Elastocaloric Cooling of Additive Manufactured Shape Memory Alloys with Large Latent Heat

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Abstract
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Keywords
additive manufacturing, three-dimensional (3-D) printing, shape memory alloys, elastocaloric cooling, latent heat, linear superelasticity

Disciplines
Materials Science and Engineering | Metallurgy

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**Elastocaloric Cooling of Additive Manufactured Shape Memory Alloys with Large Latent Heat**

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Abstract:
The stress-induced martensitic phase transformation of shape memory alloys (SMAs) is the basis for elastocaloric cooling. Here we employ additive manufacturing to fabricate TiNi SMAs, and demonstrate compressive elastocaloric cooling in the TiNi rods with transformation latent heat as large as 20 J g$^{-1}$. Adiabatic compression on as-fabricated TiNi displays cooling $\Delta T$ as high as $-7.5$ °C with recoverable superelastic strain up to 5 %. Unlike conventional SMAs, additive manufactured TiNi SMAs exhibit linear superelasticity with narrow hysteresis in stress-strain curves under both adiabatic and isothermal conditions. Microstructurally, we find that there are Ti$_2$Ni precipitates typically one micron in size with a large aspect ratio enclosing the TiNi matrix. A stress transfer mechanism between reversible phase transformation in the TiNi matrix and mechanical deformation in Ti$_2$Ni precipitates is believed to be the origin of the unique superelasticity behavior.

Keywords: additive manufacturing, three-dimensional (3-D) printing, shape memory alloys, elastocaloric cooling, latent heat, linear superelasticity
I. INTRODUCTION

Elastocaloric cooling is an emerging refrigeration mechanism alternative to vapor-compression technology.[1-3] Elastocaloric cooling has one of the largest energy savings potentials among all non-vapor compression technologies.[1, 4] In elastocaloric cooling, a shape memory alloy undergoes a stress-induced solid-solid diffusionless martensitic phase transformation between austenite and martensite,[2, 5] and cooling is achieved during the endothermic reverse transformation from martensite to austenite upon stress unloading.[2, 6] The elastocaloric effect with isothermal change in entropy was reported in CuZnAl alloys in 2008. The cooling effect with adiabatic change in temperature was demonstrated in NiTi and NiTiCu alloys in 2012.[6, 7] The efforts to explore new elastocaloric materials have gone from binary TiNi alloys [6-8] to ternary and quaternary TiNi-based alloys,[7, 9-13] Cu-based alloys,[14-16] and magnetic alloys.[17-22] At the same time, there have also been development of prototypes of elastocaloric systems and devices based on compressive thermoelastic tubes [23, 24], tensile sheet/ribbons,[25] and bending films.[9]

From the heat exchange point of view, materials geometries with large surface areas and porosity can enhance heat transfer and lead to better cooling performance as manifested in active magnetic regenerators.[1, 26, 27] However, conventional production techniques of shape memory alloys (SMAs) typically only allow certain fixed shapes such as tubes, rods, sheets, and wires. Although their mechanical integrity under stress needs to be carefully addressed, it would be of great interest to explore formation of SMAs with other structures such as mesh-shaped and honey-comb geometries which can be very effective as heat exchangers.[28]

Additive manufacturing, also known as three-dimensional (3D) printing, allows the highest freedom in terms of shape design among various manufacturing techniques, and it can
enable customization of SMAs.[29, 30] Broadly speaking, casting and powder metallurgy are two categories of manufacturing techniques for SMAs, and additive manufacturing is in the category of powder metallurgy.[30, 31] The casting technique utilizes arc or induction melting under vacuum followed by metal forming and machining to achieve final shapes, while powder metallurgy employs powders as starting materials and undertakes consolidation processes such as sintering at near melting temperatures to produce near-net-shape components. In contrast to conventional powder metallurgy such as spark plasma sintering, and hot isostatic pressing (for a review on conventional powder metallurgy see reference [31]), additive manufacturing builds materials by sequentially adding melted layers to form the desired geometry controlled by an automated computer model. The potentially attractive feature of additive manufacturing for elastocaloric cooling is its ability to generate near-net-shape SMAs that possess large surface areas for fast heat exchange and robust mechanical properties for structural integrity.

