Journal of
Ceramic Science
and Technology

J. Ceram. Sci. Technol., **08** [4] 525-530 (2017)
DOI: 10.4416/JCST2017-00032
available online at: http://www.ceramic-science.com

Mechanical Properties of Zirconia Y-TZP Core Veneered for Dentistry Applications

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received May 15, 2017; received in revised form September 4, 2017; accepted November 7, 2017

Abstract

The objective of this work is to compare the mechanical properties of sintered yttria tetragonal zirconia polycrystalline (Y-TZP) micro- and nano-particles, and evaluate the influence of a layer of veneer aesthetic ceramic (annealing from 600 °C to 935 °C, surface finishing) on Y-TZP mechanical properties. The specimens were cut from four Y-TZP pre-sintered blocks, sintered, polished and coated with feldspathic ceramic. One experimental Y-TZP block was made with Y-TZP nano-particles and three commercially available blocks were made with Y-TZP micro-particles from different companies (ProtMat, Ivoclar and Vita). One group of ProtMat Y-TZP micro-particles specimens was not coated. The zirconia with nano-particles showed the highest flexural strength (1020 MPa) and fracture toughness (11.2 MPa·m$^{-1/2}$). ANOVA statistical analysis did not show statistically a difference in the flexural strength (~ 850 MPa), hardness (~ 1300 HV), fracture toughness (~ 9 MPa·m$^{-1/2}$) and shear strength (~ 12.97 MPa) among the zirconia specimens with micrometer-sized particles.

Keywords: Y-TZP, zirconia nano-particles, dental prosthesis, zirconia core veneered

I. Introduction

Zirconia modified with yttria (Y-TZP) is currently used in dentistry to meet the increasing aesthetic demands of patients, to improve the performance of prostheses in the oral cavity and to reduce the costs of dental treatment. Y-TZP is used in CAD-CAM manufacturing systems and allows the preparation of metal-free dental prostheses with good aesthetic quality [1–5].

Besides displaying excellent properties, such as mechanical strength and fracture toughness, yttria-doped zirconia is inert in physiological media and has higher flexural strength than alumina [6–9]. In addition to the high hardness and wear resistance, zirconia, when polished, has favorable biocompatibility and aesthetics [3]. According to Kosmac and Oblak [10], yttria-doped tetragonal zirconia polycrystal is a ceramic material with better mechanical properties than other dental ceramics. The higher strength of zirconia is known to be associated with a stress-induced phase transformation mechanism [5].

There is a lack of data about the properties of zirconia/ceramic composites that result from aesthetic feldspathic ceramic coating. The aim of this study was to determine the influence of a layer of veneer ceramic on mechanical properties (four-point bending strength, hardness and toughness) of four Y-TZP commercial products. The specimens were cut from pre-sintered disks used in the machining of prostheses by a CAD-CAM system. The hypothesis tested was that the strength of Y-TZP for CAD-CAM systems is affected by surface finishing and layer of veneer ceramic.

II. Materials and Methods

In the present work, four pre-sintered Y-TZP blocks from three manufacturers and with different zirconia particle sizes were used:

a) Y-TZP blocks made with nano-particles (Y-TZP Nano);
b) Y-TZP blocks made with micro-particles from ProtMat Materiais Avançados, Juiz de Fora, MG, Brazil (Y-TZP micro);
c) Y-TZP blocks made with micro-particles and named as IPS e.max ZirCAD from Ivoclar Vivadent AG, Schaan/Liechtenstein (e.max);
d) Y-TZP blocks made with micro-particles and named as VITA 2000 YZ CUBES form VITA Zahnfabrik, Bad Säckingen Germany (In Ceram).

Since ZrO_2 nano-particles tend to behave differently from ZrO_2 micro-particles [8,16], we decided to include both types in the experimental groups.

(1) Sample preparation and characterization

Two hundred and twenty specimens were cut from the pre-sintered Y-TZP blocks using a cutting machine (Buehler LTD. – Bluff, Illinois, USA). Considering that the final desired samples size for the 4-point bending test

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was 45 × 4 × 3mm and during sintering a contraction of the order of 25 % occurs, the samples were cut from the pre-sintered blocks with larger dimensions. The samples were divided into three groups. In Group 1: thirty samples (60 × 5.3 × 4 mm) of each Y-TZP type were cut for four-point bending tests. In the Group 2: fifteen specimens of each Y-TZP type with dimensions of 15 × 15 × 4 mm were used in complementary tests. Among the samples from Group 2, five were used for shear tests, five for Vickers Hardness tests, and five for analysis of the microstructure. In Group 3: thirty samples (60 × 5.3 × 5.3 mm) of micro-particles Y-TZP ProtMat were cut for four-point bending tests, this group did not receive any coating.

