Original article

Fatigue behavior of 3%Y₂O₃-doped ZrO₂ ceramics

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ABSTRACT

The objective of this work was to evaluate the cyclic fatigue strength of a commercial pre-sintered tetragonal zirconia ceramics for dental systems, and to determine the main mechanical properties. Samples were sintered in air at 1600 °C for 120 min with heating and cooling rate of 10 °C/min. The sintered specimens were characterized by X-ray diffraction and scanning electron microscopy. Hardness and fracture toughness were determined using the Vicker’s indentation method. The strength was determined by four-point bending tests. The cyclic fatigue tests were realized as four-point bending tests within a frequency of 25 Hz and a stress ratio R of 0.1. The Weibull analysis was employed in order to perform failure probability calculations. Sintered specimens presented average values of hardness, fracture toughness and bending strength near to 23.5 GPa, 8 MPa m¹/² and 900 MPa, respectively. The fatigue tests results allow concluding that the fatigue strength limit over 5 x 10⁶ stress cycles is about 550 MPa or around 63% of the static strength of this material. The tetragonal-monoclinic (t-m) zirconia transformation observed by X-ray diffraction of fractured surfaces occurs during cyclic loading and the fracture of specimens. The 3Y-TZP samples clearly present a range of loading conditions where cyclic fatigue can be detected. The fatigue strength limit around 550 MPa is appropriate for application in dental implant parts.

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1. Introduction

Ceramic components for structural engineering applications are generally subjected to continuous operation in a variable load environment [1]. Usually, ceramics are characterized in regard to hardness, toughness and bending strength. However, the failure under fatigue conditions, at loads much below the critical failure strength is a common phenomenon in all materials, including ceramics [2]. Consequently, it is very important to investigate the fatigue strength of ceramics.

The development of advanced ceramics during recent years followed several fascinating concepts, e.g., to increase strength, reduce brittleness, and increase high temperature stability. However, the development of structural ceramics for dental materials with improved fatigue resistance was not considered. The existence of cyclic fatigue effects has been proven for several ceramic materials, and clear experimental evidence has been obtained for a limited range of test conditions [3].

Another possibility of application for ceramic materials is as biomaterials. In this case, the use of advanced ceramics...
started in the 1970s, and since then a continuous improvement of these materials in various applications can be noted. An important improvement has been possible the use of ceramics as dental materials. They present advantages such as esthetic, biocompatibility and chemical inertness [4–6].

Zirconia is the most promising bio-ceramic, due to its excellent biocompatibility. The main advantages of ZrO₂ are its higher fracture strength and fracture toughness, and lower Young’s modulus [7–13]. It is of common knowledge that ZrO₂ additions may increase the fracture toughness of ceramic materials. This effect is based on the tetragonal to monoclinic phase transformation of ZrO₂, accompanied by an increase of the specific volume in the order of 3–6% [7]. This volume increase generates stresses in the ceramic matrix, which difficult crack propagation. When such a ceramic is used for implants such as artificial joints or dental abutment, it undergoes cyclic loading for a fairly long period [14].

Cyclic fatigue of ceramics recently became a highly attractive research field for material scientists. There is a strong demand to generate design-relevant fatigue data which are required for many of the projected applications of structural ceramics. On the other hand, knowledge of fatigue in ceramics is insufficient so far and information about the correlation between microstructural parameters and fatigue properties is still missing for most ceramic systems. Besides this lack of understanding a number of fundamental questions still have not been answered unambiguously for many of the most important ceramics [15–18].

It is essential in engineering applications of ceramic materials for structural purposes to determine the fatigue behavior under appropriated static or cyclic loading. A considerable number of reports have been published on the fatigue of glass, alumina and zirconia ceramics. There have been few critical studies published regarding the cyclic and static fatigue at room temperature of advanced ceramics, although activity in this field has increased recently. Furthermore, fatigue testing applied to brittle materials imposes a number of problems. One of them is the wide scatter in data, which sometimes obscures the fatigue tendency. This scatter is considered to derive intrinsically from a defect distribution in the specimens [19].

