Ceramic laminates have been fabricated with thin layers, containing a mixture of unstabilized zirconia (MZ-ZrO$_2$) and alumina (Al$_2$O$_3$), sandwiched between thicker layers of alumina that contain a small fraction of Y$_2$O$_3$-stabilized tetragonal ZrO$_2$ to inhibit grain growth. The MZ-ZrO$_2$ undergoes a tetragonal-to-monoclinic phase transformation during cooling to produce biaxial compressive stresses in the thin layers. Cracks that extend within the thicker alumina layers can be arrested by the compressive layers to produce a threshold strength, i.e., a strength below which the probability of failure is zero. Laminates composed of Al$_2$O$_3$ layers 315 ± 15 μm thick and Al$_2$O$_3$/MZ-ZrO$_2$ layers 29 ± 3 μm thick exhibit a threshold strength of 507 ± 36 MPa, regardless of the MZ-ZrO$_2$ content, for volume fractions ≥0.35. These results, piezoelectric stress measurements, and microstructural observations suggest that microcracking produced during the transformation reduces the magnitude of the compressive stresses achieved, which in turn limits the magnitude of the threshold strength.

I. Introduction

The strength of ceramics must currently be described by statistical parameters because of the uncontrolled distribution of flaws or cracks that cause failure.\(^1\)\(^\text{1-4}\) Unlike ductile materials that exhibit plastic deformation mechanisms limiting the relationship between small flaws and strength, the failure strength of most elastic ceramic materials typically is inversely dependent on the size of small flaws or cracks that, in many cases, are detectable only by observations of fracture origins. Today, the statistical nature of ceramic strength must be taken into account by designing for an acceptable failure probability.

There are several new approaches that can be used to improve the reliability of ceramic materials. One is to reduce the size of the heterogeneities within the powder by passing a dispersed slurry through a filter, and then forming the component from the slurry state, as recently introduced by Yu and Lange.\(^1\)\(^\text{1-3}\) Filtration during the formation of monolithic bodies is essential because processing, even in a clean room, has no effect on the strength degrading heterogeneities within the powder. A second approach is the use of equally spaced, thin compressive layers that prevent cracks from producing catastrophic failure below a threshold stress.\(^4\) A crack originating in a thicker tensile layer extends at a low stress, arrests at the interfaces of the thin compressive layers, and then extends through the compressive layers with increasing applied stress. Failure occurs at a threshold stress (σ$_\text{THR}$) that causes the crack to fully extend through the compressive layers. With alternating compressive and tensile layers of thickness $t_1$ and $t_2$, respectively, a biaxial compressive strain ($\epsilon_b$) arises when the thinner $t_1$ layers either have the lower coefficient of thermal expansion (CTE) or exhibit a volumetric increase because of either a phase transformation or a chemical reaction. The residual stresses in the thin and thick layers are given by\(^5\)

\[ \sigma_1 = \sigma_c = \epsilon_b E_i \left( 1 + \frac{t_1}{E_1 E_2} \right) \]

and

\[ \sigma_2 = -\sigma_1 \frac{t_1}{t_2} \]

respectively, where $\sigma_c$ is the biaxial compressive stress, $E_i = E_i/(1 - \nu_i)$, $E$ is the Young’s modulus, and $\nu$ is the Poisson’s ratio. The tensile stresses in the thick layer are small when $t_1/t_2$ approaches 0, i.e., the same conditions that maximize $\sigma_c$.

A stress-intensity factor was developed for the extension of the crack straight through the compressive layers with increasing applied stress.\(^4\) By rearranging the stress intensity function, the smallest stress (σ$_\text{THR}$) required to cause the crack to fully extend through the bounding compressive layers can be expressed as\(^6\)

\[ \sigma_{\text{THR}} = \frac{K_c}{\pi \left( t_2 \left( 1 + \frac{2t_1}{t_2} \right) \right)^{1/2}} + \sigma_c \left[ 1 - \left( 1 + \frac{t_1}{t_2} \right)^2 \sin^2 \left( \frac{1}{1 + \frac{2t_1}{t_2}} \right) \right] \]

where $K_c$ is the critical stress intensity factor of the compressive layer material. In effect, the compressive layers truncate the statistic strength distribution usually observed for brittle materials. A quick examination of Eq. (2) shows that the threshold strength increases with $\sigma_c$, $K_c$, and is inversely proportional to the distance between the compressive layers. Factors that maximize the threshold strength under specific conditions have been described elsewhere.\(^6\)

