Non-monotonic grain size dependence of phase transformation behavior in NiTi microscale samples

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Abstract

Superelastic NiTi shape memory alloy (SMA) cuboidal micropillars (1 μm × 1 μm × 3 μm) with average grain sizes (GS) of 26 nm, 127 nm and 421 nm are compressed by flat-tip nanoindentation. Increasing GS from 26 nm to 127 nm enhances the transformation by promoting nucleation and growth of martensite. Nevertheless, by further increasing GS to 421 nm, the overall transformation is significantly suppressed, leading to a non-monotonic variation in transformation stress, recoverable strain and hysteresis loop area with GS. Such strong effects of GS on microscale phase transformation behavior of SMA are quantitatively elucidated by a simple three-length-scale model in this paper.

Keywords:
- Grain size effect
- Shape memory alloys (SMA)
- Martensitic phase transformation
- Compression test
- Micromechanical modeling

Application of shape memory alloys (SMAs) in nanoelectromechanical systems (NEMS) and microelectromechanical systems (MEMS) [1,2] involves a considerable reduction of external length scale of SMA components. Such length scale changes can significantly affect the behavior of the materials and the structure. Size effects on behavior and properties of materials caused by both internal and external constraints are actively investigated by researchers in different areas of materials science [3–8]. Recent studies have shown that grain size (GS) reduction down to the nanoscale can considerably suppress the martensitic phase transformation (PT) and that the property and performance of bulk nanocrystalline (nc) NiTi SMAs can be fundamentally changed by changes in the phase transformation mechanism [9–17]. For coarse-grained samples, it has been shown that transformation behaviors of SMA oligocrystals are also significantly different from those of their polycrystalline counterparts [18–23]. For microscale polycrystalline NiTi samples, however, a recent preliminary study on tapered cylindrical micropillars [24] has found a non-monotonic grain size dependency in phase transformation behavior when the GS is increased from 10 nm to 421 nm which is close to the external size of the micropillars (diameter = 0.5 μm). It is conjectured that such a non-monotonic trend is a result of the combined effects of internal and external length scales of the samples on the phase transformation response of the material. However, clear understanding of the roles of different length scales in such size effects and the associated mechanisms are still not available but will be critical for small-scale applications of SMAs in MEMS and NEMS.

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This paper aims to examine the effects of grain size (internal length scale of SMA material) and its interaction with sample size (external length scale) on the PT behavior of cuboidal micropillars of uniform cross-section under compression. The physical nature of the interaction among different length scales in the observed GS dependent response is explored and a simple multiscale continuum model is used to reveal the mechanism underlying the observed phenomena.

Commercial grade NiTi polycrystalline sheets (NDC, USA) with 50.61 at.% Ni, were homogenized at austenite phase stability temperature of 800 °C for 60 min and subsequently quenched in cold water. Multiple pass cold rolling was then used to achieve a final thickness of 1 mm (42% thickness reduction). Polycrystalline samples with grain sizes of 26 nm, 127 nm and 421 nm were obtained by subsequent heat treatment of the cold rolled sheets in a Nabertherm furnace for 105 s at 485 °C, 900 s at 520 °C and 510 s at 600 °C respectively [24]. An FEI Helios G4 UX dual-beam focused ion beam was used to prepare TEM samples and cuboidal micropillars along the cold rolling direction.

 Grain size measurements were carried out with an FEI G2F30 high resolution TEM. Using a recently developed multistage fabrication method, cuboidal micropillars were milled out of an initial normal cylindrical rough cut of a larger diameter [25]. Subsequently, the sides of the cuboidal micropillars were milled using a low current ion beam to reduce the Ga ion damage and remove the damaged layer induced by the higher current of the rough-cut stage. Accordingly, five non-tapered cuboidal micropillars (1 μm width and 3 μm height) were fabricated for each grain size (see Fig. 1). The main advantage of the cuboidal micropillar over the widely used tapered cylindrical micropillar is that it has a uniform cross-sectional area along the pillar height. Consequently, a more
Fig. 1. SEM images of fabrication stages and resulting cuboidal micropillars with average grain sizes of 26 nm, 127 nm and 421 nm (see TEM images).

