Reversible elastocaloric effect at ultra-low temperatures in nanocrystalline shape memory alloys

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1. Introduction

Superelasticity and elastocaloric effect (ECE) are the two distinct properties that accompany the martensitic phase transformation (PT) in ferroelastic SMAs [1]. In recent years, the ECE of SMAs has been successfully exploited in solid-state refrigeration as an alternative to vapor-compression-based cooling [2]. In typical single-crystalline and polycrystalline superelastic SMAs, the reversible martensitic PT occurs via reversible nucleation and growth of martensite under mechanical loading and unloading [3]. Consequently, typical superelastic SMAs exhibit the common features of first-order PTs, such as stress hysteresis [4], deformation instability [5], and a strong temperature-dependence of the PT stress and the ECE [6]. These features impose the following limitations on superelastic SMAs as solid-state refrigerators: hysteresis reduces the cooling efficiency [4], deformation instability is a source of poor fatigue life [7], and the strong temperature dependence limits the operating temperature span to a certain/narrow range [8]. The last issue leads to a vanishing of the ECE when the operating temperature falls below the temperature range that stress-induced martensitic PT can be triggered by stress, which renders the typical SMAs unviable as solid-state refrigerators in low-temperature ambient.

Over the last years, novel SMAs that maintain superelasticity and ECE at low temperatures have been developed [8–11]. The strategies employed so far are to design novel SMAs with low transformation temperatures [8–10,12] and tailoring the mode of martensitic PT towards a weakly first-order mechanism to broaden the transformation temperatures [13]. Although superelasticity as low as 4.2 K has been recently discovered [12], to the best of our knowledge, 175 K is the lowest operating temperature of ECE reported so far [11]. Recently, we have studied the role of grain size

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and internal defects on the mechanism of martensitic PT and superelastic properties of NiTi [14,15]. We showed that with a reduction of austenite grain size into the nanocrystalline range, the mode of superelastic deformation changes from large hysteresis plateau-type superelasticity (with a narrow temperature range of superelasticity) to slim-hysteresis superelasticity with extended temperature window of superelasticity down to 200 K [6].

Here, we report on the temperature-dependent ECE of the nanocrystalline NiTi fabricated by severe cold-rolling. We first show that the nanocrystalline NiTi preserves slim hysteresis superelasticity down to an ultra-low temperature of 18 K. Then, we show a crossover in the mode of ECE with lowering ambient temperature $T_{\text{amb}}$; from a stress-induced martensitic PT dominated mechanism for $175 \, K \leq T_{\text{amb}} \leq 300 \, K$, to an ECE that exhibits an opposite sign for $18 \, K \leq T_{\text{amb}} \leq 90 \, K$. We present results of in-situ low temperature neutron diffraction experiments and molecular dynamics (MD) simulations in order to unveil the origin of such ECE at ultra-low temperatures. Finally, we discuss the feasibility of exploiting such ECE in cryogenic refrigeration applications.

2. Materials and experiments

The material used here is a severely cold-rolled superelastic NiTi with a chemical composition of Ni$_{50.6}$Ti$_{49.4}$ [16]. Temperature-dependent resistivity $R(T)$ and heat capacity $C_p(T)$ were measured with a Quantum Design Physical Precision Measurement System (PPMS). $R(T)$ measurements were performed with rectangular bars with dimensions of $10 \times 2 \times 0.5 \, \text{mm}^3$ with cooling rate of 2 K/min. $C_p(T)$ measurements were performed on circular disks with diameter of 4 mm using the standard relaxation method. In-situ cooling XRD diffractograms were recorded with a Rigaku SmartLab (9 kW XRD) equipped with a CuK$_{\alpha 1}$ radiation source with $\lambda = 0.154056 \, \text{nm}$ [16]. The frequency-dependent storage modulus is measured with a Netzsch 242E Artemis dynamical mechanical analysis (DMA) in cantilever mode.

