Low temperature degradation of a Y-TZP dental ceramic

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Bars of Y-TZP ceramic for dental restorations were subjected to hydrothermal degradation via in vitro exposure to water steam at 140 °C for 7 days. X-ray diffraction, atomic force microscopy and scanning electron microscopy techniques were applied to observe and quantify the tetragonal–monoclinic (t–m) phase transformation associated with the process. Nanoindentation was used to assess the ceramic’s mechanical properties before and after hydrothermal degradation. Texture associated with martensitic t–m transformation was observed at the grain surface. The t–m transformation followed nucleation-and-growth kinetics, with predominance of the nucleation process. The transformation occurred within a layer of 6 μm below the surface.

Mechanical properties deteriorated with hydrothermal degradation, resulting in a 30% reduction of Young’s modulus and hardness. A strong correlation was found between the increasing monoclinic fraction and the decline in mechanical response. It was thus concluded that the emergence of the monoclinic phase and the associated microcracking were the most likely causes for the degradation of mechanical properties.

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1. Introduction

The development of high-toughness ceramics [1–3] has led to an increased usage of yttria-stabilized tetragonal zirconia (Y-TZP) in clinical applications. Current dental Y-TZP ceramics consist of uniform 0.2–0.5 μm diameter equiaxed grains prepared from fine ZrO2 particles and 1.75–3.5 mol.% (3.5–8.7 wt.%) Y2O3. Depending on composition, firing time and temperature, Y-TZP ceramics may contain mixtures of tetragonal and cubic phases [4–6].

Problematically, yttria-stabilized tetragonal zirconia undergoes an unfavorable transformation known as “low temperature degradation” (LTD) [7], which has been extensively documented in previous reports [see the comprehensive reviews by Lawson [8], Chevalier et al. [9] and Lughi and Sergo [10]]. The LTD phenomenon is characterized by the following. In the initial stages and in the presence of water, a tetragonal-to-monoclinic (t–m) phase transformation takes place at fairly low temperatures (65–300 °C), the degradation process proceeding gradually from the surface into the bulk of the ceramic. Subsequently micro- and macrocracks develop in the wake of the expansion in volume associated with the phase transformation [11]. Ultimately, LTD results in surface roughening [12,13] and detrimentally affects the Y-TZP’s mechanical properties [14,15].

Several hypotheses were proposed to explain the cause-and-effect relationship between the presence of water and the t–m phase transformations. According to Sato and Shimada [11], surface chemisorbed water induces the breakage of Zr–O–Zr bonds and the formation of Zr–OH, thereby resulting in stress corrosion. Another hypothesis postulated that water promoted the formation of Y(OH)3, thus depleting the stabilizer Y2O3 and triggering the t–m transformation [16]. The latter assumption, however, has since been disproved [17]. In an alternative explanation, the phase transformation was attributed to internal stresses associated with the diffusion of water radicals within the zirconia lattice [17,18] by an oxygen vacancy diffusion mechanism [19–22].

The susceptibility of Y-TZP to LTD depends on a variety of factors. Degradation increases when the Y2O3 content is low [23] and the grains are large in size [24–26]. Moreover, the rate of phase transformations augments with increasing temperature and aging time [11,12,15]. Additional effects may stem from residual stresses induced by surface preparation [27] and the cubic phase acting as nucleation sites for the t–m transformation [28].

Controlling the hydrothermal aging of Y-TZP still remains a challenge. It has been reported that the addition of CeO2 or Al2O3 to Y-TZP might inhibit the t–m transformation [23,29–31]. For instance, no monoclinic phase was formed in 3Y-ZrO2 and 4Y-ZrO2 alloyed with CeO2 in excess of 10 wt.%. Moreover, supplementing the zirconia with up to 40 wt.% Al2O3 decreased the t–m transformation rate, but did not fully inhibit the transformation [23]. More recently, results by Tsubakino et al. [31] indicated that the
inclusion of 1.2–12 wt.% Al₂O₃ limited the t–m phase transformation to the surface layers. At variance with Tsukabiko et al., Li and Watanabe [29] were able to suppress the t–m phase transformation during hydrothermal degradation of 2Y-TZP and 3Y-TZP by adding 3–5 vol.% Al₂O₃.

LDT was most specifically described in zirconia implants of femoral heads [13,32,33]. In a “leading opinion” paper on the future of zirconia as a biomaterial [34], Chevalier was marveling at the dental community realizing the benefits of zirconia but appeared as largely indifferent to its degradation due to aging.

Indeed, although LTD might roughen surfaces, cause wear and decrease the hardness and strength of Y-TZP restorations, only little information is available regarding low temperature aging of Y-TZP dental ceramics [35–38]. In this context, data by Papanagiotou et al. [36] indicated that LTD did not reduce the flexural strength of a dental zirconia ceramic. Still the t–m phase transformation slowly propagates from the surface into the bulk in the LTD process. The depth of the transformed layer is time dependent and was estimated to a few micrometers [33]. In consequence of which, methods focusing on surface characterization should be applied and related to the alterations in mechanical properties after LTD.

Nanoindentation is a popular method to assess a material’s small scale mechanical properties. Moreover, contact stiffness can be determined on a continuous scale at any point along the loading curve by applying the continuous stiffness measurement (CSM) technique [39,40] and thus simultaneously providing elasticity and hardness measurements as a function of indentation depth. Methods suitable for analyses of surface topographies [41], such as scanning electron microscopy (SEM) and atomic force microscopy (AFM), might also be of value to characterize surfaces during the hydrothermal aging of Y-TZP ceramics.

