Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics

Massimiliano Guazzatoa,*, Mohammad Albakrya, Simon P. Ringerb, Michael V. Swaina

aBiomaterials Science Research Unit, Faculty of Dentistry, University of Sydney, United Dental Hospital, 2 Chalmers Street, Surry Hills, NSW, Australia 2010
bAustralian Key Centre for Microscopy and Microanalysis, University of Sydney, Sydney, NSW, Australia

Received 11 December 2002; received in revised form 2 May 2003; accepted 29 May 2003

KEYWORDS
Strength; Fracture toughness; Dental ceramic; Microstructure; Zirconia

Summary Objective: The present study is the second part of an investigation of strength, fracture toughness and microstructure of nine all-ceramic materials. In the present study, DC Zirkon, an experimental yttria partially stabilized zirconia, In-Ceram Zirconia slip and In-Ceram Zirconia dry-pressed were compared.

Methods: Strength was appraised on ten bar-shaped specimens for each material (20 × 4 × 1.2 mm) with the three-point bending method. The fracture toughness (Indentation Strength) was measured on twenty specimens (20 × 4 × 2 mm) for each ceramic. The volume fraction of each phase, the dimensions and shapes of the grains and the crack pattern were investigated with SEM. Phase transformation was investigated with X-ray diffraction. Data were compared with an ANOVA and Sheffe’s post hoc test (p = 0.05).

Results: Means of strength (MPa) and fracture toughness (MPa m^{1/2}) values and their standard deviation were: In-Ceram Zirconia dry-pressed 476 (50)1, 4.9 (0.36)1; In-Ceram Zirconia slip 630 (58)2, 4.8 (0.50)1; the experimental yttria partially stabilized zirconia 680 (130)2, 5.5 (0.34)2; DC-Zirkon 840 (140)3, 7.4 (0.62)3. Values with the same superscript number showed no significant statistical difference. Microscope investigation and X-ray diffraction revealed the important role played by the tetragonal to monoclinic phase transformation and by the relationship between the glassy matrix and the crystalline phase in the strengthening and toughening mechanisms of these ceramics.

Significance: the zirconia-based dental ceramics are stronger and tougher materials than the conventional glass-ceramics. Better properties can have positive influence on the clinical performance of all-ceramic restorations.

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Introduction

The development of advanced dental material technologies has recently led to the application of...
zirconia-based ceramics in dentistry. The remarkable mechanical properties of zirconia, already exploited in several medical and engineering applications, are mainly due to the tetragonal to monoclinic (t → m) phase transformation. The t → m transformation, which can be induced by external stresses, such as grinding, cooling and impact, results in a 4% increase of volume that causes compressive stresses. These stresses may develop on a ground surface or in the vicinity of a crack tip. It is this clamping constraint about the crack tip that must be overcome by the crack in order to propagate, explaining the increased fracture toughness of zirconia compared to other ceramics. Transformation toughening can occur when the zirconia particles are in the metastable tetragonal form, and on the verge of transformation. The metastability of the transformation is dependent on the composition, size, shape of the zirconia particles, the type and amount of the stabilizing oxides, the interaction of zirconia with other phases and the processing.1 Further-

1. Stabilizing oxides, the interaction of zirconia particles, the type and amount of the stabilizing oxides, the interaction of zirconia with other phases and the processing. 

2. Literature has shown contradictory results and modest improvement of the strength and fracture toughness of IZ over IA.7–10 There is a lack of studies comparing the slip to the dry-pressed, although the dry-pressed material is thought to have better mechanical properties as a result of more consistent processing.

DZ is an isostatically hot-pressed and fully sintered 5 wt% Y2O3 TZP. A framework is obtained by milling a dry-pressed block of this ceramic with a specifically designed CAD/CAM system, the DCS Precident milling system.

