

# LABORATORY REPORT

## Characterization Studies of Transformation-Toughened Ceramics

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### Abstract

The goal of this study was to characterize transformation-toughened zirconia ceramics and determine the effect of environment on strength and crystal phases. Eight commercial ceramics and three laboratory-prepared high-purity  $ZrO_2$  specimens containing 2, 3, and 4 mol%  $Y_2O_3$  were used for this investigation. The effects of exposure to temperatures ranging from 150° to 800°C in varying atmospheric conditions (aging) on the crystal phases of the toughened ceramics were evaluated. Four-point flexural strength measurements were made at several selected stressing rates and temperatures (25° to 1050°C) in dry  $N_2$  and  $N_2$  with 10 vol%  $H_2O$ . X-ray diffraction was used to evaluate phase changes during low-temperature aging.

The toughened ceramics showed premature tetragonal-to-monoclinic phase transformation caused by low-temperature aging. The magnitude of the aging effect depended on the environment and the chemical composition and microstructure of the ceramic. The flexural strengths measured for the eight commercial ceramics at 25°C were two and three times those reported for nontoughened  $ZrO_2$  and  $Al_2O_3$  ceramics. At 1050°C, flexural strength decreased 52% to 72% from values found at 25°C. Flexural strength values among the eight toughened commercial ceramics also showed considerable variation.

### Introduction

The very high strength and toughness reported for transformation-toughened ceramics have generated interest in their use in severe environments. Since their development more than a decade ago, these ceramics have been the subject of numerous investigations.<sup>1-3</sup> The dramatic improvement in the strength and toughness of these  $ZrO_2$ -based ceramics compared to conventional  $ZrO_2$  ceramics depends on a stress-induced marten-

sitic phase transformation from the tetragonal to the monoclinic crystal form. Effective use of these toughened ceramics for structural applications in severe environments depends strongly on their mechanical reliability and cost.

Transformation-toughened ceramics include partially stabilized zirconia (PSZ), tetragonal zirconia polycrystals (TZP), and zirconia-toughened alumina (ZTA). MgO and CaO are stabilizers used for PSZ ceramics, while  $Y_2O_3$  and  $CeO_2$  are stabilizers used for TZP ceramics. In PSZ ceramics the toughening mechanism is due to the small metastable tetragonal precipitates in large ~50- $\mu m$  cubic matrix grains. The TZP ceramics consist of fine tetragonal grains (0.3-3  $\mu m$ ). Transformation of these fine grains to the monoclinic phase during crack propagation produces the toughening observed.<sup>1-3</sup> The ZTA ceramics consist of 15% to 20% fine-grained transformable tetragonal  $ZrO_2$  dispersed intergranularly in larger  $Al_2O_3$  grains.

In this study, eight transformation-toughened zirconia ceramics and three laboratory-prepared YTZP ceramics were investigated. The microstructure, chemistry, crystal structure, density, hardness, and coefficient of thermal expansion of the as-received commercial ceramics were determined. Test specimens of all eight ceramics were then subject to a number of temperatures, stressing rates, and environments. The effects of these conditions on flexural strength were then examined.

### Experimental Procedures

The two MgO-PSZ, three  $Y_2O_3$ -TZP, two ZTA, and one  $CeO_2$ -TZP commercial ceramics evaluated are identified and briefly described in Table I. The microstructure, chemistry, crystal structure, density, hardness, and coefficient of thermal expansion of these ceramics were determined.

Flexural strength was measured at selected temperatures from 25° to 1050°C using a four-point flexure fixture in a universal testing machine (Instron Model 1123, Instron Corp. (Canton, MA)). Both dry  $N_2$  and  $N_2$  with 10 vol%  $H_2O$  atmospheres were used in a specially designed environmental control chamber for all flexural strength measurements. All test specimens were 6.35 cm  $\times$  0.51 cm  $\times$  0.255 cm with the tensile surface

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\*Member, American Ceramic Society.

