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THERMALLY-INDUCED MARTENSITIC TRANSFORMATIONS IN Cu-BASED SHAPE MEMORY ALLOY MICROWIRES

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Prior studies on shape memory alloys have identified size effects on the superelastic, i.e. stress-induced, hysteresis of martensitic transformations. However, literature on thermally-induced transformations and size effects upon stored elastic energy is rather limited. In this work, a complementary sample size effect on the stored elastic energy of the transformation, and its effect on variant selection, is elaborated. Shape memory alloy microwires of a CuAlMnNi alloy are drawn with diameters varying between 45 and 255 microns and processed to obtain bamboo grain structures, where the grain boundaries lay almost perpendicular to the wire axis. Calorimetric and thermomechanical analyses of the microwires establish a decreasing contribution of stored elastic energy to the free energy of martensitic transformation as the wire diameter is reduced. This in turn affects the transformation ranges and macroscopic strain generated in constrained thermal cycling. The effect is shown to be associated with a decrease in number of interacting martensite variants as well as relaxation on free surfaces. The presented results indicate that thermal actuation of lightly biased SMA wires is enhanced in finer wires.

Keywords: shape memory, martensitic transformation, elastic strain energy, size effects

Introduction

It has recently been found that micro-scale pillars and wires of various shape memory alloys (SMAs) show sample size-dependent properties below $\sim 100\text{ }\mu\text{m}$ diameter [1–7]. For example, transformation temperatures and stresses increase at smaller sample scales in Cu-Al-Ni [1], while hysteresis over a cycle of forward and reverse transformations increases in several Cu- and Ni-

based SMAs [1–3, 8]. These property changes may be associated with a transition from multi-domain to single-domain transformation morphology observed as the wire diameter is decreased [5]. It has been suggested that at submicron scales additional effects may emerge, such as the complete suppression of martensitic transformation as seen in NiTi [9, 10].

Sample size effects such as those above imply significant interactions of the thermoelastic martensitic transformation with free surfaces, which is also in line with observations that martensite appears at free surfaces at temperatures far above the bulk transformation temperature [11]. By extension, surfaces must affect the balance between chemical and non-chemical energies that drive the transformation. The driving force for the transformation is the chemical free energy difference (ΔG_{ch}) between the austenite and martensite phases; this energy is nominally reduced to zero at an equilibrium temperature (T_0) in the absence of any resisting non-chemical energies [12, 13]. Non-chemical energies that superimpose upon this scenario include frictional work that is done during the transformation (W_{fr}) and stored elastic energy produced by the transformation mismatch (ΔG_{el}):

$$\Delta G = -\Delta G_{ch} + (\Delta G_{el} + W_{fr}) \quad (1)$$

While ΔG_{ch} is essentially a material property that depends on chemical composition and temperature, the two non-chemical terms ΔG_{el} and W_{fr} are significantly affected by microstructure. In addition to permitting some microstructural control over the shape memory properties of the alloy, these terms are therefore also the domain of sample size effects.

The frictional work term, W_{fr} , speaks to the loss of energy when the transformation interfaces propagate through the sample; it is usually associated with the interaction of the phase interfaces with defects, or pinning points [1, 14]. Heat is lost in an additive fashion over both forward and reverse transformations, and is therefore responsible for hysteresis. Size effects on hysteresis during superelastic loading have been extensively studied [1, 3–5], with the overarching conclusion that frictional dissipation is higher in smaller structures; W_{fr} rises as sample size, D , decreases. Ueland and Schuh [5] found that the scaling of this relationship ($\sim 1/D$) was consistent with surface-obstacle control rather than volume-obstacle control for samples with $D < 100 \mu m$,

suggesting that frictional dissipation at obstacles on the wire surface is the dominant source of energy damping in small scale SMAs.

Unlike W_{fr} , the elastic term ΔG_{el} is reversible over the course of a full forward/backward transformation cycle, because it represents the stored elastic energy associated with volume and shape mismatch between austenite and martensite. Size effects upon this term are less studied, although greater prominence of free surfaces should certainly be expected to affect the stress state in a sample undergoing transformation. Chen and Schuh [1] calculated the elastic field around an ellipsoidal region in a finite matrix undergoing a shear distortion, and found that the internal stresses and the stored elastic strain energy decrease with sample dimension due to relaxation at the free surfaces. Since these stresses tend to oppose martensite formation (and conversely, promote reversion to austenite), their relaxation at free surfaces is expected to shift the transformation temperatures (and stresses) in favor of martensite. Chen and Schuh also reported calorimetry results consistent with this, i.e., a shift towards higher transformation temperatures as the wire diameter decreased, i.e., less undercooling or applied stress is necessary for martensitic transformation.

However, apart from this single qualitative observation we are not aware of a more explicit evaluation of sample size effects on ΔG_{el} . This open area is especially interesting and relevant for shape memory properties triggered by thermal excursions (as opposed to superelastic stress cycles), because thermally- and mechanically-induced martensite differ significantly in number of variants and transformation morphology [13, 15–18]. It is the purpose of this study to explore sample size effects on thermally induced transformations, and in particular to shed more light on sample size effects upon the martensitic transformation ranges and ΔG_{el} .

Materials and methods

Microwires of CuAlMnNi were produced and characterized. These quaternary alloys are relatively less studied compared to the other Cu-based SMAs such as CuAlNi and CuZnAl and of interest for their high temperature shape memory properties, for use over 100 °C [19–27]. Replacing part of the Al content with Mn in more conventional CuAlNi alloys suppresses brittle γ_2 precipitation [23] and enhances thermoelastic and pseudoelastic properties [26], and ductility

[26, 28]. According to Ref. [24], for this alloy the disordered BCC high temperature β phase undergoes DO₃ ordering to β_1 during quenching and then transforms to the 18R β'_1 martensite at lower temperatures, generating reversible strains between 2-10 % depending on the crystal orientation [25]. Bulk alloys with a nominal composition of Cu-25Al-4Mn-2.8Ni (at%) were first prepared by induction melting of high purity elemental powders under argon atmosphere. The as-cast alloy is in the β phase at room temperature, and shows shape memory properties with characteristic temperatures of Ms=103 °C, Mf=10°C, As=24°C and Af=134°C (martensite start and finish, austenite start and finish, respectively). The as-cast bulk alloy had a mean grain size of 170 μ m which increased up to 1200 μ m when it was annealed at 900 °C for 2 hours. These samples were prepared and characterized to compare with the wire form of the same alloy.

