Elastocaloric effect in a textured polycrystalline Ni-Mn-In-Co metamagnetic shape memory alloy (Postprint)

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Abstract

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Full Text

Preamble

Elastocaloric Effect in a Textured Polycrystalline Ni-Mn-In-Co Metamagnetic Shape Memory Alloy

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By direct measurements, the elastocaloric effect at various temperatures in a [001]-oriented $Ni_{45\cdot7}Mn_{36\cdot6}In_{13\cdot3}Co_{5\cdot1}$ metamagnetic shape memory polycrys-

tal has been investigated. A reversible temperature change of 6.35 K, due to the relatively low stress (100 MPa) induced martensitic transformation, was observed at room temperature. A theoretical analysis based on the Debye description has revealed that the adiabatic temperature change arising from lattice vibration plays a dominant role in the large elastocaloric effect for Ni-Mn-In-Co alloys.

Introduction

Caloric effects stem from the thermal changes of a given material in response to changes in external stimulus.[?] The application of external driving fields such as magnetic field, uniaxial stress, isotropic pressure, and electric field result in magnetocaloric, elastocaloric, barocaloric, and electrocaloric effects, respectively. Giant magnetocaloric effect (MCE) at room temperature has been reported sequentially in GdSi$_4$- Ge ,[?] LaFe$_{13}$- Si H,[?] Mn-Fe-P-As,[?] and Ni-Mn-In-Co.[?] Recently, the mechanocaloric effect (including elastocaloric effect and barocaloric effect) in shape memory alloys (SMAs), originated from superelasticity or giant volume change on martensite transformation (MT), has been increasingly acquired attention.[?, ?, ?] Compared with magnetic refrigeration, mechanical cooling exhibits obvious advantages: (i) large and reversible adiabatic temperature change (ΔT); (ii) wide temperature window and (iii) relatively lower driving forces.\cite{8-11} A Ni-Ti wire has shown a giant temperature rise of 25 K upon stretching,[?] and a large ΔT of 6-7 K was observed by compressing Cu-Zn-Al polycrystalline bulk samples over a large temperature span of 130 K.[?] It should be mentioned that to date, these directly measured elastocaloric effects were only reported in the conventional (temperature or stress driven) SMAs.

For mechanocaloric effects in magnetic SMAs, previous studies focus on the barocaloric effect in Ni-Mn-In and elastocaloric effect in Fe- or Co-doped Ni-Mn-Ga.\cite{12-14} However, caloric effects in Ni-Mn-based alloy systems were characterized indirectly by isothermal entropy change ΔS. Direct measurement of ΔT, which is more reliable and straightforward to assess the field-induced thermal phenomena,[?] is still lacking for the elastocaloric effect in magnetic SMAs.

Material Selection and Objectives

Here, a Ni-Mn-In-Co magnetostructural transition alloy is selected as a model system for elastocaloric effect study based on the following considerations. First, martensitic transformation occurs from ferromagnetic austenite to antiferromagnetic martensite in Ni-Mn-In-Co.[?, ?] The peculiar metamagnetic transition character is different from that in conventional non-magnetic and ferro-ferromagnetic transition alloys. Second, critical transformation stress (CTS) to drive MT in Ni-Mn-In-Co is relatively lower than that in conventional Ni-Ti and Ti-Ni-Cu SMAs.[?, ?, ?, ?] In other words, the magnitude of the driving stress for elastocaloric cooling is expected to be low, which is crucial for practical applications. Third, despite intensive investigations on MCE in Ni-Mn-In-Co, elastocaloric temperature change and possible contributions in this magnetostructural transition material is still unclear.

In this letter, we investigate in a textured polycrystalline Ni-Mn-In-Co alloy, temperature dependence of isothermal stress-strain response and fast-loading-unloading induced sample temperature change near adiabatic conditions. A reversible elastocaloric temperature change of 6.35 K has been observed at room temperature by applying a uniaxial compressive stress of 100 MPa. The physical origin of the adiabatic temperature change is further analyzed.

Experimental Methods

A highly oriented polycrystalline rod of $Ni_{45\cdot7}Mn_{36\cdot6}In_{13\cdot3}Co_{5\cdot1}$ was grown by a hot-mold casting technique.[?] The texture of the sample was analyzed by electron backscatter diffraction (EBSD) on a scanning electron microscope. Martensitic transformation temperatures were determined by magnetization versus temperature curves (M-T) using a superconducting quantum interference device (Quantum Design MPMS-5S).