Table I. Transformation-Toughened Ceramic Materials Selected for Evaluation

| Material supplier          | Material designation | Material description*  | Material type |
|----------------------------|----------------------|--|---------------|
| Ceramtec, Inc.             | ZTA-XS121            | ZrO <sub>2</sub> -toughened Al <sub>2</sub> O <sub>3</sub>   | ZTA           |
| Kyocera International      | DTA-AZ301            | ZrO <sub>2</sub> -toughened Al <sub>2</sub> O <sub>3</sub> (19% ZrO <sub>2</sub> )                               | ZTA           |
| (USA) Nilcra Ceramic, Inc. | MS-PSZ               | 3% MgO-stabilized ZrO <sub>2</sub> (heat-treated for high strength)  | PSZ           |
| (USA) Nilcra Ceramic, Inc. | TS-PSZ               | 3% MgO-stabilized ZrO <sub>2</sub> (heat-treated for high thermal-shock resistance)                              | PSZ           |
| Ceramtec, Inc.             | YTZP-XS241           | 5% Y <sub>2</sub> O <sub>3</sub> -stabilized ZrO <sub>2</sub> (with 10% Al <sub>2</sub> O <sub>3</sub> addition) | TZP           |
| NGK Locke, Inc.            | Z191                 | 5% Y <sub>2</sub> O <sub>3</sub> -stabilized ZrO <sub>2</sub>  | TZP           |
| Kyocera International      | PSZ-Z201             | 5.4% Y <sub>2</sub> O <sub>3</sub> -stabilized ZrO <sub>2</sub>  | TZP           |
| Ceramtec, Inc.             | CTZP                 | CeO <sub>2</sub> -stabilized ZrO <sub>2</sub> (with 10% Al <sub>2</sub> O <sub>3</sub> addition)                 | TZP           |

\*All compositions are in weight percent.

Table II. Property Characterizations of Transformation-Toughened Ceramics

| Material Designation                                       | Nilcra MS-PSZ                             | Nilcra TS-PSZ                             | Kyocera DTA-AZ301                             | Kyocera PSZ-Z201                                      | NGK-Z191                                 | Ceramtec ZTA-XS121  | Ceramtec YTZP-XS241   | Ceramtec CTZP   |
|--|---|---|---|---|--|---|---|---|
| Density (g/cm <sup>3</sup> )*                              | 5.7                                       | 5.7                                       | 4.2   | 5.9   | 5.9                                      | 4.4   | 5.4   | 5.7   |
| Hardness (kg/mm <sup>2</sup> )†                            | 1099                                      | 1025                                      | 1939  | 1282  | 1292                                     | 1172  | 1120  | 864   |
| Coefficient of thermal expansion (× 10 <sup>-6</sup> /°C)‡ | 10.3                                      | 9.5                                       | 8.4   | 11.0  | 10.1                                     | 9.4   | 9.9   | 10.7  |
| Major microstructural features§                            | Porous coarse-grained (30–60 μm) material | Porous coarse-grained (30–60 μm) material | Dense two-phase material with grains 0.3–2 μm | Dense fine-grained material (0.2–0.5 μm, avg. 0.3 μm) | Dense fine-grained material (0.2–0.4 μm) | Fine-grained multiphase material (0.5–2.5 μm, avg. 1.5 μm). Uniform distribution of pores (0.2–2 μm). | Fine-grained multiphase material (2–4 μm). Uniform distribution of pores (0.5–4 μm) | Fine-grained two-phase material (1–4 μm). Uniform distribution of pores |

\*By water immersion method. †Vicker's microindent hardness tester. ‡Theta Industries Dilatronic II (Model 6024). §JEOL (Tokyo, Japan) JSM-840 SEM/EG&G Ortec System 5000 on polished and etched specimens.

ground and polished to a 0.4-μm finish. The tensile surface edges were rounded to a radius of 0.1 of the test bar thickness, and all surfaces were parallel to 0.0025 cm. Machine crosshead speeds of 6.4×10<sup>-3</sup> cm/s and 4×10<sup>-5</sup> cm/s were used.