This research is focused on the processing, mechanical properties and cyclic fatigue life of a commercial Y₂O₃-stabilized ZrO₂ ceramic. Specifically, the fatigue behavior of tetragonal zirconia polycrystals (TZP) with 3 mol% of Y₂O₃ stabilized (3Y-TZP), produced by solid-state sintering at 1600 °C was investigated by means of cyclic four-point bending load controlled tests. The occurrence of the t-m transformation during the fatigue tests was observed.

2. Experimental procedure

2.1. Processing

High-purity Y-TZP commercial zirconia, ZrO₂–3 mol%Y₂O₃ pre-sintered blocks (ProtMat Materiais Avançados®, Guaratingueta, Brazil) was used in this study. Blocks with 55 mm x 15 mm x 15 mm were cutted and sintered at 1600 °C in a MoSi₂ resistance furnace heated for 2 h, with heating and cooling rate of 10 °C/min [5,11,12].

In order to obtain the specimens for the four-point flexure tests, the dense ceramic blocks cutted and grinded in rectangular bars of 3 mm x 4 mm x 45 mm, with an automatic grinding machine. After grinding, the samples were polished with diamond pastes of 15, 9, 6, 3 and 1 µm.

2.2. Characterization

The bulk density of the sintered samples was measured by the Archimedes’ method in distilled water. The crystalline phase content was determined by X-ray diffractometry (XRD) using Cu-Kα radiation in the 2θ range of 20–80°, with a step width of 0.05° and 2 s of exposure time per position. The monoclinic phase fraction was calculated using the Garvie and Nicholson [20] method and the monoclinic volume fraction was then obtained using the equation proposed by Toraya et al. [21].

The calculation of the penetration depth of the X-rays of the analyzed surface was based on the absorption of the X-rays by the material. The penetration depth of X-rays is given by Eq. (1) [22]:

\[ h = \frac{\tan \theta}{2} \left( \frac{1}{\mu \rho} \right) \ln \left( \frac{I}{I_0} \right) \]  

where \( h \) is the penetration depth [µm]; \( \theta \) is the diffraction angle; \( I \) is an intensity of diffracted X-ray beam; \( I_0 \) is an intensity of X-ray beam; \( \mu \) is the coefficient of absorption; \( w \) is the weight fraction of element or component; \( \mu / \rho \) is the coefficient of mass absorption [cm²/g] (Zr = 143, O = 11.5, Y = 134) and \( \rho \) is the specific mass [g/cm³] (Zr = 6.511, O = 1.354, Y = 4.472, ZrO₂, 3Y₂O₃ = 6.051).

Polished and thermal etched surfaces of the sintered samples and fractured surfaces of the mechanically tested specimens, were examined by scanning electron microscopy (SEM), using a LEO-1450VP microscope.

2.3. Microhardness and fracture toughness

Hardness and fracture toughness (KIC), were determined using a Vickers Indentation method. In each sample, 21 indentations were measured, under a load of 2000 gf for 30 s. The fracture toughness has been calculated by measurement of the relation between cracks length (c) and indentation length (a), using the relation proposed by Niihara et al. [23], valid for Palmqvist crack types, which present \( c/a \) relation <3.5.

2.4. Modulus of rupture (MOR)

The modulus of rupture (MOR) was determined by four-point bending tests, using a servo-hydraulic testing machine MTS model 810.23M. For the accomplishment of the bending tests, batches of 21 samples were grinded and polished, obtaining bars of 4 mm x 3 mm x 45 mm, according ASTM C 1116-94. The tests were conducted using a four-point bending device with
outer and inner spans (\(l_1\) and \(l_2\)) of 40 and 20 mm respectively. The speed of the crosshead displacement was 0.5 mm/min. The bending strength of the samples was calculated by the following equation.

\[
\sigma_f = \frac{3}{2} \frac{F_A}{b} \times \left(1 - \frac{l_2}{l_1}\right)
\]

(3)

where \(\sigma_f\) is the bending strength [MPa]; \(F_A\) is the rupture load [N]; \(b\) is the width of the samples [mm]; \(h\) is the height of the samples [mm]; \(l_1\) is an Outer span [mm]; \(l_2\) is an inner span [mm].