Metallic microwires with diameters ranging from 45 to 255 μ m were produced via the Taylor wire drawing process described elsewhere [1, 3]. Aluminosilicate glass is used to draw the wires in order to minimize Al reaction with glass. The coated wires were quenched in ice water after annealing at 900 °C for 2 hours under a static Argon atmosphere to induce grain growth into an oligocrystalline structure. The final composition of the wires was Cu-21.5Al-4Mn-2.8Ni (at%). Compositional variations among the wires were less than 1 at%. The diameter of each wire was measured with a scanning electron microscope (JSM-6610LV SEM). Two of the produced wires are shown in Fig. 1. The wires mostly have uniform diameters with grain boundaries perpendicular to the wire axis (Fig. 1a) and visible martensite plates on the surface at room temperature (Fig. 1b).

A TA Instruments Q800 Dynamical Mechanical Analyzer (DMA) was used to study two-way shape memory behavior of the microwires. The cross-head displacement was measured by a high resolution linear optical encoder within the instrument, with a nominal resolution of 1 nm. The gauge length varied over the range 6-11 mm for different wires. In every case the wire was much longer than the grain size. Transformation temperatures of each wire were determined by employing constrained thermal cycling between somewhat below room temperature and ~230 °C, with cooling and heating rates of 4°C/min, under various constant tensile stresses as well as under a stress-free condition. The transformation temperatures were taken as the first points deviating from linearity in the strain-temperature plots, with a typical error of ± 2 °C. The results

of a series of thermal cycling experiments with different cooling and heating rates showed that the thermal lag between the test chamber and the wires led to misreading of the actual sample temperature, especially at high rates. Therefore, the transformation temperatures reported herein were corrected by calibration to a reference wire with 100 μm diameter, by extrapolating to infinitely slow heating/cooling rates. Measured and corrected forward transformation intervals, stored elastic strain energy, interaction stress and transformation strain generated between M_s and M_f under different constant stress are summarized in Table 1. For calculation of stored elastic strain energy and interaction stress refer to the next section.

The bulk polycrystalline parent alloy in as-cast and annealed states and some of the wires were subjected to thermal cycling in a TA Instruments Q1000 Differential Scanning Calorimeter (DSC), in order to obtain transformation temperatures and ranges under stress-free conditions.

Framework for data analysis

Our main goal in this work is to understand the separate contributions of the energetic terms in Eq. (1) on a quantitative basis. Accordingly, we analyze the data in the light of a one dimensional thermomechanical model developed by adapting prior works of Patoor [29] and Hamilton [16]. The model is developed by considering the N possible martensite variants available to a wire as it undergoes the transformation. Here, the term *variant* refers to the martensite plates oriented in a certain direction, which is dictated by the orientation of the parent phase and the direction of the external stress, if any. Depending on the crystal structure of the parent and the martensite phases, up to 24 variants can form in SMAs [30]. Variant n is associated with volume fraction ξ^n and a constant transformation strain ε_{tr}^n , which is taken as a scalar, i.e., considering only the projection along the loading direction. The total transformation strain is then the sum over the strains of the various variant volumes:

$$\varepsilon_{tr} = \sum_n \xi^n \varepsilon_{tr}^n \quad (2)$$

Since the transformation strains are recoverable, we write the total recoverable strain (ε_{tot}) as the sum of the average elastic strain field (ε_e) and transformation strain (ε_{tr}).

The chemical free energy difference (ΔG_{ch}) in Eq. (1) is assumed to vary linearly between the equilibrium temperature T_0 and a given temperature T :

$$\Delta G_{\text{ch}} = \Delta S^{A \rightarrow M} (T - T_0) \sum_n \xi^n \quad (3)$$

where $\Delta S^{A \rightarrow M}$ is the entropy difference between martensite and austenite.

The stored elastic energy produced by the transformation mismatch (ΔG_{el}) is assumed to be the summation of the elastic strain energy and the interaction energy between the martensite variants, i.e.

$$\Delta G_{\text{el}} = \frac{1}{2} E (\varepsilon_{\text{tot}} - \varepsilon_{\text{tr}})^2 + W_{\text{int}} \quad (4)$$

where E is the elastic modulus, which was assumed to be equal for both phases, and W_{int} is interaction energy.

For the interaction energy, Patoor et al. [29] introduced a quadratic form, $\frac{1}{2} h^{mn} \xi^m \xi^n$ where ξ^m is the fraction of a second martensite variant, and h^{mn} is defined as interaction stress which accounts for the compatibility between variant m and n . Typical values of h^{mn} are 1/1000 of the shear modulus for self-accommodating variants and 1/150 of the shear modulus for non-self-accommodating variants in the CuZnAl alloys in their work [31]. However, this quadratic form is rarely used in multivariant polycrystalline modeling of SMAs [32, 33], because of the challenge associated with calibrating the value of this interaction matrix for a specific SMA alloy [32]. Gao and Brinson [34] took the interaction energy as a small, constant contribution to frictional resistance to transformation (F_c) as previous micromechanical model calculations reveal a very small magnitude of interaction energy when calculations and comparisons to experimental data are made. As the interaction energy is considered important in describing the size-dependent effects of interest in this paper, we propose the following form in which h is not ignored but homogenized.

$$W_{\text{int}} = \frac{1}{2} h \xi^2 \quad (5)$$

In general, h depends on the local microstructure of the sample, such as grain size and arrangement of martensite variants. To simplify the model and to focus on sample size effects, we assume further that the dependence is only through the wire diameter, $h = h(D)$. This assumption will be shown to be reasonable in the following sections where the relationship between wire diameter and martensite structure is developed experimentally.

The frictional work, W_{fr} in Eq. (1), evolves gradually over the course of an individual transformation, and we assume it to be proportional to the transformed volume fraction as is typical [29, 32, 33]:

$$W_{fr} = \pm F_c \Delta \sum_n \xi^n \quad (6)$$

where the sign is positive for forward and negative for reverse transformation, such that W_{fr} is always positive. F_c is a positive constant specifying the energy dissipation due to phase transformation, and which may be sample size dependent.

Phase transformation occurs when $\frac{\partial \Delta G}{\partial \xi^n} = 0$, which can be evaluated by combining Eqs. (1-6).

