Mechanical Properties of Hot-Pressed TZP Ceramics Doped with \( Y_2O_3 \) and \( Nb_2O_5 \)

Deuk Yong Lee*, Dae-Joon Kim** and Kyeong-Sik Cho**

*Department of Metallurgical and Materials Engineering, Daelim College of Technology, Anyang 431-715, Korea

**Ceramics Division, Korea Institute of Science and Technology, Seoul 130-650, Korea

\( Y_2O_3 \) and \( Nb_2O_5 \) co-doped tetragonal \( ZrO_2 \) polycrystals (TZPs) were synthesized by hot-pressing (HPing) at temperatures in the range of 1300 to 1500°C to investigate the effect of alloying on the mechanical properties of TZPs. TZPs (89.25 mol% \( ZrO_2 \)-5.75 mol% \( Y_2O_3 \)-5.00 mol% \( Nb_2O_5 \) and 90.24 mol% \( ZrO_2 \)-5.31 mol% \( Y_2O_3 \)-4.45 mol% \( Nb_2O_5 \)), prepared by HPing at 1400°C for 1 h, showed a negligible monoclinic (m-) \( ZrO_2 \) content (<1%), the highest flexural strength of about 1 GPa, and the fracture toughness of above 7.5 MPa m\(^{1/2}\). Both low and high temperature (250 to 1000°C) aging for up to 100 h was carried out to evaluate the phase stability. TZPs, aged at temperatures higher than 400°C, suffered from strength degradation due to the extensive cavitation caused by graphite oxidation. The carbon incorporated in TZPs was identified as either an ether-type C-O or a carbonyl-type C=O. On the other hand, the specimens aged at temperatures lower than 400°C maintained the phase stability and mechanical properties.

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**Keywords:** tetragonal zirconia polycrystal (TZP), hot-pressing (HPing), aging, phase stability, graphite oxidation

I. Introduction

\( Y_2O_3 \) stabilized tetragonal \( ZrO_2 \) polycrystals (Y-TZPs) possess a number of desirable properties, such as excellent fracture toughness and strength for structural applications. Nevertheless, losses in strength and fracture toughness after long-term use at low temperatures (100 to 400°C), so called low temperature degradation (LTD), limit widespread applications of Y-TZP. In order to overcome these problems, there have been several efforts to develop Y-TZP with improved low temperature mechanical properties by alloying oxides\(^{(10)}\), such as \( CeO_2 \), \( TiO_2 \), etc., into Y-TZP, which leads to the low-temperature phase stability of Y-TZP.

Kim and Tien\(^{(5)}\) reported the compositional region of transformable and nontransformable t-\( ZrO_2 \) solid solutions along with the phase boundary of c-\( ZrO_2 \) solid solutions in the system \( ZrO_2-Y_2O_3-Ta_2O_5 \). In a similar system \( ZrO_2-Y_2O_3-Nb_2O_5 \), Lee et al.\(^{(6)}\) observed that the t-\( ZrO_2 \) solid solution (monolith, 2.06 \( \mu \)m) of 90.24 mol% \( ZrO_2 \)-5.31 mol% \( Y_2O_3 \)-4.45 mol% \( Nb_2O_5 \), sintered for 10 h at 1550°C in air, possesses the highest strength and toughness of above 500 MPa and 8 MPa m\(^{1/2}\), respectively, without suffering t→m phase transformation after aging up to 1000 h in the temperature range of 200 to 1000°C. For the comparison, 3Y-TZP (0.85 \( \mu \)m), prepared under the same sintering condition, exhibited the strength and toughness of 600 MPa and 4.8 MPa m\(^{1/2}\), respectively, but 64% of t-\( ZrO_2 \) transformed to m-\( ZrO_2 \) during aging for 100 h at 220°C.

Notably, greater bend strength of Y-TZP was achieved by HPing\(^{(5)}\) or hot-isostatic pressing (HIPing)\(^{(6)}\).

Masakii\(^{(9)}\) examined Y-TZPs prepared by HPing as a function of \( Y_2O_3 \) content and reported that a 3-point bend strength and fracture toughness determined using an indentation method according to Niihara\(^{(8)}\) for 2.5 mol% \( Y_2O_3 \)-TZP (2.5Y-TZP) were about 1700 MPa and 5 MPa m\(^{1/2}\), respectively.

Thus, the purpose of the present study is to investigate the mechanical properties of \( Y_2O_3 \) and \( Nb_2O_5 \) co-doped TZPs and 3Y-TZP prepared by HPing and the phase stability of t-\( ZrO_2 \) solid solution under the aging at low and high temperatures.