The samples made with Y-TZP micro-particles were sintered in a furnace VITA Zyrcomat (VITA Zahnfabrik, Bad Säckingen) at 1530 °C for 120 min, using a rate of heating and cooling of 10 °K/min. The samples of Y-TZP nano-particles were sintered in a MAITEC F1650 furnace (MaitecSP-Brazil) at 1350 °C with the same rates of heating and cooling. Different furnaces were used to meet the manufacturers' recommendations.

The Y-TZP samples were weighed and measured before and after sintering. The bulk density of the sintered samples was measured with the Archimedes method in distilled water, and the relative density was determined by correlating the bulk density with the theoretical density ($\varrho_T = 6.05$ g/cm^3). The crystalline phases of the sintered specimens were investigated by means of X-ray diffraction, using a Shimadzu XRD-6000 diffractometer (SHIMADZU-Japan) with CuKα radiation for angles between 20° and 80°, an angle step of 0.05° and a speed of 3 counts/second. The peaks were identified based on comparison with standard ICDD (International Centre for Diffraction Data) diffraction files.

The sample surfaces were polished with diamond paste before the samples were sintered. A scanning electron microscope (JEOL, JSM-5800LV, Tokyo, Japan) was used for microstructural analysis. Thermal etching was used to determine the average grain size, as described by Moraes *et al.* [8].

Samples cut from micro-particles Y-TZP ProtMat blocks (Group 3) were uncoated and were used as a reference to analyze the influence of the aesthetic coating on the Y-TZP mechanical properties. All other samples from Group 1 and Group 2 of each Y-TZP type were veneered with aesthetic feldspathic ceramic. The zirconia samples received a one-sided coating of CZR-Cerabien Zr ceramic (Noritake-Shinmachi, Nagoya, Japan) A3 color. Annealing was performed from 600 °C to 935 °C with 1-min steps, under a pressure of 4 kPa. After annealing heat treatment, the feldspathic coating on Group 1 for the 4-point bending test had a thickness of 1.0 mm and the samples in Group 2 for shear testing had a coating thickness of 4.0 mm. Fig. 1 shows one sample for shear testing. During sintering, the zirconia undergoes contraction of the order of 25 %. After sintering, the nominal dimensions of samples for the four-point bending test were 45 x 4 x 3 mm, as recommended by technical standard JIS R 1601and ASTM C1161 (Standard Test Method for Flexural Strength of Advanced Ceramics at Ambient Temperature) [11–12].

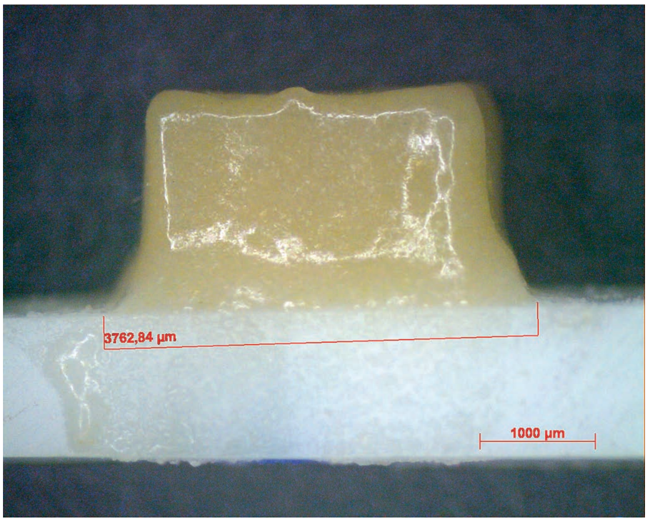

Fig. 1: The coating on zirconia sample for shear test.

Shear tests were performed to determine the adhesion of the coating material (Group 2). The layered aesthetic feldspathic ceramic was applied with the help of a silicone mold, thus creating an interface with an angle of ninety degrees between the zirconia and ceramic. The shear load was applied parallel to the zirconia-coating interface.

