Hardness and Fracture Toughness of Alumina-Doped Tetragonal Zirconia with Different Yttria Contents

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The 0.75 to 3.0 mol% Y$_2$O$_3$-stabilized tetragonal ZrO$_2$ (Y-TZP) and Al$_2$O$_3$-Y-TZP fine-grained ceramics with 0.2 to 0.7 mass% of alumina were produced by a colloidal technique and low-temperature sintering. Trace alumina addition enhanced the densification of Y-TZP. The influence of the resulting density, microstructure, the yttria-stabilizer and the alumina content on the hardness and toughness were studied. The bulk 2.7Y-TZP ceramic with an average grain size of 110 nm reached a hardness of 13.6 GPa and fracture toughness of 11.2 MPa m$^{1/2}$. Y-TZP ceramics with a reduced yttria-stabilizer content were found to reach a fracture toughness of 13.8 MPa m$^{1/2}$ (2Y-TZP), and 14.5 MPa m$^{1/2}$ (1.5Y-TZP). A nano-grained alumina dispersed zirconia with 3 mol% Y$_2$O$_3$ with an average grain size of 97 nm was obtained, and the hardness increased to 16.8 GPa. Y-TZP/alumina ceramics with a 0.35 mass% Al$_2$O$_3$ were found to reach a fracture toughness of 15.7 MPa m$^{1/2}$ (2Y) and 15.3 MPa m$^{1/2}$ (1.5Y).

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1. Introduction

The fabrication of tough and strong ceramics, long a goal of ceramic scientists, is difficult to achieve because of their inherent brittleness. Tetragonal zirconia (TZP) or zirconia-based ceramics have attracted special attention because of their excellent mechanical properties and attractive possibility of obtaining a nano-grained bulk ceramic with a controllable microstructure and improved properties.

The tetragonal-monoclinic ($t \rightarrow m$) phase transformation in zirconia has received much attention, because the anisotropic and large ($\sim 3\%$) volume increase upon transformation often causes severe cracking if the zirconia-based ceramics are cycled through the transformation. Martensitic transformation in the stress fields of propagating cracks leads to dramatic increases in the toughness of two-phase ceramics. A fine-grained single-phase tetragonal zirconia can be produced, which undergoes the martensitic transformation to monoclinic symmetry during fracture. Optimization of the toughening that can be achieved by such transformations is a research goal of major importance. The strong dependence of the transformation toughening effect in zirconia with grain size is also known.

There is a controversy regarding the values of the fracture toughness ($K_{IC}$) in the literature. Lange et al. reported a $K_{IC}$ value of 6.73 MPa m$^{1/2}$. This value was based on a transformation-toughened composite, i.e., one that occurred during the crack propagation. The very poor fracture toughness values of the nanocrystalline 3 mol% yttria-stabilized zirconia ceramic was reported by Mayo et al. due to overstabilization of the tetragonal phase by the fine grain size, so that it could not transform to a monoclinic phase during crack propagation. Cottom and Mayo showed that without phase transformation toughening, the $K_{IC}$ is in the range of 2.25 to 4.25 MPa m$^{1/2}$, a value comparable to brittle ceramics. However, there was a problem with their data analysis. The crack geometry was the Palmqvist type at the loads they used, however, instead of using an equation related to the Palmqvist geometry, they used an equation for the median crack geometry. This should result in an error even though the trend in toughness should be valid.

The $K_{IC}$ of nanocrystalline zirconia could be significantly increased by allowing the phase transformation ($t \rightarrow m$) to occur by decreasing the thermodynamic stability of the tetragonal phase, i.e., reducing the amount of yttria-stabilizer. Bravo-Leon et al. reported the preparation of the fully tetragonal zirconia samples with 1.0 and 1.5 mol% Y$_2$O$_3$ with the optimum $K_{IC}$ value of about 16 MPa m$^{1/2}$. In this case, the grain size for the optimum $K_{IC}$ was just below the critical grain size for transformation in the material, and decreasing of the grain size was reported to lower the $K_{IC}$ in the 1.0Y-TZP and 1.5Y-TZP ceramics to a value of 2-3 MPa m$^{1/2}$, similar to monoclinic zirconia. However, the density of the ceramic samples in the above investigation was relatively low (88.9-95.3%) and some times the crack propagation could possibly be stopped by the intersection of the crack with a pore. As a result, the measured crack length and calculated $K_{IC}$ value could be incorrect.

