Novel process for the production of 3Y-TZP ceramics: comparison between ageing in artificial saliva and accelerated ageing

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Abstract
The degradation of tetragonal zirconia polycrystalline (3Y-TZP) ceramics prepared by a novel film growth technique, and by sintering at 1400 °C, was evaluated for one year using two processes: (i) degradation under oral conditions in artificial saliva (37 °C and pH 6.8) and (ii) accelerated degradation by autoclaving at 134 °C at 0.2 MPa of pressure. X-ray diffraction analysis of 3Y-TZP ceramics sintered at 1400 °C showed a phase transformation (tetragonal to monoclinic) in 3Y-TZP ceramics after the fifth month in artificial saliva. After 12 months in artificial saliva, there was ~11% of monoclinic phase present in 3Y-TZP ceramics, but only ~2% of monoclinic phase in samples that were subjected to accelerated degradation for 5 h. No correlation was found between the level of ageing during accelerated degradation and degradation in artificial saliva. There was no degradation of 3Y-TZP ceramics prepared by a novel film growth technique, independently of the degradation method used, which suggests that this material could be used for dental prosthetics.

1. Introduction
The formation of dental cavities and other oral diseases can lead to permanent damage, which will make necessary the use of a dental prosthesis.

Tetragonal zirconia polycrystalline (3Y-TZP) ceramics are biocompatible materials with excellent mechanical strength, which are commonly used for dental prostheses [1, 2]. A disadvantage of 3Y-TZP ceramics is low-temperature degradation (LTD), sometimes referred to as ‘ageing’.

According to ISO 13356 standard [3], accelerated degradation in water steam has been used to determine the integrity of 3Y-TZP ceramics. However, it is necessary to compare the effects of accelerated degradation in water steam to the effects of saliva at conditions resembling those of the mouth (i.e. oral conditions), and there are very few reports regarding the useful life of zirconia ceramics under oral conditions.

Chevalier et al [4], studied the degradation of zirconia ceramics occurs in a humid environment or in the presence of water and usually begins on the surface of the material. As water enters the structure, tension force is formed within the atomic lattice, inducing destabilization of the crystal structure which shifts from tetragonal to monoclinic phase. During this shape shift (phase transformation) the unit cell volume expands, inducing micro-cracks and allowing water to penetrate into the core structure, which causes the mechanical properties and the durability of the material to decrease [5, 6].

Great efforts have been made to develop alternative processes for producing 3Y-TZP ceramics that are not affected by Ltd. Alternative processes are: to use a zirconia-toughened alumina composite [7–9], or zirconia doped with transitions metals or other elements [10–12]. Another alternative process is to use coatings on the zirconia surface [13–15]. The creation of alternative production processes requires the elucidation of the factors that induce degradation of ceramics (e.g., critical grain size and content of stabilizing agents in zirconia), and the determination of the stress component that takes place during the transformation of the crystal structure [16, 17].
It is well known that, according to the ISO 13356 standard [3], the study of the lifetime of biomedical grade zirconia is based only on accelerated ageing tests [18–24]. This test requires the immersion of the ceramic in water steam in an autoclave at 134 ± 2 °C, at a pressure of 0.2 MPa for 5 h. Sanon et al [24] reported that 1 h of accelerated ageing corresponds to 2 years of degradation at 37 °C. However, it must be noted that the degradation mechanism of zirconia ceramics is still a matter of debate, which makes it necessary to study the effect of oral conditions (e.g., artificial saliva at 37 °C for one year) on the degradation of zirconia ceramics, and to compare these effects with those of accelerated ageing tests, specifically because the pH of the human body could affect the mechanism of phase transformation. There are very few reports addressing the lifetime of zirconia under oral conditions [25, 26].

In this work, two degradation methods for 3Y-TZP ceramics were evaluated under atmospheric conditions. One of these methods is similar to oral conditions (3Y-TZP ceramics were exposed to artificial saliva at 37 °C with a pH of 6.8 for one year), while the other one is an accelerated degradation process. In addition, the degradation under oral conditions of 3Y-TZP ceramic samples produced by sintering at 1400 °C was analysed, and the degradation of 3Y-TZP ceramic samples that were produced using a novel film growth technique (patent number MX/a/2010/005719, henceforth ‘film growth process’) [27]. The results indicate that the degradation of 3Y-TZP ceramics is faster under oral conditions than in the accelerated ageing process.