To fabricate TiNi alloys two types of additive manufacturing have hitherto been explored: powder-bed-based and flow-based.[30, 31] The powder-bed-based approach employs a high-energy laser beam to fuse small powders together for creating 3D shapes. Selective Laser Sintering (SLS) is one such powder-bed-based technique. The SLS is the first commercialized additive manufacturing technique and thus far, it is the technique of choice for most of reported 3D printed TiNi,[30] as well as some Cu-based alloys.[32] The flow-based approach, on the other hand, injects flux of powders into a molten pool while simultaneously a laser beam is pointed at the injected powders. A typical flow-based technique is Laser Engineered Net Shaping (LENS).

The flow-based LENS can produce fully dense materials with high strength and form refined microstructure with limited segregation. Components with dimension as large as 30 cm
$\times 30 \text{ cm} \times 15 \text{ cm}$ can be produced by LENS. LENS can even be used to fabricate graded materials with composition and porosity gradient across sections.\cite{31, 33} Fabrication of Ti, Ti-Al-V \cite{34} and recently superelastic TiNi alloys \cite{35} have been demonstrated using LENS. There have been many reports of SMAs fabricated using additive manufacturing, but to date there has not been investigation of elastocaloric properties of additive manufactured SMAs.

We report on elastocaloric cooling properties of TiNi SMAs fabricated by a flow-based additive manufacturing technique. We have produced cylindrical TiNi rods 7 mm in diameter by fusing Ni and Ti powder using a LENS system. Calorimetric measurements of the as-fabricated TiNi using differential scanning calorimetry has allowed us to probe the presence of phase transformation, transformation enthalpy, and transformation temperatures. We have investigated their superelastic behaviors, and characterized their cooling ability under different applied strains. Microstructural morphology and elemental distributions of the alloys were investigated to shed light on the influence of structural constituents on the mechanical properties of the as-fabricated TiNi.

II. EXPERIMENT

1. Material fabrication and sample preparation

Additive manufacturing of TiNi alloys was conducted using a directed energy deposition system (LENS MR-7, Optomec Inc.). The system allows multiple powder feeds for deposition, uses a laser for full consolidation, and employs a computer-aided design model to achieve automatic building of metallic alloy layers. The process was in a controlled inert gas environment suitable for highly reactive materials. The starting power was set to be 360 W, and it was slowly reduced to 200 W at the end of each build under a laser beam spot size of 0.5–1.0 mm. The powder feed rate was $\approx 10.0 \text{ g min}^{-1}$ for both Ni powders and for Ti powders. The Ni
powders and Ti powders had a size of 45–125 µm. The design to achieve four orthogonal hatching sequences (45, 135, 225, and 315 degrees) was performed at every four layers. Each layer thickness was 0.254 mm, and the hatch distance was set to be 0.381 mm. The deposition substrate was a Ti plate, and the laser scanning speed with respect to the substrate motion was 63.5 mm s$^{-1}$. To avoid overbuilding, each build was interrupted every 6–8 mm in height in order to refocus the laser beam. The flow rate of the carrier Ar gas and the shielding Ar gas was $6.7 \times 10^{-5}$ m$^3$ s$^{-1}$ and $3.3 \times 10^{-4}$ m$^3$ s$^{-1}$, respectively. The input energy density from the laser beam to volume of each scan was estimated to be $45.6$ J mm$^{-3}$ using an equation including the processing parameters of effective laser power, laser scanning speed, the layer thickness, and the hatch distance.[36] The dimensions of the produced TiNi rods are listed in Table 1.