The data for dense nano-sized zirconias are required to clarify the effect of the yttria contents on the $K_{IC}$.

The addition of one ceramic to another often produces a composite with more desirable properties than the individual components. Small quantities of alumina (Al$_2$O$_3$) are known to aid densification, and have been shown by Sakka et al. to enhance the tensile deformation during superplastic flow of the zirconia ceramic. The addition of alumina to yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) has produced ceramics with improved toughness. Y-TZP ceramic with slightly different yttria contents (2-3 mol%) showed the opposite trend in $K_{IC}$ values after the alumina addition. Also, the $K_{IC}$ values of Al$_2$O$_3$/ZrO$_2$ composites showed a dependence on the testing and evaluation techniques. Fukuhara showed that the alumina addition to Y-TZP increased the hardness, but decreased the $K_{IC}$. Examples of
the effect of a small alumina addition (0.375-1.5 mol% Al2O3) have been shown by Kihara et al.16) The KIC increased by 17% and 15% with the addition of 1 and 4 vol% Al2O3, respectively. However, the results have not always been consistent. Bhaduri et al.18) reported that the nanocrystalline Al2O3/ZrO2 fully-dense composite had an average hardness and a KIC of 4.45 GPa and 8.38 MPa-m1/2, respectively. Lange4,5) reported a hardness of 15 GPa for a conventionally processed nano-ceramic.

The 1.5 to 3.0 mol% Y2O3-stabilized tetragonal ZrO2 (Y-TZP) and Al2O3/Y-TZP nano-composite ceramics with 1-5 mass% of alumina were produced and the influence of the ceramic processing conditions, resulting density, microstructure, and the alumina content on the hardness, toughness and density were studied.12) The bulk nanostructured 3 mol% yttria-stabilized zirconia ceramic with an average grain size of 112 nm was shown to reach a hardness of 12.2 GPa and KIC of 9.3 MPa-m1/2. A nano-grained bulk alumina/zirconia composite ceramic with an average grain size of 94 nm was obtained, and the hardness increased to 16.2 GPa. Nano-grained tetragonal zirconia ceramics with a reduced yttria-stabilizer content were shown to reach a KIC value between 12.6-14.8 MPa-m1/2 (2Y-TZP), and 11.9-13.9 MPa-m1/2 (1.5Y-TZP). The main discrepancies in these results4,5,11,12) should be attributed to the different starting materials and fabrication routes.

In the present study, we expected that the KIC of the yttria-stabilized zirconia might be increased if the thermodynamic stability of the tetragonal zirconia decreased (for occurrence of the phase transformation from tetragonal to monoclinic upon the introduction of cracks during indentation). Tetragonal zirconia (Y-TZP) ceramics with a 0.75-3.0 mol% yttria-stabilizer content were produced and then examined in order to optimize the KIC. The influence of the alumina content in 0.35 and 0.7 mass% Al2O3-doped zirconia and the lowering of the yttria-stabilizer content from 3 to 0.75 mol% Y2O3 on the hardness and KIC of the bulk nano-ceramic were considered. The tetragonal zirconia nano-ceramics (doped and undoped with alumina) with the highest hardness and KIC were produced.

2. Experimental

2.1 Sample preparation

The yttria-stabilized zirconia (Y-TZP) nanopowder preparation technique as well as the properties of its colloidal consolidation were previously well described.22-24) The γ-alumina powder (Al2O3 Nanotek, CI Chemical Co., Tokyo, Japan) with an average particle size of 30 nm was dispersed in the suspensions within 2 h prior to the zirconia powder addition. Consolidations of the suspensions by slip casting and subsequent cold isostatic pressing (CIP) at 400 MPa were applied. The samples were sintered under ambient pressure in air at the temperature of 1150°C and times ranging from 2 to 30 h in order to produce a ceramic with a range of densities and grain sizes.18-24) The samples were heated at 5°C/min to the desired temperatures, held for the prescribed times, and then furnace cooled.

2.2 Characterization methods

The density of the sintered bodies was measured by Archimedes method in water. The relative density of the zirconia ceramic was based on 6.06 g/cm3, and the relative densities of the zirconia-alumina composites were calculated according to the mass% of Al2O3 in each composite, assuming the α form (d = 3.98 g/cm3).