For forward transformation, for each variant this leads to

$$\sigma \epsilon_{tr}^n + \Delta S^{A \rightarrow M} (T - T_0) - h \xi^n = F_c \quad (7)$$

where $E(\epsilon_{tot} - \epsilon_{tr}^n)$ has been replaced by the uniaxial stress, σ , using Hooke's law. In the stress-assisted thermally induced case, the martensite start temperature under a constant stress σ , denoted as M_s^σ satisfies

$$\sigma \epsilon_{tr}^n + \Delta S^{A \rightarrow M} (M_s^\sigma - T_0) - h \xi^n = F_c \quad (8)$$

Rearranging the equation for M_s^σ yields

$$M_s^\sigma = \frac{\sigma \epsilon_{tr}^{n^*} - F_c}{-\Delta S^{A \rightarrow M}} + T_0 \quad (9)$$

Since $\Delta S^{A \rightarrow M} < 0$ and $\xi^n = 0$ at this stage, n^* is the first forming, i.e. most favorable variant such that $\sigma \epsilon_{tr}^n$ is maximized.

Further cooling may activate more variants, and at the end of the transformation, i.e. at $T = M_f^\sigma$, $\xi = \sum_n \xi^n = 1$. Assuming the last activated variant is \tilde{n} , the driving force at the end of the transformation is given as

$$\sigma \varepsilon_{tr}^{\tilde{n}} + \Delta S^{A \rightarrow M} (M_f^\sigma - T_0) - h = F_c \quad (10)$$

Rearranging the equation for M_f^σ yields

$$M_f^\sigma = \frac{\sigma \varepsilon_{tr}^{\tilde{n}} - F_c - h}{-\Delta S^{A \rightarrow M}} + T_0 \quad (11)$$

Using equations (9) and (10), the forward transformation range can be defined as:

$$M_s^\sigma - M_f^\sigma = \frac{\sigma(\varepsilon_{tr}^{n*} - \varepsilon_{tr}^{\tilde{n}})}{-\Delta S^{A \rightarrow M}} + \frac{h}{-\Delta S^{A \rightarrow M}} \quad (12)$$

Eq. (12) suggests that the width of the transformation range is reflective of the number of variants, n , each of which may be triggered at a separate temperature depending on their favorability with respect to the direction of applied stress. In other words, less favorable variants will require more chemical energy support in the form of undercooling, whereas the most favorable one forms almost immediately at M_s .

The first term in Eq. (12) accounts for the effect of external stress on the transformation range. In a defect-free single crystal, only one variant appears such that $\varepsilon_{tr}^{n*} = \varepsilon_{tr}^{\tilde{n}}$, i.e. the first and the last appearing variants are the same, making the first term zero. In the multi-variant case, a difference between ε_{tr}^{n*} and $\varepsilon_{tr}^{\tilde{n}}$ emerges, which causes the first term to increase with increasing external stress. In this case, the value of $\varepsilon_{tr}^{n*} - \varepsilon_{tr}^{\tilde{n}}$ depends on the characteristic transformation strain of orientations available in the structure and their fraction through Eq. (2). Therefore, it increases with increasing external stress as higher transformation strains are achieved as a consequence of increased volume fraction of favorably oriented variants [16]. Both σ and a non-zero value of $\varepsilon_{tr}^{n*} - \varepsilon_{tr}^{\tilde{n}}$ terms result in an enlargement of $M_s^\sigma - M_f^\sigma$ interval as external stress increases.

The second term in Eq. (12) shows that the transformation range is enlarged when there is greater interaction between variants, i.e., a larger value of h . As noted above, higher h values

would physically correspond to, e.g., a greater number of incoherent variants that would tend to inflate elastic strains; such strains become more severe as the transformation progresses, delaying the martensite finish temperature.

In the absence of external stress, the first term in Eq. (12) becomes zero. The transformation interval in that case depends only on the interaction stress, which expands as the number of incoherent variants increases. Re-introducing Eqs. (4) and (5) more explicitly shows how the transformation width is a measure of the variant interaction energy (W_{int}) when the forward transformation is completed, i.e. $\xi=1$:

$$\Delta G_{el} = W_{int} = \frac{h}{2} = \frac{-\Delta S^{A \rightarrow M} \cdot (M_s - M_f)}{2} \quad (13)$$

Eq. (13) is the same equation proposed by Wollants et al. [35] which gives the maximal amount of energy that could be stored elastically in a thermally induced martensitic transformation. Assuming that the fraction of martensite in a polycrystalline specimen increases linearly between M_s and M_f , Eq. (13) suggests that the stored elastic energy is directly proportional to the forward transformation interval ($M_s - M_f$), i.e. amount of undercooling necessary to complete the forward transformation.

The implications of the above developments on experimentally measurable quantities are shown in Fig. 2, where the left hand column shows the flow of heat that would be measured in a calorimetry experiment, and the right-hand column shows the evolution of the martensite volume fraction (ξ) which might be measured by entropy change (ΔS). For simplicity Fig. 2 focuses on the condition of zero applied external stress.

The upper row of Fig. 2, panels (a) and (b), shows the effect of the chemical energy (ΔG_{ch}) alone; in the absence of any opposing forces, the forward and reverse transformations occur at the equilibrium temperature (T_0) at which the free energies of the high and low temperature phases are equal, giving a singular sharp peak in the calorimetric plot (Fig. 2a). The corresponding martensite fraction (ξ) change shows itself as a sudden jump upon cooling and a sudden decline to zero upon heating, both at T_0 (Fig. 2b). A strain measurement of a single

variant martensitic transformation will yield a graph of the same nature, with a sudden expansion upon cooling and a sudden contraction upon heating. As noted in the introduction, there are no effects of microstructure or sample dimensions on the chemical energies of the phases, so the situation in Fig. 1a and b is a baseline, idealized case.

The middle row of Fig. 2 shows the effect of the chemical energy with the added presence of the interface friction term (W_{fr}). The change in phase fraction occurs rapidly, i.e., at a single temperature for each transformation, but each transformation is “delayed”, requiring undercooling ($T_0 - T_M$) or overheating ($T_A - T_0$) in order for the transformation to overcome the frictional resistance to interfacial motion. This internal friction is the source of the transformation hysteresis (Figs. 2c and d). Because frictional resistance of the transformation is closely associated with microstructure and surface effects, the hysteresis is indeed significantly affected by sample size, as studied in Refs. [1, 3, 8, 36].