(2) Mechanical tests

The shear tests were performed on a universal mechanical testing machine (EMIC-DL 10000 – Emic Equipment and Test Systems Ltda., Paraná, Brazil), and had the purpose of evaluating the shear strength of the interface between the zirconia and the veneered aesthetic feldspathic ceramic. Fig. 2 shows the set-up for shear testing. A load cell of 5000 N and a loading rate of 1 mm/min were used. The shear test finished with fracture or displacement of the feldspathic ceramic from the zirconia.

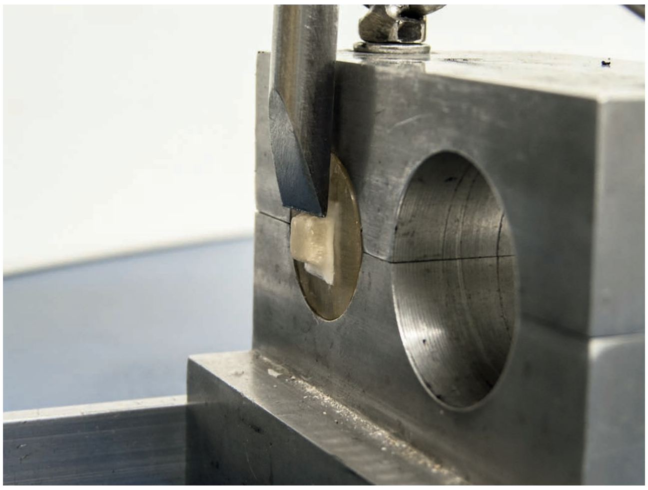

Fig. 2: Zirconia veneered with aesthetic feldspathic ceramic mounted in test apparatus for the shear test.

After the shear test, all specimens were observed in an optical microscope (Pantec, Panambra, Brazil) with a magnification of five and twenty times for inspection of the zirconia-coating interface and determination of the fracture type. The images were analyzed with ScopePhoto 6.0

software (Microimaging, Orakei, New Zealand). The data were subjected to analysis of variance (ANOVA) and comparison of means of Tukey's test with a significance level of 5 %.

The four-point bending tests were conducted in accordance with Technical Standards JIS R 1601. A universal testing machine MTS-250kN (MTS, Eden Prairie, MN USA) was used, with distances between supporting pins (I_1) of 40 mm and between loading pins (I_2) of 20 mm and a loading rate of 0.5mm/s. During loading the coated sample surface was facing down (Fig. 3).

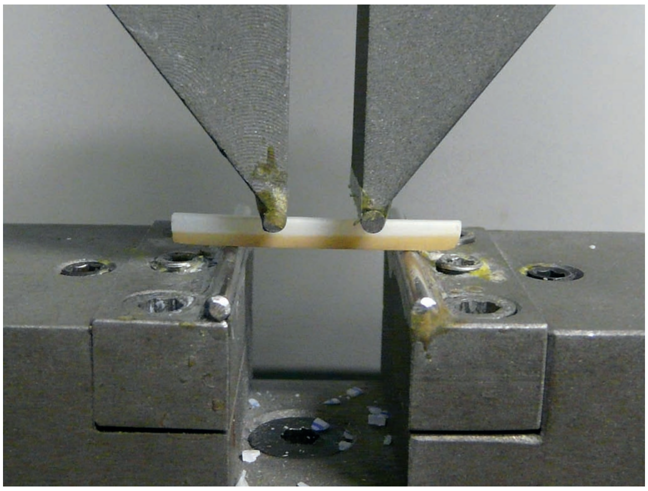

Fig. 3: Set-up for the 4-point bending test.

The flexural strength was calculated according to Equation (1)

$$\sigma_f = \frac{3}{2} \times F_A \times \frac{(I_1 - I_2)}{b \times h^2} \quad (1)$$

where F_A is the applied fracture force and b and h are width (± 4 mm) and height (± 3 mm) of the sample, respectively, measured before the test.

The hardness was measured on the zirconia surface and feldspathic ceramic of five veneered samples from Group 2 and uncoated sub-group samples cut from micro-particles Y-TZP ProtMat. The hardness of each sample was measured on the zirconia surface without coating using 20 N loading for 15 s and on the surface with the feldspathic ceramic layer using a 3 N loading for 15 s. The hardness of the samples was considered as the average of 21 Vickers indentations. In this test, a Micromet 2004 durometer (Buehler, USA) was used. The tests were performed according to ASTM C1327 and ASTM C1424 [13, 14]. The fracture toughness (K_{IC}) was calculated from the results of the hardness tests.

