-ray diffraction patterns (XRD) employing Cu-K\(_\alpha\) radiation. The actual composition is \( \text{Ni}_{48.4}\text{Mn}_{34.8}\text{In}_{16.8} \) (at.\%) determined by subsequent energy-dispersive spectroscopy.

After annealing at 1173 K for 24 h, compression samples were cut from the directionally solidified rods into rectangular prisms with nominal dimensions of \( 3 \text{ mm} \times 3 \text{ mm} \times 6 \text{ mm} \). The compression axis was parallel to the crystal growth direction. The compression experiments were conducted using an MTS screw driven test frame. A high temperature extensometer was used to measure the strain from the tips of the compression platens. In the present work, the compressive protocol comprised the following steps: First, the sample was loaded at a very low strain rate of \( 1.7 \times 10^{-4} \text{ s}^{-1} \) up to the safe strain of about 1.4%. Second, the sample was allowed to be hold at constant stress for temperature recovery. Third, the sample was unloaded at a strain rate of \( 1.7 \times 10^{-3} \text{ s}^{-1} \). To measure temperature change, a K-type thermocouple was attached to the mid-point of the gauge length of the specimen. The output of the thermocouple was read by a measurement computing data acquisition device (DAQ) at a frequency of 50 Hz and the temperature of the sample was continuously monitored.

This alloy shows a mixture of austenite and martensite phases at room temperature (Fig. 1). This suggests its martensitic transition temperature is close to room temperature, so that the desired caloric effect occurs in a temperature range that is useful for practical applications. Along the crystal growth direction (Fig. 1), large columnar grains grow into a textured structure with a preferred direction (the L2\(_1\) (220) plane of austenite phase, see the inset in Fig. 1). Compression experiments were conducted along the crystal growth direction to evaluate the elastocaloric effect.

The measurements for isothermal entropy and adiabatic temperature changes were collected on two different samples. It is very important to stress the fact that these compression tests are not possible with the arc-melted polycrystals because they often fail after 1 cycle, while the textured structure allows successful testing multiple times, which is very helpful to gather data for the GEC in Ni–Mn based MSMAs.

Figure 2 shows the isobaric (constant stress) strain-temperature histories of the Ni–Mn–In samples at selected uniaxial compressive stress levels. The martensitic transition results in a sharp change in uniaxial strain, which increases with the compressive stress. The small thermal hysteresis (<10 K) between cooling and heating sequences is associated with the first order character of the martensitic transition. Meanwhile, the martensitic transition under a larger compressive stress is distinctly shifted to a higher temperature region. This is expected and is related to the positive Clausius–Clapeyron slope [9,10]. Finally, there is some residual strain at large stresses, which is indicative of the occurrence of micro-plastic strain. This is one reason that mechanical breakdown occurs during thermal and mechanical cycles.

The GEC effect is usually quantified by an isothermal entropy change, which can be calculated using the Clausius–Clapeyron relation [2,9]:

\[
\Delta S = -v_0 \Delta \epsilon \left( \frac{dT_m}{d\sigma} \right)^{-1}
\]

where \( v_0 \) is specific volume, \( 1.399 \times 10^{-4} \text{ m}^3/\text{kg} \) (calculated using the lattice parameter of the parent phase), \( \Delta \epsilon \) is the strain change between austenite and martensite phases in

![Figure 1](image1.png)

**Figure 1.** X-ray patterns of the transverse section (perpendicular to the crystal growth direction) in directionally solidified Ni\(_{48}\)Mn\(_{34.8}\)In\(_{16.8}\) rods, indicating a mixture of austenite and martensite phases at room temperature. The inset shows large columnar grains growing into a textured structure along the crystal growth direction.

![Figure 2](image2.png)

**Figure 2.** (a) The strain as a function of temperature at selected values of uniaxial compressive stress in directionally solidified Ni\(_{48}\)Mn\(_{34.8}\)In\(_{16.8}\) MSMA polycrystals. The inset shows the martensitic transformation temperature as a function of stress. Dashed line corresponds to a linear fit to the critical stress. (b) Stress evolution as a function of applied strain (about 1.4\%) at selected temperatures.
the transition regime, $dT_m/\sigma$ is the stress field-driven shift in transition temperature ($T_m$) obtained from transition start or finish temperatures on cooling or heating (0.24 K/MPa, the inset in Fig. 2a).

