Evidence for a toughening contribution from domain switching, a deformation mode akin to twinning, has been sought in uniaxial tension and compression, biaxial compression, and on the fracture surfaces of several tetragonal zirconia polycrystalline (TZP) ceramics. Only in biaxial compression was domain switching found. In other cases, textures of both the tetragonal and monoclinic phases were due to stress coupling with transformation shear strain. The lower bound of the critical stress for domain switching is placed at the bend strength of TZP, which can exceed 1000 MPa. Although thermal activation may lower the critical stress sharply, at lower temperatures, domain switching is not likely to be an important toughening mechanism.

A mechanically induced transformation from a tetragonal (t) to a monoclinic (m) polymorph near the crack tip is responsible for a high fracture toughness, relative to other ceramics, for many zirconia-containing ceramics. As a toughening method the mechanically induced t-to-m transformation suffers from inherent limitations. First, the upper limit for transformation toughening is determined by the t-to-m equilibrium temperature, which in pure ZrO₂ is around 1150°C. Equilibrium temperatures in partially stabilized zirconia (PSZ) are even lower. Second, the toughening contribution has a steep temperature dependence, decreasing rapidly as the temperature is raised. Other toughening methods applicable for a wider temperature range with a lower temperature sensitivity are of interest in view of these inherent limitations. Recently, an alternative toughening mechanism based on ferroelastic domain switching in a tetragonal zirconia polycrystalline (TZP) was proposed. In this mechanism, the stress-induced alignment of the c axis of the t phase along the maximum principal stress axis results in a shape change of a pure shear type. The magnitude of the pure shear, on the order of 0.04 or less, arises from the different cell spacing along c and a directions. Virkar and Matsumoto suggested that the higher-than-expected toughness in some untransformable TZP, including a Ce-TZP that they studied, could be due to this novel mechanism. They also suggested that domain switching can operate in both the metastable and the stable tetragonal phase regimes, thus serving as an active toughening mechanism at very high temperatures. Nonetheless, results presented by Reidinger and Whalen on Y-TZP and results on other zirconia alloys (Yb-, Sc-, and Ce-TZP) from our laboratory suggest that the toughening contribution via domain switching is minimal in its extent and occurrence.

The "transformation" strain in zirconia due to domain switching can be ascertained from single-crystal experiments of the type performed by Lankford and coworkers. Their experiments revealed a thermally activated strain burst of ~0.005 in axisymmetric compression of (100) oriented PSZ single crystals at room and elevated temperatures. These (100) cubic single crystals of yttria-doped zirconia were reported to contain 50 vol% of tetragonal precipitates in a cubic matrix. Each precipitate consisted of approximately equal-size tetragonal domains with c axes parallel to each of the cubic (100) axes. The maximal strain available for domain switching in the (100) PSZ single crystals is roughly 0.0033 for compression and 0.0066 for tension. The strain values come about from assuming a tetragonality (c/a) ratio of 1.02 and an initial volume fraction of the t variant oriented with parallel to the stress axis of ¼. Thus, some other deformation mechanisms must contribute to accommodation of the strain burst observed in compression. Nonetheless, even if contributions from other deformation mechanisms are not distinguished, the strain burst prior to exhaustion of domain switching is very small. In fact, the t-to-m transformation strain for some Ce-TZP loaded in compression is almost 10 times greater.

The toughness increment due to domain switching can be estimated following a similar line to the reasoning behind the McMeeking–Evans equation for transformation toughening. In essence, the toughness increment should be proportional to the shape strain, and inversely proportional to the critical stress. As already established above, the magnitude of the shape strain from domain switching is very small compared to what is known for the t-to-m transformation, which entails a simple shear of ~0.16 in addition to a volumetric increase of ~0.05 of the unit cell. Therefore, in order to qualify as an effective toughening mechanism, domain switching must involve a relatively low critical stress, thus permitting formation of the relatively large crack tip process zone needed to confer significant toughening in light of the small shape strain for domain switching. In theory, the mechanics of domain switching should be similar to other shear-based deformation modes, e.g., twinning and dislocation slip. The magnitude of the critical stress to trigger domain switching can be directly measured in tension or compression tests as they yield identical results. The domain switching zone near the crack tip should be similar in shape to the plastic zone commonly observed in metals. The mechanics of domain switching are distinctly different from that of the t-to-m transformation, which is a form of dilatant plasticity.