Tensile loading and unloading experiments were performed under vacuum using a custom-built loading frame equipped with a Gifford-McMahon cryo-cooling chamber with dog-bone shaped specimens as shown in Fig. 1(a–c) [17]. Indium foil was placed between the specimen and the jigs to enhance the thermal contact. A thin layer of Apezion N grease was pasted between the jigs and Indium foil to further enhance the thermal contact. To measure adiabatic temperature changes $\Delta T_{\text{ad}}$, the stress is slowly increased up to maximum stresses of 600–1250 MPa, then rapidly released at a strain rate of 0.18 s$^{-1}$. Measurements were performed from 350 down to 18 K. To explore the reversibility of the ECE, cyclic loading and unloading with a strain rate of $1.5 \times 10^{-2} \, \text{s}^{-1}$ were conducted. Temperature changes are measured with Chromel-Au/Fe (0.07 at.%) thermocouple wires spot-welded to the mid-point of the gauge length and the output signal of the thermocouple was recorded by a Graphitec data logger at a sampling interval of 250 ms. Neutron diffraction spectra were recorded under tensile loading and unloading at temperatures of 300 and 35 K with a high resolution time-of-flight neutron diffractometer at TAKUMI (Beamline 19) at the Materials and Life Science Facility in the Japan Proton Accelerator Research Complex (J-PARC) [18]. Diffraction spectra are recorded for about 60 min in the d-spacing range of 0.67–3.33 Å.

3. Molecular dynamics simulations

MD simulations were performed using the LAMMPS code [19] with a recently developed interatomic potential [20], which accurately reproduces the grain size dependence of temperature- and stress-induced phase transformations in the NiTi SMA [21]. Initially, a nanocrystalline cell was generated using the Voronoi construction method [22] with random positions and crystallographic orientations of the B2 austenite phase. A cube-shaped cell with a total of 30 grains and an average grain diameter of 4 nm was considered. A relaxation at the designated temperature was performed with a time step of 2 fs in an isobaric-isothermal (NPT) ensemble at zero-pressure considering full relaxation of cell parameters under the periodic boundary condition. The superelastic response of the nanocrystalline cell was investigated based on stress-controlled cyclic tensile loading and unloading with a maximum stress of 2 GPa and loading and unloading rates of $\pm 6.25 \, \text{MPa/s}$, allowing the relaxation of cell dimensions orthogonal to the loading direction. The evolution of the microstructure was identified using the adaptive cutoff common-neighbor analysis (AC-CNA) algorithm [23,24].

4. Results and discussion

4.1. Microstructure and PT behavior

As shown previously, the microstructure of the severely cold-rolled NiTi is comprised of a mixture of nanocrystalline austenite (B2) with an average grain size of $\sim 5 \, \text{nm}$, densely-distributed dislocations, and nanodomains of stabilized B19' martensite [16]. Details of the microstructural features of the severely-deformed NiTi can be found elsewhere [25–27]. The PT behavior of the nanocrystalline NiTi is compared with a typical coarse-grained NiTi in Fig. 2(a–d). In the coarse-grained sample, PT is realized by a sharp behavior with $M_s \sim -M_f \sim -25 \, K$ and a rapid loss of superelasticity at 250 K (dashed curves in Fig. 2(d)). In contrast, the nanocrystalline NiTi shows a weak and broad PT over a wide temperature range $-175 \, K < T < 300 \, K$, as can be seen from the deviation in $C_p(T)$ from the Debye-Einstein curve (red line in Fig. 2(a)) and a narrow hysteresis in the electrical resistance curve (Fig. 2(b)). The XRD diffractograms recorded at different temperatures (Fig. 2(c)), confirms that the PT range is $-175 \, K < T < 300 \, K$ in which the B2 phase transforms partially to B19' and the majority of the microstructure remains as B2 with further cooling to 5 K. As it is seen in Fig. 2(d), the nanocrystalline NiTi maintains the slim hysteresis superelasticity over a wide temperature range of $18 \, K < T < 300 \, K$ [see Ref. [28] for the values of Young’s modulus and hardness of the severely-rolled NiTi].