An experimental 3 mol% Y2O3 TZP (YZ) (corresponding to 6 wt% Y2O3 TZP) has been recently developed by one of authors (MS) from commercially available powders. A restoration is made from this material by milling a block of partially sintered ceramic, which is then sintered to full density at approximately 1400°C. Better mechanical properties are expected from DZ and YZ, when compared to IZ, as a result of processing and the absence of a low modulus infiltrating glass phase.

The aim of this study, which is divided in two parts, was to compare the strength, fracture toughness and microstructure of nine dental ceramics. In part I, IPS Empress (E1), Empress 2 (E2), a new experimental pressable ceramic (EC), IA dry-pressed and IA slip were discussed. The present paper focuses on IZ slip, IZ dry-pressed, DZ and YZ and compares these ceramics to peer materials already discussed in part I.11

Materials and methods

Preparation of the specimens

All specimens were obtained by cutting bars from several blocks that in turn were processed using different methods according to the material and the manufacturer’s recommendations. IZ slip specimens were obtained by preparing some blocks pouring an aqueous-based slip (lot 6214P, Vita Zahnfabrik, Bad Säckingen, Germany) as recommended by the manufacturer and described in part I.11 IZ dry-pressed (lot 6434R Vita In-Ceram Blank for Cerec, Vita Zahnfabrik, Bad Säckingen, Germany) was provided already sintered by Vita. YZ specimens were prepared by sintering some blocks of 3 mol% of Y2O3 ZrO2 powder at 1450°C for 1 h at the heating and cooling rate of 5°C/min. DZ specimens were cut from a block (lot No 521) of fully sintered material. After the preparation of the bars all specimens were ground and wet polished with diamond discs of nominal grit size 120, 70, 30 and 15 μm to the final dimensions. Finally, the specimens were cleaned using an ultrasonic bath with acetone at room temperature for 15 min. Ten samples for each material, with final dimensions of approximately 20 × 1.2 × 4 mm wide were used to test strength. Twenty specimens for each material with final dimensions of approximately 20 × 3 × 4 mm were used to appraise the fracture toughness.

Uniaxial flexural strength

Strength was measured with a three-point bending technique as described in part I and reported by ISO 6872.11,12
Fracture toughness, elastic modulus and hardness

Fracture toughness was assessed using the indentation strength method as proposed by Chantikul et al. Young’s modulus and hardness are parameters of the equation to calculate the fracture toughness and were determined according to the ASTM 1259-94 and ASTM C 1327-99.

Equation and experimental conditions were as reported in part I, whereas the following range of loads was used: IZ slip, IZ dry-pressed and YZ 20, 60, 120 and 200 N; DZ 40, 80, 160 and 300 N.

Statistics

All data were compared with one-way ANOVA and a series of Sheffe` post-hoc tests. The alpha value (p) was set at 0.05.

Microscopy

The volume fraction of each phase, porosity, fracture behavior, and grain shapes and sizes were determined from SEM (XL 30, Philips, Eindhoven, Holland and JSM 6000 FSEM, Jeol, Tokyo, Japan) micrographs. The specimens for SEM observation were polished to 1 μm and carbon coated, while those for field emission SEM were polished, etched and coated with platinum (20 nm). IZ slip and dry-pressed specimens were etched for 30 min with an ion beam (gun current 1.0 mA and gun voltage 5.5 mV) (Dual Ion Mill, Model 600, Gatan Pleasanton, California USA), whereas DZ and YZ specimens were thermally etched for 10 minutes at 1400°C. For YZ and DZ the average grain size was determined by the line-intercept technique. For this purpose, five micrographs and five lines were used for each material. In the case of IZ, due to the presence of multiple phases and the variety of the shape of the grains, means of length and width or diameter were calculated.

X-ray diffraction

X-ray diffraction (Diffractometer D5000, Siemens, Germany) analyses were conducted to determine the relative amount of the monoclinic phase of the as-sintered and fractured surfaces. Specimen surfaces were scanned with Cu Kα X-ray from 20 to 40° 2θ degrees with a step size of 0.04° and 5 s step interval. The relative amount (XM) of the monoclinic phase was calculated as suggested by Garvie and Nicholson.