III. Results and Discussion

The mechanical properties of zirconia and ceramic have been investigated in the past [5, 8, 15 – 18], but there is a lack of data about the properties of zirconia/ceramic composites that result from aesthetic coating. The shear test proposed in this work aims to simulate clinical use. Adhesion of the aesthetic coating is achieved by annealing the composite, and this may affect its mechanical properties, especially at the interface. This justifies the conditions chosen for this experiment. Boudrias [1], Sundh, Molin [19], and Yilmaz and Dincer [20] used a similar testing model, but they analyzed the adhesion between ceramic and metal and did not analyze the influence of an aesthetic coating on the mechanical properties (flexural strength, toughness and hardness).

The results of measurements of values of physical and mechanical properties of several types of zirconia are shown in Table 1. This table shows that the four Y-TZP blocks used in this work have similar coefficients of thermal expansion. Consequently, we used the same material for the aesthetic layer.

The X-ray diffractogram patterns of the sintered samples are shown in Fig. 4. Qualitative analysis of the diffractograms groups showed no peaks characteristic of the monoclinic phase after the samples had been annealed and polished. The annealing temperature is higher than the transformation temperature of the monoclinic to the tetragonal phase, which is retained at room temperature by the presence of yttria as substitutional impurity. The presence of the tetragonal phase is responsible for a high mechanical strength of this material [10, 21].

The monoclinic phase forms spontaneously on the surface of zirconia after sintering annealing owing to thermal stresses and the lack of restriction at the surface, but can be removed if the annealed zirconia is carefully polished [11, 21 – 22].

Measurements on the blocks after annealing showed no difference in density between the different types of zirconia (Table 1). All samples showed a relative density higher than 99 % of theoretical density. The high values of density help to enhance the mechanical properties of zirconia, since the presence of voids in the material reduces fracture toughness by reducing the area of resistance and concentrating the stress [8, 10, 18].

There were no significant differences in the values of shrinkage and mass loss of the zirconia samples from different manufacturers. This facilitates the use of zirconia for prostheses manufacturing, since there is no need to change the programming of annealing furnaces and the CAD/CAM scanning system of the prosthetic model when zirconia from a different manufacturer is used.

Image analysis of scanning electron microscopy data was used to measure the average grain size after thermal treatment (Fig. 5). Zirconia prepared with nano-particles (Y-TZP Nano) had smaller grain sizes than zirconia prepared with micro-particles (Table 1). These results corroborate those of Moraes *et al.* [8] and Danilenko *et al.* [17]. The average grain size is an important parameter influencing the metastability of the tetragonal phase at room temperature and the mechanical properties of the material.

Table 1 shows that sintered samples cut from zirconia blocks made with nano-particles have the highest Vickers hardness (1390 + 35 HV). Reduction in particle size increases the surface available for adhesion. The smaller the average grain size, the greater the number of grains per unit area and the best accommodation and the contact between the particles [7]. These features facilitate the adhesion process. Moreover, as stated by Daguano *et al.* [23], there is an increase in hardness and fracture toughness of the material, owing to the very large number of contours to be overcome by a crack during propagation. Thus, the material with finer microstructure shows higher toughness since it requires higher energy for crack growth.