4.2. Temperature-dependent ECE

The sample's temperature variations $T_{\text{sample}}$ during cyclic loading/unloading and during rapid release of 1250 MPa tensile stress are shown in the first and second rows of Fig. 3(a–f), respectively. For $175 \, K \leq T_{\text{amb}} \leq 300 \, K$ (transformation range), the nanocrystalline NiTi exhibits a conventional ECE as evidenced by heating during loading and cooling with unloading, because of the release and absorption of stress-induced heat of PT (Fig. 3(a) and (b)). The amount of released/absorbed heat and the degree of temperature variations are weaker than those of coarse-grained NiTi due to the nanocrystalline microstructure [6]. In this temperature range, $T_{\text{sample}}$ drops when the stress is released rapidly, leading to $\Delta T_{\text{ad}} < 0$. Typical of ferroic PT materials [11], the ECE degrades gradually with a decrease of $T_{\text{amb}}$, and completely disappears below the transformation range at $T_{\text{amb}} = 150 \, K$ (Fig. 3(c)). Due to a weakly first-order nature of stress-induced martensitic PT in the nanocrystalline NiTi [29,30], the temperature span of the conventional ECE is wider than typical coarse-grained SMAs as shown in Fig. 4. At lower ambient temperatures ($100 \, K \leq T_{\text{amb}} \leq 150 \, K$), there is no discernible temperature changes. However, at $T_{\text{amb}} < 75 \, K$, an anomalous reversible ECE appears. During cyclic loading and unloading, the stress and $T_{\text{sample}}$
are no longer in phase. In the loading process, the specimen mostly cools and in the unloading process it mostly heats, although a small amount of heating with loading and cooling with unloading can be detected. In this temperature range, a jump in $T_{\text{sample}}$ ($\Delta T_{\text{ad}}>0$) is observed when the stress is released rapidly. In stark contrast with the conventional ECE that degrades with a decrease of $T_{\text{amb}}$, this reversible ECE intensifies gradually with decreasing $T_{\text{amb}}$ down to 18 K as shown in Fig. 4. At $T_{\text{amb}} = 18$ K, the $\Delta T_{\text{ad}}$ reaches a relatively large value of ~3.4 K.

As a short summary, we have observed that the ECE of the nanocrystalline NiTi, which maintains slim-hysteresis superelasticity over a wide temperature span, crosses over from stress-nanocrystalline NiTi, which maintains slim-hysteresis superelasticity over a wide temperature span, crosses over from stress-induced PT dominated mechanism to an unprecedented ECE well below the PT range. This new ECE exhibits a change in sign and intensifies with a decrease of temperature. It should be noted that despite the similarity between the observed ECE and the inverse ECE ($\Delta T_{\text{ad}} < 0$ when stress is applied), this ECE does not fall into the category of inverse ECE [31]. According to the definition of inverse ECE [32], increasing the driving field (tensile or compressive stress) will cause $\Delta T_{\text{ad}} < 0$. In other words, the sign of $\Delta T_{\text{ad}}$ does not depend on the direction of the applied field. However, as it is discussed in section 4.5, reversing the direction of the applied stress from tensile to compressive will change the sign of $\Delta T_{\text{ad}}$.

1 The origin of the heating during loading and cooling with unloading is unknown to us. However, the measurement of the temperature evolution of the jigs shows that the jigs heat with loading and cool with unloading (joule heating effect). Because of the non-adiabatic condition during cyclic loading/unloading, this heat effect from the jigs may flow to the specimen, which causes heating/cooling with loading/unloading respectively. The other possibility for the heating with loading and cooling with unloading could be due to twin boundary activities of the residual martensite.

4.3. Mechanism of low-temperature superelasticity: insights from in-situ neutron diffraction experiments and dynamical mechanical analysis