From LENS-manufactured rod materials, disk samples with diameter of 3 mm and thickness of 1.5 mm, and rod samples with a length of 10 mm and diameter of 5 mm were machined using electrical discharge machining. As-machined disk samples were used to characterize phase transformation using differential scanning calorimetry (DSC Q100, TA Instrument Inc.) with a scan range from $-50$ to $150$ °C. The scan rate was fixed to be $10\pm0.5$ °C min$^{-1}$ following an ASTM F2004 standard for nickel-titanium alloys.[37] The samples for scanning electron microscopy (SEM) were mechanically polished in an Allied High Tech MetPrep System using colloidal silica at the final step for a surface finish of 0.05 µm. The rod samples for compression tests, as per ASTM E9 Standards, had the length-to-width ratio of 2, and both ends of the samples were kept flat and parallel. Compression is the preferred mode of stress application because in contrast to tension, compression tends to prevent cracks or pores from growing to failure that takes place along the direction perpendicular to the loading axis.[38] In order to compare the properties of LENS-manufactured TiNi with TiNi fabricated in a more
conventional way (casting), we also prepared casted TiNi tubes with 50.73 at.% Ni (purchased from Confluent Medical, Inc.) for compression tests.

2. **Composition measurement**

The compositions of LENS-manufactured TiNi alloys were analyzed using wavelength dispersive spectroscopy (Electron Probe Microanalyzer 8900R, JEOL Inc.) with calibrated standards. The results are summarized in Table 1.

3. **Mechanical property characterization and temperature measurements**

Mechanical tests were conducted using a 100 kN hydraulic universal testing machine (810, MTS Systems Corp.) equipped with an annular furnace allowing a sustained temperature up to 1200 °C. Pairs of grips were customized using precipitation-hardening stainless steels (Yield strength higher than 1,000 MPa) to serve as a rigid housing for accommodating the compression samples inside the furnace. A lubricant (Dupont Teflon, McMaster Inc.) was applied at both ends of compression samples to mitigate the surface friction and the resulting non-uniform transverse deformation. The isothermal testing was conducted with a strain rate of 0.0002 s\(^{-1}\), consistent with isothermal strain-rate of 0.0004 s\(^{-1}\) or less previously reported in [39, 40]. The adiabatic condition was achieved using a strain rate of 0.2 s\(^{-1}\), consistent with an adiabatic limit confirmed in experiments and in simulation.[39, 41] Due to limited space in the furnace for an extensometer, only displacement-derived strain readings were available to record, which typically has uncertainty of 0.8 %. A T-type thermocouple (36 gauge, Omega Inc.) was attached to the middle of rod samples using electrically-and-thermally conducive silver paste (Structure Probe, Inc.). Readings of the thermocouple was recorded using a portable data acquisition system (cDAQ-9171, National Instruments Corp.) with a sampling rate of 0.5 s and
were stored using a customized program in a LabVIEW system design software (LabVIEW 2015, National Instruments Corp.).

4. Microstructural characterization

The microstructure of the TiNi samples was characterized using a field emission scanning electron microscope (FE-SEM) (SU-70, Hitachi Ltd.) in a backscattered electrons (BSE) mode under 10 kV accelerating voltage. The FE-SEM was equipped with an energy dispersive x-ray (EDX) detector (XFlash 4010, Bruker Corp.) possessing energy resolution less than 125 eV and input count-rate higher than 700,000 count s\(^{-1}\).

III. RESULTS AND DISCUSSION

Figure 1. (Color online) Photographs of TiNi alloy rods produced by LENS. The number above each picture is their sample ID. Their dimensions and compositions are summarized in Table 1.

Binary TiNi alloys was chosen for synthesis here because among SMAs, TiNi is the most investigated and is thus far the only one commercially available. As a result, extensive information including phase diagram, transformation temperatures, transformation paths, etc are available which can serve as a benchmark for additive-manufactured TiNi. Figure 1 shows the
LENS-manufactured TiNi alloys in the shape of rods with a diameter of 7 mm and of different heights. The details of fabricated sample dimensions are listed in Table 1. In order to demonstrate the composition control capability of LENS, we have fabricated a series of samples in the slightly Ti-rich range (Table 1). The rod shape was used in order to help accommodate superelastic tests in a compression mode.

![DSC thermogram](image.png)

Figure 2. Differential scanning calorimetry thermo-grams of representative LENS-manufactured TiNi alloys. Four transformation temperatures, $M_s$, $M_f$, $A_s$, $A_f$, are identified using the tangent method. Latent heat, $\Delta H_{A \to M}$, $\Delta H_{M \to A}$ are calculated using the area under peaks. The values of transformation temperatures and latent heat are shown in Table 1.