The samples for the Vickers indentation tests were squares with an approximate 4 mm height and 12 mm sides. The surface on which the indentations were performed was previously polished with diamond paste in an ordinary metalliclographic polisher. The quality of the finishing was checked by optical microscopy in order to avoid the presence of any scratches on the surfaces prior to testing. Grain sizes were measured by a linear analysis of SEM micrographs of the polished and etched (1100°C for 1 h) surfaces. Hardness indentations (Hardness Testing Machine (MVK-H2), Akashi Co. Japan) were obtained by applying the forces of both 4.9 N and 9.81 N (0.5 kg and 1 kgf, respectively) for a dwell time of 15 s. For each sample, 10 indentations were used to obtain the average hardness and standard deviation value. The high load (98 N and 196 N × 15 s) indentation tests (Hardness Testing Machine (AVK-A), Akashi Co. Japan) were performed on each sample to generate cracks, and from them, the fracture toughness values were obtained. The higher force of 196 N (20 kg mass) was applied to generate cracks on the surfaces of the Y-TZP nano-ceramics with a reduced yttria content. An average fracture toughness and standard deviation for each sample were computed from the total number of fracture toughness values per sample (12 values).

Because zirconia cracks in a Palmqvist mode, the KIC was obtained from the expression given by Niihara et al.25) for the Palmqvist cracks in brittle materials:

\[
K_{IC} = \frac{H \cdot d^{1/2}}{E \cdot \varphi} \cdot \frac{H}{E \cdot \varphi} = 0.035 \cdot \left(\frac{\varphi}{2\varphi - 1}\right)^{-1/2}
\]

where \(H\) is the Vickers hardness, \(E\) is the Young’s modulus, \(2\varphi = d\) is the diagonal of the indentation, \(\varphi\) is the constrain factor, and \(l\) is the crack length. The so-called Palmqvist cracks \((l)\) begin only at the end of the diagonals of the indentation, and the criteria for such cracks are as follows: 0.25 = \(l/a\) = 2.5.23) The expression for the fracture toughness (eq. 2) was obtained from the above relation (eq. 1):

\[
K_{IC} = 9.052 \cdot 10^{-3} \cdot H^{3/2} \cdot E^{2/5} \cdot d \cdot l^{-1/2}
\]

A value of \(E = 210 \text{ GPa}\) has been assumed for all the ceramic samples irrespective of their compositions. In addition, the crack lengths were immediately measured after the indentation was carried out in order to avoid slow crack growth after removing the load.9,23)

3. Results and Discussion

3.1 Sintering behavior

The isothermal sintering behavior was studied at 1150°C. The sintering behaviors for the 3Y-TZP and 0.2 to 0.7 mass% alumina-doped 3Y-TZP samples are shown in Fig. 1, where the relative densities are plotted as a function of the sintering time. At this sintering temperature, the grain size remained in the nano-scale range.9-12,19-21,24)
ceramic sample prepared from the 3Y-TZP powder reached 92% during heating (5 °C/min) to the prescribed temperature, and 95% after a 2-h hold. The densification, D = 97.5%, was attained by sintering at 1150 °C for 12 h. Sintering at 1150 °C with the longer hold of 30 h produced a ceramic that was 99.1% dense.

The addition of a small amount of alumina allowed the densification rate to be increased in comparison to the alumina-free 3Y-TZP samples. The 0.35 mass% Al₂O₃-doped zirconia ceramic exhibited 95.4% densification during heating (5 °C/min) to 1150 °C and 99.2% densification after a 12-hour hold. A nearly full-dense ceramic was obtained after a 20-hour hold. No significant differences were found necessary for the sintering conditions of the Y-TZP ceramics with a reduced yttria-stabilizer content.

Figure 2 shows the SEM microstructure of the 0.35 mass% Al₂O₃/2.7Y-TZP composite sintered at a temperature of 1150 °C for 20 h. The addition of the alumina enhanced the sintering process, shortened the sintering time (Fig. 1) and allowed the ceramic microstructure to remain in the nanoscale region. The average grain size is about 97 nm. The ceramic samples had varied densities (97 to 100% relative density) and grain sizes (60 to 160 nm) depending of the sintering parameters and composition.