The bottom row of Fig. 2, panels (e) and (f), show the situation when all of the energetic terms of Eq. (1) are in play, including not only the chemical energy and friction term, but now adding also the elastic energy (ΔG_{el}), which depends upon the interaction of variants. As established in the development of Eq. (13), elastic strain energy causes the sharp transformation temperature to blur over a wider transformation range, with the characteristic “start” and “finish” temperatures required to describe it (Fig. 2e). The strain around growing martensite plates opposes the forward transformation, demanding more driving force—in the form of undercooling—to overcome the free energy barrier; this transformation range manifests itself with a gentler slope in phase fraction (ξ) versus temperature plots (Fig. 2f). Conversely, a steep slope implies a low elastic strain stored in the material during forward transformation [12, 16, 37]. Anything that increases internal elastic strain mismatch, e.g., interaction of phase domains with other variants, grain boundaries, dislocations, precipitates, will increase the stored elastic strain energy, and by extension the Ms-Mf and As-Af transformation ranges. It is worth noting that asymmetry between the martensite and austenite transformation ranges can provide information about differences between forward and reverse transformation.

Results

i. Surface effects: Comparison of bulk and microwire forms

In order to study the effect of grain and sample size on transformation characteristics, an as-cast bulk piece, an annealed bulk piece, and a microwire with 60 μm diameter drawn from the same alloy were characterized by DSC. For comparison, the bulk samples were around 4 mm in diameter. The as-cast alloy had the smallest average grain size which was measured as 170 μm . The grains were grown up to 1200 μm by annealing at 900 $^{\circ}\text{C}$ for 2h in the annealed bulk piece. Figure 3a shows the heat evolution profiles, normalized with respect to sample weight, of bulk polycrystalline CuAlMnNi alloys in as-cast and annealed conditions, in comparison with the microwire. There is obviously a downward trend in the transformation temperatures with increasing sample size, as expected from the increasing elastic constraints. Nevertheless, it should be recognized that transformation temperatures are highly sensitive to slight fluctuations in composition and subtle variations in long-range order of the parent phase [37]. These temperatures are not consequential individually as they may vary from specimen to specimen for such reasons.

A more subtle but very physically important difference among the curves in Fig. 3 pertains to the width of the transformation ranges. Transformations occur over a considerably wider range in the as-cast alloy with an average grain size of 170 μm ($\sim 92^{\circ}\text{C}$ as compared with 24°C in the microwire). Since the transformation heats of bulk and wire samples are comparable ($\sim 5\text{-}7\text{ J/g}$), the narrower transformation range in wire form renders the transformation peaks more pronounced. The bulk sample in the as-cast condition has considerably more constraint upon the transformation, first by virtue of having less free surface at which to relax transformation strains, and also due to its fine grain size and relatively higher proportion of grain boundary area, all of which increases the interaction energy term (h) in Eq. (12). Because grain boundaries are barriers to the propagation of the transformation, a finer grain size is more constrained than a coarse-grained one. This is also evident when comparing the as-cast bulk sample with one that was annealed for 2 h at 900 $^{\circ}\text{C}$. Although both of these samples have transformation ranges

that are wider than the microwire, the increase in grain size narrows the transformation ranges and sharpens the definition of the DSC peaks. And, all of these differences in transformation ranges are revealed even more obviously when the heats of transformation are converted to martensite fractions by integrating and normalizing the area under the forward transformation peaks (Fig. 3b).

According to Eq. (13), the elastic energy of domain interactions controls the transformation range, and can now be quantified by the measurements in Fig. 3 if the entropy of the transformation is known. The entropy is the ratio of chemical enthalpy of transformation (ΔG_{ch}) and equilibrium temperature (T_0), both of which are material properties, so the transformation entropy has a single value for all of the different physical forms of the same alloy in Fig. 3, provided that the heat capacities of the two phases are equal [12]. The entropy change due to forward transformation is calculated here using two methods: (i) via the Classius-Clapeyron equation ($\partial\sigma/\partial T = \Delta S/\epsilon_{tr}$) based on a measurement of the slope ($\partial\sigma/\partial T$) and transformation strain (ϵ_{tr}) in stress assisted thermal cycling in the DMA (which is relevant to the wire but not the bulk pieces) and (ii) via an empirical relation between entropy change and electron/atom ratio in Cu-based shape memory alloys proposed by Romero and Pellegrina [38]. The results obtained by the two methods are in good agreement giving an entropy change of 0.026 J/g°C. Table 2 shows the elastic strain energy (ΔG_{el}) values calculated using Eq. (13), which demonstrates that the stored elastic strain energy decreases with decreasing grain boundary density and sample size. Table 2 also gives the interaction stress, h , between martensite variants calculated using Eq. (12) for a pure thermal transformation. The significantly lower interaction stress obtained in the microwire conform to the expectation that free surfaces relieve mismatch stresses; the wire structure may also promote a higher fraction of coherent martensite variants, or variants oriented parallel to one another and not competing with respect to shape change.

ii. Effect of external stress

We next conduct a series of experiments with increasing constant external applied stress during thermal cycling. Fig. 4 shows the strain-temperature response and corresponding measured phase diagram for the forward transformation of a wire with 110 μm diameter. Elongation is recorded

when transforming to martensite upon cooling and contraction upon reversion to austenite during heating (Fig. 4a). Applied stress results in formation of preferred martensitic variants oriented to promote elongational strains. The transformation strain is completely recovered after a full thermal cycle, and increases with increasing external stress.

The transformation temperatures, which were taken as the first point deviating from linearity in the strain-temperature plots, are seen to increase with increasing external stress, as described by the Clausius–Clapeyron equation. Figure 4b shows the evolution of the martensite fraction assuming a linear scaling of strain and volume fraction, and that the transformation achieves 100% completeness for each cycle. Interestingly, the increase in forward transformation temperatures was observed to differ between the M_s and M_f temperatures, the effect of external stress level being more pronounced on M_s . In other words, external stress enhances martensite nucleation, however, the growth and completion of the transformation requires larger energy input to overcome the elastic energy term as the external stress rises. This leads to broadening of the transformation range (M_s - M_f) at higher applied stresses (Fig. 4c). A similarly increasing trend in M_s - M_f interval with increasing external stress was also observed in CuAlNi microwires [1]. Comparing Eqs. (9) and (11) shows that this effect arises from the transformation strain of the least favorable variant, $\varepsilon_{tr}^{\tilde{n}}$, which is much smaller than the transformation strain of the most favorable variant, $\varepsilon_{tr}^{n^*}$.