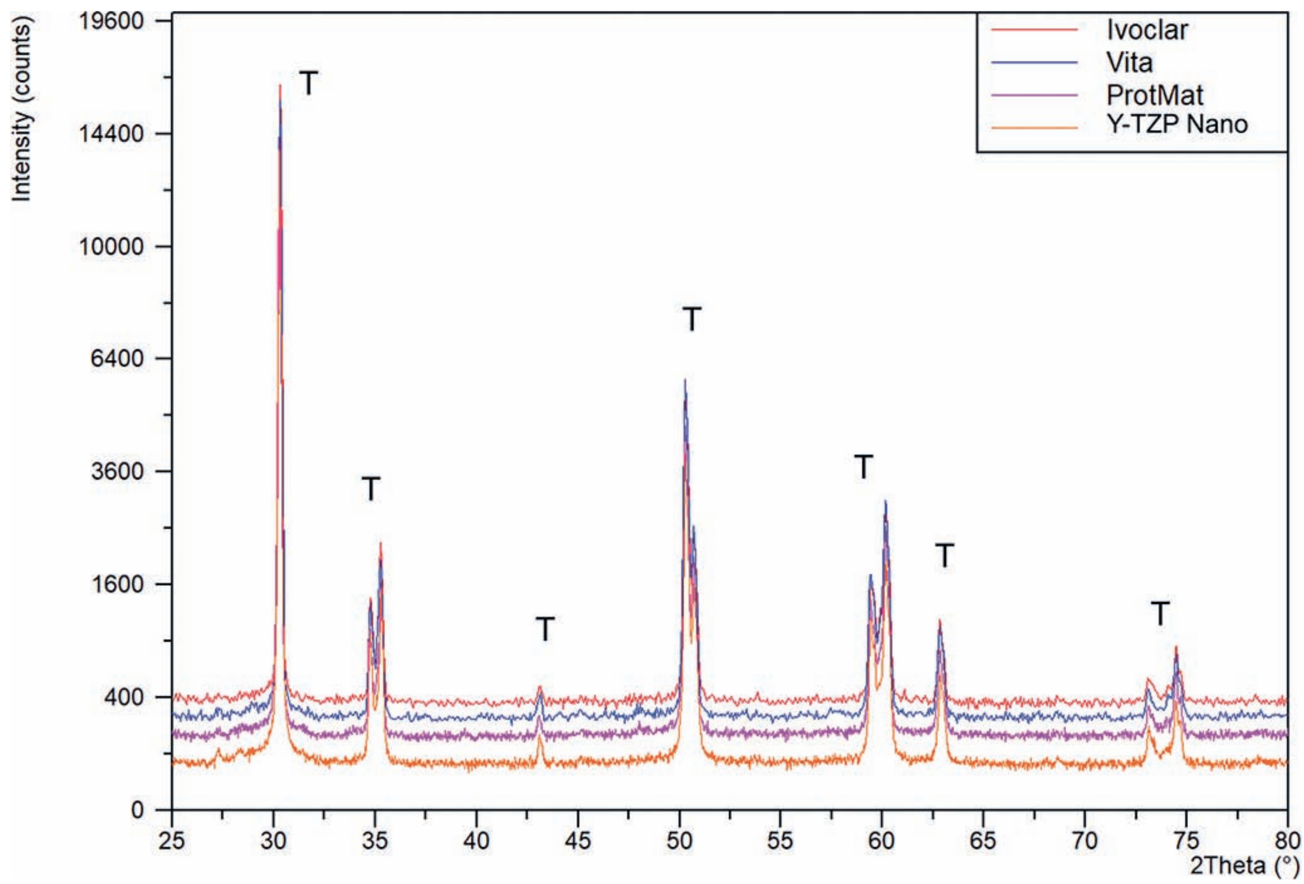

Fig. 4 X-ray diffraction pattern of samples. Ivoclar e.max; Y-TZP micro from ProtMat sintered at 1530 °C; Y-TZP Nano from ProtMat sintered at 1350 °C; In Ceram from Vita sintered at 1530 °C.

Table 1: Number of samples (N), physical and mechanical properties of zirconia Y-TZP core veneered with aesthetic feldspathic ceramic.

Property	N	Y-Zr nano	Y-TZP micro (ProtMat)	Y-TZP micro No coating (ProtMat)	e.max (Ivoclar)	In Ceram (Vita)
Relative density after annealing (%)	30	99.06 ± 0.4	99.50 ± 0.4	99.34 ± 0.1	99.3 ± 0.3	99.2 ± 0.6
Linear retraction (%)	30	24.1 ± 0.6	24.5 + 0.3	24.5 ± 0.3	24.4 ± 0.5	24.3 ± 0.4
Shear strength (MPa)	30	14.32 + 2.01	11.88 + 2.03	-	10.45 + 3.27	8.97 + 1.28
Flexural strength (MPa)	30	1020 ± 245	855 ± 240	1099 ± 213	870 ± 260	862±230
Fracture toughness ($MPa \cdot m^{1/2}$)	5	11.2 ± 0.2	8.90 ± 0.3	10.64 + 1.9	9.1 ± 0.4	8.8 ± 0.2
Particle grain size (nm)	5	260	840	840	820	830
Sintering temperature (°C)		1350	1530	1530	1530	1530
Vickers hardness – Zirconia (HV)	5	1390 ± 35	1324 ± 29	1320 + 70	1303 ± 23	1297 ± 46
Vickers hardness – Noritake (HV)	5	581 ± 22	545 ± 44	-	531 ± 70	477 ± 93