### 3.2 Mechanical properties

The Vickers hardness data vs. relative density for the fully tetragonal yttria-stabilized alumina-free zirconia ceramic with (a) 3.0 mol%; (b) 2.7 mol%; (c) 1.5%; and (d) 0.75 mol% yttria-stabilizer contents, and zirconia doped with 0.35 and 0.7 mass% alumina are shown in Fig. 3. As can be seen from Fig. 3, the hardness increases with density, and after a maximum, decreases. The undoped, nearly fully dense yttria-stabilized zirconia 2.7Y-TZP ceramic (dotted lines) exhibited an average hardness of 13.6 GPa (for 99.2% dense). The 1.5Y-TZP and 0.75Y-TZP ceramics had reduced average hardness values in comparison with the samples with the higher yttria-stabilizer contents. For all the Y-TZP specimens, the maximum hardness was observed at a somewhat lower density rather than at full density. A longer hold at temperature allowed the density to be increased to nearly 100%. However, during such holdings, the average grain size of the zirconia samples (Fig. 4) also slightly increased from 82 nm (2-h hold) to 118 nm (30-h hold). As a result, after some maximum value, the average hardness of the Y-TZP ceramics with 0.75 to 3 mol% of yttria-stabilizer (Figs. 3(a-d)) gradually decreased.

The trace-addition of alumina (0.35 and 0.7 mass% of Al₂O₃) allowed the hardness to increase for the alumina/zirconia composites of all yttria-stabilizer contents (Fig. 3). The relative hardness of the 0.35 mass% alumina/zirconia composite with a 3 mol% yttria-stabilizer reached the maximum value of 16.1 GPa at the relative density of 99.1% (Fig. 3(a)). The average hardness of the alumina/zirconia composite with the same alumina content, but with a slightly lower yttria-stabilizer content (2.7Y-TZP) reached the highest value of 16.8 GPa at the relative density of 99.5% (Fig. 3(b)). The maximum hardness of the 0.7 mass% Al₂O₃/1.5Y-TZP and 0.35 mass% Al₂O₃/0.75Y-TZP ceramic samples were only 13.9 GPa (relative density 99.6%) and 13.7 GPa (relative density 99.2%), respectively. We can conclude that reducing the yttria-stabilizer amount lowers the hardness of the zirconia and alumina/zirconia composite ceramics.

The fracture toughness vs. yttria-stabilizer content for the fully tetragonal zirconia ceramics and 0.2-0.7 mass% Al₂O₃/ Y-TZP composites is shown in Fig. 5. The average value of 8.62 MPa·m¹/² was measured and calculated for the 3Y-TZP ceramics. The significant increasing of KIC with decreasing yttria-stabilizer content can be seen. The fracture toughness reached the average value of 13.5 MPa·m¹/² by decreasing the Y₂O₃ content to 2 mol% and 14.2 MPa·m¹/² for the 1.5 mol% yttria stabilizer. Compared to this result, the 0.35 mass% alumina/3Y-TZP composite ceramic showed the maximum fracture toughness value of 7.86 MPa·m¹/² and reached the maximum for the 1.5-2 mol% yttria-content. For these compositions, the average fracture toughness was found to be 15.7 MPa·m¹/². However, further increasing the alumina content leads to a sharply reduced KIC.

### 4. Conclusion

We showed that dense yttria-stabilized (0.75-3 mol% Y₂O₃) tetragonal zirconia and 0.2 to 0.7 mass% alumina/zirconia nano-ceramics were obtained by a colloidal technique and low-temperature sintering at 1150 °C. The yttria-stabilized tetragonal zirconia ceramic with a higher fracture

**Fig. 1** Densification behavior during the sintering at 1150 °C.

**Fig. 2** SEM micrograph of 0.35 mass% Al₂O₃/2.7Y-TZP ceramic sintered at 1150 °C for 20h.
toughness was obtained by reducing the yttria-stabilizer content (preventing over-stabilization) from 3 mol% to 2.1.5 mol%. The addition of 0.2-0.35 mass% alumina produced an increasing fracture toughness. However, the 0.7 mass% Al$_2$O$_3$ doped tetragonal zirconia ceramic with a 1.5-3 mol% Y$_2$O$_3$ stabilizer content showed a significant reduction in $K_{IC}$ when compared to the alumina-free and 0.2-0.35 mass% alumina doped zirconia ceramics.

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