Compressive tests of a specimen with a size of 3 mm × 3 mm × 7 mm were conducted using a testing machine (Autograph AG-I 50 kN Model M1, Shimadzu).[?] A low strain rate of 5×10^{-5} s^{-1} was chosen to ensure isothermal conditions. The strain was measured by a strain gage (KFL-02-120-C1-11, KYOWA). For elastocaloric measurement, a much higher strain rate of 0.13 s^{-1} was selected to approximate the adiabatic condition. At each temperature, the sample was loaded from 0 to 100 MPa, and subsequently unloaded from 100 to 0 MPa after holding the stress for 30-35 s. The loading-releasing loop was cycled two times at each temperature. The temperature change of the stressed sample was monitored by a T-type thermocouple welded to the sample surface.

Results and Discussion

Figure 1 [Figure 1: see original paper] shows thermo-magnetization curves at a low field of 10 mT for $Ni_{45\cdot7}Mn_{36\cdot6}In_{13\cdot3}Co_{5\cdot1}$. On heating, the non-magnetic martensite transforms to ferromagnetic austenite in a temperature range between austenite start temperature A = 268 K and finish temperature A_f = 294 K. Upon cooling, the martensite starts to form at M = 284 K and finishes at M_f = 255 K. As illustrated by the schematics in Fig. 1, the microstructure evolves from a single martensite (T = 270 K), coexistence of martensite and austenite phases to a single austenite phase (T = 280, 290 and 300 K), (T = 320 K). The fraction of austenite phase f_A at a given temperature T on the heating direction can be obtained by integrating the transition distribution function resulting from M-T data upon heating.[?] At 280 K, the corresponding f_A can be estimated to be about 50% while more than 90% at 300 K.

Figure 2 [Figure 2: see original paper] presents isothermal compressive stress-strain curves of the rectangular sample above room temperature. To avoid crack initiation, the applied stress is limited up to 100 MPa. From the EBSD mapping, the deviation of orientation of columnar grains from the [001] axis (in parent phase coordination) is rather small, indicating that the compressive force is almost parallel to the austenitic [001] direction. A typical superelastic behavior occurs at 300 and 310 K. The value of CTS to induce martensitic transformation at 300 K is about 80 MPa, which is lower than that of $Ni_{45}Mn_{36\cdot5}In_{13\cdot5}Co_5$ [001] single crystal (about 150 MPa at 300 K).[**?**, **?**] This is caused by different MT temperatures. At higher temperatures, it needs a higher stress to induce the martensitic transformation. Since the critical stress should be higher than 100 MPa when the operating temperature above 320 K, there is nearly the elastic deformation of austenite observed.

To characterize the elastocaloric effect, direct measurements of adiabatic temperature change are conducted. Figure 3 [Figure 3: see original paper] plots the temperature change as a function of time for $Ni_{45\cdot7}Mn_{36\cdot6}In_{13\cdot3}Co_{5\cdot1}$. It is clear that the magnitude of ΔT and its reversibility strongly relies on the initial temperature and f_A. At 270 K, the sample is nearly in its martensite state and a small value of about $±$0.35 K for both ΔT_{loading} and ΔT_{unloading} might be due to the reversible rearrangement of martensitic variants by stress. At 280 K (12 K above A), the sample contains the mixture of martensite and austenite. A large ΔT_{loading} (4 K) but a small ΔT_{unloading} (−0.5 K) observed in the first cycle suggest that the austenite fully transforms to martensite but only a small part of stress-induced martensite transforms back to the austenite during stress release. In the second cycle, ΔT_{loading} and ΔT_{unloading} drastically decrease down below 1 K. This irreversible stress-induced phase conversion occurs at temperatures above A . Similarly, irreversible magnetostructural transition has been observed in Heusler alloys when approaching A .[**?**]

At the temperature close to A_f (290 K), the temperature-time profile in the second cycle slightly reproduces that in the first cycle despite an asymmetry between ΔT_{loading} (3.5 K) and ΔT_{unloading} (−2.5 K). At temperatures above A_f (T = 300-330 K), symmetric temperature changes upon loading and unloading as well as reproducible time-temperature profiles can be observed. Considering transition volume directly reflects the temperature change,[**?**] the stress-induced transition fraction of austenite is proportional to the elastocaloric temperature change upon loading. As the value of ΔT_{loading} at 300 K is close to that at 280 K (about 4 K in the first cycle loading, f_A = 50%), it can be deduced that only half of the austenite participates in phase transition at 300 K. Meanwhile, as illustrated in Figure 2, the incomplete transformation strain at 300 K is about 1.0%, much smaller than that reported in single crystal along the [100] orientation (5.2%).[**?**] The application of higher stress above 100 MPa is prone to intergranular fracture for the present polycrystalline Ni-Mn-In-Co due to the deformation incompatibility of small crystals (about 1 mm in width). In future experiments, coarse columnar grains are necessary to realize a full transition and corresponding higher ΔT.