To elucidate the mechanism of such anomalous ECE, we performed in-situ neutron diffraction under tensile stresses spanning a wide range of temperatures. Fig. 5(a) and (b) show the evolution of 100B2 diffraction profiles along the loading direction at 300 K and 50 K, respectively. At 300 K, at which slim hysteresis superelasticity is accompanied by a conventional ECE, a simultaneous decrease in the diffracted intensity and an increase in the d-spacing with loading, which are fully reversible with unloading are observed. As discussed previously, these features indicate a continuous (second-order) stress-induced B2 $\leftrightarrow$ B19$'$ martensitic PT [6,29]. Note that the relative change in the integrated intensity of the 100B2 peak is only ~3.7% for 1300 MPa change of stress, which indicates that only a small volume of the B2 phase transforms to B19$'$. At 50 K, at which smooth hardening superelasticity is accompanied by an anomalous ECE, much less discernible changes occur in the diffracted intensity, but, a significant reversible peak shift is still present. Because the reversible changes in diffracted intensity reflects the B2 $\leftrightarrow$ B19$'$ lattice change, it appears that with lowering the $T_{\text{amb}}$ to below the transformation range, the contribution from the stress-induced B2 $\leftrightarrow$ B19$'$ in the superelastic deformation disappears. Meanwhile, the smooth hardening superelasticity (Fig. 2(d)) originates from the large elastic deformations of the nanocrystalline microstructure (reversible peak shift). Quantitatively speaking, at 50 K, and under a tensile stress of 1300 MPa, the measured elastic strain of the B2 lattice along the RD ($y_{\text{RD}}$) and ND ($y_{\text{ND}}$) reach 1.8% and ~0.58%, respectively. It is worth mentioning that 1.8% of lattice elastic strain (from non-transformational mechanism) at such low temperatures is unprecedented in typical structural materials with ~ 0.2% of

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Fig. 1. Experimental setup for low-temperature elastocaloric measurements. (a) Gifford-McMahon cryo-cooling loading machine used for elastocaloric measurements and in-situ neutron diffraction experiments, (b) inside the loading chamber, and (c) schematic drawing of the dog-bone specimen that is electro-discharge machined from the severely-rolled sheet. The Chromel-Au/Fe (0.07 at.%) thermocouple is spot-welded to the center of the gauge length.
elastic limit and stiffening elastic constants with lowering temperature \cite{33}.

Smooth hardening superelasticity\(^2\) with slim-hysteresis below the PT transformation temperatures has been widely reported in strain glass SMAs \cite{34-37}. One of the distinct features of strain glass SMAs is the frequency dependence of the temperature at which a dip (minimum) in storage modulus \(T_{g(u)}\) occurs \cite{36}. In Fig. 5(c) it is seen that the nanocrystalline NiTi exhibits this feature of strain glass and \(T_{g(u)}\) follows the Vogel-Fulcher relation (inset). Based on this similarity, we believe that the ultra-low temperature ECE that we have observed in the nanocrystalline NiTi, could potentially be observed in other families of SMAs with smooth hardening superelasticity such as strain glass \cite{34-37}, aged SMAs with rubber like stress-strain behavior \cite{38,39}, and Gum metal \cite{40}.

4.4. MD simulations

Fig. 6 shows the results of MD simulations on nanocrystalline NiTi with an average grain size of 4 nm performed at temperatures of 300 K and 20 K. In line with experimental observations \cite{41} and previous micromechanical modeling \cite{42}, our MD simulations show that after a number of cyclic loading and unloading (Fig. 6(a1) and (b1)), the degeneration of superelastic properties saturate and the nanocrystalline NiTi exhibits a fully recoverable slim-hysteresis superelasticity from 300 K down to 20 K (Fig. 6(a2) and (b2)). The snapshots from the simulation cells at different applied stresses are shown in Fig. 6(a4) and (b4). The blue spheres correspond to B2 crystals, gray spheres to grain boundaries, and red spheres to B19\(^0\) martensite. At both temperatures, little discernible stress-induced martensitic PT can be observed with loading, which indicates that the major deformation mechanism carrying superelastic deformation is not stress-induced PT. Instead, the reversible deformation originates mainly from the large elastic deformations of the nanocrystalline microstructure (B2 grains, stabilized nano domains of martensite, and grain boundaries), which is accompanied by a large change in the volume of the simulation cell as presented in Fig. 6(a3) and (b3). The relative volume change \(e\) reaches \(6.2 \times 10^{-3}\), which is in the order of the measured \(e\) (5.48 \(\times 10^{-3}\)) from in-situ neutron diffraction experiments \(e = (1 - 2\nu)\varepsilon_0\) (\(\nu\) is poison's ratio).