Differential scanning calorimetry (DSC) measurements (Figure 2) of all five samples (two plotted here) show there is only one peak in both cooling and heating, indicating the typical one-stage transformation path from austenite phase with the B2 crystal structure to martensite phase with the B19' monoclinic phase in TiNi.[5, 42] The austenitic finish temperature ($A_f$) as well as martensitic start temperature ($M_s$) of the two samples in Figure 2 are nearly the same,
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despite the difference in martensitic finish temperature ($M_f$) and austenitic start temperature ($A_s$).
The measured values of $M_s$, $M_f$, $A_s$, $A_f$, and the latent heat for the five samples are listed in Table 1.

The measured $A_f$ is about 100 °C. It is important to point out that $A_f$ is the temperature most relevant to superelasticity and thus elastocaloric cooling. Complete superelasticity only takes place above the $A_f$, and fully reversible transformation from stress-induced martensite to austenite for elastocaloric cooling comes into completion exclusively above the $A_f$. Cooling below $A_f$ induces residual martensite and thus incomplete reversible transformation occurs, hindering the possibility of achieving large elastocaloric cooling $\Delta T (\Delta T_c)$. The high $A_f$ values are consistent with the known composition-dependent transformation temperature in TiNi-based SMAs: Ti-rich TiNi tends to show high transformation temperatures over a wide composition range [43, 44]. Despite the slight difference in the Ni concentration, the transformation temperatures of the present sample are nearly the same. As a comparison, we have also fabricated several TiNi rods with composition in the Ni-rich region (51.5±0.6 Ni at. %). The $A_f$ of these Ni-rich samples were found to be around 0 °C, again consistent with the known trend in the casted TiNi alloys.

Table 1  Physical properties and transformation-related properties of LENS-manufactured TiNi alloys.

| Sample ID | Produced Dimension | Composition [at.% Ni] | Transformation Temperatures | Thermal hysteresis | Latent heat | | | |
|-----------|--------------------|------------------------|-----------------------------|-------------------|-------------|--------|--------|
|           | Height [mm] | Diameter [mm] | $M_s$ [$^\circ$C] | $M_f$ [$^\circ$C] | $A_s$ [$^\circ$C] | $A_f$ [$^\circ$C] | $A_f - M_s$ | $\Delta H_{A-M}$ [J g$^{-1}$] | $\Delta H_{M-A}$ [J g$^{-1}$] |
| 1         | 25.00   | 7.00     | 49.8±1.7   | 63.1     | 47.6     | 89.4     | 106.6   | 43.5     | 12.8   | 12.3   |
| 2         | 28.00   | 7.00     | 47.3±1.5   | 60.8     | 46.4     | 82.9     | 102.3   | 41.6     | 1.1    | 1.5    |
| 3         | 28.00   | 7.00     | 47.0±0.8   | 63.7     | 45.4     | 87.9     | 106.9   | 43.2     | 15.4   | 15.2   |
| 4         | 31.00   | 7.00     | 46.6±3.8   | 60.5     | 43.0     | 86.1     | 104.5   | 44.0     | 16.1   | 15.7   |
| 5         | 34.00   | 7.00     | 45.0±1.3   | 62.8     | 41.7     | 84.7     | 105.4   | 42.6     | 21.0   | 20.9   |
In addition to the large range over which the transformation temperature can be tuned in SMAs, it is known that elastocaloric cooling can be observed for a large temperature range (above $A_f$) for a given SMAs material. Cooling operational temperature window of 100 °C or more have been reported in CuAlMn [16], CuZnAl [14], and NiFeGaCo [19]. The large operational temperature range combined with significant tunability of the transformation is very unusual among different classes of caloric materials, i.e. compared to electrocaloric and magnetocaloric cooling, and it makes elastocaloric cooling in SMAs very attractive from the application point of view. In Table 1, the latent heat of exothermic transformation ($\Delta H_{A \rightarrow M}$) from austenite to martensite is slightly larger than the latent heat of endothermic transformation ($\Delta H_{M \rightarrow A}$) during the reverse transformation. This difference is due to hysteric energy dissipation explained in a later Section. Both transformation latent heat are on the order 10 J g$^{-1}$, and the maximum is 20.9 J g$^{-1}$. 
Figure 3. Comparison of reported endothermic latent heat, $\Delta H_{M\rightarrow m}$, for different alloy systems.