As illustrated in Figure 4 [Figure 4: see original paper], the largest reversible adiabatic temperature change occurs at 300 K. With the increase of temperature, the value of CTS is increased, thus elastocaloric effect is smeared. It should be pointed out that the stress-induced temperature change behavior of Ni-Mn-In-Co has a difference from that driven by magnetic field.[**?**] No reduction of elastocaloric ΔT_{ad} in the second stress cycling occurs at 300 K but a significant reduction of magnetocaloric ΔT_{ad} in the second magnetic field cycling.[**?**] More importantly, only a uniaxial stress of 100 MPa is desired for elastocaloric cooling while a driving magnetic field of 2 T is needed for magnetocaloric cooling.

As compared to elastocaloric effects in Cu-Zn-Al, Ni-Ti and Fe-Pd,\cite{9-11,20} a significant advantage of Ni-Mn-In-Co is its low driven stress and high specific elastocaloric effects (|ΔT|/|Δσ|). As seen in Table I, our $Ni_{45}\cdot_7Mn_{36}\cdot_6In_{13}\cdot_3Co_5\cdot_1$ sample shows a highest |ΔT|/|Δσ| of 35 K/GPa among recently reported SMAs. In addition, it is expected that the elastocaloric temperature window in Ni-Mn-In-Co can be broadened by increasing the applied stress, as experimentally verified in Fe-Pd and Cu-Zn-Al alloys.[**?**, **?**]

Physical Origin of the Elastocaloric Effect

To clarify the physical origin of the large elastocaloric behavior, it is necessary to analyze the source of ΔT. On the macroscopic scale, dissipated energy related to the interfacial friction contributes to the sample temperature change. As presented in Figure 4 [Figure 4: see original paper], a common feature of adiabatic temperature change at various temperatures is that ΔT_{loading} is always slightly larger than ΔT_{unloading}. This temperature change discrepancy may be attributed to the release of frictional heat generated from martensite/austenite and martensitic variants interfaces, which enhances the heating effect upon loading but counterbalances the cooling effect upon unloading. Meanwhile, Young' s modulus of the parent phase at various temperatures is almost the same, quite different from that in Fe-Pd,[**?**] suggesting a negligible modulus contribution.

In principle, electronic contribution (resulting from electronic states near the Fermi level), vibrational contribution (related to the vibrations of the atoms around their equilibrium positions in the crystal lattice), and magnetic contribution (due to metamagnetic feature upon martensite transformation) should be taken into account for Ni-Mn-In-Co. The adiabatic temperature change is expressed as

$$\Delta T = \Delta T_{vib} + \Delta T_{elec} + \Delta T_{mag} + \Delta T_{fri}$$

where ΔT_{vib}, ΔT_{elec}, ΔT_{mag}, and ΔT_{fri} denote the vibrational contribution, electronic contribution, magnetic contribution, and frictional heat, respectively.

Based on the Debye theory,[?] the vibrational entropy for one mole substance can be estimated as

$$S_{vib}(\theta_D) = -3Nk_B \ln\left(1 - \exp\left(-\frac{\theta_D}{T}\right)\right) + 12Nk_B\left(\frac{\theta_D}{T}\right)^3 \int_0^{\theta_D/T} \frac{x^3}{e^x - 1}dx$$

where N is the number of atoms per mole, k_B is the Boltzmann constant, and _D is the Debye temperature.

Accordingly, vibrational entropy change upon martensite transition ΔS_{vib} = S_{vib}(_D) - S_{vib}(_D^0), where _D and _D^0 represent the Debye temperature of the martensite and austenite phase, respectively. Considering similar compositions between the reported $Ni_{45}Mn_{36\cdot 5}In_{13\cdot 5}Co_5$ and the present $Ni_{45\cdot 7}Mn_{36\cdot 6}In_{13\cdot 3}Co_{5\cdot 1}$, _D = 304 K and _D^0 = 322 K are utilized.[?] The resultant vibrational entropy at T = 280 K is -1.354 J mol^{-1} K^{-1}. The adiabatic temperature change associated with the vibrational contribution to elastocaloric effect can be estimated as ΔT_{vib}   -TΔS_{vib}/C, where C is the specific heat which is assumed to be stress independent. For Ni-Mn-In-Co, the value for the specific heat at T = 280 K is approximately 30 J mol^{-1} K^{-1} for both martensitic and austenite phases.[?, ?] For an adiabatic loading involving the full phase transition, the maximum expected vibrational temperature change is 12.6 K. In case of transformed austenite fraction 50%, a ΔT_{vib} of 6.3 K at an ideal adiabatic condition is expected at 280 K. Moreover, considering the imperfect adiabatic deformation, there exists a strong dependence of measured ΔT on the applied strain rate, as recently proposed in Ni-Ti.[?] By referring to the profile of ΔT vs. strain rate in Ni-Ti, we therefore estimate a reasonable ΔT_{vib}   5.5 K at the current strain rate of 0.13 s^{-1} for Ni-Mn-In-Co.