The change in elastic strain energy (ΔG_{el}) with external stress is quantified using Eq. (13) as shown in Table 3. Table 3 also shows that the interaction stress, which was assumed to depend only on the wire size in our model, has an indirect dependency on external stress through wire size. The decrease in interaction stress with increasing external stress level indicates reduced incoherency, i.e. interaction stress, due to an increasing fraction of favorably oriented martensite plates biased by the external stress. In other words, the enlargement of the transformation range with increasing external stress is due to the first term in Eq. (12) rather than the domain interactions captured by the second term, which should diminish with external stress due to the formation of more coherent martensite variants.

iii. Size effects on macroscopic strain generation in thermal transformations and stored elastic strain energy

In order to observe the variant structure of forming martensite domains clearly, some of the wires were electropolished prior to thermomechanical characterization, following the approach of Ref. [5]. Fig. 5a shows montaged SEM images of such a wire with 60 μm diameter, after five stress-assisted thermal cycles under 60 MPa external stress, and cooling down to room temperature, i.e. below M_f , under this constant stress. Fig 5b shows a sketch that illustrates the orientations of the variants more clearly. This wire is like the majority of such relatively thin wires in the sense that it exhibits martensite domains in parallel groups spanning the wire diameter. There are large patches of such aligned groups of domains, which may be related to the oligocrystalline austenite grain structure of the wire. The martensite structure in a somewhat larger wire with a diameter of 100 μm that was cycled under identical conditions, on the other hand, contains plates with various orientations, some of which exhibit large included angles between domains (Fig. 6a). Domains of each variant group overlap in some regions, unlike the thinner wire, which is seen more clearly in the schematic in Fig. 6b. In a still thicker wire, with an average diameter of 210 μm (Fig. 7a), domain overlap is even more commonly seen throughout most all of the wire (Fig.s 7b, c and d); in this case we show a cross-sectional optical micrograph, as the martensite plates were not clearly visible on the surface of the wire when viewed in the SEM.

The observations in Figs. 5-7 are typical of our observations of the martensite structure on microwires in general, and suggest that finer wires tend to favor fewer interacting variants, even at the same applied stresses. A series of systematic thermomechanical tests employed on microwires with diameters varying over the range 45-255 μm also bear out these trends in a more quantitative sense based on the trends in recoverable transformation strain and transformation range. As shown in Fig. 8a, an average strain of only 1.5 % was observed in all wires undergoing pure thermal transformations regardless of wire diameter, although an occasional wire showed reversible strains up to 2.2 % (not shown) probably due to incidental favorable texture. Under external stress, on the other hand, a strong size effect was observed,

with the transformation axial strain increasing substantially with decreasing wire diameter (Fig. 8b).

A summary of many experiments of the kind shown in Fig. 8 are compiled in Fig. 9, for both stress-free and various applied stress levels, across a range of wire diameters. For reference, the maximum theoretical transformation strain that can be achievable in a favorably oriented CuAlMn single crystal is calculated as 10.3 % [25]. The total macroscopic strain generated due to stress-free martensitic transformation does not vary much with wire diameter, whereas it increases to values as high as 8 % with decreasing wire diameter when the thermal cycles are repeated under biasing external tensile stress. These trends align with the morphological differences among the variously-sized wires shown in Figs. 5-7; the smaller wires favor single variant conditions that promote greater axial strain, whereas larger wires have more variant competition and correspondingly lower strains. As a result, the finer wires are more responsive to a biasing stress than are the larger ones.

Another noteworthy observation regarding size effects in this series of wires is that the nucleation and completion rates of martensitic transformation are higher in thinner wires. Fig. 10 shows the thermal hysteresis curves for three different wires obtained during thermal cycling under a small constant external stress of 20 MPa. Nucleation and growth of martensite plates is almost instantaneous in thinner wires, evident from the sharper edges and steeper slope of the hysteresis curves. The transformations occur more gradually as the sample dimensions increase, which is consistent with a stronger opposing forces against martensite nucleation and growth, i.e., more competition among variants as observed microstructurally.

The trend in Fig. 10 is expanded upon in Fig. 11, which shows the transformation ranges for all the wires (extrapolated to the zero stress condition) as a function of the wire diameter. Despite some scatter, this data reinforces the presence of a significant size effect, with a clear decrease in the martensitic transformation range with decreasing wire diameter. Following Eqs. (12-13), this shows that the amount of elastic strain energy stored in the material during forward transformation is reduced with the sample size. On secondary axes, Fig. 11 also shows the stored elastic strain energy extracted using Eq. (13), as well as the variant interaction stress, h ,

calculated using Eq. (12). These axes provide an estimate of the quantitative effects of the morphological size effect seen in Figs. 5-7; the interaction stress of ~ 7 MPa and stored elastic strain energy of 0.5 J/g seen in a millimeter-scale sample are more than double those in the finest wires. The low values in microwires are considerably below those calculated for different single crystal multivariant models that vary between 18 and 270 MPa [31], and nearly an order of magnitude below the values in Table 1 that we measured on bulk fine grained samples of the same material. The relaxation effect of free surfaces thus favors the formation of fewer variants, suppresses competition among variants, leading to less elastic mismatch and a narrower transformation range.

Discussion

The assemblage of the data obtained in prior reports and the present work on SMA microwires points out a significant size dependence on non-chemical energy (frictional work (W_{fr}) and elastic strain energy (ΔG_{el})) terms in Eq. (1) as well as the transformation strain (ϵ_{tr}) in the sample diameter range from ten to hundreds of microns (Fig. 12). Smaller sample size favors high energy dissipation (Fig. 12a) and high thermally activated transformation strains (Fig. 12b) while storing less elastic strain energy (Fig. 12c) during forward transformation.

The origins of size effects on transformation stresses, temperatures and hysteresis in shape memory microwires have been discussed in detail by Chen and Schuh [1], with specific reference to superelastic cycling rather than thermal cycling. Taking into account various size related contributions to the thermodynamic balance, such as interfacial, surface and stored elastic energies in addition to acoustic emission and heat transfer, they concluded that stored elastic energy and internal friction are the most important factors. They argued that the prominence of free surfaces in smaller samples is responsible for relaxing elastic strains, shifting the transformation stresses (and temperatures). They also argued that the frictional term of Eq. (1) must have a sample size dependence to explain the larger energy dissipation in smaller wires. Subsequent work on superelastic behavior in SMA microwires revealed differences in martensite plate density depending on sample size [5]. However, these studies focused their consideration of size effects primarily on superelastic hysteresis, i.e., stress induced transformations at a constant

temperature above A_f where generally only one of the 24 variants grows in a given grain. In contrast, the present study shows that the variant formation kinematics in temperature induced transformations are rather complicated due to self-accommodating multivariant plates; whereas uniaxial load biases the selection of a preferred variant, thermally-induced martensite domains are not biased and therefore more randomly oriented. And yet, we still observed similar size effects on the martensite structure after thermal transformation (Figs. 5-7) as were reported during superelastic loading.

