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Crystal orientation dependence of stress-induced martensitic transformation in shape memory zirconia

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Abstract

Small volume samples of zirconia can survive stress-induced martensitic transformation without cracking, which enables in-depth explorations of martensite mechanics using micro-scale specimens. Here we present a systematic investigation of the orientation dependence of tetragonal crystals undergoing a uniaxial stress-driven martensitic transformation to the monoclinic phase, in single crystal zirconia pillars doped with yttria and titania. The Young's modulus, martensitic transformation stress and transformation strain are highly dependent on the crystallographic orientation, and generally align with expectations based on known tensor properties and transformation crystallography. However, in some orientations, fracture or plastic slip are apparently preferred to martensitic transformation, and thus crystallography favors certain orientations if superelasticity or shape memory properties are specifically desired in zirconia ceramics.

Keyword: Shape memory effect (SME), Small volume zirconia, Crystallographic orientation, Martensitic transformation, Microcompression

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1. Introduction

Since the discovery of stress-induced martensitic transformation in zirconia [1], numerous studies have been devoted to understanding the shape change due to the rapid and reversible lattice transformation [2-7], with some studies indicating zirconia's potential as a shape memory material [8, 9]. Crystallographic studies have revealed that the phase change between the tetragonal and monoclinic lattices is highly anisotropic [10-12]. Therefore, it is expected that the measureable shape memory properties such as the transformation stress and strain will also be orientation dependent, much as is observed in shape memory metals [13-15]. However, a systematic experimental assessment of the orientation dependence of the shape memory effect in zirconia has yet to be carried out, likely due to the propensity for cracking during the transformation [16-19]. Recently, we have identified a method to avoid cracking in martensitic ceramics, by eliminating grain boundaries and using small samples with large surface-to-volume ratios [20-22], thereby reducing transformation mismatch stresses. With the ability to reversibly transform without cracking, such samples enable the possibility of systematically studying the orientation dependence of the martensitic transformation in ceramics.

In this work, we present a characterization of the effect of crystal orientation on martensitic transformations in zirconia ceramics. Using single crystal micro-pillars of zirconia doped with titania and yttria, an assessment of shape memory properties in terms of critical stress, transformation strain, and Young's modulus is conducted. Property orientation maps are calculated to facilitate comparison of the experimental results with theoretically expected values.

2. Materials preparation and characteristics

For studies of martensitic transformation in zirconia at room temperature, the composition must be tuned to bring the tetragonal/monoclinic transformation temperatures into the range of ambient conditions, and the ability to retain the austenitic tetragonal phase at room temperature is specifically desired. Accordingly, a variety of samples with different compositions were first produced, and thermally and structurally characterized to assess their suitability for studies of stress-induced martensitic transformation. We denote composition with the shorthand $x\text{Y}_2\text{O}_3\text{-}y\text{TiO}_2\text{-ZrO}_2$, with x and y indicating the molar percentage of yttria and titania respectively. Polycrystalline zirconia compacts were prepared using conventional ceramic fabrication procedures, the details of which can be found in our earlier work [22]. Nanosized powders of ZrO_2 , Y_2O_3 and TiO_2 were ball milled and compacted into pellets, followed by sintering at 1700°C for 6 hours in air. Differential scanning calorimetry (DSC, STA 449, Netzsch) was conducted in air from 25 to 1000°C on pellets with a range of compositions, with a heating and cooling rate of $10^\circ\text{C}/\text{min}$. X-ray diffraction (XRD, D8, Bruker) was conducted on bulk samples at room temperature, using copper k_α radiation at a scan rate of $0.02^\circ/\text{step}$ with 2θ ranging from 25 to 65° .

The inset in Figure 1(a) shows an exemplar DSC curve, with exothermic heat release on cooling through the martensitic transformation (to the monoclinic phase), and a corresponding endotherm during reversion to the austenite (tetragonal) phase on heating. The characteristic transformation temperatures A_s , A_f , M_s , M_f (respectively corresponding to austenite start and finish—the transformation to the tetragonal phase, and martensite start and finish—the transformation to the monoclinic phase) all decrease linearly with yttria concentration, as shown in Figure 1(a), until around 2 mol% Y_2O_3 , beyond which the clear thermal DSC peaks are no longer present, and the lines in Figure 1(a) are extrapolations. For

2 mol% yttria, the extrapolated lines lie well above room temperature, which suggests that in principle, these materials should have fully transformed to monoclinic martensite on cooling, but they did not, as explicitly confirmed with the XRD data shown in Figure 1(b). Therefore, the retained tetragonal phase at room temperature is metastable, giving these samples the unique ability to undergo stress induced transformation from the tetragonal phase to the monoclinic phase, and to then permanently retain the equilibrium monoclinic phase after unloading.