Aging was investigated in the eight commercial toughened ceramics. Temperature treatments of 150°, 250°, 300°, and 800°C were chosen to evaluate these effects. Test specimens were held at these temperatures for 25 to 250 h in N<sub>2</sub> with 10 vol% H<sub>2</sub>O, for 168 h in vacuum (10<sup>-3</sup> torr), and for 24 h in dry N<sub>2</sub>.

X-ray diffraction (XRD) (Norelco/Phillips Electronic Instruments, (Mahwah, NJ) XRD system (CuKα radiation)) was used to determine the chemical elements, compounds, and crystalline phases in the treated materials. Peak height values from the XRD spectra were used to calculate the percentage of the crystalline phases by the method of approximate triangles.<sup>4,5</sup>

To better understand the effect of aging, three YTZP ceramics with 2 to 4 mol% Y<sub>2</sub>O<sub>3</sub> stabilizer were prepared in the laboratory. These specimens were made by mixing chemically pure ZrO<sub>2</sub> powder (provided by personnel from the Materials Laboratory, Wright-Patterson AFB, OH (prepared by alkoxide decomposition)) with 2, 3, and 4 mol% Y<sub>2</sub>O<sub>3</sub> stabilizer. The mixed powder was then compacted into discs and sintered at 1400°C for 20 h. The sintered discs were theoretically dense and had an average grain size of 0.7 μm (0.25–1.25 μm). These specimens were aged at 250°C in N<sub>2</sub> with 10% H<sub>2</sub>O (24 h), dry N<sub>2</sub> (24 h), and vacuum (16 h), in the same manner as they were for the commercial ceramics, and phase transformation was determined by XRD. The mechanical properties of the laboratory prepared YTZP ceramics were not determined.

## Results and Discussion

The characterization results are shown in Table II. The Kyocera DTA-Z301 (Kyocera International (Vancouver, WA)) had the highest hardness, 1939 kg/mm<sup>2</sup>. The six ZrO<sub>2</sub>-based ceramics had

hardness values ranging from 860 to 1300 kg/mm<sup>2</sup>. The coefficient of thermal expansion for the six ZrO<sub>2</sub>-based ceramics ranged from 10 to 11×10<sup>-6</sup>/°C.

## Flexural Strength Studies

The flexural strength measurements are presented in Table III. The strongest material under all measurement conditions was Kyocera ZTA-AZ301. The three Y<sub>2</sub>O<sub>3</sub>-TZP ceramics (Z191, Z201, and XS241) ranked next in flexural strength. Interestingly, these three materials had the smallest average grain size. The two Nilcra MgO-PSZ ceramics (MS and TS) (Nilcra Ceramics, Inc. (Elmhurst, IL)), and Ceramtec ZTA-XS121 and CeO<sub>2</sub>-TZP (Ceramtec, Inc. (Salt Lake City, UT)) followed in descending order of flexural strength.

All eight commercial ceramics showed significant loss of flexural strength at 1050°C. Generally, as the test temperature was increased from 25° to 1050°C flexural strength decreased by 52% to 72%, but with considerable variation among the commercially available toughened ceramics. Following Larsen *et al.*,<sup>6</sup> the decrease in strength is attributed to a decrease in the driving force for the tetragonal-to-monoclinic transformation at the higher test temperatures.

The toughened ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> ceramics were stronger at room temperature than the conventional form of these ceramics. Fully stabilized ZrO<sub>2</sub> has an average room-temperature flexural strength of 250 MPa,<sup>7</sup> whereas, the toughened ZrO<sub>2</sub> ceramics investigated were two to four times stronger. Similarly, the ZrO<sub>2</sub>-toughened Al<sub>2</sub>O<sub>3</sub> ceramics were one and a half to three times stronger than conventional Al<sub>2</sub>O<sub>3</sub> (600 MPa).<sup>7</sup> Even at 1050°C, the toughened ceramics were stronger than nontoughened ZrO<sub>2</sub> (145 MPa at 1000°C) and Al<sub>2</sub>O<sub>3</sub> (400 MPa at 1000°C) ceramics.<sup>7</sup>