Evidence of domain switching in zirconia was originally offered following XRD examination of ground surfaces. Two primary observations were made:

1. No monoclinic phase was detected;
2. The XRD pattern indicated that the c axis aligns preferentially normal to the ground surface. Since the stress state of the ground surface is one of biaxial compression, with zero stress normal to the ground surface, these observations are in accord with domain switching. Simultaneous observations have been reported for surface treatment of BaTiO₃,12–14 which, along with KNO₃,15 single crystals, among others, can be deformed through motion of domain boundaries under an applied stress. Domain boundaries in these materials, analogous to twin boundaries, move under an applied stress such that the domains which produce the most favorable accommodation of the current stress state expand at the expense of the less favorably oriented domains.

We have verified the above results under the same stress state using a different technique in a hot-pressed sample containing 2.25 mol% Yb₂O₃. This zirconia is slightly oxygen deficient at the completion of hotpressing, allowing the introduction of a biaxial compressive stress state in the near surface region by locally restoring the oxygen stoichiometry during a short air anneal. The restoration of oxygen stoichiometry to the surface typically produces a whitened surface layer surrounding a darker core. XRD of the surface area (A in Fig. 1) reveals nearly the same relative peak heights as for a tetragonal zirconia with a ground surface, but with a smaller amount of peak broadening. Peak height ratios for (002) and (113) reflections are shown in Table I for a random powder and hot-pressed, oxygen-
This is also contradictory to the expected response from a domain switching mechanism, which should produce an alignment of the c axis along the stress axis but not normal to the tensile surface. Similar findings have been obtained for Y-TZP, Sc-TZP, and Ce-TZP in our laboratory.

The above results raise some questions concerning the effectiveness of domain switching as a toughening mechanism. For all the TZP examined to date in our laboratory, formation of the m phase was coincident with the inelastic deformation which yields toughening. No evidence for domain switching of the t phase was found on the fracture, tensile, or compressive surfaces of bend specimens. Hence, the critical stress for domain switching must be very high, at least higher than the bend strengths of these TZP. Indeed, an upper bound of the critical stress for domain switching can also be estimated, based on its occurrence in planar surfaces under a biaxial compressive stress state. In this case, the effective stress for domain alignment is equivalent to a tensile stress (normal to the plane) of a magnitude equal to the biaxial compressive stress. Noting that the dominant (t-m) transformation is entirely suppressed in the present case, because of its strong pressure sensitivity,4,9,11 inasmuch as the biaxial stresses for such a state cannot exceed the uniaxial yield stress of a highly stabilized TZP, we estimate the critical stress for domain switching to be on the order of 3 GPa by referring to the compressive yield stress data of fully stabilized cubic zirconia obtained by an indentation method.26

In view of these high critical stresses, no significant contribution of domain switching to toughness is expected for low and moderate temperatures. Evidence for the operation of domain switching in favorably aligned single-crystal Y-Psz obtained by Lankford and co-workers5,6 confirms the relatively high critical stress. However, like the yield stress of the fully stabilized cubic zirconia,16,26 this critical stress decreases with temperature rather steeply,5,6-8 raising the possibility of a toughening benefit from domain switching at higher temperatures. A strong contribution of thermal activation is reasonable if we envision coherent interface motion as the rate-determining step in domain switching. Direct microscopic observations of this type have been provided by Chiao and Chen in orthorhombic-to-monoclinic transformation of ZrO$_2$ using an in situ TEM technique.17 They found that the interface migrates by a glide mechanism of interface dislocations, for which thermal activation volume (i.e., in forming the critical double-kink configuration before each unit glide step) should be small. This is consistent with the large thermal activation observed by Lankford and co-workers in domain switching5 by and Reyes-Morel in transformation plasticity.9,18 On the other hand, although the stress responsible for domain alignment in hot-pressing at 1400°C is very low, on the order of 30 MPa, it seems more likely that the process could be partly assisted, if not entirely dominated, by a diffusive mechanism during powder densification and grain growth. And yet, an essentially diffusion-controlled phase transformation has no utility for toughening, since fracture is a relatively fast process.