Based on the above results, a single composition was selected for further study, namely, $2Y_2O_3-5TiO_2-ZrO_2$. The sintered zirconia pellet was firstly polished with diamond slurry and heat treated at $1650^{\circ}C$ for 30 minutes to enhance grain boundary contrast. After coating with carbon (~ 20 nm in thickness), the surface morphology was imaged with scanning electron microscopy (SEM, in a JEOL 7600F with a field emission gun), as seen Figure 2(a). Since we are concerned specifically with small-scale samples having dimensions finer than the grain size of the bulk-processed material, we performed local chemical analysis with electron probe micro-analysis (EPMA, JXA-8500F, JEOL) to verify the composition, using a wavelength dispersive X-ray spectrometer at low accelerating voltage of 15 kV. The EPMA results indicate that all the pillars studied in this article have a composition of $2Y_2O_3-5TiO_2-ZrO_2$. The crystal orientation of each grain was determined with electron backscatter diffraction (EBSD, EDAX) and the orientation map can be seen in Figure 2(b). The crystal orientation was obtained by indexing the Kikuchi bands using a tetragonal zirconia phase file ($a = 3.608 \text{ \AA}$, $c = 5.184 \text{ \AA}$ [22]) and was considered successful if the confidence index was greater than 0.15. Each color corresponds to a different surface normal crystal orientation of tetragonal zirconia, as represented by the color coded stereographic triangle in Figure 2(b). Once the grain orientation was determined, individual

grains were subsequently milled with a focused ion beam (FIB, Nova600i Nanolab, FEI) with a constant accelerating voltage of 30 kV and variable currents. A three-step milling procedure was employed that includes creating a 40 μm diameter trench with 2.5 μm depth at 21 nA (to avoid tip-substrate interference as shown in Figure 2(c)), milling to the desired pillar size at 0.92 nA and final polishing at 28 pA. The final microscale pillars have diameters much smaller than the grain size, resulting in single crystal pillars as exemplified in Figure 2(d).

3. Pillar Micro-Compression and Martensitic Transformation

All the pillars reported in this study were based on the same elemental and phase composition, and differed only in crystallographic orientation. The pillars were compressed uniaxially from the top at room temperature, with a blunt cono-spherical diamond tip (20 μm in diameter) using a nanomechanical test platform (PI 85, Hysitron), as schematically illustrated in Figure 2(e). The load was applied in open loop control mode with a loading/unloading rate of 100 $\mu\text{N/s}$. The load and displacement were both measured along the laboratory z-axis. A typical single crystal pillar (pillar 2) is shown in Figure 3(a), with its corresponding load-displacement curve during compression illustrated in Figure 3(e). At the start of the compression test, the pillar was in the tetragonal phase and the slope of the initial linear elastic loading region corresponds nominally to the modulus of the tetragonal phase. Once the critical load was reached, a sudden and abrupt martensitic transformation from the tetragonal phase to the monoclinic phase took place in less than 2 ms and resulted in a large displacement plateau. After the transformation, there was continued elastic loading followed by elastic unloading when the applied load was removed. The residual displacement after unloading indicates that the pillar permanently changed shape and the magnitude of the residual displacement corresponds to the height change of the pillar in

Figure 3(b). Looking at the residual displacement in Figure 3(e) and the as-deformed pillar morphology in Figure 3(b), we observe a large shear distortion away from the compression axis. However, the top portion of the pillar where the tip was in contact remains essentially plumb and flat; the shape change seen in this pillar is not due to bending from off-axial loading, but rather is a result of the mandatory transformation shear associated with the martensitic transformation. The transformation appears to have occurred monolithically across all of its unconstrained volume in a single martensite domain, which is consistent with the observation of a single displacement burst in Figure 3(e).

For all of the pillars studied here, it was clear that only a partial transformation occurred, as revealed by the surface morphology after transformation, as in Figure 3(b). In this pillar and all the others studied, constraints at the top and bottom of the pillar apparently suppressed shape change near those regions, and in some pillars there was incomplete transformation within other regions in the pillar midsection as well. Such partial transformation is important when carrying out strain calculations (as will be described later in section 4.6), and to account for this, each pillar was examined via SEM after compression to evaluate the fraction transformed (f_{trans}) using a linear intercept method along the pillar axis as shown in Figure 3(b). Some pillars had clear demarcations between the phases, others showed less distinct markings, leading to uncertainty in the determination of transformation percentage and by extension the measured strains.

Martensitic transformations are reversible upon heating to a temperature higher than the austenite finish temperature, A_f . The thermally induced shape recovery of pillar 2 was examined by first heating to 450°C, where no recovery was observed (Figure 3(c)). Upon subsequent heating to 550°C, the pillar became erect again; in Figure 3(d) this is shown for Pillar 2 where the single martensite domain completely disappeared. These results indicate

that the austenite reversion temperature is above 450°C but below 550°C, which aligns very well with the extrapolations in Figure 1(a), which would expect the reversion to begin at 460°C and be completed by 520°C for this composition.

Another two pillars were prepared to directly observe the phase changes associated with the behaviors seen above, by FIB milling the single crystal pillars into thin lamellae that could be examined using transmission electron microscopy (TEM, 2100F, JEOL) and selected area electron diffraction (SAED). One pillar was prepared directly after FIB milling in the undeformed state and is shown in Figure 4(a). A high-resolution image was taken and the corresponding diffraction pattern shows that the image corresponds to the tetragonal phase aligned along the $[1\bar{1}\bar{1}]$ zone axis. The other pillar was subjected to similar uniaxial compression as described in Figure 3 and the deformed pillar was subsequently cut into lamellae and imaged by TEM (Figure 4(b)). Electron diffraction was performed across the specimen and two sets of SAED patterns were obtained. The pattern in the pillar center was best indexed as the monoclinic phase with a zone axis of $[101]$, whereas the pattern at the bottom of the pillar was best indexed as the tetragonal phase with a zone axis of $[111]$. This observation agrees with the as-deformed SEM image in Figure 3(b), confirming that the pillar is partially transformed. The lamellar TEM sample of the second pillar was then heat treated at 550°C and imaged by TEM again. The film was found to be straightened after heat treatment (Figure 4(b)) and the diffraction pattern was best indexed as tetragonal with a zone axis of $[11\bar{2}]$. These results offer further more direct evidence of the forward and reverse martensitic phase transformations inferred from the responses in Figure 3.