Results

The mean values of flexural strength, fracture toughness, elastic modulus and hardness are reported in Table 1, along with the material tested in part I. As far as strength is concerned, statistics show that the materials were divided into five groups in which ceramics of the same group (indicated by the superscript number) do not show any statistical difference. In a decreasing order, DZ proves to be the strongest material; there is no statistical difference between YZ, IZ slip and IA slip; IA slip is statistically as strong as IZ dry-pressed and IA dry-pressed. There is no statistical difference between IA dry-pressed, E2 and EC. Finally, E1 is the weakest material. In respect of the fracture toughness, the materials are divided into 5 groups with (in increasing order) E1 in group 1; EC, E2 and IA dry-pressed in group 2; IZ dry-pressed, IA slip and IZ slip in group 3; YZ in group 4; and DZ in group 5.

The volume fractions of each phase, the glassy matrix and porosity of DZ, YZ and IZ slip and dry-pressed are reported in Table 2. The microscopic observations show that IZ dry-pressed and slip are microstructurally very similar (Fig. 1), unlike IA slip.

<table>
<thead>
<tr>
<th>Material</th>
<th>Strength (MPa)</th>
<th>Fracture Toughness (MPa m^1/2)</th>
<th>Elastic Modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E1</td>
<td>106 (17)^1</td>
<td>1.2 (0.14)^1</td>
<td>65 (1.5)</td>
<td>6.5 (0.4)</td>
</tr>
<tr>
<td>EC</td>
<td>303 (49)^2</td>
<td>3.0 (0.65)^2</td>
<td>90 (3.7)</td>
<td>5.5 (0.2)</td>
</tr>
<tr>
<td>E2</td>
<td>306 (29)^2</td>
<td>2.9 (0.51)^2</td>
<td>105 (4.8)</td>
<td>5.3 (0.2)</td>
</tr>
<tr>
<td>IA dry-pressed</td>
<td>440 (50)^2,3</td>
<td>3.6 (0.26)^2</td>
<td>265 (10)</td>
<td>11 (1.1)</td>
</tr>
<tr>
<td>IZ dry-pressed</td>
<td>476 (50)^2</td>
<td>4.9 (0.36)^2</td>
<td>240 (9.0)</td>
<td>11 (0.9)</td>
</tr>
<tr>
<td>IA slip</td>
<td>594 (52)^3,4</td>
<td>4.4 (0.48)^3</td>
<td>265 (10)</td>
<td>11 (0.3)</td>
</tr>
<tr>
<td>IZ slip</td>
<td>630 (58)^2</td>
<td>4.8 (0.50)^3</td>
<td>240 (9.0)</td>
<td>10.5 (0.2)</td>
</tr>
<tr>
<td>YZ</td>
<td>680 (130)^5</td>
<td>5.5 (0.34)^4</td>
<td>240 (9.5)</td>
<td>13 (0.3)</td>
</tr>
<tr>
<td>DZ</td>
<td>840 (140)^6</td>
<td>7.4 (0.62)^5</td>
<td>220 (7.5)</td>
<td>12 (0.2)</td>
</tr>
</tbody>
</table>

The superscript number indicates (for materials with the same number) groups with no significant statistical difference.

Materials discussed in Part I 11.
and dry-pressed as discussed in part I. In both materials the three sizes of particles of alumina seen in IA slip are also present (Fig. 1). However, in IZ the elongated alumina grains are significantly finer (average 6 long, 2 μm wide) and not oriented. Indentations made on the polished surfaces of both materials show symmetric cracks. Zirconia grains are observable in two forms: large faceted grains (mean grain size 2 μm) and fine spherical grains (mean grain size <1 μm). Agglomerates with a cluster of zirconia or alumina grains are also seen (Fig. 1A). The crack pattern is consistently transgranular for the zirconia grains (Fig. 1B and C), whereas it is intergranular for alumina grains, except when the crack tip propagates perpendicularly to the elongated grains. Microscopy shows evidence of crack deflection and crack shielding (bridging and pull-out of elongated grains) and microcrack toughening (Fig. 1B and C). The only noticeable difference between IZ slip and dry-pressed is the porosity (Table 2), being greater in IZ dry-pressed.