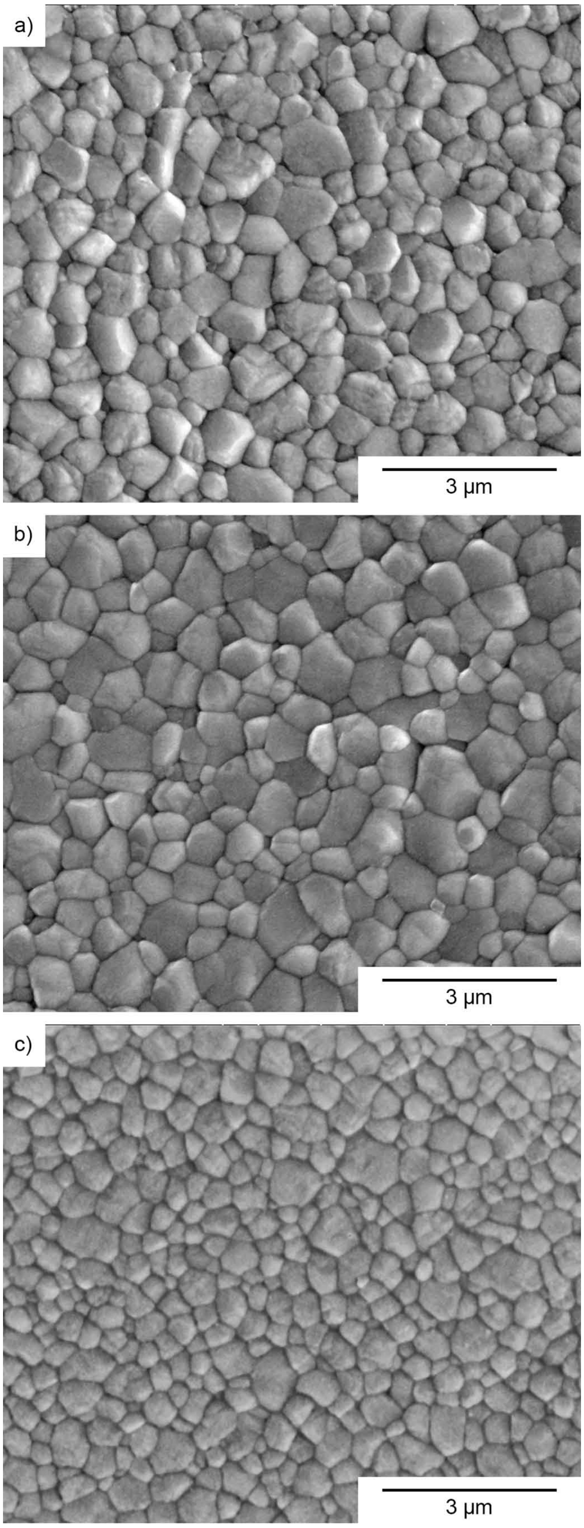

Fig. 5: Surface morphology of zirconia after sintering. (A) Ivoclar e.max micro particles sintered at 1530 °C; (B) Y-TZP micro-particles from ProtMat sintered at 1530 °C; (C) Zirconia nano-particles sintered at 1350 °C.

Tukey's test indicated that only the tested group of zirconia made with nano-particles showed a significant difference to other groups. The higher fracture toughness and flexural strength of Y-TZP nano-particles compared to micro-particles can be associated with a smaller average grain size. ANOVA statistical analysis indicated that there was no statistically significant difference in flexural strength and fracture toughness between the zirconia groups made with micro-particles.

Tinschert and Zwez [24] mention that the four-point bending strength of zirconia partially stabilized by yttria is 913 MPa. The hardness results of the present study for Y-TZP micro-particles were slightly higher and varied between 1297 and 1303 HV.