4. Orientation Effects on the Martensitic Transformation

4.1. Micro-Pillar Compression

Similar micro-compression data to that of Figure 3(e) were gathered for a variety of pillars with the same dimensions but different crystallographic orientations. Figure 5(a) shows the orientations of all the pillars' compression axes on the tetragonal standard stereographic triangle. A diverse range of responses is observed, with the majority of the pillars experiencing martensitic transformation as exhibited by the signature load plateaus on their load-displacement curves, as well as clear phase contrast in subsequent SEM imaging, as shown in Figure 5(c). In contrast, some pillars fractured upon loading, as exemplified by the load-displacement curve and post-fracture pillar image in Figure 5(d). A third class of responses is illustrated Figure 5(b), in which there is evidence of planar slip in the as-deformed pillar image, with permanent deformation sustained by plasticity, and which was not recoverable upon heating up to 600°C. In Tables 1 and 2, data for all the pillars tested are compiled, including the pillar dimensions, orientations, and characteristic shape memory properties, all of which will be discussed in turn in subsequent sections.

4.2. Elastic Modulus

For tetragonal pillars, the theoretical elastic modulus along the z-axis can be calculated from the known orientation information and the compliance tensor of tetragonal zirconia. This is accomplished by rotating the standard compliance tensor into the specified lab frame, written using the full Einstein tensorial notation as [23],

$$\begin{aligned} \frac{1}{E_{33}} &= s'_{33} = s'_{3333} = a_{3m}a_{3n}a_{3o}a_{3p}s_{mnop} \\ &= (a_{31}^4 + a_{32}^4)s_{11} + (2a_{31}^2a_{32}^2)s_{12} + (2a_{31}^2a_{33}^2 + 2a_{32}^2a_{33}^2)s_{13} + (a_{33}^4)s_{33} + \\ &\quad (a_{32}^2a_{33}^2 + a_{31}^2a_{33}^2)s_{44} + (a_{31}^2a_{32}^2)s_{66} \end{aligned} \quad (1)$$

where the a_{ij} terms represent the components of the rotation matrix found from the EBSD orientation data in Table 1, and the compliances of tetragonal zirconia $S_{11}, S_{33}, S_{44}, S_{66}, S_{12}, S_{13}$ are taken from Kisi [24].

The loading moduli of the tetragonal pillars were measured based on the slope of the loading curve during compression and the geometry of pillars in Table 1. They are plotted against the theoretically predicted values from Equation 1 in Figure 6(a). While the measured modulus is reasonably correlated with the theoretical value, there is better quantitative agreement at higher moduli. We attribute the experimental variation to several aspects of the micro-compression testing such as substrate and tip compliance, minor misalignments, indentation compliance at the point of contact of the tip; these are all known deficiencies of microcompression testing and the present apparently high compliance is in line with results from the field on other materials [25, 26].

A more nuanced view of orientation dependence of Young's modulus of tetragonal zirconia is provided in the stereographic triangle in Figure 6(b). The theoretical Young's modulus is highly anisotropic, ranging from 160 GPa near (111) to 290 GPa near (100). The loading moduli of our pillars follow the correct general trends, with orientations close to (111) having smaller moduli, typically less than 100 GPa, whereas pillars with larger moduli, greater than 100 GPa, are for orientations close to (001) and (100).

Since the compression tests trigger a transformation from tetragonal to monoclinic zirconia, it should be possible to examine the monoclinic elastic modulus upon unloading. However, as noted earlier, most pillars did not fully transform to the monoclinic phase, so the elastic behavior during unloading should reflect the mixed properties of tetragonal and monoclinic phases; the unloading modulus is therefore not analysed here.

4.3. Transformation Correspondences and Thermodynamics

The transformation in zirconia can be described by the lattice correspondence between the tetragonal unit cell and the resulting monoclinic unit cell [13, 27]. For tetragonal zirconia, there are three possible correspondences each producing the same final monoclinic structure but differing on whether the tetragonal c axis becomes the monoclinic a, b, or c axis [13, 28]. Here we use the mathematical formalism presented by Simha [29] but refer to the correspondences as A, B, and C as described by Kriven [30]. For each correspondence there are four possible variants, leading to 12 possible routes through which the transformation can occur. Ideally, in general modes of loading, only one variant is preferred. In what follows, we rule out any variant from correspondence A because it is not favored thermodynamically, as correspondence A has larger principal distortions than B [30] (sum of the squares of the eigenvalues of the Bain strain), which is often taken as a measure of the strain energy. Furthermore, correspondence A is also not observed experimentally in the literature [2, 10], leaving only correspondence B and C with 8 total possible variants. The preference among correspondence B and C will be discussed in more detail in section 4.4.