As indicated in Table III, the two Y<sub>2</sub>O<sub>3</sub>-TZP ceramics (Z191 and Z201) exhibited major plastic deformation at 1050°C when subjected to slow stress application rates in both dry N<sub>2</sub> and

Table III. Summary of Flexural Strength Results

| Test conditions  |                      |                        | Material/average strength for candidate materials (MPa) (CV (%))* |          |           |          |          |          |          |         |
|------------------|----------------------|------------------------|---|----------|-----------|----------|----------|----------|----------|---------|
| Temperature (°C) | Atmosphere           | Crosshead speed (cm/s) | AZ301   | MS       | Z191      | CTZP     | Z201     | 121      | 241      | TS      |
| 25               | Dry N <sub>2</sub>   | 0.0064                 | 1265 (11)   | 679 (6)  | 1004 (16) | 481 (4)  | 957 (5)  | 556 (4)  | 777 (19) | 677 (3) |
| 25               | Dry N <sub>2</sub>   | 0.00004                | 1106 (12)   | 621 (7)  | 1014 (9)  | 472 (1)  | 775 (23) | 567 (6)  | 761 (13) | 583 (3) |
| 25               | 10% H <sub>2</sub> O | 0.0064                 | 849 (29)  | 638 (4)  | 831 (13)  | 473 (2)  |          |          |          |         |
| 25               | 10% H <sub>2</sub> O | 0.00004                | 932 (12)  | 566 (4)  | 821 (8)   | 422 (7)  |          |          |          |         |
| 250              | Dry N <sub>2</sub>   | 0.0064                 | 897 (12)  | 540 (12) | 900 (8)   | 523 (13) | 714 (17) |          |          |         |
| 250              | 10% H <sub>2</sub> O | 0.0064                 | 1036 (19)   | 525 (6)  | 827 (5)   | 433 (10) | 690 (19) |          |          |         |
| 250              | 10% H <sub>2</sub> O | 0.00004                | 892 (7)   | 448 (11) | 862 (6)   | 341 (24) | 709 (10) |          |          |         |
| 800              | Dry N <sub>2</sub>   | 0.0064                 | 832 (13)  | 299 (8)  | 460 (4)   | 216 (7)  | 320 (27) |          |          |         |
| 800              | 10% H <sub>2</sub> O | 0.0064                 | 729 (30)  | 282 (8)  | 325 (21)  | 202 (12) | 391 (11) |          |          |         |
| 800              | 10% H <sub>2</sub> O | 0.00004                | 463 (36)  | 270 (9)  | 261 (16)  | 218 (5)  | 396 (8)  |          |          |         |
| 1050             | Dry N <sub>2</sub>   | 0.0064                 | 662 (36)  | 248 (6)  | 319 (1)   | 181 (14) | 264 (22) |          |          |         |
| 1050             | Dry N <sub>2</sub>   | 0.00004                | 590 (23)  | 248 (5)  | 120 (4)†  | 191 (15) | 175 (6)† |          |          |         |
| 1050             | 10% H <sub>2</sub> O | 0.0064                 | 554 (24)  | 225 (4)  | 296 (6)   | 186 (13) | 247 (20) | 252 (12) | 217 (6)  | 251 (7) |
| 1050             | 10% H <sub>2</sub> O | 0.00004                | 620 (24)  | 254 (6)  | 115 (12)† | 154 (23) | 173 (6)† | 251      | 248 (2)  |         |

\*CV—Coefficient of variation ((standard deviation/mean)×100). †At the slow stressing rate at 1050°C in N<sub>2</sub> and N<sub>2</sub>+10% H<sub>2</sub>O, both the 191 and 201 ceramics plastically deformed during flexural testing.