An important implication of the above results is that the elastocaloric effect of the superelastic nanocrystalline NiTi is comprised of two contributions; heat of PT associated with stress-induced crystal change from B2 to B19\(^0\) and thermoelastic effect associated with elastic deformations. In the temperature range that the

\(^2\) Smooth hardening superelasticity refers to a type of superelasticity that stress increases with increasing strain and strain evolves smoothly/uniformly in the gauge area of the tensile specimen. These features are in contrast to the plateau-type superelasticity in typical SMAs where stress remains constant with increasing strain and deformation is highly localized.
PT can be triggered by stress the ECE is dominated by the heat of PT since the entropy change is larger than the entropy change from the elastic deformations (thermoelastic effect). With lowering the ambient temperature to below the transformation range, the PT mechanism vanishes while the thermoelastic effect continues to exist as long as the material preserves the superelastic behavior.

4.5. Analysis of temperature-dependent thermoelasticity (entropic elasticity)

Now, let us link such large elastic deformations to the observed ECE at ultra-low temperatures. According to theory of elasticity, for a solid material with linear elastic stress-strain behavior, the entropy change originates from the relative volume change \( \varepsilon \) \(^43\). With the assumptions of constant volumetric coefficient of thermal expansion \( \alpha \) and constant bulk modulus \( K \) (temperature-independent), the entropy change \( \Delta S \) is calculated as:

\[
\Delta S = K \alpha \varepsilon
\]  

(1)

For a change in stress \( \Delta \sigma \), the adiabatic temperature change \( \Delta T_{ad} = T - T_{amb} \) can be obtained by solving the following equation \(^44\):

\[
\int_{T_{av}}^{T} \frac{\rho c_T(T)}{T} dT + \frac{\Delta \sigma \alpha}{3} = 0
\]  

(2)

where \( \rho c_T(T) \) is the temperature-dependent specific heat per unit
Fig. 4. Dependence of $\Delta T_{ad}$ to $T_{amb}$ for temperature range of 18 K $\leq T_{amb} \leq$ 350 K. Note that at some intermediate temperatures at which the two ECEs become comparable, they compensate each other leading to no detectable $\Delta T_{ad}$.

volume at constant volume. In order to solve Eq. (2), we have assumed that $\rho c_p(T) = \rho c_p(T)$ and $\alpha = 6 \times 10^{-6}$/K. The $c_p(T)$ data from Fig. 2(a) are fitted with polynomial functions in the temperature range of 2–110 K. Then, Eq. (2) is solved numerically to find the temperature rise $T$ and the $\Delta T_{ad}$ for $\Delta T < 0$ (unloading) and $\Delta T > 0$ (loading). As it is seen in Fig. 7(a), Eq. (2) predicts a non-monotonic trend; the $\Delta T_{ad}$ increases with a decrease of $T_{amb}$ reaches a maximum at $\sim T_{amb} = 16$ K, and tends to vanish with further decrease of temperature to 0 K. Although the predicted trend cannot be fully captured in our experiments, nevertheless, it seems that the $\Delta T_{ad}$ reaches a maximum at 18 K for 600 MPa of stress (Fig. 7(b)). Since the only temperature-dependent variable in Eq. (2) is $c_E(T)$, it is concluded that the observed ECE at ultra-low temperatures originates from large entropic elasticity of the nanocrystalline NiTi i.e., it is a large thermoelastic effect. It is emphasized that Eqs. (1) and (2) are only valid approximations of $\Delta S$ and $\Delta T_{ad}$ for linear elastic materials. Thus, in case of the nanocrystalline NiTi with non-linear elastic behavior, Eqs. (1) and (2) predict lower $\Delta T_{ad}$ than the actual values. Precise calculation of $\Delta T_{ad}$ requires a non-linear thermoelastic analysis and considerations of temperature-dependent $\alpha$ and $K$ and their stress dependencies, which represents a future theoretical challenge.