The Gibbs free energy of transformation (ΔG_{Total}) from tetragonal to monoclinic is written [31, 32],

$$\Delta G_{Total} = \Delta G_{Chemical} + \Delta G_{Elastic} + \Delta G_{Friction} - \sigma_{shear} \epsilon_{Shear} \quad (2)$$

where all the ΔG terms on the right hand side represent energies that must be overcome for the transformation to occur. The chemical free energy ($\Delta G_{Chemical}$), which is a function of the enthalpy of transformation ΔH and the temperature T , can be expressed as [13],

$$\Delta G_{Chemical} = \frac{\Delta H \rho}{M} \left(1 - \frac{T}{T_0} \right) \quad (3)$$

where ρ is the density, M is the molar mass, and T_0 is the equilibrium transformation temperature between monoclinic and tetragonal zirconia. The elastic term ($\Delta G_{Elastic}$)

represents the elastic energy that is stored in the bulk region, in and around the transformed zone; this term is expected to be very small for micro-pillars since there is limited bulk material to store elastic energy, and mismatch strains are accommodated at free surfaces. The friction term ($\Delta G_{Friction}$) encapsulates any dissipated energy caused by the transformation front interacting with obstacles such as defects and free surfaces. It is possible to include additional terms such as interface and surface energies but these are typically negligible compared to the other terms [33]. The mechanical term ($\sigma_{shear}\epsilon_{shear}$) in equation 2 is the energy supplied as work by the applied stress. For the transformation to occur, this work must equal or exceed the sum of the other ΔG terms on the right hand side, bringing ΔG_{Total} to zero.

4.4. Transformation Stress

The applied stress (σ_{App}) can be resolved into a shear component (σ_{shear}) along the transformation shear direction in the shear plane [34] by using the Schmid factor (SF),

$$\sigma_{App} = \frac{\sigma_{shear}}{\cos(\chi) \cos(\lambda)} = \frac{\sigma_{shear}}{SF} \quad (4)$$

where χ is the angle between the shear plane normal and the compression axis, and λ is the angle between the shear direction and the compression axis. Equation 4 predicts an inverse relationship between the Schmid factor and the measured transformation stress. The tetragonal unit cell faces are the viable shear planes, and their plane normals effectively have indices matching the plane indices, since the tetragonal double cell [35] has only a slight tetragonality of 1.7% ($c/a = 1.017$) and the axes are therefore nearly Euclidean.

The most common criterion for choosing the preferred variant is the maximum resolved shear stress criterion [28], which predicts that the preferred variant is the one with the largest shear stress acting on its shear plane along a shear direction [13]. According to Equation 4, this selection criterion chooses the variant with the most negative Schmid factor

(SF_{max}) since this variant requires the smallest applied compressive axial stress to attain the critical condition for transformation, leading to

$$\sigma_{App} = \frac{\frac{\Delta H \rho}{M} \left(1 - \frac{T}{T_0}\right) + \Delta G_{Elastic} + \Delta G_{Friction}}{SF_{max} \cdot \varepsilon_{Shear}} \quad (5)$$

The micro-compression results exhibited a wide range of critical stresses at which the transformation occurred, ranging from 0.58 to 8.7 GPa, suggesting that the critical transformation stress depends strongly on the crystal orientation. This concept is well studied in shape memory metals [13, 34] but has yet to be explored in a shape memory ceramic material. In Figure 7 we present the orientation dependence of the measured transformation stresses, and for purposes of discussion we duplicate the presentation several times in order to explore lattice correspondences B and C individually and together. In Figure 7, the color legend is presented so that pillars in the blue regions are expected to have the lowest transformation stresses, and those in the red regions should have the higher values. Close inspection of Figure 7(a) shows that the agreement is very poor if the transformation is assumed to follow lattice correspondence B, while examination of Figure 7(b) shows a generally very good alignment for correspondence C. The combined analysis of correspondence B and C in Figure 7(c), rather than improving the alignment, merely degrades the level of agreement seen between experiment and theory in Figure 7(b). The good agreement of experiment and theory in the case of correspondence C is best illustrated by plotting σ_{App} directly against SF_{max} , which is shown in Figure 8. A least-squares fitting of the data shows a relationship of $\sigma_{Meas} = 0.53 SF_{max}^{-1}$, which matches very well with the expected form of Equation 5. The 95% confidence bands, shown by the gray shaded region, covers almost all pillars that transformed, except three outliers (pillar 2, 18

and 31) which are highlighted with asterisks and are not included in the fitting; these will be discussed later.

Based on the above analysis, we may take correspondence C as the only active correspondence in the present work, and we can now draw further insight from Figure 7(b) and (d), which respectively show the pillars that transformed (b) and fractured or slipped (d). The measured transformation stress generally increases as expected as SF_{max} decreases, as explicitly shown in Figure 7(b). But for very low SF_{max} , fracture or slip become more likely, which makes intuitive sense since those pillars, requiring larger applied loads to transform, can first exceed the cleavage or slip stress instead.

At first glance, it is unusual to observe slip in an unconfined ceramic material at room temperature, but there is precedent in small samples such as we consider here [17, 36-38]. For example, Zou and Spolenak demonstrated plastic slip for certain orientations of micron-scale pillars made from ionic crystals (NaCl, KCl, LiF, and MgO) [36], while Montagne et al. [37] and Kiani et al. [38] showed similar results in Al_2O_3 and in SiC respectively. We expect the preferred slip planes to be {110}-type in the tetragonal single cell BCT system [39], corresponding to {100} in the tetragonal double cell FCT system used in this article (crystal slip is also observed on {100} planes in cubic zirconia [40]). According to Equation 4, these planes will experience the largest shear stress when they are aligned 45° from the applied stress direction. This condition is met for pillars that have their (110) crystal plane normal aligned with the [001] direction, and indeed, the pillars that exhibit slip traces in Figure 5(b) align with this expectation in light of their near-[110] orientations as shown in Figure 7(d). A general observation in Figure 8 is that there are three distinguishable regions in terms of pillar behavior for various SF_{max} ; these are labeled across the top of the figure. For $SF_{max} > 0.3$, all the pillars transformed without any fracture or slipping, suggesting a