2.5. Cyclic fatigue by four-point bending testing

The cyclic fatigue tests were carried out by four-point bending loading in air at room temperature, with a relative humidity near 60%. The specimen dimensions and the testing machine were the same as employed in the bending strength tests. The cyclic fatigue was studied under a sinusoidal stress wave form with a frequency of 25 Hz and a constant stress ratio (\(R\)) between the minimum stress (\(\sigma_{min}\)) and maximum stress (\(\sigma_{max}\)) of 0.1. The number of specimens used in fatigue tests varied between 13 and 23 samples at each stress level, under the maximum stress values of 570, 610 and 650 MPa. In the lower stress levels, 500 and 530 MPa, only 3 specimens were tested. The tests were interrupted when the surviving samples reached a number of stress cycles between 2 and \(5 \times 10^6\) cycles.

Interrupted samples were submitted to XRD and SEM characterization according to procedures previously mentioned.

2.6. Statistical analysis

For the statistical evaluation of the fracture strength and cyclic fatigue resistance, the two-parameter Weibull distribution function, given by Eq. (4), was used.

\[
P(x) = 1 - \exp \left(-\left(\frac{x}{b}\right)^m\right), \quad \text{for } x > 0 \quad \text{and} \quad P(x) = 0, \quad \text{for } x < 0
\]

(4)

where \(P\) is the probability associated to \(x\) value (or failure probability); \(m\) is the modulus of Weibull distribution; \(b\) is the scale parameter or characteristic strength; \(x\) is the bending strength (static tests) or the number of cycles to failure (fatigue tests).

The Weibull parameters, \(m\) and \(b\), are obtained by the linearization of Eq. (4), see Eq. (5), and plotting \(\ln \ln [1/(1 - P(x))]\) vs. \(\ln x\):

\[
\ln \ln \left(\frac{1}{1 - P(x)}\right) = m \ln x - m \ln b
\]

(5)

The stress value for 50% of rupture probability was estimated as reference and also for direct comparison with the average fracture strength. The Weibull parameter “\(m\)” for the static tests, was determined using a correction factor of 0.938, corresponding to 21 samples, in agreement with the German norm DIN-51-110.

In the case of the static tests, this is done by fitting a straight line using the conventional least-squares method. However, this procedure is inappropriate for fatigue results, because it is not able to take account the censored results, often found in these testing. Thus, the Weibull parameters for the fatigue tests are determined by maximum likelihood method [24].

3. Results and discussion

3.1. Characterization

Fig. 1 presents X-ray diffractogram (XRD) patterns of the \(\text{ZrO}_2\) samples, before and after sintering at 1600 °C and of the fracture surface after bending testing.

It can be observed that the pre-sintered ceramic, as received, presents a certain amount of residual monoclinic \(\text{ZrO}_2\) phase, which was estimated, according to Toraya et al. [21], to 13 vol%. After sintering, the processing conditions used in this work allowed a total stabilization of the tetragonal \(\text{ZrO}_2\) phase, during cooling. The XRD patterns of the fracture surfaces of the bending tested specimens show clearly that there was a considerable amount of stress-induced t–m transformation of around 10 vol%, due to the tensile stress to which the grains of these surfaces were submitted. It is known that the application of stresses to tetragonal \(\text{ZrO}_2\) grains may start the martensitic t–m transformation [5].

Fig. 2 presents a micrograph of the polished and etched \(\text{ZrO}_2\) surface and the fracture surface of a specimen tested in fatigue.