Fig. 2. (a) Variation in stress-strain curves of the representative micropillars with grain size (GS) at maximum stress levels ($\sigma_{\text{max}}$) of 850 MPa and 950 MPa, and variation in (b) hysteresis loop area ($H$), (c) total recoverable strain ($\varepsilon_r$) and (d) transformation start stress ($\sigma_{\text{tr}}$) and strain hardening modulus ($\beta$) with GS.
uniform nucleation and growth of the martensite phase can be achieved in cuboidal micropillars, which is in contrast to the case of tapered micropillars where higher stress level and concentration at top and bottom of the pillar can induce an early nucleation of martensite phase. Moreover, cuboidal micropillars are more suitable for observation of morphology alteration during the phase transformation in in-situ experiments. The micropillars were compressed at a fixed stress rate of 100 MPa/s up to the maximum stress ($\sigma_{max}$) of 850 MPa and 950 MPa at room temperature in a Hysitron TI 950 nanoindenter. A 60° conical flat end diamond indenter of 10 μm diameter was used to compress the micropillars. To ensure a complete contact between the micropillar and the flat indenter, a preload of 50 MPa was applied to the micropillars in all compression cycles. Additional (quadratic) drift correction was applied to all indentation results.

Fig. 2(a) shows the measured representative stress-strain curves of the cuboidal micropillars of the three different GS compressed up to $\sigma_{max}$ of 850 MPa and 950 MPa. It is seen that during the stress-induced phase transformation under uniform compression, the transformation start stress ($\sigma_{tr}$), the strain hardening modulus ($\beta$), the hysteresis loop area ($H$) and the total recoverable strain ($\epsilon_{re}$) of the micropillars strongly depend on and vary non-monotonically with GS. Fig. 2(b) and (c), show the variations in $H$ and $\epsilon_{re}$ with GS for the micropillars compressed up to $\sigma_{max}$ of 850 and 950 MPa. Fig. 2(d) shows the variation in $\sigma_{tr}$ and $\beta$ with GS. At first, by increasing the GS from 26 nm to 127 nm, the phase transformation is significantly enhanced with a rapid increase in $H$ and $\epsilon_{re}$. However, by further increasing the GS from 127 nm to 421 nm which is close to the width of the micropillars (1 μm), the phase transformation is suppressed with significant decreases in both $H$ and $\epsilon_{re}$. A similar non-monotonic variation of $H$, $\epsilon_{re}$, $\sigma_{tr}$ and $\beta$ with GS was also observed in the previous experiment on tapered cylindrical micropillars [24]. Such a non-monotonic grain size dependent phase transformation behavior of the micropillar NiTi samples is in stark contrast to the monotonic grain size dependence of the bulk samples in which the largest grain size is still much smaller than the dimensions of the sample [9,11,24].