N<sub>2</sub> with 10 vol% H<sub>2</sub>O (Fig. 1). Both ceramics have very fine-grain microstructures (~0.3 μm); this suggests that deformation is caused by grain-boundary sliding. Larsen<sup>6</sup> has reported significant creep in these materials due to grain-boundary sliding at 1000°C.

As shown in Table III, strengths in dry N<sub>2</sub> were higher than those in N<sub>2</sub> with 10 vol% H<sub>2</sub>O (90% of the measurements). In addition, strengths at the more rapid loading rates tended to be higher (85% of the measurements). These results suggest a stress corrosion effect. However, the use of dynamic fatigue analysis to determine a stress corrosion coefficient ( $n$ ) was not effective because sufficient data points at each test condition were not available for statistically conclusive findings.<sup>6</sup>

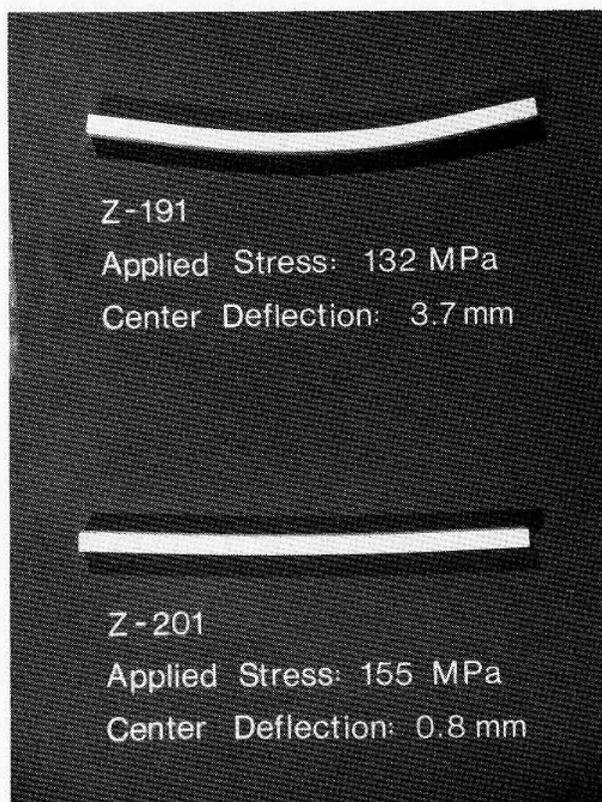


Fig. 1. Plastic deformation of slow-loaded Z191 and Z201 test specimens.

### Aging Studies

**Commercial Toughened Ceramics:** The results for the commercial toughened ceramics are presented in Table IV. Seven of the eight commercial ceramics showed some degree of phase transformation due to aging. CTZP did not exhibit any phase changes and the TZP ceramics, Z191 and Z201, showed only minimal phase change.

Tsukuma *et al.*<sup>9</sup> and Watanabe *et al.*<sup>10</sup> investigated premature transformation behavior in the YTZP ceramics and identified a critical grain size below which aging degradation no longer occurred. As the concentration of Y<sub>2</sub>O<sub>3</sub> stabilizer in the material was increased, the critical grain size increased. At 2 mol%, the material was prone to aging effects unless the grain size was less than 0.2 μm. At 5 mol%, aging effects occurred if the grain size was above 0.7 μm. These findings would account for the minimal transformation found for the Z191 and Z201 ceramics, which contain 3 mol% Y<sub>2</sub>O<sub>3</sub> and have an average grain size of 0.3 μm.

Matsumoto<sup>11</sup> reported that 5% to 10% additions of Al<sub>2</sub>O<sub>3</sub> inhibited premature transformation due to aging. These results would account for the absence of aging effects observed for CTZP which contained 10% Al<sub>2</sub>O<sub>3</sub>.

Aging at 250°C in N<sub>2</sub> with 10 vol% H<sub>2</sub>O resulted in the largest amount of transformation, while aging in dry N<sub>2</sub> resulted in a lower amount of transformation. The amount of transformation followed a consistent pattern, increasing with the following order of aging atmospheres: vacuum, dry N<sub>2</sub>, and N<sub>2</sub> with 10 vol% H<sub>2</sub>O.