Initial studies to test Eqs. (1) and (2) were conducted with ceramic laminates composed of thick layers (600 μm) of Al$_2$O$_3$ and thin layers (37 μm) of Al$_2$O$_3$/mullite containing a residual compressive stress of ~1 GPa, which produced a threshold strength of 482 ± 20 MPa.\(^4\) Although the threshold strength was in close agreement with that predicted from Eq. (2), it was observed that the crack bifurcated within the compressive layer instead of propagating straight through, as in the derivation of Eq. (2). More recent experiments by Rao et al.\(^1\) have shown that the crack will propagate straight through the compressive layer and...
result in a threshold strength predicted by Eq. (2) when either the compressive stress or the compressive layer thickness is small. On the other hand, the crack is observed to bifurcate through the compressive layer and produce a threshold strength much larger than that predicted by Eq. (2) when the compressive stress or compressive layer thickness is larger.\textsuperscript{8} The phenomena causing bifurcation and the stress intensity function that describes bifurcation are under development.\textsuperscript{8}

For experiments reported here, thick Al\(_2\)O\(_3\) layers and thin compressive layers containing a mixture of Al\(_2\)O\(_3\) and unstabilized zirconia (MZ-ZrO\(_2\)) were used to produce the composite. Previous work with Al\(_2\)O\(_3\)/MZ-ZrO\(_2\) mixtures has shown that compressive stresses can be formed in both a three-layer composite, with Al\(_2\)O\(_3\)/MZ-ZrO\(_2\)/TZ-ZrO\(_2\) outer layers surrounding a central Al\(_2\)O\(_3\)/stabilized zirconia layer,\textsuperscript{9,10,15} and in laminates composed of Al\(_2\)O\(_3\)/MZ-ZrO\(_2\) layers sandwiched between either Al\(_2\)O\(_3\) or Al\(_2\)O\(_3\)/stabilized zirconia layers.\textsuperscript{13} The compressive surface stresses were shown to enhance the strength of the three-layer bars, as compared with a monolithic Al\(_2\)O\(_3\)/zirconia material, and internal Al\(_2\)O\(_3\)/MZ-ZrO\(_2\) layers under a compressive stress are expected to improve mechanical performance as well.

In our system, the compressive stress was produced by the combination of a phase transformation and a thermal expansion mismatch. On cooling from the densification temperature, the MZ-ZrO\(_2\) in the thin layers transforms from the tetragonal to the monoclinic structure, accompanied by a volume expansion of \(\sim 4\%\).\textsuperscript{14} This volume increase, combined with the thermal expansion mismatch between the layers, creates a residual, biaxial compressive strain given by

\[ \epsilon = [(\alpha_t - \alpha_c)\Delta T]_{10} + \epsilon_T + [(\alpha_t - \alpha_c)\Delta T]_{1m} \quad (3a) \]

and

\[ \epsilon_T = 0.013\phi \quad (3b) \]

in which \(\alpha\) are the CTEs of the thin (denoted as “1”) and thick (denoted as “2”) layers before \((t)\) and after \((m)\) the transformation, \(\Delta T_1\) is the change in temperature from the densification to the transformation temperature, \(\Delta T_2\) is the change in temperature from the transformation to room temperature, and \(\epsilon_T\) is the linear dilatational strain produced during the phase transformation of the ZrO\(_2\), where \(\phi\) is the volume fraction of the MZ-ZrO\(_2\) in the thin layers. Because of the differential thermal expansion, small tensile stresses are developed in the thin layers before the transformation and small compressive stresses are developed after the transformation, but the majority of the residual compressive stress is produced by the phase transformation. As shown below, the high-residual compressive stresses predicted from Eqs. (1) and (3) were not observed, apparently because of the microcracking that accompanied the phase transformation. However, large threshold strengths were observed despite the apparent lack of very high-compressive stresses.