The physical mechanism of the above observed non-monotonic grain size dependent phase transformation behavior of micropillar samples can be described as schematically shown in Fig. 3(a). According to the length scale of grain size ($l_g$), grain boundary thickness ($l_b$) and sample size ($L$), the observed grain size dependent behavior can be divided into three regions. Region I where $L \ll l_g \gg l_b$ is the nanocrystalline region. In this nanograined region (the case of GS $\approx 26$ nm), investigations [9–11] have shown that the large volume fraction of grain boundary and its strong constraint on the phase transformation of the enclosed crystallite leads to a significant suppression of PT owing to the interfacial energy dominance and that the hysteresis loop area and total recoverable strain are greatly reduced. As the GS is increased from 26 nm to 127 nm, the microstructure and the resulting behavior enter into Region II where $L \gg l_g \gg l_b$ (the case of GS $\approx 127$ nm). In this region the transformation of a grain in a representative layer (as shown in Fig. 3(a) and (b)) is no longer strongly constrained by the grain boundary but is rather constrained by the surrounding poly crystal (see the grey area in Fig. 3(a)) which acts as an effective matrix. The constraint effects will be quantified by a model in the next paragraph. It must be noticed that most of the commercial NiTi polycrystals belong to this region. Compared to Region I, the constraint imposed by the grain boundary (‘shell’) on the crystallite (‘core’) is much weaker and the PT of a grain proceeds via the usual nucleation-growth mode inside each grain. In another word, the significant suppression of PT from grain boundary constraints in Region I is now much released which in turn leads to a significant reduction in $\sigma_{tr}$ and $\beta$ along with the appearance of the typical large $\epsilon_{re}$ and $\sigma - \epsilon$ hysteresis loop area. However, when $L$ is further increased to 421 nm which is close to the width of the cuboidal micropillar, the PT response enters into Region III. In this region, the size of the grains is further increased and consequently the number of the grains inside the micropillar is decreased significantly. In this case, the transformability of a rather large grain inside a micropillar depends not only on its orientation relative to the loading direction but also on the degree of the imposed constraints by its neighboring grains [26–28] and the effective matrix (grey colored area in Fig. 3(a)). Compared to Region II, both of the above-mentioned constraints are much enhanced owing to the considerably increased GS ($l_g$) (Fig. 3). Strictly speaking, such a variation in granular constraints with the internal length scale (GS) for a given microscale sample of size $L$ is of a 3D nature and is rather complicated. To reveal the nature of the length scale interactions and to identify the key governing parameters, further simplification of the constraints into a 2D and even an effective 1D model is needed.

To quantify the GS effect, three most important relevant length scales of grain size ($l_g$), grain boundary thickness ($l_b$) and micropillar size ($L$) should be introduced in the modeling. As shown in Fig. 3(b), the micropillar (of size $L \times L \times 3L$) consists of a layer of grains (like a beam) and an effective homogenous matrix (like an elastic foundation) [29–32]. The grains inside the layer have different orientations and each grain consists of a transformable crystallite and a non-transformable grain boundary. When $l_g$ approaches $l_b$, the energy of the non-transformable grain boundary becomes dominant in the transformation process of the grain, which leads to a decrease in superelastic hysteresis loop area with a decrease in $l_g/l_b$ [9–11]. When $l_g$ is increased and becomes comparable to the external length scale $L$, the transformation of each large grain becomes mainly constrained by its neighboring grains and the matrix. The quantitative feature of such grain-matrix interactions can be effectively captured by modeling the micropillar as a sandwich of beam-on-foundation in a 1D setting [29–32] in which the misfit energy between the grain and the elastic foundation only depends on the difference between their displacements. The total energy of the 1D beam-on-foundation system consists of two parts, i.e., strain energy of the grains (local term) and grain-to-foundation interaction energy (non-local term). The displacements at the two ends of the ith grain are denoted as $u_{i-1}$ and $u_{i}$, the boundary conditions are $u_{0}=0$ and $u_{n}=\pi$, where $n=(-L/l_g)$ is the number of the grains. The total Helmholtz free energy ($\Phi$) of the system can be expressed as a function of strain $\epsilon_i$ of each grain ($\epsilon_i=(u_i-u_{i-1})/l_g$):

$$\Phi = \sum_{i=1}^{n} \left[ \varphi_g (\epsilon_i) + \varphi_f (\epsilon_i) \right]$$

(1)

where the strain energy density $\varphi_g (\epsilon_i)$ of the ith grain can be expressed as a function of the non-dimensional length scale $l_g/l_b$, the angle $\theta_i$ (between the ith grain orientation and the loading direction) and the strain $\epsilon_i$ of the ith grain:

$$\varphi_g (\epsilon_i) = f (l_g/l_b, \theta_i, \epsilon_i)$$

(2)