The presence of moisture accelerated phase transformation. Several mechanisms have been proposed for this acceleration.<sup>12</sup> They include (a) stress corrosion by H<sub>2</sub>O at the Zr–O–Zr bonds, (b) hydroxide formation, and (c) catalytic action of water. Irrespective of the particular mechanism, the presence of moisture during low-temperature aging reduces nucleation energy for the tetragonal-to-monoclinic phase transformation.<sup>12</sup>

Past work<sup>13–17</sup> has attributed premature transformation to the formation of hydroxides; however, that was not observed in this work. XRD analysis and subsequent Raman and attenuated total reflection Fourier transform infrared radiation (ATR-FT-IR) analyses<sup>18</sup> before and after aging did not reveal the presence of hydroxides. To further investigate the role of OH and H<sub>2</sub>O on the surface of aged specimens, high-resolution XPS surface analysis was conducted on several MS-PSZ and TZP-XS241 specimens before and after aging (Table V). The oxygen present on the surface of the as-received specimens in the form of H<sub>2</sub>O and OH compounds decreased after aging for both the PSZ and TZP ceramics. The aging treatment apparently promotes chemical desorption and dehydration of the H<sub>2</sub>O suggesting

Table IV. Results of XRD Analysis After Aging

| Material | As-received | Percent monoclinic (MP)*            |  |                                |                        |
|----------|-------------|-------------------------------------|--|--------------------------------|------------------------|
|          |             | After 250°C in 10% H <sub>2</sub> O | After 300°/800°C in 10% H <sub>2</sub> O | After 250°C dry N <sub>2</sub> | After vacuum treatment |
| Z191     | 7 (t)       | 9 (t)                               | 10 (t)                                   |                                |                        |
| AZ301    | 28 (t)      | 33 (t)                              | 27 (t)                                   | 26 (t)                         |                        |
| Z201     | 3 (t)       | 4 (t)                               | 4 (t)                                    |                                |                        |
| CTZP     | 0 (t)       | 0 (t)                               | 0 (t) <sup>†</sup>                       |                                |                        |
| XS121    | 30 (t)      | 64 (m)                              | 60 (m)                                   | 48 (t)                         |                        |
| XS241    | 15 (t)      | 46 (c)                              | 42 (c)                                   | 36 (c)                         | 15 (t/c)               |
| MS-PSZ   | 24 (c)      | 33 (c)                              | 33 (t) at 800°C                          | 28 (c)                         |                        |
| TS-PSZ   | 32 (c)      | 49 (c)                              | 41 (t) at 800°C                          | 44 (c)                         | 39 (c)                 |

\*MP is major ZrO<sub>2</sub> crystal phase: (m) monoclinic, (t) tetragonal, (c) cubic. <sup>†</sup>CTZP is 0% m at 300° and 150°C.

that the acceleration of phase transformation in the presence of moisture (aging) is not caused by the formation of OH compounds.

As shown in Table IV, the MS-PSZ and TS-PSZ ceramics were susceptible to heat treatment at 250°C and 800°C in N<sub>2</sub> with 10 vol% H<sub>2</sub>O. The amount of transformation to the monoclinic phase was about the same at both temperatures. The monoclinic phase, after aging in dry N<sub>2</sub>, increased 4% and 12% for MS and TS, respectively. TS-PSZ also transformed when heated in a vacuum at 250°C. At 800°C, the increased presence of the monoclinic crystal phase may be due to eutectoid decomposition or formation of an ordered anion vacancy δ-phase (Mg<sub>2</sub>Zr<sub>5</sub>O<sub>12</sub>) as reported by Ferber and Hine.<sup>19</sup>

The two ZTA ceramics responded very differently after aging in dry N<sub>2</sub>. The AZ301-ZTA showed essentially no change in the amount of monoclinic phase after aging in dry N<sub>2</sub>, while the XS121-ZTA showed an 18% increase. The XS241-TZP showed the largest increase in monoclinic phase after aging in dry N<sub>2</sub>. These results clearly showed that aging at 250°C is sufficient to promote premature transformation for some toughened ceramics.