For each system, the bar represents the range of values reported. The maximum value of the latent heat for each alloy is marked to the right of the bar. The TiNi alloys in this work have large latent heat and are highlighted in yellow. Please see Table S1 in Supplementary Materials for detailed values and the references.

The latent heat is one of the most important materials parameters for the elastocaloric effect. In Figure 3 we have summarized the reported endothermic latent heat in various SMA systems. TiNi-based alloys with the most available data possess the largest latent heat with maximum value $> 30 \text{ J g}^{-1}$ in contrast to copper-based (maximum $6.8 \text{ J g}^{-1}$) and other alloys (maximum $9.3 \text{ J g}^{-1}$). The latent heat of $30 \text{ J g}^{-1}$ can in principle give rise to a elastocaloric
cooling $\Delta T$ ($\Delta T_c$) as high as 54 °C using a heat capacity $C_p = 0.55$ J g$^{-1}$ C$^{-1}$ and an equation $\Delta T_c = \Delta H_{M\rightarrow A} / C_p$. Recently, a heating $\Delta T_h$ as large as 58 °C was reported in casted Ti-50.5 at.% Ni with $A_f$ of 20 °C, indicating the potential of TiNi alloys to achieve large $\Delta T_c$. We have placed the latent heat values of LENS-manufactured TiNi alloys in this work in Figure 3. In one sample, we have observed 20.9 J g$^{-1}$, which is in the middle of the reported latent heat range for casted TiNi. The value is consistent with a reported endothermic latent heat of $19 \pm 2$ J g$^{-1}$ in Ti-rich TiNi with $A_f = 105$ °C fabricated using laser based directed energy deposition.[45] It is worth mentioning that the current TiNi alloys are in the as-fabricated state, and increase of latent heat could be potentially achieved using heat treatment, or by adding elements to TiNi such as Hf.[46]

Figure 4. Compressive stress-strain curves of LENS-manufactured TiNi alloys at different strains under isothermal and adiabatic conditions. The strain rate was varied to achieve the isothermal condition and the adiabatic limit in two measurements. The maximum load was held for 30 s for natural cooling to ambient temperature, followed by unloading. Due to the relatively high $A_f$ (≈100 °C) of the fabricated alloy, the measurements were carried out at ≈122 °C.
The superelastic behavior is essential for elastocaloric cooling, and Figure 4 shows the stress-strain curves of LENS-manufactured TiNi under the strain rate of 0.0002 s$^{-1}$ for isothermal case and 0.2 s$^{-1}$ for the adiabatic case. Under both isothermal and adiabatic conditions, fully reversible behavior exists up to 5.0 % strain. At 6.0 %, plastic deformation begins to take place with yielding stress of $\approx$1280 MPa in loading, and upon unloading partial recovery leaves residual strain of $\approx$0.78 %. The stress hysteresis is the difference between the middle of forward transformation and that of reverse transformation, and it increases with applied strain. The stress hysteresis is 100 MPa at 3.0 %, 157 MPa at 4.0 %, and 228 MPa at 5.0 %. Strikingly, under full recovery at 3–5% strain, adiabatic stress-strain curves appear to nearly overlap the isothermal ones with slightly larger stress. The non-plateau transformation behaviors with small hysteresis here are similar to those of reported TiNi alloys with Ti$_2$Ni precipitates that are fabricated also using LENS and tested at strain rate of 0.001 s$^{-1}$.[35]
Figure 5. Temperature vs time in superelastic loading-unloading tests under adiabatic (top) versus isothermal conditions (bottom). The values of temperature change for heating ($\Delta T_h$) during loading and for cooling ($\Delta T_c$) during unloading as well as the corresponding applied strains are shown. The test temperature for loading-unloading is $\approx 122 \, ^\circ\text{C}$.