Thus, the origins of size dependence of the martensitic structure would appear to lie in two fundamental differences between smaller and larger structures: the prominence of free surfaces and obstacles to the transformation. The large proportion of free surfaces per unit volume that is available in thinner wires enhances the forward transformation in two ways. First, surfaces are easy nucleation sites; when nucleation occurs on a free surface elastic strain energy is marginalized, which renders nucleation spontaneous [12, 37]. Second, after nucleation, when elastic mismatch strains are normally the main barrier to continued transformation, the free surfaces of fine wires promote elastic relaxation and thus speed the transformation progress. In bulk samples or thick wires, the large elastic opposition to martensite growth leads to multiple nucleation and variant competition. Thus, a natural corollary of the more rapid transformation in fine wires is a tendency for a single variant, even in the absence of biasing stress.

As shown in Figs. 8 and 9, the axial strain achieved in thermally induced martensitic transformation is also found here to be significantly sample size dependent. To our knowledge, this size effect has not been reported previously in shape memory alloys. We explain this size effect as being a natural corollary of the sample size-dependent martensitic structure evolution described above. In polycrystalline structures, the recoverable strain is the average of the strains produced by each domain with a different orientation, as formulated in Eq. (2). In stress-free thermal cycling, martensite variants tend to accommodate themselves in a way to minimize elastic strain, yielding a small average axial strain by diversifying the orientations of the local transformation strains. Therefore, wire diameter has no considerable effect on strain generated and recovered during purely thermal martensitic transformation. However, under external biasing stress the most favorable variant grows at the expense of others and gives the largest strain [39].

Because the smaller wires have lower barriers to domain growth, the first one to form spans the wire diameter and dominates the transformation kinematics, leading to a larger axial strain along the bias direction than can be obtained in a larger system where multiple nucleation and variant competition takes place. The overall average strain may still be small if the majority of the available orientations in the thin wire are unfavorable with respect to the applied stress direction, which we believe is the source of scatter in Fig. 9. Nucleation-dominated transformation in larger samples, on the other hand, tends to produce variants with various orientations, some of which may interfere destructively with the overall macroscopic strain. The condition leading to the formation of incoherent variants, i.e. variants with large angles between one other as shown in Figs. 7 and 8, is that the stress biasing the orientation of the new nuclei is composed of not only the external stress applied, but also the stress exerted by another growing plate which may have a different direction than the external stress. It should again be mentioned that in the case of a favorable texture and a defect free parent phase, it is possible to obtain large overall strains with large samples. Nonetheless, all other things being equal, the present study suggests that thermally-triggered actuators based on shape memory alloys may benefit from adopting a smaller scale wire. Wires with diameters below 100 μm generate strains well above 3 % under a relatively small external stress, outperforming larger wires under identical conditions by a wide margin.

Conclusions

The martensite structure and thermally induced transformation behavior of CuAlMnNi shape memory alloy microwires with a bamboo type grain structure and diameters varying over the range 45–255 μm were studied experimentally. The results show that the elastic strain energy stored during thermally induced martensitic transformation depends on sample size and external biasing stress. The origins of these dependencies are related to the variation in martensite variant structure with sample size and external stress:

- Smaller samples respond faster to temperature change, i.e. the forward transformation interval is narrower, implying less elastic constraints opposing the transformation. The elastic strain energy accumulated during martensitic transformation is directly

proportional to the wire diameter. The decrease in stored elastic energy in small diameter wires is the result of the decrease in number of martensite variants as well as relaxation on free surfaces.

- The elastic stresses caused by the transformation were quantified using a thermodynamic model, and the resulting homogenized “average” interaction stress was calculated based on the experimentally measured forward transformation intervals for each wire. The elastic interaction stress was found to decrease with wire diameter and increase with external stress applied during thermal cycles.
- External stress biases variant formation during stress-assisted thermally induced transformations. As the constant external stress increases, the fraction of self-accommodated martensite plates decreases, resulting in higher elastic strain storage evident from the larger transformation intervals at high stresses.
- The macroscopic strain generated during thermally induced martensitic transformations is independent of wire diameter in the absence of external stress, whereas it increases with decreasing wire diameter under identical external stress. This result implies that thermal actuation of lightly biased SMA wires is enhanced in finer wires, which is a favorable practical result of the sample size effects on the martensitic transformation.

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Figure Captions

Fig. 1 Micrographs of some of the CuAlMnNi microwires **(a)** with a diameter of 45 μm (grain boundaries perpendicular to the wire axis are shown with the arrows), and **(b)** with a diameter of 125 μm showing the martensite plates spanning the wire diameter

Fig. 2 The calorimetry profile and corresponding temperature-strain graphs of the cases where **(a, b)** there is no non-chemical energies, **(c, d)** there is only frictional work and **(e, f)** both frictional work and elastic strain energy are at play, respectively

Fig. 3 (a) DSC peaks normalized by sample weight and **(b)** martensite fraction variation with temperature of small and large grained bulk alloy and the microwire with 60 μm diameter. Martensite start temperatures are equalized for better comparison on forward transformation intervals

Fig. 4 (a) Strain and **(b)** martensite fraction variation with temperature in a wire with 110 μm diameter under various external stresses. Martensite fraction was taken as normalized strain, assuming that the strain is directly proportional to transformed martensite fraction. **(c)** Phase diagram of the same wire

Fig. 5 (a) Montaged SEM images showing martensite plates spanning the wire's diameter aligned parallel to each other in a wire with 60 μm diameter after stress assisted thermal cycles. **(b)** Sketch showing the orientation of the martensite variants

Fig. 6 (a) Montaged SEM images showing multivariant plates in a wire with 100 μm diameter after stress assisted thermal cycles. **(b)** Sketch showing the orientation of the martensite variants

Fig. 7 (a) Cross section of the wire with 210 μm diameter after stress assisted thermal cycles. Martensite variants are seen to be oriented in different directions within the same grain. **(b)** Sketch showing the orientation of the martensite variants. **(c)** and **(d)** SEM image of the surface showing differently oriented and overlapped variants shown in higher magnification