reliable transformation region for shape memory ceramics in orientations lying in the blue or dark blue regions of the maps of Figure 7(b). For $SF_{max} < 0.1$, on the other hand, the pillars either fractured or slipped, as seen in the red regions in Figure 7(b). Interestingly, the boundary between transformation and fracture/slip in orientation-space is not sharp; upon close inspection we observe signs of a gradual transition region between these two states at intermediate values of SF_{max} between 0.1 and 0.3, i.e. for orientations lying in the light blue or cyan regions of the maps of Figure 7(b). In these regions, we suspect that the normal stresses are approaching values high enough to cause cleavage, which at these intermediate orientations is beginning to compete with the transformation. In fact, in a few pillars, the competition between transformation and cracking is abundantly clear, with evidence of both occurring in a single pillar. Figure 9 shows two views of pillar 6 showing regions of transformation and a small axial crack near the top of the pillar.

At a given Schmid factor in Figure 8, some pillars like pillar 6 apparently both transform and crack, while others only transform or only crack; which response is triggered in a given pillar must depend upon some aspect other than the maximum Schmid factor alone. For example, small variations in factors such as pillar geometry (pillar taper, aspect ratio), mechanical loading (pillar-tip alignment) and orientation (EBSD identification) could be involved here. These factors might further help explain the three outlier pillars marked with asterisks in Figure 7 and 9. Pillar 2 and pillar 31 have very low Schmid factors, 0.03 and 0.003 respectively, so are not expected to transform when, somewhat surprisingly, they do. A plausible explanation for this is orientation identification error, for example if these pillars had spanned multiple grains along their height, and were indexed only to a single orientation not dominant in the transformation response. Outlier pillar 18 has an intermediate Schmid factor (0.19) so might be expected to either transform or fracture, but

it transforms at much lower stresses than other similar pillars. Again, pillar taper, pillar-tip misalignment, or even a surface defect that initiates the transformation are all possible source of error.

Another possible physical origin for the scatter, outliers, and differentiation among pillars of similar Schmid factor in Figure 7 and 9 is the effect of other stress components on the transformation. The transformation of zirconia, while dominated by shear, also involves volume change and thus non-shear tensor terms also contribute to its activation. The competing mechanisms of slip and cracking also have normal- or hydrostatic-stress dependencies. We have conducted a Schmid analysis with an added, adjustable normal stress term acting on the shear plane, opposing the volume change of the transformation. We find that this can produce a modest improvement in the trends of Figure 8, but with no major change in interpretation; the analysis is omitted here for brevity.

The slope of the fit line in Figure 8 represents the sum of all the ΔG terms divided by shear strain (ϵ_{Shear}) from Equation 5. The theoretical value according to the chemical free energy is calculated to be 0.69 GPa by using Equation 3 and the values shown in Table 3, and this value is surprisingly close to the measured slope of 0.53 GPa. The agreement, while encouraging, is subject to some caveats. First, though the elastic energy term is close to zero for micro-pillars as stated earlier, the determination of the frictional free energy contribution is very challenging without knowledge of the types of defects present and their distribution. Second, the enthalpy of transformation used in the calculations here was measured from a bulk specimen and that would incorporate the elastic free energy, which in turn, would cause the bulk enthalpy to be larger than the micro-pillar enthalpy. Nonetheless, the chemical energy term is expected to be the most important term in Equation 5 for

micro-pillars, so the agreement between its value and the experimental one is considered good.

4.5. Size Effects

The above section outlined multiple possible sources of scatter in the micro-compression tests (possible pillar-tip misalignment, orientation uncertainty, slight variation in pillar taper and aspect ratio, normal stress effects, etc.). Beyond these factors, however, there is one systematic physical contribution to scatter which is relatively unexplored in shape memory materials of any kind: orientation-dependence of sample size effects. It is reasonably well established that sample size has a strong effect on the critical transformation stress in martensitic materials [41, 42], and although we are not aware of prior study of orientation effects upon size dependency, it seems possible that the various free energy terms in Equation 5 which are sensitive to structure/sample size may also be sensitive to sample orientation.

Sample size effects have not, to our knowledge, been explored before in single crystal ceramic shape memory materials with control on crystal orientation, and our data in Figure 10 present a first preliminary examination of these effects. Interestingly, as shown in Figure 10(a) and (b), generally the critical stress for martensitic transformation increases with the pillar diameter. This observation agrees with the results reported in our earlier work, for similar zirconia pillars without orientation control [21]. However, this trend is of opposite to those in shape memory metals [33, 42], and may speak to a dominance of a different term in the energy balance of Equation 5 for the present materials vis-à-vis metals. For example, one major difference between metals and ceramics is their stiffness; comparing the isotropic Young's modulus of zirconia to a Cu-Ni-Al shape memory alloy [43] (200 vs 25 GPa, respectively), zirconia is notably stiffer. This extends to other measures of

elastic stiffness [44] such as the cubic bulk modulus, (176 vs 130 GPa), and the boundaries of the cubic shear moduli (μ' - μ'' , 114-59 vs 9-95 GPa). As a result, the elastic strain energy term on martensitic transformation in Equation 5 might be much more significant in ceramics than in metals.