Figure 5 shows the direct measurements of temperature change, $\Delta T_c$ (cooling $\Delta T$) and $\Delta T_h$ (heating $\Delta T$), under isothermal vs adiabatic superelastic conditions. The adiabatic temperature increases during loading and decreases upon unloading, while nearly constant temperature is observed under isothermal loading-unloading as expected. Both $\Delta T_c$ and $\Delta T_h$ increase monotonically as a function of increasing applied strains. $\Delta T_c$ increases from $-4.2 \, ^\circ\text{C}$ at 3.0 % strain to $-6.7 \, ^\circ\text{C}$ at 6.0 % strain with the maximum $\Delta T_c$ of $-7.5 \, ^\circ\text{C}$ at 5.0 %. $\Delta T_h$ also increases from 4.2 °C at 3.0 % strain to 11.3 °C at 6.0 % strain.
Under the same mechanical strain, $\Delta T_c$ is often smaller than $\Delta T_h$. We see $-7.5 \, ^\circ C (\Delta T_c)$ vs $+9.5 \, ^\circ C (\Delta T_h)$ at 5.0 % strain. We also note that under zero-loading thermal cycling in DSC, $\Delta H_{M\rightarrow A}$ is less than $\Delta H_{A\rightarrow M}$ (Table 1). Both effects are associated with the intrinsic hysteresis of a martensitic transformation. The hysteretic behavior is an energy dissipative process primarily taking place via the mechanism of plastic relaxation of coherent strains between austenitic phase and martensitic phase, manifested through emitting dislocation segments throughout an austenite-martensite interface for reducing the elastic strain energy.[47] Friction can also contribute to the dissipated energy when austenite-martensite interface moves across the austenitic phase [47] or precipitates.[48, 49] The strain energy stored via forward transformation from austenite to martensite for heating is thus dissipated, and only a fraction of stored energy becomes available in reverse transformation for cooling, thereby resulting in smaller $\Delta T_c$ compared to $\Delta T_h$. 
Figure 6. Compressive stress-strain curves of a TiNi alloy made by the LENS additive manufacturing versus those of a TiNi alloy made by the conventional casting method. Isothermal and adiabatic curves are superposed in each case, and the applied strain is 4.0%.

The mechanical behavior of LENS-manufactured TiNi in Figure 4 are rather unusual. In Figure 6, we compare stress-strain curves of LENS-manufactured TiNi to casted TiNi. A striking feature is the linear superelasticity and the overlap of adiabatic and isothermal stress-strain behaviors in LENS-manufactured TiNi. In contrast, a casted TiNi displays the conventional transformation plateau behavior, and the adiabatic behavior is notably different from the isothermal one showing a much larger stress hysteresis and a greater transformation slope. The stress hysteresis under adiabatic and isothermal conditions is nearly identical and it is 157 MPa in the LENS-manufactured TiNi, while in casted TiNi, the adiabatic hysteresis is 480 MPa, much larger than the isothermal one of 250 MPa.

When work recovery is properly used, a small hysteresis in stress-strain behavior can give rise to a reduced input work, leading to an increased coefficient-of-performance in materials (COP$_{\text{mat}}$). There have been different definitions and formulations of COP$_{\text{mat}}$ proposed to date. In one, the COP$_{\text{mat,}\Delta T}$ can be defined as extracted latent heat (measured heat) divided by required input work,[50] given by equation (1):

\[
\text{COP}_{\text{mat,\Delta T}} = \rho \times \Delta T \times C_p / \int \sigma d\varepsilon, \quad (1)
\]

where $\sigma$ is stress and $\varepsilon$ is strain, provided that work recovery is utilized via reverse transformation upon unloading. With a heat capacity $C_p = 0.55 \text{ kJ kg}^{-1} \text{°C}^{-1}$ [6], a density $\rho = 6.5 \times 10^3 \text{ kg m}^{-3}$ [51], and the hysteric area of 7.69 MJ m$^{-3}$, the COP$_{\text{mat,\Delta T}}$ of the current LENS-manufactured TiNi is 3.5.
We have previously also proposed another coefficient-of-performance taking into account the Brayton-like cycle under which most elastocaloric materials are to be operated in a cooling system. The \( \text{COP}_{\text{mat.}\Delta S} \) is given by equation (2):