Looking at a typical microstructure of the sintered samples, Fig. 2(a), the presence of fine microstructure composed of equiaxial grains smaller than 0.5 μm can be observed. No abnormal grain growth of \(\text{ZrO}_2\) grains has been observed in this material. In Fig. 2(b) a typical brittle fracture surface which clearly shows that the initial crack nucleation and propagation
region are located in the upper side of the picture, corresponding to the region of maximum tensile stress in the bending test.

### 3.2. Microhardness, fracture toughness and modulus of rupture (MOR)

Table 1 presents the relative density and mechanical properties of the sintered samples.

<table>
<thead>
<tr>
<th>Relative density (%)</th>
<th>Vickers hardness (GPa)</th>
<th>Fracture toughness (MPa m^{1/2})</th>
<th>MOR (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.7 ± 0.2</td>
<td>13.5 ± 0.2</td>
<td>8.15 ± 0.25</td>
<td>880 ± 35</td>
</tr>
</tbody>
</table>

The high densification (>99.5) of the sintered samples indicates that the sintering conditions used in this work were satisfactory to eliminate most of the porosity and maintain a microstructure with fine grains, see Fig. 2(a). This typical microstructure and the results of the X-ray diffraction analysis, shown in Fig. 1(b), indicate the predominance of the tetragonal phase, justifying the high K_{IC} and MOR values presented in Table 1. Toughening by the t–m phase transformation and crack deflection are the main mechanisms actuating to improve the mechanical properties of this material [25]. The t–m phase transformation, allows the MOR to reach the elevated values, near 900MPa. Furthermore, the hardness values were about 13.5GPa. Results obtained in a previous work by Grathwohl and Liu [15], for ZrO$_2$–3mol%Y$_2$O$_3$, report hardness, fracture toughness and modulus of rupture of 12.3GPa, 4.8MPa m^{1/2} and 656MPa respectively, but in general, the results obtained in this work are typical and consistent with literature data [8].

### 3.3. Cyclic fatigue

The cyclic fatigue tests were interrupted at $N_f = 2 \times 10^6$ cycles, condition in which the material is estimated to provide infinite life. The specimens which did not fracture in the test are marked by an arrow symbol (run out). The six maximum stress levels ($\sigma_{\text{max}}$) were selected in relation to the initial strength. The fatigue strength limit is around 550MPa, which corresponds to 62.5% of the modulus of rupture evaluated in this work (880MPa).

At the lowest stress levels ($\sigma_{\text{max}} = 500$MPa and 530MPa), neither spontaneous nor fatigue fracture were observed. As $\sigma_{\text{max}}$ increased, some specimens reached $N_f = 2 \times 10^6$ cycles without failure, but some specimens failed spontaneously, i.e., below $10^5$ loading cycles. On the other hand, the number of specimens failing at $10^3 < N_f < 2 \times 10^6$ was relatively large. In an amount of 13 specimens tested at $\sigma_{\text{max}} = 650$MPa, 4 specimens failed below a hundred cycles, 9 failed during cycling and none of them achieved $10^6$ cycles. The 23 specimens tested at $\sigma_{\text{max}} = 610$MPa revealed the following: 1 specimen failed below a hundred cycles, 19 failed during cycling, 3 specimens survived $2 \times 10^6$ cycles. The 13 specimens tested at $\sigma_{\text{max}} = 570$MPa revealed that 1 specimen failed below hundred cycles, 9 failed...
during cycling, 3 specimens survived $2 \times 10^6$ cycles. At the stress levels above 550 MPa, the majority of the specimens failed in the range of $10^3 < N_f < 2 \times 10^6$ cycles. Samples that failed under low cycles ($N_f < 10^3$ cycles), are more frequent under higher stresses, while the reduction of the maximum applied stress lead to a significant increase in the number of no failed samples ($N_f > 2 \times 10^6$ cycles).

Figs. 4 and 5 present XRD patterns and SEM micrographs, respectively, of the polished surfaces submitted to tensile stress, in survived samples after fatigue testing.