The size effects in shape memory metals are usually observed to be dominated by internal friction, but if we hypothesize that in the ceramics the elastic energy is dominant, then in fact smaller samples may be expected to have lower transformation stresses as we see in Figure 10. For example, Chen and Schuh [33] showed with elastic calculations that in Cu-Ni-Al shape memory alloys (with Young's modulus of 26 GPa), the critical stress could increase by ~20 MPa as the pillar diameter increased to a "bulk" response. With an order of magnitude higher stiffness, it is reasonable to expect hundreds of MPa of increase in transformation stress of zirconia ceramics at bulk size scales. This issue will require further study, but it does point to unique possible size effects in shape memory ceramics as a class.

What is more interesting for the present discussion is that the size dependency in shape memory zirconia appears to be orientation dependent; Figure 10(c) shows that the slope of the size-effect trendline appears to be different for the two different crystallographic orientations studied here. Given that several terms in Equation 5 are known to be influenced by the interaction of martensite with sample surfaces, it seems possible that by extension they may depend upon crystallography of how the martensite variant interacts with the surface. We are not aware of significant discussion of this issue for any thermoelastic martensitic material, and clearly more work is needed. For the main part of the present study this effect has been minimized: for all of the orientation studies in Figure 5-8, we specifically strove to keep the pillar diameter constant. However, the sample size

effect in Figure 10 appears to be very sensitive, and small variations in pillar diameter could add to the experimental scatter in our results.

4.6. Transformation Strain

A characteristic feature of the mechanical response of a shape memory material is the strain plateau caused by the rapid phase transformation, and many such plateaus were observed in the specimens tested in this work. To properly estimate the transformation strain associated with a given orientation's transformation, the variation of transformation fraction (f_{trans}) discussed in Figure 3 and 4 must be accounted for. The reported axial transformation strain ($\Delta\epsilon_{trans, meas}$) is then a corrected measured strain,

$$\Delta\epsilon_{trans, meas} = \frac{\Delta h_{plateau, meas}}{f_{trans} * H_{pillar}}, \quad (6)$$

where $\Delta h_{plateau, meas}$ is the displacement measured in the plateau region.

To calculate the theoretical transformation strain, we used the Bain strain tensor (B) which can be derived from polar decomposition of the lattice deformation tensor, F , which converts a tetragonal unit cell to a monoclinic one [29]. Here it is assumed that the biasing stress applied during micro-compression results in the formation of only one variant of martensite and therefore no lattice invariant shear was included in the calculation. The transformation strain can then be calculated for all variants for any vector v as

$$\begin{pmatrix} v'_x \\ v'_y \\ v'_z \end{pmatrix} = B \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} \quad (7)$$

To calculate the expected axial strain during a pillar compression test, we begin with the [001] vector and apply the Bain strain tensor to obtain a new vector, v' . The deformation along the compression axis is represented by the component v'_z that lies along the compression direction, and the true strain can then be found using the following equation.

$$\varepsilon_z = v'_z - 1 \quad (8)$$

In order to apply this analysis to all possible crystal orientations, we rotate the Bain strain tensor over all of orientation space using,

$$\begin{pmatrix} v'_x \\ v'_y \\ v'_z \end{pmatrix} = RBR^T \begin{pmatrix} v_x \\ v_y \\ v_z \end{pmatrix} \quad (9)$$

where R and R^T represent the rotation matrix generated from the Euler angles and its transpose, respectively. Figure 11(a) maps the expected strain for all tetragonal orientations for correspondence C, as well as the measured experimental strain of transformed pillars.

The map in Figure 11(a) shows that there is a large range of possible transformation strains from positive 3% (i.e., the transformation would actually favor tensile elongation along the compression axis) to negative 7% (i.e., a compressive transformation strain). Several important features emerge from Figure 11(a). For example, areas with the largest expected strains are identified as being near the [101] pole. It is generally true that pillars with orientations near the bottom central regions of the stereographic triangle seem to be those that achieve the most transformation strain without fracture. Another especially interesting feature of Figure 11(a) is those regions near the [001], [100], and [110] poles, where positive strains are expected from crystallographic analysis. Since a positive strain is not compatible with the applied compressive stress, we would expect that these orientations could not transform during compression. It is therefore an encouraging point of agreement that the pillars in these regions tended to exhibit fracture or crystal slip without transformation.

Figure 11(b) plots the theoretically expected strains against the measured strains for all transformed pillars. The outlier pillars in terms of transformation stress are also highlighted with asterisks and as expected, they are also outliers in terms of strain. Apart

from these outliers and some experimental scatter, the agreement between theory and experiment is reasonable. The least-squares linear fit and the 95% confidence bands shown in gray cover most of the data, and encompass the expected $\epsilon_{\text{Meas}} = \epsilon_{\text{Theo}}$ trend.

5. Conclusions

We have experimentally examined the strong crystallographic orientation dependence of the martensitic transformation behavior for shape memory zirconia micro-pillars during compressive loading. By identifying a composition of zirconia that is in the tetragonal phase at room temperature and which transforms to the monoclinic phase under load, and by further compressing a variety of micro-pillars with diverse orientations, the following major conclusions were drawn:

- The orientation effect leads to large, systematic variations in the mechanical properties of shape memory zirconia. The loading modulus in the tetragonal phase varies by over a factor of two across orientation space, in a trend that agrees with expectations based on rotation of the compliance tensor.
- Pillars with different orientations transform at different stress levels, in rough agreement with a simple Schmid factor shear projection analysis, and the experimental data fits best with tetragonal-monoclinic transformation correspondence C. However, there is a transition between stress-induced transformation and fracture/slip for unfavorably oriented crystals; orientations near [001] and [100] require such large applied stress for the transformation that fracture occurs before the transformation is triggered. Pillars with orientations near [110] exhibit crystal slip and we attribute this to favorable alignment of slip planes with the maximum resolved shear stress.