The grain-foundation interaction energy density $\varphi_f (\epsilon_i)$ of the ith grain can be expressed as:

$$\varphi_f (\epsilon_i) = \frac{E_a}{L^2} \left( u_i - \frac{i \pi}{n} \right)^2 = \frac{E_a}{l_g} \left( \frac{l_g}{L} \right)^2 \sum_{k=1}^{i} \epsilon_k - i \epsilon$$

(3)

In Eq. (3), an overall uniform deformation ($\pi/2 \leq \pi \leq L$) of the elastic foundation is assumed and an effective elastic modulus ($E_a$) of the foundation is used in calculating the misfit energy which comes from the incompatibility between the overall displacement of the foundation and the local displacement of the individual grains [29]. The introduction of the elastic foundation energy term $\frac{E_a}{L^2} (u_i - \frac{i \pi}{n})^2$ can satisfactorily quantify the constraints imposed by the matrix on the grains, especially for the case where GS is comparable to $L$. For given micropillar size $L$ and texture, the effects of the grain-to-foundation constraint (Eqs. (3)) is more pronounced in the micropillar of large GS than in the micropillar...
of small GS. Consequently, the phase transformation of the grains would be significantly suppressed when GS approaches $L$.

The displacement $u_i$ of the grains can be solved numerically by minimizing the total Helmholtz free energy with $\partial \Phi / \partial u_i = 0$. The nominal stress-strain curve and the hysteresis loop area ($H$) in one loading-unloading cycle for a given $L$ can be calculated accordingly. Fig. 3 (c) shows the variation in the calculated normalized hysteresis loop area ($\overline{H}$) with GS ($l_g$) and the corresponding scaling laws.

\[
\overline{H} = \left(1 - C_1 \frac{l_b}{l_g}\right) \left[1 - C_2 \left(\frac{l_g}{L}\right)^\gamma\right]
\]

where $C_1, C_2$, and $\gamma$ are coefficients related to material constants. It must be noticed that, although Eq. (4) can be constructed phenomenologically.
based on the general understanding of the sources of the constraint, here it is derived from the energy dissipation of the stress-strain curve based on Helmholtz free energy of the crystal (see references [9,11] for the lengthy mathematical derivations).

From Eq. (4), it is seen that for small GS where \( l_0/l_s \) is ignorable, \( \Pi \) decreases with decreasing \( l_0/l_s \) since the grain boundary energy gradually dominates the nanoscale phase transformation [9–11]. Similarly, for large GS where \( l_0/l_s \) is ignorable, \( \Pi \) decreases with increasing \( l_0/l_s \) owing to the dominance of the effects of granular constraints. In this case, both the existence of fewer neighboring grains and the exposure of a portion of the micropillar to the free surfaces will increase the heterogeneity in each grain and the micropillar, which can further contribute to the suppression of phase transformation by the increase in the grain–foundation interaction energy as shown in Fig. 3(b) and Eq. (3). Therefore, it becomes clear that the non-monotonic grain size dependent behavior of micropillars is a result of the competition between the two distinct mechanisms (i.e., grain boundary constraint and granular constraints) operating at the two different length scale regions.

In summary, the non-monotonic grain size dependence of phase transformation behavior in microscale samples is observed in both the tapered micropillars and the cuboidal micropillars. By increasing the GS from 26 nm to 421 nm, the total recoverable strain and hysteresis loop area under a given stress first increase, then reach their maximum and finally decrease. Such a non-monotonic grain size dependent behavior, basically independent of cross-section (shape) and fabrication method of the micropillars, reflects a change in the phase transformation suppression mechanism from grain boundary constraint dominated region at nanoscale to the granular constraints dominated region at microscale when GS approaches the sample size. The results of the simple 1D analytical model incorporating internal and external length scales support the above scenario and clearly reveal that the interactions among these length scales can indeed significantly affect the transformation behavior of microscale NiTi samples. Further utilization of such combined effects of internal and external length scales may open up new avenues for designing new material systems with superior properties.

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References