II. Experimental Procedures

Alumina (AKP-30, \(d_{50} = 0.4 \mu m\), Sumitomo Chemicals, Tokyo, Japan) and both Y\(_2\)O\(_3\)-free and 3% Y\(_2\)O\(_3\)-stabilized zirconia (TZ-0 and TZ-3YS, \(d_{90} = 0.3\) and 0.4 \(\mu m\), Tosoh, Tokyo, Japan) were used to fabricate the laminar composites. All powders were formulated as highly dispersed slurries with deionized water and tetramethyl ammonium hydroxide salt (TMA-OH), at a pH well above the isoelectric point of alumina (\(pH_{IEP} = 9\)), using an ultrasonic liquid processor (Model W-380 Sonicator, Heat Systems-Ultrasonics, Inc., Farmingdale, NY). A slurry containing 0.30 volume fraction of solids, composed of 0.95 volume fraction Al\(_2\)O\(_3\) and 0.05 volume fraction Y\(_2\)O\(_3\)-stabilized ZrO\(_2\) (TZ-ZrO\(_2\)), was used to form the thicker tensile layers. The TZ-ZrO\(_2\) was used to control the grain size of the Al\(_2\)O\(_3\) during densification. Slurries containing 0.15 volume fraction of solids, composed of Al\(_2\)O\(_3\) and 0.05, 0.2, 0.35, 0.5, 0.65, 0.8, or 0.95 volume fraction MZ-ZrO\(_2\), were prepared to form the thin compressive layers. The transformational strains associated with the MZ-ZrO\(_2\) were used to vary the amount of residual compressive stress achieved during cooling. All slurries were attrition-milled for 1.5 h (Szegvari Attritor, Union Process, Akron, OH; 3 mm 3Y-ZrO\(_2\) milling media), rolled for at least 12 h, sonicated again, and then stirred for 30 min before use.

Rectangular plate specimens \(\sim 70 \text{ mm} \times 60 \text{ mm} \times 2.5 \text{ mm}\) were produced by a sequential slip-casting procedure, which has been described elsewhere.\textsuperscript{15} Each laminate was composed of four Al\(_2\)O\(_3\)/MZ-ZrO\(_2\) compressive layers (29 \(\pm 3 \mu m\) thick), alternately sandwiched between the thicker Al\(_2\)O\(_3\)/TZ-ZrO\(_2\) tensile layers (315 \(\pm 15 \mu m\) thick). Each plate was dried in air at 70°C, and then fully densified by heating in air at 1500°C for 2 h. The dense laminates were diamond ground and cut into flexural bar specimens, which were diamond ground to a final dimension of \(\sim 2 \text{ mm} \times 2 \text{ mm} \times 60 \text{ mm}\). Monolithic plates of Al\(_2\)O\(_3\) (containing 0.05 volume fraction of TZ-ZrO\(_2\)) were also fabricated by slip casting; they were used as standards.

The threshold strength of each laminar material was determined by measuring the flexural strength of specimens containing a pre-existing crack introduced with a Vickers indenter. One of the lateral faces (perpendicular to the layer orientation) of each specimen was diamond polished to facilitate layer visibility and the placement of a small Vickers indent. A single Vickers indent of 0.5, 1.5, or 2.5 kg was placed in the center thick Al\(_2\)O\(_3\) layer of each flexural specimen to produce small precracks of varying size, which were measured with an optical microscope (Model Eclipse ME600P, Nikon, Japan). These indents were carefully placed to ensure that the precracks remained centered in the layer, far from the compressive layer interfaces. Monolithic specimens were also polished and indented at identical loads. For each laminate or monolith, at least five specimens with the 0.5 kg indent were tested, and at least two specimens were tested for both the 1.5 and 2.5 kg indent conditions. Additionally, unindented monoliths were tested for strength variability comparisons. Unindented laminate specimens were not tested, because failure would have initiated from very small processing or machining flaws at a very high stress, and as a result the critical stress (\(\sigma_{f,CR}\)) required to drive the crack through the compressive layer would not have been measured.