The penetration depth of X-rays of the analyzed surface, based on the absorption of the X-rays by the material and calculated by Eq. (1) was of 7.3 μm. As shown in Fig. 4, this penetration depth of X-rays allowed detecting the t–m phase transformation in the central region of the polished surface which was submitted to the maximum tensile stress during the bending fatigue tests. The value fraction of the transformed phase was estimated around 7–10%. The slit formation (microcracks) observed in this surface, see Fig. 5, is visible. However the crack shielding presented by the martensitic ZrO$_2$ transformation produces compressive stresses that cause crack arrest.

Fig. 6 presents the fracture surfaces micrographs of the sintered samples fractured during fatigue tests.

The specimens rupture in fatigue starts in the polished tensile surface of the sample and occur in a brittle mode, being a function of the critical flaw size. This flaw must overcome the compression stresses generated by the t–m phase transformation in order to propagate. Therefore, the t–m transformation as observed by Grathwohl and Liu [15] increases the critical flaw size and results in improved strength and fatigue resistance. Cyclic testing of Y-TZP provides interesting results concerning fatigue behavior, threshold phenomena, and the strengthening effect of this transformation-toughened ceramic. The range of fatigue is not clearly delimited while it is clear that this fine-grained ceramic is particularly prone to cyclic fatigue.

3.4. Weibull distribution

The results of the statistical analysis of the MOR using the two-parameter Weibull approach are presented in Fig. 7.

It was observed for a large amount of ceramic materials that the “m” value depends on processing, the amount of inclusions, microstructure, pore distribution and surface finishing degree. These values are usually between 3 and 15 for ceramics, which means that materials with $m=15$ have a lower spreading of fracture strength values than ceramics with $m=3$. High values of $m$ represent less scattering of the fracture strength and thus more reliable materials. Quinn [26] says that groups of ceramic materials with $m$ higher than 10

![Fig. 4 - XRD patterns of the polished surface of ZrO$_2$(3%Y$_2$O$_3$) (a) before and (b) after fatigue bending testing.](image)

![Fig. 5 - SEM micrographs of the polished surface in survived samples after fatigue bending testing: (a) 530 MPa; (b) 610 MPa.](image)
can be considered good and reliable for structural applications. In this work, a Weibull modulus $m = 9.8$ was found for the ZrO$_2$ samples. The predominant factors for this resistance behavior are the microstructural characteristics and the high relative density.

Fig. 6 and Table 2 present results of Weibull analysis of the samples tested in fatigue, in which the spontaneous failure data ($N \leq 10^3$ cycles) were excluded of the calculations. In this case, the Weibull parameters were determined for each stress level. The very low $m$ values reflect the low uniformity of the fatigue data. The characteristic life at each stress level is given by the $b$ values. A tendency is observed of the $m$ values to increase and the $b$ values to decrease as $\sigma_{\text{max}}$ is increased. The Weibull parameters allow also for reliable life estimates to be formed, with the use of an appropriate reliability function.

### 4. Conclusions

In this work, the mechanical properties and cyclic fatigue behavior of tetragonal zirconia polycrystalline (3Y-TZP) has been evaluated. The adopted processing route allowed to obtain highly dense (99.7%) materials. The modulus of rupture (880 MPa), Vickers hardness (13.5 GPa) and fracture toughness
(8.15 MPa m^{1/2}), as well as the Weibull modulus (9.8) qualify this material for applications in metal-free dental restorations.

Cyclic fatigue tests by four-point bending were conducted in order to obtain the stress life $\sigma \times N$ curve for the material. The experimental results clearly indicate that 3Y-TZP ceramic material suffered cyclic fatigue fracture. Phase analysis results indicate that the material suffers t-m phase transformation due to cyclic as well as static loading. It was found that the fatigue strength limit is around 550 MPa (62.5\% of the MOR). The Weibull analysis of the fatigue results obtained low $m$ values, reflecting the high scattering of the fatigue data.

Conflicts of Interest

The authors declare no conflicts of interest.

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References