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Shape Memory and Superelastic Ceramics at Small Scales

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Abstract: Shape memory materials are a class of smart materials able to convert heat into mechanical strain (or strain into heat), by virtue of a martensitic phase transformation. Some brittle materials such as intermetallics and ceramics exhibit a martensitic transformation, but fail by cracking at low strains and after only several applied strain cycles. Here we show that such failure can be suppressed in normally brittle martensitic ceramics by providing a fine-scale structure with few crystal grains. Such oligocrystalline structures reduce internal mismatch stresses during the martensitic transformation, and lead to robust shape memory ceramics capable of many superelastic cycles to large strains; here we describe samples cycled up to 50 times, and samples which can show strains over 7%. Shape memory ceramics with these properties represent a new class of actuators or smart materials with a unique set of properties that include high energy output, high energy damping, and high temperature usage.

One Sentence Summary: Fine-scale shape memory ceramics capable of many actuation cycles to strains up to 7%.

Main Text: Shape memory materials are solid-state transducers, able to convert heat to strain and vice versa. They exhibit two unique properties: 1) the shape memory effect, which is the ability to transform to a "remembered" pre-defined shape upon the application of heat and 2) superelasticity, which is the ability to deform to large strains recoverably, while dissipating energy as heat. The underlying mechanism in crystalline shape memory materials is a thermoelastic martensitic transformation between two crystallographic phases that can be induced thermally (shape memory effect) or with the application of stress (superelasticity) (*1, 2*). The ability to transduce heat and strain renders shape memory materials useful in a wide variety of actuation, energy damping, and energy harvesting applications (*3-7*). To be of practical use, the material must be able to accommodate the extreme deviatoric strains associated with the

phase transformation without cracking or otherwise sustaining damage. There are, however, a number of materials with martensitic transformations that cause cracking, most often because shape distortions in adjacent crystal grains are incommensurate with one another, inducing large mismatch stresses and triggering fracture.

One conspicuous class of brittle materials—ceramics—falls into this category. A number of brittle ceramics exhibit martensitic transformations, and thus are candidate shape memory materials (*8-10*). For example, zirconia has a well-studied martensitic transformation (*8, 11-14*) between tetragonal and monoclinic phases with associated shear strains of up to 15% (*15, 16*). However, the mismatch stresses in polycrystalline zirconia prevent shape memory behavior. At strains of only about ~2%, cracking is observed after only a few transformation cycles (*17*). This is unlike shape memory metals such as Ni-Ti, which can access large strains up to ~8% and, at lower strain levels can be reversibly transformed up to millions of cycles (*18*).

As the fundamental cause of cracking in ceramics with martensitic transformations is transformation mismatch stresses, our strategy is to reduce these stresses through two main approaches. First, we reduce the size scale of the specimen itself—a smaller ceramic has a higher surface area to volume ratio, and the free surfaces can contribute to stress relaxation. Second, we strive to reduce the number of crystals within the volume of the specimen—an "oligocrystalline" or even single crystalline material contains fewer grain junctions where the individual grain transformation strains will compete. Both of these concepts have been explored in shape memory metals (*7, 19-21*); here we extend their application to ceramics.

Our experiments employed polycrystalline zirconia doped with either ceria, yttria or both, processed into solid polycrystalline specimens using conventional methods (*22, 23*). From these polycrystalline specimens, micron-scale pillars were fabricated using focused ion beam milling. The resulting pillars were sized to be smaller than or near the average grain size of the ceramics, and so were either single crystalline or oligocrystalline (defined in (*21*) as having more surface area than grain boundary area) in every case. We applied loads to pillars both in a mode of axial compression and in bending, using a Hysitron nano-mechanical test platform with a blunt conospherical tip (*24*).