From this value and the experimentally observed $\Delta$e, the maximum values of the isothermal entropy change at each constant stress are calculated: 2.3 J Kg$^{-1}$ K$^{-1}$ for 25 MPa, 4.0 J Kg$^{-1}$ K$^{-1}$ for 50 MPa, 6.4 J Kg$^{-1}$ K$^{-1}$ for 75 MPa. Considering the effect of hysteresis losses (Fig. 2a), these entropy changes become smaller (2.2 J Kg$^{-1}$ K$^{-1}$ for 25 MPa, 3.7 J Kg$^{-1}$ K$^{-1}$ for 50 MPa, 5.5 J Kg$^{-1}$ K$^{-1}$ for 75 MPa), but they are still comparable to other caloric effects in this class of materials (GBC effect in Ni$_{49.26}$Mn$_{36.08}$In$_{14.66}$ [5]: 10 J Kg$^{-1}$ K$^{-1}$ at a hydrostatic pressure of 1kbar; GMC effect in Ni$_{50}$Mn$_{34}$In$_{16}$ [11]: 7 J Kg$^{-1}$ K$^{-1}$ for 17). It should be noted that a larger entropy change at a higher stress could be obtained (10.3 J Kg$^{-1}$ K$^{-1}$ for 150 MPa), but this results in an unacceptable level of residual strain (not shown here). Therefore, during direct adiabatic compression tests, we conducted the experiments up to a total of about 1.4% strain to obtain near fully reversible martensitic transformation (Fig. 2b), which implies a good reversibility of the GEC [12]. These adiabatic stress–strain curves present fully recoverable superelasticity of about 1.1% transformation strain. This transformation strain correspondingly leads to an entropy change of 6.4 J Kg$^{-1}$ K$^{-1}$, obtained by Eq. (1). Similarly, this entropy change should be subtracted by the irreversible part resulted from the hysteresis losses (Fig. 2b) and then becomes 5.9 J Kg$^{-1}$ K$^{-1}$. In addition, it should be noted that a partial recovery of 0.7% during unloading is observed at 310 K, which results in a relatively small entropy change of 3.6 J Kg$^{-1}$ K$^{-1}$.

In order to directly measure the adiabatic temperature change, the sample was loaded at a very low strain rate of 1.7 × 10$^{-3}$ s$^{-1}$ up to the safe strain level of about 1.4%, and then unloaded at a strain rate of 1.7 × 10$^{-3}$ s$^{-1}$ (Fig. 3a). The sample was unloaded quickly to promote adiabaticity. Figure 3b shows a typical example of the recorded temperature change upon loading and unloading the sample. Upon loading, there is a small heating due to the latent heat of the martensitic transformation. In contrast, a significant cooling (|$\Delta T_{ad}$|) of about 4 K is measured when the stress is released, corresponding to the reverse transformation of the sample from martensite to austenite.

To reproduce the temperature changes, we have conducted successive loading cycles at different temperatures, as shown in Figure 3c. It is shown that the experimental values for the adiabatic temperature change slightly decrease with increasing test temperature, which is ascribed to the fact that the increase in the critical stress for the martensitic transition results in the decrease of the transformed martensite phase fraction and some irreversible micro-plasticity also takes place (Fig. 2b).

The theoretical temperature change during the first order phase transformations can be estimated using a simple approach recently described in [13,14], which is shown to yield a good match with indirectly measured $\Delta$S$_{iso}$ and directly measured $\Delta T_{ad}$ values. In this approach, the relationship between the calculated temperature change ($|\Delta T_{ad}$|) and the indirect $\Delta$S$_{iso}$ is given by:

$$\Delta T_{ad} = \frac{\Delta S_{iso} \cdot \Delta T_M}{\Delta S_{iso} + \Delta T_M \cdot \frac{C_{mart}}{4T_m}}$$

(2)

where the $\Delta T_M$ represents the shift of the transition temperatures for a stress change of $\Delta$e, i.e., $\Delta T_M = (dT/\sigma) \cdot \Delta e$ (where the $\Delta e$ is about 230 MPa, see Fig. 2b). The value obtained is $\Delta T_M = 55$ K. $C_{mart}$ is the heat capacity of martensite (400 J Kg$^{-1}$ K$^{-1}$), which was obtained using a commercial relaxation calorimeter, Physical Property Measurement System manufactured by Quantum Design.