2. Materials and methods

High purity 3Y-TZP powder (Tosoh Corporation, Japan), was ground in a Spex milling apparatus for 5 min and compacted to cylindrical pellets 8 mm in diameter and 4 mm thick. The powder was pressed without binders at 140 MPa using a uniaxial press. The compacted pellets were placed in a latex container and compacted again at 216 MPa for 8 min using a cold isostatic press (model CIP 50 M, TMI Corporation, USA). Some of the resulting pellets were sintered at 1400 °C for 1 h using a heating and cooling rate of 5 °C·min⁻¹. Other samples were prepared according to the novel film growth process for producing zirconia ceramics stabilized with 3 mol% Y₂O₃ using a thin film growth technique through cathodic erosion [27]. These samples were manufactured using commercial 3 mol% yttria- stabilized zirconia powder; the powder was conditioned by grinding in nylamide Spex mills with 5 and 10 mm zirconia balls as grinding media for 5 min. After conditioning, the powder was recovered, homogenized in agate mortars, and uniaxially-pressed immediately for subsequent sintering. The resulting ceramic bodies were polished using metallographic techniques until the stripes on the surface disappeared, or until low surface roughness was attained.

An artificial saliva solution was prepared according to the procedure of Macknight-Hane and Whitford [28]. To reproduce the conditions of the oral environment (i.e. 37 °C and pH of 6.8), 36 3Y-TZP samples that were sintered at 1400 °C (placed into 12 vials, 3 samples per vial) were aged for one year in a thermal bath Ex200 containing artificial saliva. Each vial contained 15 ml of artificial saliva. Three samples were recovered each month for evaluating the extent of degradation. The same procedure was applied to 3Y-TZP samples generated by the film growth process [27]. For the accelerated degradation process, samples were immersed in water steam at 0.2 MPa in an autoclave at 134 °C for 5 or 10 h. Before and after the degradation process, samples were analysed by Scanning Electron Microscopy (Field Emission JSM-7401F, JEOL, Japan) through secondary electrons, 2.0 kV, working distance = 8.0, at magnifications of 5000, 14000, and 20,000×. The average grain size was obtained using the ImageJ software. X-ray diffraction (XRD) patterns were obtained using a PANalytical X’pertPRO diffractometer, using Cu Kα (λ = 1.5418 Å) radiation. Diffraction patterns were recorded in a 2θ range of 20° to 90°, step size of 0.017°, and a counting time of 100 s. The Rietveld method was applied to all experimental XRD data to quantify the amount of the final monoclinic phase [29]. The experimental patterns were refined using the FULLPROF software. The background of experimental data was adjusted using a polynomial function. XRD profiles were fitted by the refinement of U, V, and X parameters. Fracture toughness was obtained by Evans and Charles equation (1) [30].

\[
K_{IC} = 0.0752P/C^{3/2},
\]

where \( P \) is the load applied through the indenter (9.81 N) during 15 s, and \( C \) is the length of the crack in microns.

Indentation was performed based on the ASTM C 327-03 standard, using a Vickers indenter model FM-7 from Future-Tech Corp, Tokyo, Japan.

3. Results

In general, the morphology of samples was not homogeneous for both sintering processes; the grain size and shape were irregular (figure 1). The grain size distribution was 195 nm ± 68 nm in samples obtained by the film.
growth process [27] (figure 1(a)). On the other hand, the grain size distribution was 264 nm ± 98 nm in samples sintered at 1400 °C (figure 1(b)). Figure 2 shows XRD patterns corresponding to 3Y-TZP samples sintered at 1400 °C for 1 h, and samples prepared by the film growth process aged in artificial saliva for one year. Figure 3(a) shows the presence of monoclinic ZrO2 in 3Y-TZP samples sintered at 1400 °C for 1 h and then aged in artificial saliva, the XRD pattern is characterized by a major diffraction peak at 2θ = 28.1°. In contrast, figure 3(b) shows only the main diffraction peak corresponding to the tetragonal ZrO2 phase at 2θ = 30.16° in samples prepared by the film growth process and then aged. The absence of monoclinic zirconia phase in figure 3(b) suggests that there is some resistance to LTD under the experimental conditions tested.

During the first month of ageing in artificial saliva, lack of formation of the monoclinic phase (characterised by the reflection (−111)m) revealed no LTD of samples sintered at 1400 °C. However, after 2 months in artificial saliva, an increase in reflection (−111)m was observed, which led to a decrease in reflection (101). There was 11% monoclinic phase after 12 months of ageing in artificial saliva. Figure 4 shows the XRD patterns of samples subjected to accelerated degradation for 5 or 10 h. A small reflection peak (−111)m corresponding to the monoclinic phase was evident after 10 h. The maximum amount of monoclinic phase in the accelerated degradation test was 2%.

Figure 4 shows the influence of ageing time on the hardness of 3Y-TZP samples sintered at 1400 °C for 1 h and then kept in artificial saliva for one year. There was a slight decrease in hardness as ageing time increased. Fracture toughness was 4.08 MPa·m1/2 MPa·m1/2 and 6.73 MPa·m1/2 for samples with 0 and 12 months of ageing, respectively. Figures 5(a) and (c) show SEM images corresponding to the footprints Vickers indentations of 3Y-TZP ceramics sintered at 1400 °C for 1 h before and after ageing, respectively. The length of the cracks was approximately 10 μm in samples with no ageing (figure 5(b)), and approximately 5 μm after 12 months of ageing (figure 5(d)).