The structural transition heats the sample due to the stress-induced exothermic austenite → martensite transition by a magnitude of (|ΔT_{vib} + ΔT_{elec}|) whereas magnetic disordering results in a temperature drop of |ΔT_{mag}|. Due to the counterbalance effect between structural and magnetic contribution, the overall temperature change at 280 K upon to 100 MPa is |ΔT_{vib} + ΔT_{elec}| - |ΔT_{mag}| + |ΔT_{fri}| = 4 K.

As |ΔT_{mag}| is about 2 K in pure magnetic transition of Ni-Mn-In-Co,[?] the contribution from conductive electron, lattice vibration, and friction heat is about 6 K. Therefore, ΔT_{elec} is estimated to be negligible (0.2 K), provided that ΔT_{fri} = 0.3 K deduced from the temperature difference (0.6 K) between the 2nd loading and unloading (Fig. 4). The conclusion can therefore be drawn that in our Ni-Mn-In-Co system, the vibrational term (+5.5 K) contributes positively and predominately, whereas magnetic part (-2 K) works against, to the total cooling effect. This agrees with the case of MT in Cu-Zn-Al where lattice contribution amounts 90% for the overall entropy change,[?]

but is different from the magnetovolume phase transition Fe-Rh alloys where the conduction electron is the leading factor for the overall entropy change.[?] In addition, due to the large difference in the magnetization of martensite and austenite, the magnetic contribution in Ni-Mn-In-Co is expected to be significant, which cancels out the vibrational contribution and results in reduced net value of total entropy change.[?] This may explain that elastocaloric ΔT_{ad} in metamagnetic Ni-Mn-In-Co is much smaller than that in non-magnetic Ni-Ti and Cu-Zn-Al shape memory materials. It implies that elastocaloric ΔT of magnetic SMAs might be enhanced by the minimization of the magnetic contribution.

Summary

In summary, adiabatic temperature change and its cycle reversibility upon loading and unloading in textured polycrystalline $Ni_{45\cdot7}Mn_{36\cdot6}In_{13\cdot3}Co_{5\cdot1}$ strongly relies on the operating temperature and applied stress. To achieve a reversible magnetostructural transition, a sample temperature higher than A_f and a proper applied stress to induce phase transformation are required. The strength of elastocaloric effect in $Ni_{45\cdot7}Mn_{36\cdot6}In_{13\cdot3}Co_{5\cdot1}$ at 300 K reaches 35 K/GPa, exceeding that in conventional polycrystalline Cu-Zn-Al and Ni-Ti alloys. Due to the negative contribution of magnetic entropy change to the total entropy change in metamagnetic phase transformation, it is suggested that maintaining but minimizing the magnetic contribution is desirable to achieve large elastocaloric effect in Ni-Mn-based Heusler alloys.

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TABLE I. The change of stress to induce elastocaloric effect $|\Delta\sigma|$, adiabatic temperature change from direct measurements $|\Delta T|$ and strength of elastocaloric effects ($|\Delta T|/|\Delta\sigma|$) in materials exhibiting martensitic transformation around room temperature.

Alloy comp. (at. %)	Sample status	T (K)	$\Delta\sigma$	(GPa)
$Cu_{68}Zn_{16}Al_{16}$	Polycrystal	296		
$Ni_{50}Ti_{50}$	Polycrystal	346		
$Ti_{54\cdot9}Ni_{32\cdot5}Cu_{12\cdot6}$	Thin film			
$Fe_{68\cdot8}Pd_{31\cdot2}$	Single crystal			
$Ni_{45\cdot7}Mn_{36\cdot6}In_{13\cdot3}Co_{5\cdot1}$	Textured polycrystal			35

FIG. 1. Temperature dependence of the magnetization in a magnetic field of 10 mT for $\mathrm{Ni_{45\cdot7}Mn_{36\cdot6}In_{13\cdot3}Co_{5\cdot1}}$ alloy. The insets schematically show the microstructure evolution with temperatures. The hatched area denotes martensite and the residual area austenite.

FIG. 2. Stress-strain curves of the $\mathrm{Ni_{45\cdot7}Mn_{36\cdot6}In_{13\cdot3}Co_{5\cdot1}}$ polycrystalline sample compressed up to 100 MPa at various fixed temperatures. The inset shows the EBSD orientation mapping, where the color bar indicates the deviation angle of crystal growth from [001] axis.

FIG. 3. Temperature-time profiles of the $\mathrm{Ni_{45\cdot7}Mn_{36\cdot6}In_{13\cdot3}Co_{5\cdot1}}$ polycrystalline sample during fast loading up to 100 MPa and unloading at various temperatures by two cycles.

FIG. 4. Temperature dependence of adiabatic temperature changes upon loading and unloading during the first and second cycles.

Note: Figure translations are in progress. See original paper for figures.

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