II. Experimental Procedure

The powder preparation procedure of nontransformable TZP (89.25 mol% \( ZrO_2 \)-5.75 mol% \( Y_2O_3 \)-5.00 mol% \( Nb_2O_5 \)), monolith (90.24 mol% \( ZrO_2 \)-5.31 mol% \( Y_2O_3 \)-4.45 mol% \( Nb_2O_5 \)), and 3Y-TZP was reported elsewhere\(^{(1)}\). The powders were uniaxially pressed into rectangular plate (34 mm × 34 mm × 5 mm) at 98 MPa. The plates were inserted in a graphite die and hot-pressed (HPed) in the temperature range of 1300 and 1500°C under Ar atmosphere. The heating rate was 12°C/min and the holding time at each sintering temperature was 1 h. A pressure of 5 MPa was applied up to HPing temperature and then the pressure increased to 30 MPa at the sintering temperature. After sintering, the pressure was reduced to 15 MPa and then released completely at 1200°C. The final dimension of HPed material was 34 mm × 34 mm × 4 mm. The sintered specimens were ground and polished down to a 1 \( \mu \)m diamond finish.

The bulk density of the specimen was determined by the Archimedes method. The elastic modulus was meas-
ured acoustically using the pulsed-echo overlap method (Model MK-5 Grindasonic, J. W. Lemmens N. V., Belgium)\(^9\). Fracture toughness of bar was measured using the dummy indentation method\(^{[10,11]}\) by placing three equally-spaced Vickers diamond indents of 294 N on the tensile-sided surface after polishing to a 1 \(\mu\)m diamond finish. The flexural strength was measured in 4-point bending with outer and inner spans of 20 and 8 mm, respectively, at a crosshead speed of 0.5 mm/min (Model 4204, Instron, UK).

Both low and high temperature aging was carried out at 250 to 1000 °C for up to 1000 h\(^{[6,9]}\). Phase stability of t-ZrO\(_2\) after aging was studied by using X-ray diffractometry. The proportion of the \(t\), \(m\), and \(c\)-phase was estimated from the X-ray diffraction (XRD) peak heights of \((11\overline{1})_t\), \((11\overline{1})_m\), \((11\overline{1})_c\), \((004)_t\), \((400)_m\), and \((400)_c\), after Garvie and Nicholson\(^{[12]}\). XRD patterns were obtained from the CuK\(\alpha\) radiation at 40 kV and 30 mA within the scan angles \((2\theta)\) of 27.5° to 76°.

Chemical analysis and trace elements, especially carbon and carbide, were determined by X-ray photoelectron spectroscopy (XPS). XPS analysis\(^{[13]}\) was performed with a Surface Scientific Instrument Model 2803-S spectrometer having a base pressure of \(2 \times 10^{-8}\) Pa. XPS data were obtained with AlK\(\alpha\) radiation (\(H\nu=1486.6\) eV, 1 eV=1.602 \(\times 10^{-19}\) J), X-ray monochromator, and a concentric hemispherical analyzer, and the test could reach an energy resolution of 0.48 eV and a spatial resolution of 100 \(\mu\)m. An Ar ion sputter gun \((E_p=5\) keV, current of roughly 5,000 mA for 5 s) was used to remove a small amount of carbon contamination as well as a hydrated layer through a slight etching. Each spectrum was taken after identifying an absence of the C 1s line and a lack of the hydroxyl-like tail usually observed in O 1s core levels. Charging effect was neutralized using a flood gun operated at 4 eV kinetic energy. Curve fitting of the C 1s and O 1s core-level spectra was accomplished via a series of iterations to find the best fit as defined by the minimized X-squared statistics of a Gaussian function. Binding energies for each of these lines were referenced to the C 1s peak at 284.6 eV.

A scanning electron microscope (SEM, Model S-4200, HITACHI, and Model JSM-840A, JEOL, Japan) was used to examine the surfaces of polished and fractured bars and to determine the average grain size with the use of a correction factor of 1.56 after Mendelson\(^{[16]}\).

### III. Results and Discussion

Figure 1 shows the results for bulk density against HP-ing temperature. Final densities of >99.6% theoretical were obtained for all specimens sintered above 1300°C. But both monolith and nontransformable TZPs, HPed at 1500°C, were cracked and the as-HPed nontransformable TZP at 1300°C was also cracked. Grain size and \% m-ZrO\(_2\) content of specimens are summarized in Table 1.