A typical stress-strain curve for a 16 mol% CeO_2-ZrO_2 superelastic specimen loaded in compression is shown in Fig. 1A. Loading begins in the tetragonal phase (which here, in the context of shape memory materials, is referred to as "austenite") and after an initial linear elastic

response a critical stress is reached that induces the phase change into the monoclinic phase (which is referred to as "martensite"). This is seen as a slope reduction in the curve, which evolves as the transformation progresses to large strains of ~7%. Upon unloading, there is a linear elastic response of the martensite phase until another critical stress—that for reversion to austenite—is reached and a second lower plateau is seen. Complete unloading leads to a full recovery of the strain. The total energy dissipated during the cycle is quantified by the area within the curve and is listed in Table S1.

The stress-strain curve shown in Fig. 1A is characteristic of the many hundreds that we have measured on a variety of fine-scale austenitic zirconia ceramic pillars. We find these samples exhibit all the attributes of a good superelastic material. This includes large strains up to 7% in some pillars as well as the ability to cycle reversibly through the transformation many times. A series of typical stress-strain curves during cycling are shown in Fig. 1B and show that superelastic properties are present over many cycles. There is a gradual evolution of the stress-strain hysteresis loop with cycling that is expected as a superelastic material becomes "trained" to a particular kinematic transformation pathway (25). In addition to the results in Fig. 1, a variety of other specimens were cyclically loaded without failing to dozens of cycles; up to 50 cycles have been applied to a single pillar. More stress-strain curves exhibiting a range of different achievable stress and strain combinations for different pillars can be found in Fig. S4-S11. Some pillars did experience cracking (see (24) for more details), but only after many more cycles than have been previously reported in polycrystalline specimens (17).
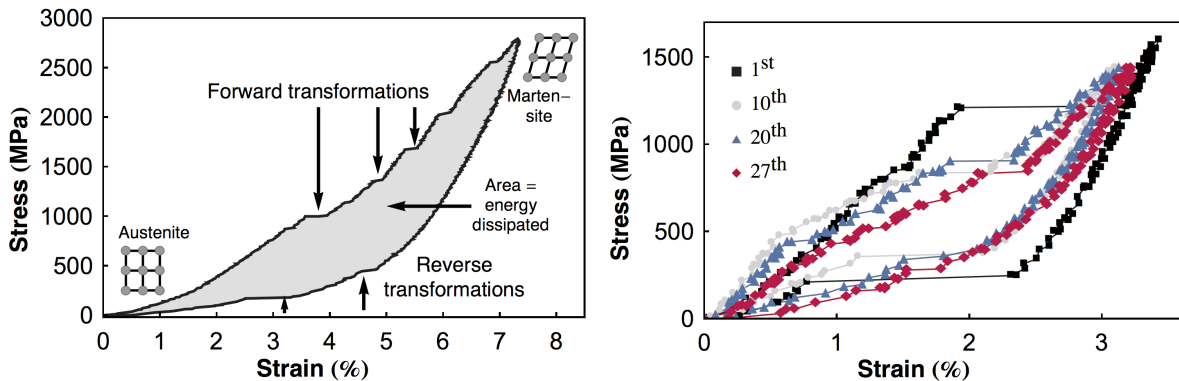

Fig. 1. (A) Micro-compression stress-strain curve for superelastic zirconia pillar, (effective diameter d_{eff}=1.82 μm, pillar B in (24)) in which initial elastic loading of austenite is followed by

forward transformation plateaus during the formation of martensite. This is followed by elastic unloading and reverse transformation plateaus with a reversion to austenite. (**B**) stress-strain curves for a pillar with d_{eff}=1.19 μm (Pillar G in *(24)*), the superelastic response stabilizes after ~10 cycles.