Fig. 8 Strain generated in (a) pure thermal and (b) 40 MPa external stress-assisted thermally induced transformations in various sized microwires

Fig. 9 Transformation strain recorded between M_s and M_f temperatures in thermal cycles performed under (a) stress-free, (b) 20 MPa, (c) 40 MPa and (d) 60 MPa constant stress conditions. For reference, the maximum theoretical transformation strain for CuAlMn alloys is about 10.3 % [25]

Fig. 10 Martensite fraction (ξ) variation with temperature under 20 MPa external stress in wires with 210, 110 and 60 μm diameters. Hystereses were shifted on temperature-axis for the sake of clarity

Fig. 11 Martensite transformation interval and corresponding stored elastic strain energy and interaction stress variation with wire diameter. The solid and dashed lines are drawn to assist the eye. The data point shown by a star is the data of a bulk (mm scale) piece of alloy obtained by DSC

Fig. 12 Summary of size effects observed in Cu-based SMA microwires. Martensite structure evolves as a result of the transition from volume domination to surface domination as sample size decreases. This leads to (a) larger frictional energy [3], (b) smaller stored elastic strain energy and (c) higher transformation strain under small biasing stress

References

1. Chen Y, Schuh C a. (2011) Size effects in shape memory alloy microwires. *Acta Mater* 59:537–553. doi: 10.1016/j.actamat.2010.09.057
2. Ozdemir N, Karaman I, Mara N a., et al. (2012) Size effects in the superelastic response of Ni₅₄Fe₁₉Ga₂₇ shape memory alloy pillars with a two stage martensitic transformation. *Acta Mater* 60:5670–5685. doi: 10.1016/j.actamat.2012.06.035
3. Ueland SM, Schuh CA (2012) Superelasticity and fatigue in oligocrystalline shape memory alloy microwires. *Acta Mater* 60:282–292. doi: 10.1016/j.actamat.2011.09.054
4. Chen Y, Zhang X, Dunand DC, Schuh C a. (2009) Shape memory and superelasticity in polycrystalline Cu–Al–Ni microwires. *Appl Phys Lett* 95:171906. doi: 10.1063/1.3257372
5. Ueland SM, Schuh C a. (2013) Transition from many domain to single domain martensite morphology in small-scale shape memory alloys. *Acta Mater* 61:5618–5625. doi: 10.1016/j.actamat.2013.06.003
6. Dunand DC, Müllner P (2011) Size effects on magnetic actuation in Ni-Mn-Ga shape-memory alloys. *Adv Mater* 23:216–232.
7. Sutou Y, Omori T, Yamauchi K, et al. (2005) Effect of grain size and texture on pseudoelasticity in Cu–Al–Mn-based shape memory wire. *Acta Mater* 53:4121–4133. doi: 10.1016/j.actamat.2005.05.013
8. San Juan J, Nó ML, Schuh C a. (2008) Superelasticity and Shape Memory in Micro- and Nanometer-scale Pillars. *Adv Mater* 20:272–278. doi: 10.1002/adma.200701527
9. Waitz T, Kazykhanov V, Karnthaler HP (2004) Martensitic phase transformations in nanocrystalline NiTi studied by TEM. *Acta Mater* 52:137–147. doi: 10.1016/j.actamat.2003.08.036
10. Waitz T, Antretter T, Fischer FD, et al. (2007) Size effects on the martensitic phase transformation of NiTi nanograins. *J Mech Phys Solids* 55:419–444. doi: 10.1016/j.jmps.2006.06.006
11. Lovey FC, Chandrasekaran M (1982) Diffraction effects in β Cu-Zn and β -Cu-Zn-Al surface martensite transformation and microstructure. *Le J Phys Colloq* 43:C4–583–C4–583. doi: 10.1051/jphyscol:1982491
12. Ortin J, Planes A (1988) Thermodynamic analysis of thermal measurements in thermoelastic martensitic transformations. *Acta Metall* 36:1873–1889.
13. Otsuka K, Wayman C (1999) Shape memory materials. Cambridge University Press, London

14. Ortín J, Delaey L (2002) Hysteresis in shape-memory alloys. *Int J Non Linear Mech* 37:1275–1281.
15. Wada K, Liu Y (2008) On the two-way shape memory behavior in NiTi alloy—An experimental analysis. *Acta Mater* 56:3266–3277. doi: 10.1016/j.actamat.2008.03.005
16. Hamilton R., Sehitoglu H, Chumlyakov Y, Maier H. (2004) Stress dependence of the hysteresis in single crystal NiTi alloys. *Acta Mater* 52:3383–3402. doi: 10.1016/j.actamat.2004.03.038
17. Liu Y, Favier D, Orgeas L (2004) Mechanistic simulation of thermomechanical behaviour of thermoelastic martensitic transformations in polycrystalline shape memory alloys. 115:37–45. doi: 10.1051/jp4
18. Lovey FC, Torra V (1999) Shape memory in Cu-based alloys : phenomenological behavior at the mesoscale level and interaction of martensitic transformation with structural defects in Cu-Zn-Al. *Prog Mater Sci* 44:189–289.
19. Ma J, Karaman I, Noebe RD (2010) High temperature shape memory alloys. *Int Mater Rev* 55:257–315. doi: 10.1179/095066010X12646898728363
20. Sugimoto K, Kamei K, Nakaniwa M (1990) Cu-Al-Ni-Mn: A New Shape Memory Alloy for High Temperature Applications. Butterworth-Heinemann
21. Wu M, Semiatin S, Schetky L (1994) Fabrication of a Cu- Al- Ni-Mn shape memory alloy. *Mater Charact* 246:343–348.
22. Morris MA (1992) High temperature properties of ductile Cu-Al-Ni shape memory alloys with boron additions. *Acta Metall Mater* 40:1573–1586.
23. Segui C, Cesari E (1995) Ordering and stabilization in quenched CuAlNiMnB alloys. *J Mater Sci* 30:5770–5776.
24. Chen L, Dunne D, Kennon N (1997) Determination of the parent grain orientation and habit plane normals for β' 1 martensite in a Cu–Al–Ni–Mn shape memory alloy. *J Mater Sci* 2:3769–3773.
25. Sutou Y, Omori T, Kainuma R, et al. (2002) Enhancement of Superelasticity in Cu-Al-Mn-Ni Shape- Memory Alloys by Texture Control. 33:
26. Morris MA, Lipe T (1994) Microstructural influence of Mn additions on thermoelastic and pseudoelastic properties of Cu-Al-Ni alloys. *Acta Metall Mater* 42:1583–1594. doi: 10.1016/0956-7151(94)90368-9