The tetragonal texture obtained on fracture and tensile surfaces of bend specimens in the presence of t-to-m transformation remains to be explained. These and other results19 suggest a simple pattern, namely, that the t crystallites with a c axis along the maximum principal stress axis are depleted first during t-to-m transformation. This observation can be rationalized in terms of the stress coupling with the transformation strains. The concept used here is the same as that of the Schmid factor in dislocation slip, since the stress coupling with the transformation shear strain is formally identical with the stress coupling with slip, as schematically illustrated in Fig. 2. We will assume a c correspondence between the phases and let the a plane be the habit plane, such that the shear direction coincides with c. (The following conclusion stands if we choose the c plane as the habit plane. Furthermore, the small tetragonality of the unit cell is of minor importance since it is the much larger transformation shear which dominates the stress-transformation strain coupling.) Using this analogy, we can anticipate that the most favorably oriented t variants are ones with both their c and a axes at 45° from the stress axis z. In this case, the quadratic projection of the c vector onto the stress axis, cos$^2$ (c,z), is simply ½. On the other hand, the average quadratic projection of the c axis to the stress axis in a random polycrystal, cos$^2$ (c,z), is obviously ½ by virtue of symmetry. Since the most favorably oriented t variants for t-to-m transformation have a quadratic

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<th>Table I. X-ray Diffraction Data for 2.25 mol% Yb-TZP</th>
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<td>Peak height ratio*</td>
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<td>I(002)/I(200)</td>
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<td>I(113)/I(311)</td>
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*Standard deviations for these values were generally <0.05.
projection greater than that of the average assembly, their transformation leaves an effect of a decreased (cos^2 θ) observed in our experiments.

More refined considerations must account for t reflections in tension and in compression are identical. This is largely confirmed. More refined considerations must account for all the tetragonal reflections, monoclinic reflections, and the possibility of domain switching (mechanical twinning) in the monoclinic phase as well. Elsewhere, we have demonstrated that all the features of texture evolution in both the t and m phases can be rationalized for different stress states with such considerations. Lastly, attention is drawn to a possible toughening mechanism in zirconia-containing ceramics which operates at or slightly above the t-to-m equilibrium temperature. We recently found a pseudoelectrode effect in a Ce-TZP containing 12 mol% CeO₂ wherein the t-to-m transformation and the accompanied transformation plasticity can be completely reversed during unloading. A large hysteresis in the stress-strain curve was observed, suggesting that a pseudoelectrode toughening mechanism is possible in this ceramic. The most interesting aspect of this mechanism is that no monoclinic phase can be detected on fracture surfaces of specimens loaded to failure under similar conditions. In other words, no permanent transformation zone remains near the crack surfaces. It seems likely that some “untransformable” TZP may be toughened up to a fairly high temperature by this mechanism. Indeed, evidence already exists in the literature.  

ACKNOWLEDGMENTS
We are indebted to Dr. P. E. Reyes-Morel and Mr. T. S. Sheu for fruitful discussions, and grateful for the experimental assistance of Mr. P. Yang.

REFERENCES

Comment on “Effects of Free Silicon on the α to β Phase Transformation in Silicon Nitride”  
Peter E. D. Morgan  
Rockwell International Science Center, Thousand Oaks, California 91360  

WITH reference to the above communication to the American Ceramic Society, it appears that the authors missed a key paper in which the conversion of α → β Si₃N₄ via a liquid Si phase was detailed before.  

REFERENCES  