Four-point bending tests were performed on a screw-driven mechanical testing machine under displacement control (Model 8562, Instron Systems, Canton, MA), with inner and outer spans of 13.05 mm and 30.2 mm, respectively, at a cross-head speed of 0.01 mm/min. The stress at failure was calculated by substituting the bar and loading-span dimensions into the bending beam formula for 4-point flexural loading, giving

\[ \sigma_f = \frac{3P_f(b-s_o)}{2bd^2} \quad (4) \]

where \(P_f\) is the failure load, \(s_o\) and \(s_i\) are the outer and inner span lengths, \(b\) is the specimen width, and \(d\) is the specimen height.

Fractured specimens were inspected by both reflected light optical microscopy and scanning electron microscopy (SEM; Model JSM-6300F, JEOL USA, Peabody, MA) to determine the source of failure and examine the paths of crack extension on the surface of each specimen. To observe the crack path beneath the surface, specimens were loaded close to their failure strength of each laminate and extended into the compressive layers during testing, remained intact. At least 100 \(\mu m\) of material was ground away from each tensile surface, to remove both the indent and any pre-existing edge cracks, and the specimens were repolished and inspected under an optical microscope.

The transformational strains of the thin layers containing MZ-ZrO\(_2\) were estimated by measuring the transformation strains of monolithic bar specimens (2 mm \(\times 4 \text{ mm} \times 10 \text{ mm}\)) with the same compositions as the thin compressive layers. The dilatational strains produced by these dense monoliths, during cooling from the densification temperature, were measured with a dilatometer.
fluorescence spectra of trace Cr3+ was obtained using a piezospectroscopic technique that measured the stress-induced shift of the characteristic Cr3+ fluorescence in thin layers. These measurements were compared to the expected strains produced as the two materials are constrained in a laminate structure (Eq. (3)). The measured values of the total residual strain mismatch between the MZ-ZrO2 specimens before and after transformation, were also measured, and values of the total residual strain mismatch between the MZ-ZrO2 specimens and an Al2O3/TZ-ZrO2 monolith were determined and compared with the expected strains produced as the two materials are constrained in a laminate structure (Eq. (3)). The measured values of the total residual strain, produced between the two materials, were then used to calculate the threshold strengths of the laminates based on Eq. (2).

Measurements of the residual, biaxial compression within the thin layers were accomplished using Eq. (1) and a piezospectroscopic technique that measured the stress-induced shift of the characteristic Cr3+ fluorescence in Al2O3 grains.17,18 The position of a specific peak, designated R2, shifts linearly to the left with respect to the tensile stress in the Al2O3. By measuring both the outer, thick tensile layers of the laminates and a monolithic specimen of the same composition, a peak shift can be measured that corresponds to only the tensile stresses produced by constraint in the laminate specimens. Then, using Eq. (1) and the layer thicknesses of the thick (t1) and thin (t2) layers, the corresponding compressive stresses in the thin layers can be calculated. Fully dense laminate specimens for all MZ-ZrO2/Al2O3 compositions were measured with this technique. In all specimens, fluorescence spectra data were incrementally measured across the center region of the outer tensile layer, perpendicular to the layer orientation, to avoid measurements close to an edge, where stresses are relaxed relative to the interior. Using these measurements and the values of t1 and t2 for each specimen, the values of the residual compression in the thin layers were calculated and compared with both the theoretical values of stress (assuming a volume expansion of 4% during transformation) and those calculated from the strains measured in the dilatational tests (Eq. (1)). These stresses were then used to calculate the expected threshold strengths of the laminates based on Eq. (2).

### III. Results

#### (1) Zirconia-Phase Transformation

The dilatational behavior, during cooling from the densification temperature, of monolithic specimens with the same MZ-ZrO2 volume fractions as those used in the thin compressive layers is displayed in Fig. 1. Based on this data, the strains produced during the transformation (εT), the CTEs before and after transformation, and the total residual strain mismatch produced between the t1 and t2 layer materials (εR) have been calculated and reported in Table I. The results for specimens with 0.05 volume fraction MZ-ZrO2 have not been included because no transformation strains were observed. As shown, the transformation strains produced in the monolithic materials increased with the MZ-ZrO2 volume fraction, but were much less than those predicted by Eq. (3). As a result, when the total Al2O3/MZ-ZrO2 specimen strains were compared
with the thermal expansion strains for a 0.95 Al₂O₃/0.05 TZ-ZrO₂ monolith, the differential residual strains (εₘ) produced between the two materials were also less than the values predicted by Eq. (3).