27. Ratchev P, Van Humbeeck J, Delaey L (1993) On the formation of 2H stacking sequence in 18R martensite plates in a precipitate containing Cu-Al-Ni-Ti-Mn alloy. *Acta Metall Mater* 41:2441–2449.
28. Omori T, Koeda N, Sutou Y, et al. (2007) Superplasticity of Cu-Al-Mn-Ni Shape Memory Alloy. *Mater Trans* 48:2914–2918. doi: 10.2320/matertrans.D-MRA2007879
29. Patoor E, Supe Z, Ge D, et al. (1995) Micromechanical Modelling of the Superelastic Behavior. 5:
30. Bhattacharya K (2003) *Microstructure of Martensite: why it forms and how it gives rise to the shape-memory effect*. Oxford
31. Patoor E, Lagoudas DC, Entchev PB, et al. (2006) Shape memory alloys, Part I: General properties and modeling of single crystals. *Mech Mater* 38:391–429. doi: 10.1016/j.mechmat.2005.05.027
32. Jung Y, Papadopoulos P, Ritchie RO (2004) Constitutive modelling and numerical simulation of multivariant phase transformation in superelastic shape-memory alloys. *Int J Numer Methods Eng* 60:429–460. doi: 10.1002/nme.940
33. Thamburaja P, Anand L (2001) Polycrystalline shape-memory materials: effect of crystallographic texture. *J Mech Phys Solids* 49:709–737. doi: 10.1016/S0022-5096(00)00061-2
34. Gao X, Brinson L (2002) A simplified multivariant SMA model based on invariant plane nature of martensitic transformation. *J Intell Mater Syst Struct* 13:795–810. doi: 10.1177/104538902032786
35. Wollants P, Roos JR, Delaey L (1993) Thermally- and stress-induced thermoelastic martensitic transformations in the reference frame of equilibrium thermodynamics. *Prog Mater Sci* 37:227–288. doi: 10.1016/0079-6425(93)90005-6
36. San Juan J, Nó ML, Schuh CA (2009) Nanoscale shape-memory alloys for ultrahigh mechanical damping. *Nat Nanotechnol* 4:415–419. doi: 10.1038/nnano.2009.142
37. Salzbrenner R, Cohen M (1979) On the thermodynamics of thermoelastic martensitic transformations. *Acta Metall* 27:739–748.
38. Romero R, Pelegrina JL (2003) Change of entropy in the martensitic transformation and its dependence in Cu-based shape memory alloys. *Mater Sci Eng A* 354:243–250. doi: 10.1016/S0921-5093(03)00013-3
39. Saburi T, Wayman C (1979) Crystallographic similarities in shape memory martensites. *Acta Metall* 27:979–995. doi: 10.1016/0001-6160(79)90186-X

Table 1. Data for the CuAlMnNi microwires investigated in this study. D is the average diameter, ΔM is the forward transformation interval obtained by extrapolating the transformation temperatures in stress-assisted thermal transformation cycles to zero stress. ΔM (*corrected*) is the forward transformation

Wire	D (μm)	Forward transformation interval ($^{\circ}\text{C}$)		ΔG_{el} (J/g)	h (MPa)	ε_{tr} (%)			
		ΔM	ΔM (corrected)			Stress-free	20 MPa	40 MPa	60MPa
#1	45	24.8	20.6	0.268	3.685	-	4.03	5.45	6.46
#2	50	13.9	11.6	0.150	2.066	-	4.84	8.29	9.7
#3	60	9.9	8.2	0.107	1.464	1.2	3.6	4.96	6.06
#4	60	16.6	13.8	0.180	2.467	1.74	5.8	7.4	-
#5	66	27.6	23.0	0.300	4.106	0.4	2.1	3.9	5.4
#6	72	19.5	16.2	0.211	2.892	-	2.7	3.9	4.7
#7	80	36.8	30.6	0.398	5.468	2.05	2	4.56	5.31
#8	80	23.3	19.4	0.252	3.462	0.39	3.23	4.41	5.22
#9	86	30.3	25.2	0.328	4.502	-	2.75	3.66	4.43
#10	110	40.0	33.3	0.433	5.944	2.2	3.97	4.63	5.25
#11	115	18.2	15.2	0.197	2.710	0.4	3.1	5	6
#12	125	40.5	33.7	0.438	6.011	-	1.85	3.39	-
#13	130	32.9	27.4	0.356	4.893	0.2	1.5	2	2.3
#14	140	43.7	36.4	0.473	6.494	1.1	4.4	4.89	5.15
#15	150	30.7	25.5	0.332	4.556	1.07	3.78	4.72	4.98
#16	175			-	-	~0.1	~1	~1.9	~3
#17	185	39.9	33.2	0.431	5.922	-	-	3.56	4
#18	210	32.2	26.8	0.349	4.789	0.4	1.03	1.73	1.83
#19	215	36.6	30.5	0.396	5.439	0.3	0.38	0.45	0.5
#20	255	36.4	30.3	0.394	5.409	0.3	1.68	2.1	-

interval corrected by calibration reference. ΔG_{el} is elastic strain energy stored in forward transformation under stress free condition calculated using Eq. 13. h is interaction stress calculated using Eq. 12 in stress-free condition. ε_{tr} (%) is transformation strain generated between Ms and Mf under different constant stresses.

Table 2. Entropy of martensitic transformation, transformation intervals and calculated elastic strain energies in fine and coarse grain alloys and the microwire drawn from the same alloy.

	ΔS (J/g °C)	Transformation Interval ΔM (°C)	ΔG_{el} (J/g)	h (MPa)
Fine grain bulk	-0.026	92	1.196	16.43
Coarse grain bulk	-0.026	59	0.767	10.54
60 μm wire	-0.026	24	0.312	4.29

Table 3. Variation of forward transformation interval, corresponding elastic strain energy, interaction stress and generated strain with external stress in a 110 μm diameter wire.

	Transformation Interval (Ms-Mf) (°C)	ΔG_{el} (J/g)	Transformation strain between Ms-Mf (%)	h (MPa)
No stress	15.2	0.197	0.4	2.710
20 MPa	20.5	0.267	3.1	3.046
40 MPa	22.4	0.291	5.0	1.996
60 MPa	30.2	0.392	6.0	1.787
80 MPa	32.8	0.426	6.9	0.355