Figure 3. Elastocaloric effects in directionally solidified Ni$_{48}$Mn$_{35}$In$_{17}$ MSMA polycrystals for adiabatic unloading ($\Delta T_{ad}$). (a) Compressive stress and (b) the corresponding temperature change ($|\Delta T_{ad}'|$) in the specimen as a function of time at 313.3 K, showing a significant temperature drop of $-4$ K (pink line) upon fast unloading (c) The adiabatic temperature changes at different test temperatures. $|\Delta T_{ad}'|$ is the calculated temperature changes. (d) The heat capacity by 2-r model outside the transition and the heating heat capacity during the transition are combined and shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
The heat capacity data outside the martensitic transformation temperatures is analyzed by the conventional 2-τ model [15,16] (Fig. 3d). The $T_M$ is the test temperature.

In Figure 2b, the hysteresis loss is clearly observed, which is quantified by integrating the area enclosed by the stress–strain curve and should be taken into account when calculating the temperature change. Subsequently, the entropy changes during the adiabatic compression can be obtained, and the corresponding calculated temperature changes are shown in Figure 3c. It is shown that the calculated temperature changes are around 4 K even for such a small strain. However, at 310 K, the $|\Delta T_{ad}^{Cal}|$ is only 2.6 K due to the partial recovery (Fig. 2b).

When comparing $|\Delta T_{ad}^{Cal}|$ with the $|\Delta T_{ad}^{Exp}|$, it can be seen in Figure 3c that the $|\Delta T_{ad}^{Cal}|$ is slightly higher than the $|\Delta T_{ad}^{Exp}|$, which can be ascribed to insufficient adiabatic conditions during testing that results in a heat transfer. The heat transfer effect can be confirmed by the fact that the specimen temperature recovers quickly to the test temperature after unloading.

The elastocaloric effects reported here compare well to those values in other giant caloric materials, such as GMC [6], GBC [5], GEC [9] and giant electrocaloric materials [17]. For such a small transformation strain of about 1.1$, |\Delta T_{ad}^{Exp}|$ of about 4 K is also comparable to the GBC effect of 4–7 K (under magnetic field of 2 T [6]), the GBC effect of 4.5 K (under hydrostatic pressure of 2.6 kbar [5]) in Ni–Mn–In alloys and the GEC effect of 3.5 K in Ni–Mn–In–Co alloys [12]. Here, it should be cleared that the underlying physics between the uniaxial compression and the hydrostatic pressure is different. The entropy change in the uniaxial compression is resulted from the transformation strain along the compressive direction, while the GBC effect is from the volume change in the hydrostatic pressure. In addition, a significant advantage of the uniaxial compression is its easy and good control.

From the present findings, it can be concluded that the textured structure significantly enhances the ductility of Ni–Mn-based MSMA, which allows easy determination of martensitic transformation characteristics in a uniaxial stress field and provides a potential way for tuning caloric effects (GEC and GMC) with a uniaxial stress. The GEC effects found in this work are the third caloric effect in the Ni–Mn-based MSMA, which is a consequence of the strain and entropy discontinuities at a magnetostuctural transition. In such a magnetostatical coupling system, we can anticipate that these caloric effects could be coupled to improve the refrigerant capacity [1]. In particular, when so many caloric effects occur in a single material, a larger refrigerant capability and an accurate control of the temperature change could be achieved by fine tuning several external parameters. Due to all of these caloric effects near room temperature, we anticipate that the GEC effect reported here will inspire commercial applications for efficient and accurate solid-state refrigerating devices at ambient temperature. In addition, the enhancement of the ductility in Ni–Mn-based MSMAs is important to further extend their applications for high performance sensors and actuators [18,19].

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