(2) Piezospectroscopic Measurements

Figure 2 shows the piezospectroscopy results for the residual stresses within the thick and thin layers, determined for specimens with 0.05–0.95 volume fraction MZ-ZrO₂. As expected, measurements of the surface Al₂O₃/TZ-ZrO₂ layers, using a monolithic Al₂O₃/TZ-ZrO₂ specimen as a reference, showed that the alumina phase was in tension (σₜ) because the thick layers constrained a fraction of the thin layer volume increase, produced by the tetragonal-to-monoclinic phase transformation of the MZ-ZrO₂. Accordingly, this constraint produced very high compressive stresses (σₙ) in the thin layers, governed by Eq. (1). Figure 2 shows the compressive stresses within the thin layers approached a maximum at 0.35 volume fraction MZ-ZrO₂, then decreased with increasing MZ-ZrO₂ volume fraction, a trend opposite to what was expected. Table II compares these values to the predicted compressive stresses calculated from Eqs. (1) and (3), using either the measured residual strains from the dilatational tests or by assuming a volume expansion of 4% during transformation. As shown in the table, the values of the residual, biaxial compressive stress were significantly less than those predicted by Eq. (1).

(3) Strength Data and Observations

Figure 3 reports the strengths for all Al₂O₃/MZ-ZrO₂ laminates and the Al₂O₃ monolith (0.05 TZ-ZrO₂), for specimens containing precracks introduced with either 0.5 kg (precrack of length 2a ~ 59 μm), 1.5 kg (2a ~ 119 μm), or 2.5 kg (2a ~ 166 μm) Vickers indents. The standard deviation is shown to be either within the dimensions of the data point or by the brackets associated with the data point. As shown, compressive layers containing only 0.05 volume fraction MZ-ZrO₂ did not affect the strength of the laminate relative to the monolith material containing the same pre-existing cracks, whereas laminates containing a larger volume fraction of the MZ-ZrO₂ had higher strengths relative to the monolith. It is also clear that although the strengths of the laminates were much greater than the monolith, their strengths did not significantly change for compressive layers containing ≥0.35 volume fraction MZ-ZrO₂. For comparison, the lowest strength for each laminate containing a different MZ-ZrO₂ volume fraction is displayed in Table III, along with predicted values for the threshold strength. Predicted values for σₘ were calculated from Eqs. (1), (2), and (3) by using elastic properties reported elsewhere,

\[ K_I = \frac{2 \cdot \sigma_m}{\sqrt{\pi a}} \]

and either the measured differential residual strains or the experimentally determined compressive stresses. For these calculations, it was assumed the elastic modulus of the multiphase compressive layers followed the lower bound estimate of Ravi-chandran.² The Poisson’s ratio followed a simple rule of mixtures, and all differential strains were dissipated via creep until the laminates were cooled below 1200°C.²

Figure 4 shows the strengths of both the 0.95 volume fraction MZ-ZrO₂ laminate and the Al₂O₃ monolith, for specimens with a range of precrack lengths. As shown, the strength of the Al₂O₃ monolith decreased as the precrack length increased, and was similar to the flaw-sensitive strength predicted by the Irwin equation shown in the figure. This flaw-sensitivity is also shown in Fig. 3, by the large range of failure strengths exhibited by the unindented monolith specimens. However, it is clear from both Figs. 3 and 4 that the strengths of the laminates were independent of the precrack length. The laminate specimens exhibited nearly the same threshold strength and thus were desensitized with respect to crack or flaw size, for the range of flaws introduced here (where 59 μm < 2a < t₃ layer thickness).