Fine-scale zirconia pillars in the tetragonal (austenite) phase are also found to exhibit excellent shape memory properties when deformed at a temperature in between the martensite and austenite transition temperatures, as shown in the scanning electron microscope images in Fig. 2. Upon loading at room temperature, shape change is effected by a stress-induced transformation from austenite to martensite, and when the load is removed the new shape remains. This is illustrated for an example pillar of 8 mol% CeO_2-0.5 mol% Y_2O_3-ZrO_2, loaded in a bending mode, between Figs. 2A and 2B, to an approximate strain of 8% *(24)*. The occurrence of the stress-induced martensitic transformation is also evidenced by stripe patterns formed on the lateral side of the pillar that we interpret as martensite variants, as shown in Fig. S12A. Subsequent heating above the austenite transition temperature causes the martensite to revert to austenite, which is crystallographically constrained to return the material to its original shape. This shape recovery is shown in Fig. 2C after heating the specimen to 500°C for 2 hours, and is accompanied by the near complete disappearance of the martensite variant stripe patterns on the side of the pillar (Fig. S12B).
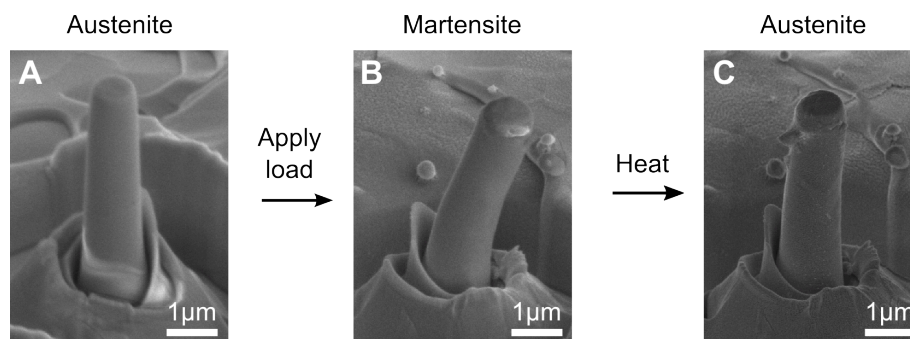

Fig. 2. (**A**) Pillar milled from austenite before deformation (d_{eff}=1.02 μm, pillar J in *(24)*) (**B**) pillar after bending at room temperature in the martensite phase (**C**) heating induces the phase transformation to austenite and leads to recovery of the original shape, which is retained upon cooling to a state comparable to that in A.

The results shown in Figs. 1 and 2 confirm that zirconia ceramics are capable of both the

shape memory effect and superelasticity, and the demonstration of these effects to large strains and through multiple cycles departs significantly from the prior literature on the martensitic transformation in zirconia. As noted earlier, the cracking and failure of zirconia ceramics during such transformations is widely known. Cracking has only been suppressed in prior work by completely eliminating the transformation itself, as for the fully stabilized zirconia ceramics in wide technological usage today (*8*). Some prior reports have suggested that shape memory properties may be possible in zirconia (*17, 26-28*), but these also reported failure at low strains (~1-2%) after only one or a few cycles.

The prospect of a new class of shape memory materials based on fine-scale ceramics is potentially technologically interesting, because ceramics occupy a different region in property-space than any other shape memory materials.

The very high strength of ceramics permits access to shape memory and superelasticity at very high stress levels relative to shape memory metals. Fig. 3A shows a single superelastic curve for one of our zirconia ceramics as compared to literature data for two common shape memory alloys; the achievable actuation stress in the ceramic is four or more times that in the metals. A more thorough evaluation of the actuation stresses and strains of shape memory ceramics vis-à-vis other actuators of many kinds is presented in Fig. 3B. Shape memory ceramics offer work output values approaching 100 MJ/m^3, and on this basis exceed not only shape memory alloys but also mechanical systems such as hydraulics.

Fig. 3A also highlights another opportunity for shape memory ceramics in the area of energy damping. The amount of mechanical energy damped into heat is reflected by the hysteresis area in the stress-strain curves of Fig. 3A. Because the ceramic is stiffer and accesses larger stresses, it has a greater opportunity to expand the hysteresis area, and can thus reversibly damp considerable mechanical energy as compared to shape memory metals. For reversible loading we calculate a damping merit index for beams in bending or compression, $\text{Merit Index} = \eta \cdot E^{1/2}$, where E is the Young's modulus and η is the loss factor (*24*). For superelastic zirconia we obtained merit index values of ~2. This value is about double that reported in Cu-Al-Ni micro-scale shape memory alloys (*7*).