\[
\text{COP}_{\text{mat.}\Delta S} = \frac{(T_c - (\Delta T_c / 2))\Delta s - A}{(T_h - T_c + \Delta T_c)\Delta s + 2A},
\]

where \( A = (\oint \sigma \delta e / 2\rho) - \Delta T_c \times \Delta s / 2 \). Here \( \Delta s = C_p \Delta T_c / T_{\text{test}} \).[52, 53] The calculation of \( \text{COP}_{\text{mat.}\Delta S} \) in the present sample is 3.0. Alternatively, we can directly use the latent heat representing the cooling potential of an elastocaloric material to calculate the coefficient-of-performance \( \text{COP}_{\text{mat.}\Delta H} \). When using the value of latent heat measured in DSC, \( \text{COP}_{\text{mat.}\Delta H} \) is 17.7. In comparison, typical casted TiNi shows \( \text{COP}_{\text{mat.}\Delta H} \) of 11.8.[6]

We note that based on DSC, the latent heat is 20.9 J g\(^{-1}\) corresponding to achievable \( \Delta T_c \) of \(-38^\circ C\), while the measured \( \Delta T_c \) is \(-7.5^\circ C\). There are several reasons for this marked discrepancy. As we discussed above, \( \Delta T_c \) cannot be larger than the difference between the testing ambient temperature (here 122 \( ^\circ C \)) and \( Af \approx 105 \( ^\circ C \), which gives possible \( \Delta T_c \approx -17 \( ^\circ C \). Another reason is related to the martensite variant morphology since thermally-induced phase transformation with zero loading in DSC leads to multi-variant, twinned martensite, while stress-induced phase transformation in superelastic tests have single-variant, detwinned martensite. The martensite morphology can impose distinct level of kinematic constraints in reverse transformation from martensite to austenite for cooling.[54]
Figure 7. Energy-dispersive X-ray spectroscopy (EDS) of LENS-manufactured TiNi sample. (A), (G) Schematics, (B), (C), (H), (I) scanning electron microscopy images, and (D), (E), (F), (J), (K), (L) EDS maps showing microstructural morphology and elemental distributions. In (A) and (G), the polished side of the TiNi sample is displayed as white and a coordinate system is as shown. The $y$-axis corresponds to the growth direction of the TiNi rod, and the $x$-axis corresponds to the planar direction. The viewing direction is denoted by the arrows. (B)–(F) is
viewed in the direction depicted in (A), the planar view and (H)–(L) under (G), the cross-sectional view. The color range in (D–(F) and (J)–(L) shows the concentration of respective element. In (C) and (I) the matrix TiNi and the precipitate Ti$_2$Ni are marked by arrows.

To obtain insight to the unusual mechanical behavior of LENS-manufactured TiNi, microstructural morphology in the growth plane and the cross-sectional views are examined in Figure 7. With a planar view (Figure 7(A)), the bright areas in Figure 7(B) have a round shape 5–10 µm in size and are surrounded by dark regions with a high length-to-width ratio. The zoomed-in view (Figure 7(C)) shows that the dark regions have a width of ~1 µm. The bright areas are identified as TiNi, and the dark regions are Ti$_2$Ni using point analysis. (See Supplementary Materials for detailed identification) The Ti$_2$Ni accounts for an area fraction of 9 % using ImageJ, and appears to be interconnected throughout the hosting plane. As previously reported,[35, 55-57] as-fabricated TiNi alloys possess the precipitates, probably due to the slow cooling rate during the additive manufacturing process. The complementary elemental map in Figure 7(D) and (E), and the added map in Figure 7(F) reveal that large amount of Ni are in the round TiNi areas, while high concentration of Ti are in the long, thin Ti$_2$Ni regions. The elemental distribution in Figure 7(D)–(F) together with the point analysis confirms the presence of two different phases, TiNi, and Ti$_2$Ni. Along the cross-sectional direction (Figure 7(G)), Ti$_2$Ni phases also have a large aspect ratio and take up an area fraction of ≈28 %. The Ti$_2$Ni phases surround the TiNi phase as seen in Figure 7(I). The relative configuration of Ti$_2$Ni enclosing TiNi can be clearly seen in Figure 7(J)–(L).