For MZ-ZrO₂ volume fractions >0.20, laminate specimens exhibited crack arrest and bifurcation behaviors, which were observed and identified previously.³ The fracture surfaces of all specimens appear similar to that shown in Fig. 5(a), where the precrack within the central thick layer propagated across the layer and down to the neutral axis of the specimen, and was arrested by the thin compressive layers on either side. This center layer appears very smooth under inspection because of the stable extension of the crack. With increased loading, this internal slit crack propagated through the thin compressive layers on either side and into the thick tensile layers, where the high applied load and lack of internal compressive stresses produced a stress concentration factor at the crack tip that caused catastrophic failure of the specimen. Figures 5(b) and (c) show the path of crack propagation at the surface of thin compressive layers changed with the volume fraction of the MZ-ZrO₂. Surface observations of

<table>
<thead>
<tr>
<th>Monolith or thin layer composition (volume fraction MZ-ZrO₂)</th>
<th>Measured thick layer stress, σₘ (MPa)</th>
<th>Thin layer compression, σₙ = σₙ † (GPa)</th>
<th>Predicted σₘ (GPa), Eq. (1)</th>
</tr>
</thead>
<tbody>
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<td>0.95</td>
<td>-19.8†</td>
<td>0.21</td>
<td>3.79</td>
</tr>
</tbody>
</table>

†Calculated from Eq. (1) using measured σₘ stresses and t₁/t₂ layer thicknesses. †Using measured results from the dilatational strain measurements. Negative values correspond to a tensile stress.
specimens containing either 0.35 or 0.50 volume fraction MZ-ZrO₂ layers showed that precracks propagated straight across to a highly visible edge crack in the compressive layer and were arrested. During catastrophic failure, the second half of the compressive layer fractured, most likely from propagation of an internal bifurcated crack branch to the tensile surface. In specimens with MZ-ZrO₂ volume fractions ≥0.65, precracks exhibited various amounts of bifurcation and/or deflection as they propagated completely through the thin compressive layers at an angle.

Figure 6 shows that the amount of surface damage in the compressive layer increased with the MZ-ZrO₂ volume fraction. Specimens with 0.05 and 0.20 volume fraction MZ-ZrO₂ showed no edge cracks within the compressive layer, whereas 0.35 volume fraction MZ-ZrO₂ specimens exhibited single edge cracks along the midplane. As the MZ-ZrO₂ volume fraction is increased above 0.35, microcracking and regions of multiple edge cracking became apparent. The compressive layers in the 0.50 volume fraction MZ-ZrO₂ specimens had both single and multiple edge cracks and showed only slight signs of microcracking on the surface, whereas specimens with >0.65 volume fraction MZ-ZrO₂ exhibited large amounts of microcracking as well as numerous "primary" edge cracks typically near the interfaces of the layers instead of at the midplane.

Examples of crack propagation beneath the surface (uncovered by removing material) are displayed in Fig. 7. It was evident that crack bifurcation occurred within the compressive layers containing MZ-ZrO₂ volume fractions ≥0.35. For specimens with MZ-ZrO₂ volume factions >0.65 the crack path was unclear because microcracking obscured the location of the crack. The average angles of bifurcation, from each bifurcated branch to its bisector, as measured from Fig. 7 are 62°, 58°, and 47° for the 0.35, 0.50, and 0.65 volume fraction MZ-ZrO₂ specimens, respectively. Although bifurcation angles varied slightly from layer to layer in specimens with identical MZ-ZrO₂ volume fractions, the angle of bifurcation gradually decreased as MZ-ZrO₂ volume fraction increased. The observed bifurcation within the Al₂O₃/MZ-ZrO₂ layers is similar to that described for the Al₂O₃/mullite materials, as is the reformation of edge cracks at the newly exposed free surface, evident by their discontinuity across the bifurcated region.

### IV. Discussion

#### (1) Tetragonal-to-Monoclinic Phase Transformation

The results of the dilatational strain measurements for the monolithic Al₂O₃/MZ-ZrO₂ specimens show that, for most materials, the transformation strains increased with the volume fraction of MZ-ZrO₂. The two exceptions were the materials containing 0.05 and 0.95 volume fraction MZ-ZrO₂ where either no transformation was detected or extensive microcracking reduced the amount of measurable transformation strain, respectively. In all cases, the transformation strains measured for the monolithic bodies were at least 28% smaller than expected based on the reported volume change for the tetragonal-to-monoclinic transformation.