Another property axis on which ceramics are generally differentiated from metals is

temperature; ceramics are generally more refractory than metals, and as such, shape memory ceramics should be thought of as a class of potential high-temperature shape memory materials. Through tuning of the composition, zirconia ceramics can exhibit transformation temperatures ranging from 0-1200ºC (Fig. S3). This is in contrast to shape memory metals which have maximum transformation temperatures of ~500ºC; a graphical comparison is made in Fig. 3C.

A final interesting prospect for shape memory ceramics is as a structural material subject to one-time mechanical loading events, where repeatable transformations are not required. In such cases the ceramic can be loaded all the way to failure, and unlike a conventional brittle ceramic, the superelastic ceramic can exhibit substantial apparent ductility (or malleability) before fracture, by virtue of the phase transformation. Fig. 3D illustrates this with two compressive stress-strain curves for zirconia. The classical response achieves elastic strains of 1-2% with some limited incipient plasticity just before brittle fracture, but the shape memory ceramic transforms, dissipating energy through a strain of about 7% in this single example, with theoretical uniaxial transformation strains up to 10% possible depending on crystallographic orientation. The result is a ceramic that dissipates exceptionally large amounts of energy upon fracture, ~35 MJ/m^3, approaching the magnitude for structural metals. The combination of ceramic strength levels with apparent ductility offers interesting opportunities in mechanical design.

While much work remains to optimize these materials for any proposed application, the unusual properties of the shape memory ceramics reported here, as well as other ceramics that exhibit martensitic transformations (*10*) and may thus exhibit similar properties, offer a strong motivation to pursue their development.
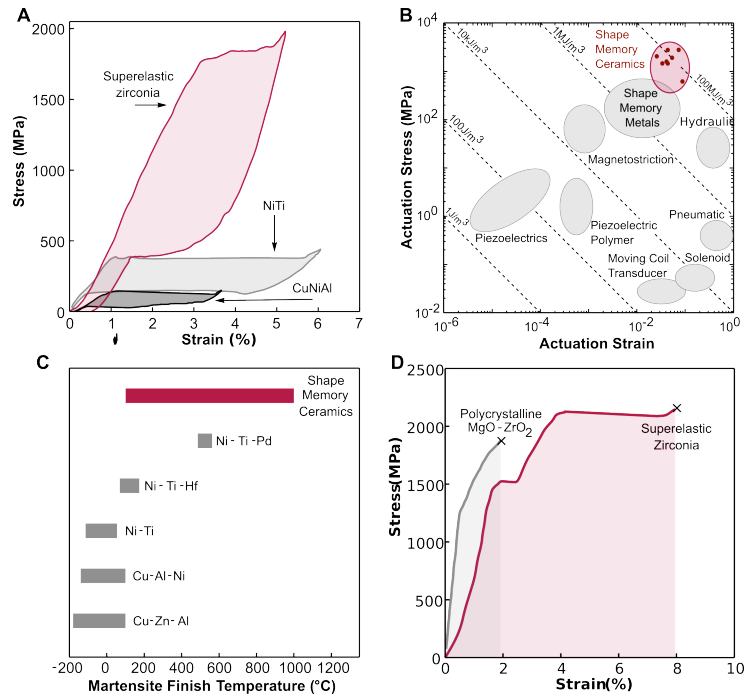
Fig. 3. (**A**) Stress-strain curves for superelastic zirconia (η=0.18, merit index =2.5), NiTi (η=0.17, merit index=1.5) (*29*), CuAlNi (η=0.19, merit index=0.9) (*7*). (**B**) actuator stress and strain for various actuator materials and systems, constant specific work indicated by dashed lines, adapted from (*3*) (**C**) martensite transformation temperatures for shape memory ceramics and metals (*30*); ceramics have much higher operational ranges (**D**) stress-strain curves for superelastic zirconia and MgO partially stabilized zirconia (*31*); upon loading to fracture significantly more energy is dissipated in the fine-scale superelastic zirconia.

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Supplementary Materials:

Materials and Methods

Figures S1-S12

Table S1

References 32-34