Vickers indentation cracks are an appropriate methodology to determine the Y-TZP toughness. In the present work, the fracture toughness was estimated by measuring the lengths of cracks emanating from Vickers indents. All Vickers indents showed cracks in the vertices and. irregular propagation, which indicates that they grew through the grain boundaries. It was found that even with the indentation performed close to the zirconia-coating interface, the crack did not grow along the interface, indicating good adhesion of the coating.

The shear strengths of the zirconia-coating interface were similar among all groups, showing that the type of zirconia does not affect the adhesion of the coating.

After shear testing, the most common fracture zirconia-coating interface was cohesive type (Fig. 6). The shear failure occurred near the application point of the force on the ceramic side. Similar result to that observed in the study of Bona [25] and work of Souza *et al.* [26].

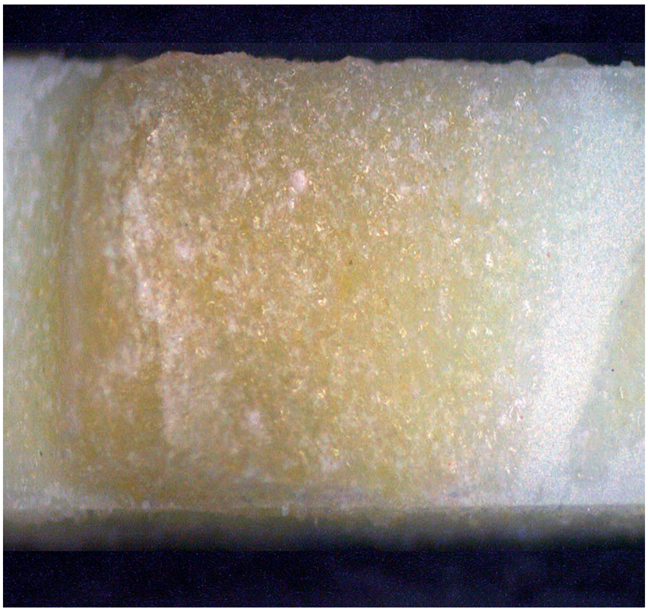

Fig. 6: Example of the fracture surface of a shear test sample.

Although the aim of this work was to evaluate the resistance of zirconia with a ceramic coating, some factors are likely to affect these results, as pointed out by Zeng *et al.* [15]. For any method of evaluation, the values for rupture of the material are directly related to the surface finishing. The precision of adaptation, as well as cementing, also affects these values. The layer of cement of a prosthetic work prevents a homogeneous distribution of tension. During chewing, the tension is not fully concentrated on the ceramic coating; the forces are transferred to the system formed by the tooth, the bonding cement and the prosthesis. If the prosthesis is etched before the implant, adhesion is improved.

Although the results are favorable in relation to the strength of zirconia partially stabilized by yttria, it is important to test them in clinical situations, i.e. after the material is processed for use in dental prosthesis. According to Tinschert *et al.* [24] and Elias *et al.* [21], machining can damage the surface, impairing the mechanical properties of the prosthesis. The same thing may happen when zirconia is etched to improve coating adhesion. The preparation of ceramic prostheses facilitates retention and adherence, but may create stress concentrators on the structure.

In clinical conditions, dental restorations are exposed to stresses and chemical interactions that are more complex and harmful than the mechanical tests performed in the laboratory. The dentist must be very careful when extrapolating results from experimental studies to clinical practice.

IV. Conclusions

The results of the present work showed that:

a) Y-TZP micro veneered with aesthetic feldspathic ceramic presented Vickers hardness (~ 1300 HV), fracture toughness (~ 9 $MPa \cdot m^{-1/2}$), flexural strength (~ 860 MPa) and shear strength (~ 10.44 MPa) suitable for use in dental prostheses.

b) Sintered zirconia blocks prepared with nano-particles have a smaller grain size (260 nm) than zirconia prepared with micro-particles (820 – 840 nm).

c) Sintered zirconia Y-TZP nano-particles samples have higher shear strength (14.32 MPa), flexural strength (1020 MPa) and fracture toughness (11.2 $MPa \cdot m^{-1/2}$) than Y-TZP micro-particles.

d) The mechanical properties of Y-TZP nano-particles veneered with aesthetic ceramic were better than blocks of Y-TZP micro-particles.

e) The use of feldspathic ceramic for aesthetic coating did not impair the mechanical properties of zirconia.

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