- The transformation strains measured experimentally also align with expectation based on projection of the transformation strain along the test axis. Pillars with orientations near [100] not only require large transformation stresses, but may never be able to transform under compressive loading due to strain incompatibilities; they favor a transformation that leads to tensile elongation under compressive loading. The actual pillar behaviors reflect a combined influence from the orientation dependence of transformation stress and strain.
- The transformation seen in the present zirconia ceramics is found to be reversible upon the application of heat, in the temperature range from ~460-550°C. In addition to the recovery of the tetragonal phase, such treatments give rise of shape recovery as well.

The crystallographic orientation dependence of shape memory microscale pillars over a wide orientation range has practical implications for micro-scale shape memory applications; the response is widely variable across orientation space, suggesting that tight control of orientation and/or texture will be an important direction for engineered shape memory ceramics.

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Graphical abstract

Figures and Tables

Figure 1: (a) Characteristic temperatures for the martensitic transformation between tetragonal and monoclinic phases of $xY_2O_3-5TiO_2-ZrO_2$ (mol%), with inset DSC curve of $1Y_2O_3-5TiO_2-ZrO_2$. (b) XRD patterns conducted at room temperature with characteristic tetragonal (t) and monoclinic (m) zirconia peaks of $xY_2O_3-5TiO_2-ZrO_2$.

Figure 2: (a) SEM image of the bulk microstructure of $2\text{Y}_2\text{O}_3\text{-}5\text{TiO}_2\text{-ZrO}_2$ (mol%) ceramic sintered at 1700°C for 6 hours, (b) an EBSD map of the corresponding grains obtained by indexing with the tetragonal zirconia phase (with the color-coded stereographic triangle of tetragonal zirconia showing surface normal orientations), (c) low-magnification and (d) high magnification SEM images of a ceramic FIB-milled pillar before compression (at a viewing angle of 52°). (e) A schematic illustration of the micro-compression on the pillars using a $20\text{ }\mu\text{m}$ cono-spherical diamond tip.

Figure 3: SEM images of Pillar 2 when (a) freshly milled, (b) after compression, (c) after heating at 450°C and (d) after heating at 550°C. The viewing angle is 52°. (e) The load-displacement curve of Pillar 2 during compression and unloading. The transformed zone in (b) was used to measure the percent transformed (f_{trans}).

Figure 4: TEM images and diffraction patterns of (a) as-milled pillar, (b) pillar after compression and lamellae after heat treatment at 550°C .

Figure 5: (a) The crystal orientations of pillars on a tetragonal standard stereographic triangle, with typical load-displacement curves and corresponding as-deformed pillar morphology for pillars that (b) slipped, (c) transformed and (d) fractured.

Figure 6: (a) The predicted Young's modulus of tetragonal zirconia as compared with the experimentally measured loading modulus for all the pillars. (b) Standard stereographic projection for the theoretical Young's modulus of tetragonal zirconia, along with data points corresponding to experimentally measured loading moduli of tetragonal pillars.

Figure 8: The measured critical stress σ_{App} vs SF_{max} for correspondence C. The fit line includes transformed pillar data only (without the three outliers), obtained by least-squares fitting the parameters a and b to the equation $\sigma_{Meas} = a SF_{max}^{-1}$, and with 95% confidence bands shown by the gray shaded region.

Figure 9: SEM micrograph of pillar 6 showing a transformation zone and an axial crack.

Figure 10: The stress-strain behaviors of pillars with diameters ranging from 0.8 to 2.5 μm and crystal orientations of (a) [257.9, 60.2, 147.4] and (b) [258.8, 42.7, 289.4]. (c) The critical transformation stress as a function of pillar diameter for pillars with two crystal orientations.

Figure 11: (a) Standard stereographic triangle of tetragonal zirconia showing the transformation strain, including contours indicating the smallest (compressive) theoretically expected strain for correspondence C. (b) Theoretical transformation strain versus experimentally observed transformation strain for correspondence C, and with 95% confidence bands shown by the gray shaded region.

Table 1

Pillar effective diameter, $d_{eff} = \sqrt{1/3(d_{top}^2 + d_{top}^2 d_{bot}^2 + d_{bot}^2)}$, (d_{top} and d_{bot} are the top and bottom pillar diameters respectively), height and orientations of all the pillars in this work.