It is known that the presence of precipitates can impose constraints on the matrix and affects the mechanical behavior of the overall materials. At the atomic level Ti$_2$Ni precipitates can be coherent with the TiNi matrix at the interface. Previously, a thin plate Ti$_2$Ni precipitate
was revealed to have a full coherency with the TiNi matrix via $<100>$ atom rows perfectly fitting that of TiNi B2 phase along the habit plane, despite lattice spacing being larger than that of the B2 phase.[58, 59] The spherically shaped Ti$_2$Ni was shown to have partial coherency with the TiNi matrix by fitting some of $(0\bar{4}\bar{1}\bar{4})$ planes of Ti$_2$Ni to $(0\bar{1}\bar{1})$ of TiNi at the interface.[60]

Hao, et al. have recently reported that Nb precipitates in intimate contact to the TiNi matrix can cause continuous, linear superelasticity with recoverable strain 6.0 % and the stress hysteresis of 180 MPa.[61] It was reported that the interaction between the nucleation of martensite in the TiNi matrix and the residual stress in Nb precipitates can induce spatially inhomogeneous initiation and propagation of martensite, causing continuous phase transformation resulting in the quasi-linear superelasticity.[62] In this picture, during the interaction the precipitates would bear the overall load in elastic deformation giving rise to the narrow hysteresis and the TiNi matrix behaves as load transfer increases with rising residual stress.[62-66] A criterion based on the large aspect ratio and the volume fraction of precipitates, and applied pre-strain is proposed to achieve the quasi-linear superelasticity in general.[62]

We believe a similar interaction is taking place here. In our scenario, the Ti$_2$Ni precipitates in Figure 7(B) and (H) have an aspect ratio of about 15 and a volume fraction close to 20 %, and a pre-strain of 5.0 % was applied (See Supplementary Materials for pretreatment). The agreement between the Ti$_2$Ni precipitate morphology observed here with the criterion above indicates that the similar precipitate-induced linear superelasticity with narrow hysteresis might also perhaps be at work. Ti$_2$Ni precipitates have thermal conduction with transformable TiNi matrix and thus promote exchange of heat to mitigate the transient effect during adiabatic testing, leading to the overlapping of stress-strain curves between the adiabatic superelasticity and the isothermal ones.
Room temperature superelasticity is essential for practical applications of elastocaloric cooling. This work demonstrates the capability of additive manufacturing to fabricate transformable TiNi alloys exhibiting elastocaloric cooling at high temperatures > 100 °C. As indicated above, we have also been able to demonstrate fabrication of LENS-manufactured TiNi with low transformation temperatures. Preliminary characterizations of the TiNi alloys with Ni-rich composition indicate that they also exhibit the linear superelasticity with narrow hysteresis near room temperature. Future work is ongoing to tune different aspects of superelastic and elastocaloric properties in additive manufactured TiNi alloys including employing post-printing heat treatment to adjust the microstructure.

IV. SUMMARY AND CONCLUSIONS

We have introduced additive manufacturing to the field of elastocaloric cooling by demonstrating the cooling capacity of TiNi SMAs fabricated using the flow-based LENS technique. As-fabricated TiNi alloys with a controllable range of compositions possess a maximum latent heat of 20.9 J g⁻¹. As-fabricated TiNi using LENS displays linear superelasticity with narrow hysteresis, which is consistent with previously reported additive manufactured TiNi and in sharp contrast to conventional casted materials. Superelasticity of as-fabricated TiNi at adiabatic versus isothermal conditions are reproducible, thereby allowing superelastic stability over a range of strain rates. Precipitates inherent in additive manufactured materials may be at the heart of a stress transfer mechanism for giving rise to the unusual linear superelasticity.

This work is an important first step in ultimately achieving elastocaloric materials of arbitrary shapes and structures for large cooling capacity with efficient transfer of heat to a
cooling medium such as water. Although much work remains to be performed in optimizing properties and structures, additive manufacturing with the maximum freedom and controllability for designs of elastocaloric materials could pave the way for pushing elastocaloric cooling toward to its full energy saving potential.[4]

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