YZ and DZ both have a very fine microstructure (mean grain size 0.21 and 0.28 μm, respectively) (Fig. 2). However, microscopy shows marked differences between the two materials. DZ is a dense material with a volume fraction of porosity less than 1% (Table 2). Pores have small diameter (<0.3 μm), spherical shape and are often located at the interboundary regions. The fracture pattern of DZ is intergranular as well as transgranular (Fig. 2B). YZ, on the other hand, has a greater porosity (9%) (Table 2). Furthermore, some pores have elongated shape and size up to 5 μm. The fracture pattern is almost exclusively intergranular with cracks occasionally propagating through the smaller particles (Fig. 2C).

The XRD analyses (Fig. 3) shows the major peaks of the tetragonal phase at 30.01, 34.5 and 35.2° (in the range 20–40° 2θ), corresponding to the (111) crystallographic plane as predicted from the x-ray Table 2 Volume fractions of each phase and porosity.

<table>
<thead>
<tr>
<th>Material</th>
<th>Phase</th>
<th>Volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DZ</td>
<td>Y₂O₃-ZrO₂</td>
<td>99 (0.2)</td>
</tr>
<tr>
<td></td>
<td>Porosity</td>
<td>&lt;1 (0.2)</td>
</tr>
<tr>
<td>YZ</td>
<td>Y₂O₃-ZrO₂</td>
<td>91 (1.4)</td>
</tr>
<tr>
<td></td>
<td>Porosity</td>
<td>9 (1.4)</td>
</tr>
<tr>
<td>IZ slip</td>
<td>Alumina</td>
<td>33.8 (1.2)</td>
</tr>
<tr>
<td></td>
<td>Zirconia</td>
<td>34.0 (1.5)</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
<td>23.0 (0.9)</td>
</tr>
<tr>
<td></td>
<td>Porosity</td>
<td>8.0 (1.1)</td>
</tr>
<tr>
<td>IZ dry-pressed</td>
<td>Alumina</td>
<td>35.5 (1.7)</td>
</tr>
<tr>
<td></td>
<td>Zirconia</td>
<td>32.2 (1.2)</td>
</tr>
<tr>
<td></td>
<td>Glass</td>
<td>21.5 (0.7)</td>
</tr>
<tr>
<td></td>
<td>Porosity</td>
<td>11.0 (1.3)</td>
</tr>
</tbody>
</table>
diffraction standards files 17-0923 (for IZ) and 14-0534 (for DZ and YZ). The monoclinic phase has the major peaks at 28.07° and 31.2° corresponding to the (111) and ð/2 (11/2) crystallographic planes as anticipated by the X-ray diffraction standard file 05-0543. The IZ analyses show the presence of the peaks corresponding to the alumina crystals (X-ray diffraction standards files 01-1243) indicated with ’A’ above the peaks in Fig. 3A. The intensity of the peaks and the relative content of each phase changes accordingly to the magnitude of the t — m phase transformation from the as-sintered surface to the fractured surface. The calculation of the relative amount of monoclinic phase shows that a significant quantity is already present in the as sintered surfaces of DZ (14%) and IZ dry-pressed (23%) (Fig. 4). A smaller amount is present in IZ slip (10%) and YZ (0.5%). This amount is increased on the fracture surfaces of DZ (46%), IZ slip (29%) and IZ dry-pressed (32%), whereas it is limited to only 6% in the case of YZ.