4. Discussion

According to our results using artificial saliva, after 12 months of ageing in artificial saliva, there was nearly 11% of monoclinic phase transformation in 3Y-TZP samples sintered at 1400 °C. This is consistent with results obtained by Miragaya et al [25], who show that 3Y-TZP samples placed into the oral cavities of twenty patients 14 h each day for 60 days exhibited between 4.7% and 7.7% of monoclinic phase transformation. Similarly, Borges et al [26] kept Y-TZP samples under oral conditions for 100 days and obtained 5.4% to 11.8% of monoclinic phase transformation.

The accelerated ageing test resulted in only 2% monoclinic phase transformation in 3Y-TZP samples sintered at 1400 °C when the ageing time was 10 h. In contrast, other reports monoclinic phase transformation of about 15%–20% after less than 1 h of accelerated ageing [18, 23]. Kohorst et al [31] reached 55% of the monoclinic phase after 8 h at 134 °C and 3 bars of pressure, but others report almost 40% monoclinic phase after accelerated degradation for over 10 h [21, 32].

Figure 5 shows that intergranular fracture predominates in 3Y-TZP samples sintered at 1400 °C and then aged in artificial saliva; this intergranular fracture is characterised by crack deflection: the crack front changes its propagation path, being more tortuous in 3Y-TZP ceramics sintered at 1400 °C for 1 h (which had a larger grain
size, figure 1(b)). The crack resulting from 12 months in artificial saliva was characterized by a small number of deviations along its propagation path, leading to an increase in the deflection mechanism, and therefore to an increase in fracture toughness. The shorter crack length (figure 5(d)) in 3Y-TZP samples sintered at 1400 °C and aged in artificial saliva may be due to structure transformation from tetragonal phase into monoclinic crystalline
phase. This transformation leads to an increase in volume resulting in a local compressive stress field around the tip of the crack that inhibits crack propagation and results in enhanced fracture toughness [33]. Conversely, in 3Y-TZP ceramics prepared by the film growth process, a lower degree of crack deflection decreased the tortuosity of the path of the crack, due to the decrease in grain size (figure 1(a)), which in turn decreased fracture toughness. The increase in fracture toughness in 3Y-TZP ceramics sintered at 1400 °C for 1 h is in agreement with the report by Piconi and Maccauro [1], who showed that transformation from tetragonal to monoclinic phase occurs in 3Y-TZP ceramics. It must be noted that if the material continues in contact with artificial saliva the transformation will continue until its mechanical properties are finally lost [34].

The present work confirms that the behaviour of 3Y-TZP ceramics is different depending on the environment; the speed of transformation is greater under conditions that are similar to the oral environment. In this work, all the samples had constant yttrium content and density; yet, 3Y-TZP samples sintered at 1400 °C and kept in artificial saliva for one year were degraded, while 3Y-TZP samples prepared by the film growth process showed no degradation after one year in artificial saliva. This difference can be attributed mainly to the critical grain size achieved during sintering at low temperature. Chevalier et al [18] stated that ‘Any extrapolation
Degradation. Nevertheless, the samples after 2-month present Low Temperature Degradation is mainly dependent on the ceramic microstructure (grain, size, yttrium content, density, etc). Therefore, LTD parameters should be specifically determined for each 3Y-TZP ceramic preparation process.

5. Conclusions

This work clearly shows that 1 h of accelerated ageing does not correspond to 2 years at 37 °C in saliva: after 12 months of ageing in artificial saliva, there was nearly 11% of monoclinic phase transformation in 3Y-TZP samples sintered at 1400 °C, while the maximum amount of monoclinic phase was 2% after 10 h of accelerated degradation.

The degradation test in artificial saliva allows the material to remain in contact with the saliva solution, so that water can infiltrate into the material grains to a higher level, causing a greater degree of phase transformation. It is possible that the composition of saliva and its pH are important factors causing higher levels of degradation.

Degradation of 3Y-TZP ceramics at low temperature depends on both the microstructure of the material and on the environment to which the ceramics will be exposed.

There was no transformation from tetragonal to monoclinic phase in 3Y-TZP ceramics prepared by the film growth process method after a year of ageing in artificial saliva; therefore, this material could be used for efficient dental prosthetics.

While 3Y-TZP ceramics sintered at 1400 °C for 1 h had excellent hardness properties, even after they were subjected to different ageing conditions. Nevertheless, the samples after 2-month present Low Temperature Degradation.

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