Figure 1 and Table I also show that the transformation temperature decreases with decreasing MZ-ZrO₂ volume fraction (i.e., increasing Al₂O₃ content). In Al₂O₃/ZrO₂ mixtures, the alumina phase is part of the constraining matrix surrounding each transforming zirconia grain. It has been shown that the constrained transformation temperature will be inversely proportional to the elastic modulus of the constraining matrix. Because the elastic modulus of Al₂O₃ is nearly twice that of ZrO₂, the elastic modulus of the constraining matrix will increase, thus decreasing the transformation temperature with increasing volume fraction of Al₂O₃. The constraint imposed by the Al₂O₃ matrix may also be the source of the lower transformational strains, because some tetragonal ZrO₂ may be retained at room temperature. Analysis of the monoliths using XRD showed that all the ZrO₂ in the 0.05 volume fraction MZ-ZrO₂ specimen remained in the tetragonal phase, whereas the 0.20 volume fraction MZ-ZrO₂ specimen contained 0.23 and 0.77 volume fraction tetragonal and monoclinic ZrO₂, respectively. Little or no retained tetragonal ZrO₂ was found for specimens with ≥0.35 volume fraction MZ-ZrO₂. It was anticipated that the constraint produced by layering these materials in a laminate structure might result in a greater amount of retained tetragonal ZrO₂. However, the phase of the ZrO₂ in the thin laminate layers was not measured by XRD because the area uncovered by bifurcation was too small for the XRD measurement.

#### (2) Measurement of Residual Stresses

As described above, values of the residual compressive stresses within the thin Al₂O₃/MZ-ZrO₂ layers were determined from Eq. (1) using the measured layer thicknesses and the measured tensile stresses in the thick Al₂O₃/TZ-ZrO₂ outer layers. Piezospectroscopic stress measurements were also performed on the thin

<table>
<thead>
<tr>
<th>Thin layer composition (volume fraction of MZ-ZrO₂)</th>
<th>Measured threshold strength, σₚ (MPa)</th>
<th>Predicted σTHR (MPa), Eq. (2)</th>
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<td>776</td>
</tr>
<tr>
<td>0.95</td>
<td>512</td>
<td>562</td>
</tr>
</tbody>
</table>

*Using results from the dilatational strain measurements. †Using results from the piezospectroscopic stress measurements.

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Figure 4. Plot of measured four-point bending failure strength versus length of precrack, produced by a Vickers indent of 0.5, 1.5, or 2.5 kg in the center thick layer. Circular and square symbols denote results for 0.95 vol% MZ-ZrO₂ laminate and Al₂O₃/TZ-ZrO₂ monolith specimens, respectively. Triangular symbols denote predicted results for monolithic Al₂O₃/TZ-ZrO₂ specimens assuming Kᵣ = 4 MPa m¹/².
(3) Microcracking and Relief of Residual Compressive Stress

A tensile stress exists at and near the free surface of a compressive layer, which is the first material system to be extensively studied for threshold strength. As shown in Figs. 5 and 6, edge cracks have also been observed in this Al2O3/MZ-ZrO2 system, in thin layers containing >0.20 volume fraction MZ-ZrO2. However, above 0.35 volume fraction MZ-ZrO2, multiple edge cracks were formed throughout the layers and near the interfaces, and regions of microcracking became apparent as the MZ-ZrO2 volume fraction increased. This microcracking, and the cracks running parallel to the layers, were formed by the high strains produced during the transformation of a critical volume fraction of ZrO2. Above 0.35 volume fraction MZ-ZrO2, the transformation strains and resulting tensile stress at the free surface of the compressive layer were sufficiently large to induce an edge crack, and then, multiple cracks oriented along the length of the compressive layer.

Although the microcracking was observed on the free surface of the compressive layers, the presence of microcracking throughout the compressive layer could not be determined (grinding away material produces a new free surface). Deep within the compressive layer, far from the tensile stresses of the free surface, microcracking might be suppressed; in fact, some transformation itself might also be suppressed deep within the compressive layers. Microcracking will relieve the compressive stresses produced during transformation, but the presence of microcracking throughout the compressive layer, and its effect on the magnitude of the compressive stress generated in the compressive layer, is uncertain.