**Laboratory Processed Ceramics:** The XRD data obtained for the 2Y, 3Y, and 4Y TZP ceramics are summarized in Table VI. As-sintered 4Y TZP showed only the presence of the tetragonal phase. All of the aged 2Y TZP specimens exhibited strong monoclinic spectra after exposure to the different aging conditions. Both the 2Y and 3Y TZP specimens showed phase transformation after aging in N<sub>2</sub> with 10 vol% H<sub>2</sub>O and dry N<sub>2</sub>. The 3Y and 4Y TZP aged in vacuum remained unchanged; however, vacuum aging caused significant transformation in the 2Y. Similar results have been reported for these 2Y TZP-type ceramics by Iio *et al.*<sup>20</sup>

These results reinforce previous findings of premature transformation in TZP ceramics with Y<sub>2</sub>O<sub>3</sub> stabilization having grain sizes larger than 0.2 μm. The presence of moisture in the aging environment tended to enhance the transformation process, but the specific mechanism by which it occurred is not clear. The formation of hydroxide (Y(OH)<sub>3</sub>) as reported by Lange *et al.*<sup>21</sup> was not observed in the X-ray spectra obtained for the TZP specimens in this study. Additional studies with IR and Raman spectroscopy on the aged 2Y and 3Y TZP did not show the presence of hydroxide formation in the near-surface region of the aged ceramics.<sup>18</sup>

Table V. Approximate Atomic Percent Surface Composition of Specimens of XS241 and MS-PSZ by XPS

| Sample      | O(H <sub>2</sub> O) | O(-OH) | O(O <sup>+</sup> ) | Zr   | Y   | Mg  |
|-------------|---------------------|--------|--------------------|------|-----|-----|
| TZP-XS241   |                     |        |                    |      |     |     |
| As-received | 9.3                 | 39.7   | 26.7               | 22.9 | 1.3 |     |
| Aged        | 5.9                 | 33.6   | 33.0               | 25.2 | 1.9 |     |
| MS-PSZ      |                     |        |                    |      |     |     |
| As-received | 9.6                 | 47.1   | 18.8               | 20.7 |     | 3.8 |
| Aged        | 4.4                 | 32.4   | 31.0               | 26.2 |     | 6.1 |

## Conclusions

The results of these studies demonstrated the existence of large differences in strength among the toughened ceramics due to variations in composition and processing procedures. Similarly, the susceptibility of these materials to loss of strength with increasing temperature varied significantly. These studies also showed that toughened ceramics can be subject to phase transformation as a result of low-temperature (150° to 300°C) aging. The degree of phase transformation is dependent on composition, microstructure, and environment.

These results clearly demonstrate the importance of tailoring the composition and microstructure of toughened ZrO<sub>2</sub>-based ceramics to avoid low-temperature aging problems. The appropriate amount of stabilizer and careful control of grain size must be employed if toughened ceramics are to be successfully used in hostile operating environments.

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Table VI. Results of XRD Analysis of the 2Y, 3Y, and 4Y TZP Discs After Aging

| Material | As-received | Monoclinic fraction (%) (MP)*       |                                   |                        |
|----------|-------------|-------------------------------------|-----------------------------------|------------------------|
|          |             | After 250°C in 10% H <sub>2</sub> O | After 250°C in dry N <sub>2</sub> | After vacuum treatment |
| 2Y       | 14 (t)      | 93 (m)                              | 88 (m)                            | 74 (m)                 |
| 3Y       | 4 (t)       | 66 (m)                              | 22 (t)                            | 0 (t)                  |
| 4Y       | 0 (t)       | 0 (t)                               | 0 (t)                             | 0 (t)                  |

\*MP is major ZrO<sub>2</sub> crystal phase: (m) monoclinic, (t) tetragonal, (c) cubic.

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