The as-HPed specimens were coated with BN film because the BN powder was sprayed on the sample to avoid the sticking problem between the specimen and the graphite die. The specimens were then mechanically

![Fig. 1 Variation of bulk density against HP-ing temperature.](Image)

**Table 1 Characteristics of hot-pressed specimens for 1 h at temperatures of 1300 to 1500°C.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Grain size (µm)</th>
<th>%m-ZrO(_2)</th>
<th>%c-ZrO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Y-TZP</td>
<td>1300</td>
<td>0.32</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1350</td>
<td>0.35</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>0.40</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>0.47</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1500</td>
<td>0.50</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Monolith</td>
<td>1300</td>
<td>*</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1350</td>
<td>0.35</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>0.48</td>
<td>&lt;1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>0.72</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>Nontransformable TZP</td>
<td>1300</td>
<td>*</td>
<td>8</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1350</td>
<td>0.39</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1400</td>
<td>0.55</td>
<td>&lt;1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>1450</td>
<td>0.78</td>
<td>4</td>
<td>20</td>
</tr>
</tbody>
</table>

* not measurable due to extensive microcracking
ground and polished down to a 1 μm finish before the experiment. However, the ground and polished specimens were not annealed due to the carbon evaporation as CO₂. Therefore, the specimens were to an extent influenced by grinding, which was confirmed by X-ray diffraction (XRD) analysis.

XRD analysis of the ground surfaces of monolith and 3Y-TZP HPeD at 1400°C, as shown in Fig. 2, exhibited the pronounced m-ZrO₂ and the asymmetric broadening of (111), peak (Fig. 1(a) and (c)). Kim et al. reported that the accumulated strain on the surface due to the grinding caused the t to rhombohedral (r) phase transformation to relax the surface strain, which was indicated by the enhanced asymmetric broadening of the (111), peak. Since polishing (Fig. 1(b) and (d)) restored the asymmetric (111), peak profile of all specimens to a symmetric one, m-ZrO₂ content of the polished specimens was negligible. However, XRD analysis of the polished monolith and nontransformable TZP revealed that t, c, and m-ZrO₂ were present, although c-ZrO₂ (13-20%) was observed only after sintering at 1450°C (Fig. 3(d)). The m-ZrO₂ content on polished surface of 3Y-TZP at 1500°C was substantially lower (~0%) than Masaki’s result(10) (10%). It could be explained by the difference in sample preparation.

Figure 4 depicts that m-ZrO₂ content of polished TZPs increases greatly at both 1300 and 1450°C, whereas 3Y-TZP shows a negligible m-ZrO₂. This observation implies that Nb₂O₅ doped Y-TZPs, sintered at temperatures lower than 1400°C, and 3Y-TZP are insensitive to temperature because m-ZrO₂ content remains unchanged even after aging at 250°C for 1000 h. However, nontransformable TZP and monolith, sintered at 1450°C, show extensive m-ZrO₂ content (~55%) after aging for 100 h at 250°C. Since LTD of TZPs is not influenced by the grain size, the increase of m-ZrO₂ content during aging may be caused by the increase of specific volume as a result of the reduction of Nb₂O₅ to NbO₂ in an oxygen deficient atmosphere. Consequently, the loss of t-ZrO₂ lattice constraint accelerates LTD.

Figure 5 shows that the flexural strength of 3Y-TZP increases with rising temperature, whereas that of monolith and nontransformable TZP increases gradually up to 1400°C (0.48 μm) and then decreases with further increase in grain size. Although the as-sintered monolith (1350°C) contains m-ZrO₂ (3%), it shows no phase transformation during aging at 250°C due to the smaller grain size (0.35 μm). In particular, monolith and nontransformable TZP HPeD at 1400°C shows the highest strength of about 1 GPa. Fracture toughness of monolith and 3Y-TZP increases sharply with rising sintering tem-
Flexural strength and fracture toughness of 3Y-TZP and monolith after HPing for 1 h at each temperature. Young's modulus of monolith and 3Y-TZP increases slightly with increasing sintering temperature, but that of monolith and nontransformable TZP, sintered at 1450°C and then aged for 100 h at 1000°C, decreases markedly (Fig. 6), resulting in a lower strength. Although Young's modulus of 3Y-TZP varies slightly after aging, it experiences the severe strength degradation due to the carbon evaporation. Therefore, it is obvious that the effect of carbon on strength is more significant than that of Young's modulus during high temperature aging.