Pillar ID	Pillar behavior	Pillar Dimensions		Orientation (Euler Angles)		
		Effective Diameter (μm)	Height (μm)	E1	E2	E3
1	Transformed	1.2	4.6	285	45	319
2		1.2	3.9	177	92	18
3		1.2	3.5	3	146	306
4		1.2	3.3	194	46	235
5		1.2	3.5	84	142	118
6		1.2	3.4	183	162	172
7		1.2	3.4	53	122	299
8		1.2	3.3	75	117	301
9		1.2	3.2	250	34	206
10		1.2	3.2	258	60	147
11		1.2	3.8	245	33	197
12		1.2	3.3	135	113	0
13		1.2	3.4	300	59	352
14		1.2	3.5	99	117	351
15		1.2	3.6	265	63	16
16		1.2	3.4	262	45	179
17		1.2	3.7	97	118	359
18		1.2	3.6	68	104	305
19		1.2	3.8	187	57	234
20		1.1	3.2	187	107	176
21		1.2	3.7	310	80	167
22		1.1	3.3	80	115	174
23		1.1	2.5	180	111	175
24		1.1	3.3	248	72	171
25		1.1	3.1	236	82	200
26		1.2	2.9	32	75	340
27		1.2	3.4	178	83	357
28		1.1	2.6	30	108	288
29		1.2	2.5	195	107	192
30		1.2	2.8	217	79	16
31		1.1	3.0	68	90	301
32	Fractured	1.2	3.6	233	15	296
33		1.2	2.7	73	101	357
34		1.2	3.6	243	72	53

35		1.2	3.6	105	98	385
36		1.1	3.6	157	9	185
37		1.1	3.5	185	17	184
38		1.2	3.7	91	104	353
39		1.2	3.3	178	88	349
40		1.1	2.4	200	90	177
41	Slipped	1.1	2.5	15	85	320
42		1.1	2.5	8	94	126
43		1.1	2.3	163	89	224

Table 2

The calculated transformation percentage, loading modulus, critical stress, transformation strain and dissipated energy for all the pillars in this work. Theoretical Schmid Factors and strains are those calculated for correspondence C.

Pillar ID	Transformation % (f_{trans})	Critical Stress		Transformation Strain (%)		Loading Modulus (GPa)	
		Experiment (GPa)	Theory (SF_{max}) (unitless)	Experiment	Theory	Experiment	Theory
1	87	0.65	0.38	3.0	4.7	59	169
2	69	2.32	0.03	3.3	3.2	137	287
3	75	1.20	0.38	3.6	5.3	70	176
4	65	0.81	0.41	3.9	4.9	52	169
5	100	1.04	0.43	4.3	5.7	77	172
6	47	2.60	0.29	1.5	4.8	103	212
7	68	0.81	0.39	4.2	4.5	67	165
8	49	1.30	0.34	3.0	4.0	88	193
9	51	1.24	0.42	4.6	5.8	76	175
10	86	1.11	0.35	3.7	4.1	69	188
11	50	0.71	0.43	4.6	6.1	67	176
12	84	0.71	0.36	6.2	4.4	79	172
13	76	0.62	0.44	6.5	5.4	72	170
14	76	0.78	0.40	5.5	4.9	69	198
15	74	0.83	0.39	5.5	4.6	69	202
16	79	0.58	0.50	6.3	6.0	61	170
17	28	0.67	0.41	2.2	5.0	70	198
18	49	0.62	0.19	1.8	5.0	56	214
19	71	0.78	0.37	4.8	4.1	80	185
20	63	2.59	0.28	2.0	3.7	191	235
21	83	3.53	0.17	2.1	1.9	209	192
22	69	1.43	0.38	1.3	5.1	139	204
23	96	2.61	0.33	4.7	4.4	160	225
24	82	2.81	0.29	3.7	3.7	198	206
25	41	3.98	0.12	1.4	1.0	204	201
26	55	3.49	0.23	2.0	2.7	163	194
27	33	3.79	0.12	2.2	1.1	265	278
28	22	2.13	0.28	2.0	3.4	174	192
29	71	2.64	0.27	2.6	3.4	127	223
30	54	3.58	0.18	3.0	2.0	170	193
31	69	4.33	0.003	5.7	-1.2	177	235
32	/	2.46	0.23	/	/	75	219

33	/	3.18	0.18	/	/	145	235
34	/	3.57	0.23	/	/	78	196
35	/	2.76	0.12	/	/	129	249
36	/	3.10	0.15	/	/	156	236
37	/	2.29	0.28	/	/	124	215
38	/	3.61	0.23	/	/	132	254
39	/	5.92	0.04	/	/	309	287
40	/	8.73	0.0002	/	/	338	240
41	/	5.77	0.07	/	/	150	255
42	/	5.20	0.05	/	/	134	277
43	/	6.57	0.02	/	/	159	250

Table 3

Related parameters for the calculation of theoretical transformation stress for $2\text{Y}_2\text{O}_3$ - 5TiO_2 - ZrO_2 (mol%). The transformation strains are taken from the Bain strain tensor of correspondence C.

Trans. Enthalpy, ΔH (KJ/mol)	Density, ρ (g/cm ³)	Molar Mass, M (g/mol)	Testing Temp. T (K)	Equilibrium Temp. T_0 (K)	Transformation Shear Strain, ϵ_{Shear}	Transformation Normal Strain, ϵ_{Normal}	Calculated $\frac{\Delta H \rho}{M} \left(1 - \frac{T}{T_0}\right) / \epsilon_{\text{Shear}}$ (GPa)
2 ^a	6.081 ^b	123.1 ^c	298	700 ^d	$\pm 8.12\%$	0.77%	0.69

^a Extrapolated from the area in the exothermic peaks in experimental DSC of bulk ceramics (

Figure 1(a))

^b Using measured lattice parameters: $a = 5.103 \text{ \AA}$, $c = 5.184 \text{ \AA}$ [22]

^c Using a weighted average of molar masses of ZrO_2 , Y_2O_3 , and TiO_2

^d $(A_s + M_s)/2$, extrapolated from the experimental DSC of bulk ceramics (

Figure 1(a))