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

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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.

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

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produced, and thermally and structurally characterized to assess their suitability for studies of stress-induced martensitic transformation. We denote composition with the shorthand xY_2O_3-$yTiO_2$-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 h 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 °C/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°/step with 2θ ranging from 25 to 65°.

The inset in Fig. 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 Fig. 1(a), until around 2 mol% Y_2O_3, beyond which the clear thermal DSC peaks are no longer present, and the lines in Fig. 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 Fig. 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.

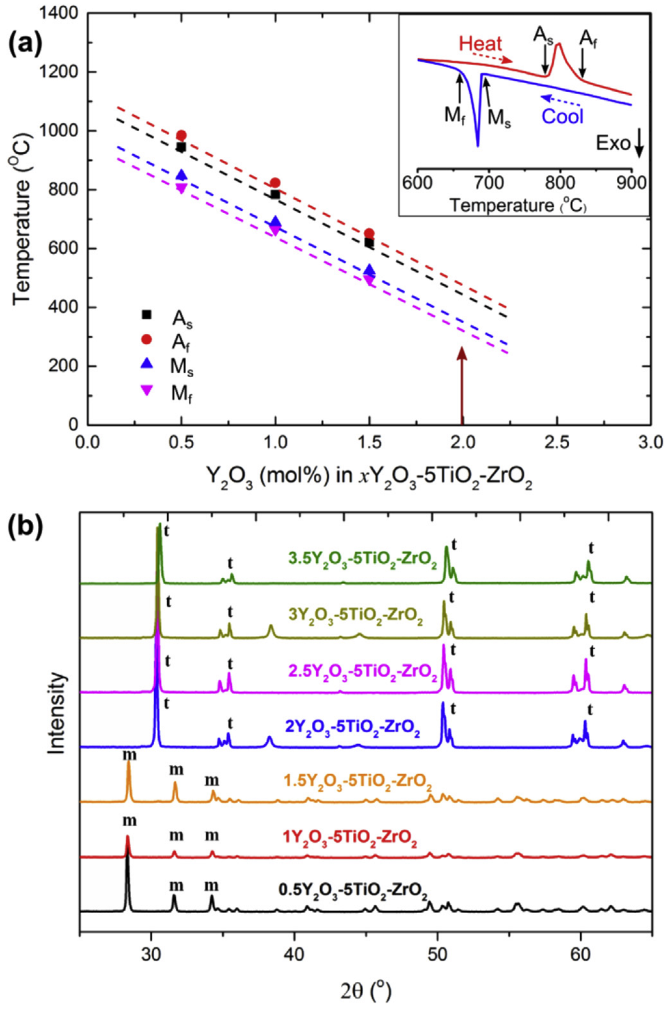

Fig. 1. (a) Characteristic temperatures for the martensitic transformation between tetragonal and monoclinic phases of xY_2O_3 $-5TiO_2$ -ZrO_2 (mol%), with inset DSC curve of $1Y_2O_3$ -$5TiO_2$ -ZrO_2. (b) XRD patterns conducted at room temperature with characteristic tetragonal (t) and monoclinic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

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 °C for 30 min 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 Fig. 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 a 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 Fig. 2(b). The crystal orientation was obtained by indexing the Kikuchi bands using a tetragonal zirconia phase file ($a = 3.608$ Å, $c = 5.184$ Å [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 Fig. 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 Fig. 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 Fig. 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 Fig. 2(e). The load was applied in open loop control mode with a loading/unloading rate of 100 μN/s. The load and displacement were both measured along the laboratory z-axis. A typical single crystal pillar (pillar 2) is shown in Fig. 3(a), with its corresponding load-displacement curve during compression illustrated in Fig. 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