Masaki measured only the variation of carbon contents before and after aging by using SIMS and laser Raman spectroscopy and reported that carbon or carbide incorporated in the specimen was responsible for the strength degradation. To verify carbon species incorporated in TZPs during HPing, surface analysis by XPS was performed in the present study for the specimen before and after aging. Only the hydrocarbon carbon C–C was observed for the monolith sintered at 1550°C for 10 h in air because free carbon was abundant inside the chamber. However, the XPS results of the as-HPed specimens demonstrated that three carbon species existed. The carbon species were identified as C–C at 284.6 eV, carbon bonded to ether-type C–O around 286.1 eV, and carbonyl-type C=O near 287.8 eV. Figure 7 shows the raw data and curve fit for the C 1s and O 1s region. An ether-type C–O (285.63 eV) and a weak peak around 284.6 eV due to a neutral hydrocarbon carbon were observed (Fig. 7(a)) for monolith HPed at 1400°C. A metal oxide (MO)
around 530.93 eV, and a weak peak (C-O) around 533.14 eV (Fig. 7(c)) were found. After aging for 50 h at 800°C, the intensity of CO decreases greatly, resulting in a weak peak C=O around 531.73 eV (Fig. 7(d)). The observed CO may be originated from the surface of graphite heating element or die due to the graphite oxidation as reported by Yamaguchi et al.16 However, no carbides, such as ZrC (281.1 eV) or NbC (281.9 eV), were observed. After HPeing, the color of specimens was changed from white to black (monolith and nontransformable TZP) and gray black (3Y-TZP). It represented that carbon contamination was more severe to Nb2O5 doped Y-TZPs than 3Y-TZP. The change of color from black (gray black) to white was observed after aging above 700°C. Thus, the oxidation of CO to CO2 during aging is probably the main reason for LTD.

In order to compare the behavior of CO, DTA/TGA were performed on monolith and 3Y-TZP. They exhibited no sign of weight gain or loss from room temperature to 1490°C, but the color of samples changed from black to white. To determine the temperature of CO2 evaporation indirectly, the flexural strength was measured after aging for 100 h at each temperature. Figure 8 indicates that CO2 evaporation starts gradually from 400°C and then completes at 800°C. The color of specimens (black/grey black) changed completely to white at 800°C (monolith) or 700°C (3Y-TZP). Unless carbon monoxide evaporates, TZPs may maintain their mechanical properties and phase stability because TZPs prepared by the conventional sintering method maintain the phase stability46 during aging at temperatures from 200 to 1000°C. Above 400°C, CO2 may start to evaporate, resulting in lowering the strength. Therefore, the strength observation suggests indirectly that 400°C is the critical temperature to the mechanical properties of HPeed TZPs.

Figure 9 illustrates that thermally etched surfaces of monolith (0.48 μm) and 3Y-TZP (0.50 μm), HPeed at 1400 and 1500°C respectively, show a few pores at the triple point (arrows). After aging for 100 h at 1000°C, however, the structure of cavities (dark area) extends across several grains (Fig. 10), resulting in high temperature strength degradation. Then, the fracture mode of aged 3Y-TZP for 100 h at 1000°C represents a typical brittle fracture as shown in Fig. 11(b).

**IV. Conclusions**

No t→m phase transformation was observed for both monolith and 3Y-TZP, sintered at lower than 1400°C, during aging at temperatures lower than 400°C because of the smaller grain size. However, CO produced by the graphite oxidation penetrates into the sintered specimen and then remains as C-O or C=O. It is expected that CO starts to oxidate gradually as a form of CO2 during aging at temperatures above 400°C, which is experimentally observed by the change of specimen color, flexural strength, and microstructure.

Nb2O5 doped Y-TZPs, monolith and nontransformable TZP, exhibit the flexural strength of about 1 GPa, the fracture toughness of above 7.5 MPa·m1/2, and no LTD behavior. The sintering condition for the mechanical properties and the excellent phase stability of TZPs is the 1 h HPeing at 1400°C in an argon atmosphere. The
above-mentioned mechanical properties are better than those of 3Y-TZP HPePed for 1 h at 1500°C and 5Y-TZP. Especially, Nb₂O₅ doping to Y-TZPs raises fracture toughness significantly without compromising strength and phase stability. The flexural strength of TZPs co-doped with Y₂O₃ and Nb₂O₅ is always higher than that of 3Y-TZP before and after the aging treatment.

Acknowledgments

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References