**Discussion**

The microstructure of IZ slip and dry-pressed (Fig. 1) are very similar and resemble that of IA slip as described in part I. Although the values of tensile strength (Table 1) may induce one to associate IA
slip with IZ slip and IA dry-pressed with IZ dry-pressed, the similarities in strength values between the two slips and the two drypressed blocks seem not to be related to the processing, but more likely to the coincident effect of the porosity. The porosity measured in IZ (slip and dry-pressed) was greater than those measured in IA (slip and dry-pressed) (Table 2). This may be explained by the poor distribution of alumina and zirconia particles and by their poor solubility with each other and the glassy phase. Kibbel et al. and Casellas et al. suggested that the poor solubility of coarse-grain alumina-zirconia glass compounds was due to the low coefficients of diffusion of Al₂O₃ and ZrO₂ within the glassy phase. They also suggested that since smaller particles have a higher solubility than larger particles, a poor solubility has to be expected in coarse Al₂O₃/ZrO₂ glass compounds with particles of different sizes, as observed in the present study. Furthermore, the low sintering temperature, used to avoid shrinkage and achieve the accuracy required in dental application, does not favor coalescence and hence a better distribution of the particles. The significance of the difference in porosity between IZ slip and IZ dry-pressed and its effect on the strength is difficult to determine, as the different distribution of the flaws may change in different batches of specimens and strength values could vary significantly if a greater number of specimens were tested. On the other hand, it is interesting to note that the fracture toughness of IZ dry-pressed and slip (which is not considered to be affected by the porosity provided this is not greater than 12%) were identical (Table 1).

The improvement of the mechanical properties of IA slip brought about by the addition of zirconia is limited to a 10% increment of the fracture toughness, while the strength is most likely related to factors such as porosity and presence of glassy phase. This value is consistent with previous studies, in which mechanical properties of IZ and IA were compared and with the XRD analyses conducted in the present study. In fact, the XRD analyses of IZ showed a modest increment of the relative amount of the monoclinic phase from the as-sintered material to the fractured surface (Figs. 3A and 4). This small amount would account for the limited contribution to the toughening mechanism by phase transformation, of IZ, and consequently, the minor difference in fracture toughness of IZ and IA slip. The difference in the relative amount of the monoclinic was also greater in IZ slip (from 10 to 29%) than in IZ dry-pressed (from 23 to 32%), however, there was no difference in the fracture toughness. An explanation for this apparent contradiction may be the limitation of the X-ray diffraction technique, the possibility that different toughening mechanisms had resulted in similar values, and the effect of the glass. The errors resulting from using the XRD analysis to measure the amount of the monoclinic phase in the surfaces of the specimens are high, as the transformed zone depth is much smaller than the x-ray penetration. However, these results are correlated to the ease of tetragonal ZrO₂ transformation and suggest that they contribute to the fracture toughness. The transformation toughening is not the only mechanism by which ZrO₂ particles contribute to the ultimate toughness of a compound. The considerable amount of monoclinic particles already transformed upon cooling and detected in the as-sintered surface of IZ dry-pressed are responsible for generating localized stresses, which together with the high tensile stresses about the crack tip can nucleate microcracks into the glass matrix (Fig. 1B). The microcracks are believed to increase the fracture toughness of the material. Therefore, microcrack toughening (Fig. 1B) may play a more important role in IZ dry-pressed, whereas transformation toughening may be the elective mechanism in IZ slip. The difference in fracture toughness between IZ and IA slip is statistically insignificant, showing that both mechanisms are scarcely effective and likely to be offset by the presence of the glassy phase (23%).