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Figure 2 and Table II show the experimental values of the residual, biaxial compression were much less than those determined by using either the differential residual strains measured during the dilatational tests or the strains calculated from the expected volume expansion during transformation (4%). In addition, the opposite to what was expected, the measured values of compressive stress decreased as the MZ-ZrO2 volume fraction was increased above 0.35. Although microcracking could be observed only on the surface of the compressive layers, it can be concluded that microcracking must also occur deep within the compressive layers, and that it is responsible for a portion of the reduction of the
compressive stresses as measured with the piezospectroscopic method. Highly microcracked layers would be unable to support large biaxial compressive stresses.

(4) Threshold Strengths

Figure 3 and Table III show that there are large differences between the experimental threshold strengths and those predicted with Eqs. (1), (2), and (3). The measured failure strengths were always greater than those predicted by using the compressive stresses measured during piezospectroscopy and, for MZ-ZrO₂ volume fractions ≥0.35, less than those predicted by using the measured differential strains because of thermal contraction and phase transformation. There were several other strength deviations that also occurred, at both low and high compressive layer MZ-ZrO₂ volume fractions.

The reduction of threshold strength with increasing precrack size, exhibited for materials containing 0.05 to 0.20 MZ-ZrO₂, can be attributed to the applied stress required to extend the precrack to the compressive layers. For low MZ-ZrO₂ volume fraction laminates, it was found that the stress required to extend the smallest precrack to the compressive layers was greater than the threshold strength of the laminate; a condition that has been described elsewhere.⁴,⁶ For this case, at an applied stress greater than the threshold stress, the crack will catastrophically extend through the compressive layers without arresting. Thus, the strengths for precracks produced with a 0.5 kg indent were greater than predicted. However, for larger precracks produced with 1.5 and 2.5 kg loads, the stress required to extend the precrack in the 0.20 volume fraction MZ laminate was less than the threshold strength, crack arrest at the compressive layer interface was observed, and a threshold strength was obtained.

For MZ-ZrO₂ volume fractions of 0.20 and 0.35, the measured values of the threshold strength were always greater than those predicted with Eq. (2). In these materials, the crack was observed to bifurcate through the compressive layer and not extend as one crack as assumed by the current model used to develop Eq. (2). It has been previously shown that an increased stress is required to extend a crack as it bifurcates through the compressive layer.⁷

At higher volume fractions of MZ-ZrO₂, the threshold strength reached an apparent plateau. As discussed above, it appears that the increasing amount of microcracking within the compressive layer with increasing volume fraction of MZ-ZrO₂ is responsible for the lower measured compressive stresses relative to those expected. Also, measurements of bifurcation within the bulk of a specimen revealed a slight decrease in the bifurcation angle as the MZ-ZrO₂ volume fraction was increased (Fig. 7). This decrease in bifurcation angle can be related to a corresponding drop in the residual compressive stresses within the layers.⁸ Therefore, although the transformation strains increase with increased volume fractions of MZ-ZrO₂, the increased microcracking limits the
development of compressive stresses, thus limiting the threshold strength as well. However, because the measured values of the threshold strength were much greater than those predicted using Eq. (2) and the measured values of residual compression, it appears that the microcracking may also serve to influence $K_C$ and/or the layer modulus, such that the threshold strength is increased but limited to a critical value.

V. Conclusions

We have shown that mixtures of unstabilized zirconia (MZ-ZrO$_2$) and alumina (Al$_2$O$_3$) create compressive stresses within thin layers that, when sandwiched between thicker Al$_2$O$_3$ layers, produce dense laminar structures that exhibit high threshold strengths of 507 ± 36 MPa. Much of the residual compression within the thin layers seems to be relieved by the microcracking that accompanies the ZrO$_2$ transformation; however, the previously studied mechanisms of crack arrest, edge cracking, and bifurcation have all been observed in the current laminar system. The transformation temperature decreased with increasing Al$_2$O$_3$ content, and eventually some unstabilized ZrO$_2$ remained tetragonal at room temperature, which was caused by the increased elastic modulus of the alumina matrix that surrounds the zirconia phase.

Fig. 7. Optical micrographs of subsurface crack bifurcation in thin compressive layers containing (a) 0.35, (b) 0.50, and (c) 0.65 volume fraction MZ-ZrO$_2$. The measured angles from each bifurcated crack branch to its bisector are 62°, 58°, and 47°, respectively.

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