The inset of Fig. 7(a) shows that the $\Delta T_{ad}$ changes sign with changing the direction of the applied stress, due to a change in the sign of the relative volume change ($e$). For tensile loading the $\Delta T_{ad} < 0$ due to the lattice dilatation ($e > 0$) and positive entropy change ($\Delta S > 0$). During unloading the $\Delta T_{ad} > 0$ due to the lattice contraction ($e < 0$) and negative entropy change ($\Delta S < 0$), which was clearly observed in Fig. 3(f). This indicates that cooling of a low-temperature ambient is possible with loading if the heating of the unloading stage is extracted from the ambient. However, hysteresis heating hinders the cooling effect with loading [45,46]. For compression test, however, cooling occurs during unloading (lower curves in the inset of Fig. 7(a)), which is devoid of the hysteresis heating. It is not possible to perform compression tests on our nanocrystalline NiTi as our samples are in the form of sheets with thickness of 0.6 mm. However, to test the above theoretical prediction, we have performed infra-red thermographic experiments on a number of structural materials at room temperature (not shown here). It was observed that the thermoelastic effect changes sign from tension to compression and that releasing a compressive stress causes cooling. Fabricating nanocrystalline NiTi in the form of a rod and performing thermometric experiments at low temperatures under compressive loads to provide direct evidence is underway.

Before closing, it is worthwhile highlighting the impact of the present results on the solid-state elastocaloric cooling. So far, the research in this field has mainly focused on elastocaloric materials that show entropy and temperature changes via structural PT mechanisms [31]. In contrast, whether thermoelastic cooling can be exploited in solid-state refrigeration has not been explored systematically, as it is generally perceived that the reversible entropy change is too small to produce significant cooling, due to the limited elasticity of structural materials. Through direct measurement of $\Delta T_{ad}$ by thermometry at ultra-low temperatures, this work underscores the potential of thermoelasticity in solid-state cooling of ultra-low temperature ambient via the model nanocrystalline NiTi that sustains large elastic deformations over a wide temperature range. As demonstrated in Fig. 7(b), not only the intensity of the ECE achieved by this mechanism can surpass barocaloric solid-state cooling materials such as CeSb [47], HoAs [48], and EuNi$_2$(Si$_{0.15}$Ge$_{0.85}$)$_2$ [49], but also conspicuously wider temperature span of ECE are achievable.

Fig. 5. Evolution of the 100B2 diffraction profile along the tensile direction (north bank) measured via in-situ neutron diffraction, (a) 300 K. (b) 50 K. The inset in (b) represents the evolution of 111B2 diffraction profile along the normal direction (south bank) showing the Poisson’s effect, (c) DMA measurements of frequency-dependent storage modulus $T_{g}(\omega)$ of the nanocrystalline NiTi with cooling. Inset shows that the $T_g$ follows the Vogel-Fulcher relation.
5. Conclusions

In summary, we have shown that the superelastic NiTi, well-known for its large room temperature ECE associated with a stress-induced martensitic phase transformation, exhibits a large and reversible ECE at ultra-low temperatures when its microstructure is severely deformed. Analyses show that such ECE originates from large elastic deformations and the ensuing entropy changes of the nanocrystalline microstructure. Considering the magnitude of the adiabatic temperature changes, its wide temperature span (18 K ≤ T_{amb} ≤ 90 K), and improved low-cycle fatigue life of the nanocrystalline NiTi [50], the model nanocrystalline NiTi suggests a new avenue for solid-state cooling in ultra-low temperature ambients.

Fig. 6. MD simulations of stress-strain response of a nanocrystalline cell with an average grain size of 4 nm at 300 K (a1) under 20 cyclic loadings, (a2) stable stress-strain response during the final (20th) cycle, (a3) stress dependence of the reversible relative volume change (ε) of the simulation cell during the final cycle, and (a4) corresponding atomic configurations of the nanocrystalline cell. (b1-b4) for 20 K. In each snapshot, blue spheres correspond to the B2 austenite structure, red spheres to the B19° martensite structure, and gray spheres to grain boundaries. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
Fig. 7. (a) Theoretical predictions of $\Delta T_{\text{f}}$ vs. $T_{\text{amb}}$ using Eq. (2). The inset compares the $\Delta T_{\text{f}}$ vs. $T_{\text{amb}}$ for releasing tensile (upper curves) and compressive (lower curves) stresses. Note that cooling effect ($\Delta T_{\text{f}} < 0$) is attainable by releasing a compressive stress. (b) Measured dependence of $\Delta T_{\text{f}}$ to $T_{\text{amb}}$ for temperature range of 18 K $\leq T_{\text{amb}} \leq$ 100 K compared with barocaloric solid-state cooling materials.

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