The fracture behavior of IZ slip and dry-pressed is also comparable, where the crack propagation is generally transgranular for the zirconia particles (Fig. 1B and C) and intergranular or occasionally transgranular, depending on the orientation of
the crack in respect of the elongated alumina grains. The phase transformation of the tetragonal zirconia particles, which occurs at the crack tip, causes compressive stresses within the transformed particles and the surrounding glassy matrix. Circumferential tensile stresses develop around the transformed zirconia particles which would attract the crack to the zirconia and appear to result in a higher incidence of transgranular fracture. The toughening mechanism operating in IZ can thus be explained as a combination of several mechanisms, such as crack deflection and contact shielding attributed to the alumina grains, and the phase transformation and microcrack nucleation mainly related to the zirconia particles.

Conversely to IZ, which contains only 33% of ZrO2 and a significant amount of glass, YZ and DZ are fully sintered zirconia, therefore better mechanical properties were expected from these materials. The variation in strength and fracture toughness (Table 1) between YZ and DZ were related to the differences in the content of the stabilizing oxide (yttria), of their grain size and in the processing method used, and the influence of these factors on the porosity and metastability of the tetragonal grains. The XRD analysis of DZ showed that a considerable amount of monoclinic was already transformed in the as-sintered material (14%) and an even greater amount was detected on the fracture surface (46%) (Figs. 3B and 4). As previously discussed for IZ, the two amounts can be related to microcrack nucleation and the transformation toughening mechanisms, which were expected to be considerably more effective in this material due to the magnitude of the $t \rightarrow m$ transformation, the lack of the glassy phase and negligible porosity (less than 1%). Conversely, the XRD analysis of YZ, showing a scarce presence of monoclinic phase in both as-sintered and fractured surfaces, indicates that the contribution of the transformation toughening must have been almost irrelevant and supports the lower than expected value of fracture toughness. Furthermore, the presence of 9% volume fraction of porosity (Table 2) is likely to be responsible for the modest strength (considering the absence of the glassy phase) which is not statistically different from IZ slip (Table 1) which has similar porosity.

The crack pattern was also significantly different. In DZ, the crack pattern showed a rather straight crack trajectory, propagating alternately through the transformed grains and into the interboundary regions (Fig. 2B), whereas in YZ the crack pattern showed a more tortuous and mainly intergranular trajectory (Fig. 2C). An interpretation of the relationship between intergranular/transgranular crack pattern and the $t \rightarrow m$ transformation was previously discussed and should be related to the compressive and circumferential stresses generated by the transformation of tetragonal grain. Such an interpretation appears to be consistent even with the fully-sintered zirconia materials, where transgranular patterns seem to be associated with transformed grains, and therefore generally seen in DZ, whereas an intergranular pattern was dominant in YZ where transformation was negligible.

### Conclusion

The present study has shown that the nine dental ceramics which are the focus of the current investigation exhibit a wide range of values in strength and fracture toughness, and highlights some aspects of the relationship existing between microstructure, toughening mechanisms, processing and mechanical properties.

A more consistent processing, as in the case of In-Ceram dry-pressed over In-Ceram slip, does not necessarily mean better mechanical properties as previously hypothesized. The present study has shown that other factors such as grain size and shape and porosity should also be considered.

The improvement of the mechanical properties due to zirconia is affected by the presence of other phases and by the metastability of the $t \rightarrow m$ transformation.

An increase of the crystalline content as seen in the pressable materials and the fully sintered zirconia generally corresponds to an improvement of the mechanical properties. However, in materials with equal crystalline content the difference in strength and fracture toughness is related to porosity and the effectiveness of each toughening mechanism.

A better understanding of the role played by such mechanisms is therefore of the utmost importance if the properties of dental ceramics are to be improved. Further studies are necessary to fully understand the influence of each toughening mechanism on the mechanical properties and clinical performance of dental ceramics.

### Acknowledgements

The first author wishes to gratefully acknowledge a scholarship from the Commonwealth Government of Australia. All authors are grateful to Vita Zahnfabrik and DCS Dental AG for providing the necessary material and also to Dr Leonhard...
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Meyer and the anonymous reviewers for their constructive comments on the manuscripts

References