The purpose of the present work was to assess the effects of hydrothermal degradation on a dental Y-TZP ceramic. To this end, the surface characteristics and mechanical properties of the ceramic were assessed before and after aging. The hypothesis tested was that the dental Y-TZP ceramic was sensitive to hydrothermal aging despite its fine crystal grain structure and the presence of small amounts of alumina in its composition.

2. Materials and methods

2.1. Specimens preparation and characterization

Five bar-shaped samples (40 × 5 × 3 mm) of Y-TZP ceramic (Lava, 3M-ESPE) as produced by the manufacturer were mirror polished using 250–600 grit diamond discs first and then refined with 3 and 1 μm diamond pastes. Subsequently the samples were thermally etched for 32 min at 1450 °C to expose the microstructure’s grain boundaries. Prior to hydrothermal degradation, each sample was characterized as described below.

The chemical composition of the ceramic was assessed with X-ray fluorescence spectroscopy using an Advant XP spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) equipped with a Cu X-ray tube in vacuum mode. The analyses were conducted using the UNIQUANT software (Thermo Fisher Scientific, Waltham, MA, USA). Instrument parameters were chosen as follows: 60 kV voltage, 120 mA current and 25 mm spot.

X-ray diffraction analysis was performed using a D500 X-ray diffractometer (Bruker AXS, Karlsruhe, Germany) with Ni filtered Cu Kα₁ (1.5406 Å) radiation at 40 kV and 35 mA. Diffraction data were collected from 2θ = 6° to 64° 2θ, with a step size of 0.01° and a counting time of 2 s/step. Rietveld refinement was applied to identify and quantify existing crystalline phases. Last, the specimens’ bulk density was determined using Archimedes’ method.

2.2. Characterization of the t–m phase transformation in hydrothermal aged samples

Low temperature degradation was produced by aging ceramic samples in 140 °C water steam at atmospheric pressure. Each sample was characterized after degradation times of 24, 96 and 168 h as follows.

Tetragonal-to-monoclinic surface phase transformations consecutive to aging were measured using the grazing incidence X-ray diffraction technique (GIXRD) with a 2θ fixed incidence angle. To this effect, the diffractometer was equipped with an Euler cradle. XRD profiles were generated from 2θ = 33° to 2θ with a step size of 0.01° and a counting time of 5 s/step. The monoclinic phase fractions Xₘ were determined using Garvie and Nicholson’s equation [42] as modified by Toraya et al. [43]. After 168 h aging, phase-depth profiles (n = 5) were generated from diffraction data obtained at fixed incidence angles varying from 1° to 15°. Subsequently, the real depth profile (fₘ) of the monoclinic fraction was calculated from the mean Xₘ fractions, using Gremillard et al.’s methodology [44].

The changes in surface topography after aging were examined by AFM. The AFM (XE-100, Park Systems Corp., South Korea) was used in contact mode, with a doped silicon probe of 10 nm tip radius. After 168 h aging, SEM images were also obtained with a high resolution field emission SEM (LEO Gemini 1225, Carl Zeiss SMT AG, Oberkochen, Germany) using the InLens detector with an accelerating voltage of 20 kV and a working distance of 2.9 mm.

2.3. Evaluation of surface mechanical properties

The mechanical properties of the surface were assessed by nanoindentation testing. An NHT nanoindenter (CSM Instruments SA, Peseux, Switzerland) equipped with a continuous stiffness measurement (CSM) module was used. This method (see Appendix A) is particularly applicable when measuring mechanical properties as a function of penetration depth within a single load cycle. For this purpose, a 2 Hz, 5 mN sinusoidal force was superimposed to the applied load. The ceramic was indented with a maximum load of 300 mN at a constant strain rate of 0.05 s⁻¹. The Berkovich diamond tip was calibrated using a fused silica standard. Hardness (H) and Young’s modulus (E) were calculated as a function of penetration depth using Oliver and Pharr’s method [39]. For computation of Young’s modulus, a Poison ratio of 0.32 was assumed. Five indentations were placed in each specimen before hydrothermal degradation and after each degradation time period.

A statistical analysis was performed on the mechanical properties registered at 400, 600 and 800 nm. The Kruskal–Wallis–H test at 5% level of significance was used to detect differences between the mechanical properties at different aging times.

3. Results

The chemical composition of the “native” material (i.e. as provided by the manufacturer) is presented in Table 1 and expressed as the weight percentages of the different oxides. The native

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<th>Chemical composition of the native material expressed as wt.% determined by XRF spectroscopy (mean ± SD).</th>
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<td>ZrO₂</td>
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<td>Y₂O₃</td>
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<td>Al₂O₃</td>
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material was a two phase 3Y-TZP ceramic with $6.09 \pm 0.02 \text{g cm}^{-3}$ bulk density. The principal phase (87 wt.%) was tetragonal, with lattice parameters $a = 3.606 \text{Å}$ and $c = 5.180 \text{Å}$. The secondary phase (13 wt.%) was cubic, with lattice parameter $a = 5.132 \text{Å}$. As hydrothermal aging progressed, monoclinic peaks $(111)$ and $(101)$ appeared in the XRD pattern at 2$\theta = 28.1^\circ$ and $31.3^\circ$, respectively. The intensities of these peaks increased with time. Aging also resulted in a shift to a lower angle (29.99$^\circ$) of the $(111)_c$ and $(101)_c$ peaks along with a significant decrease in intensity. The monoclinic mass fraction $X_m$ as calculated from the XRD patterns at different aging times is reported in Fig. 2a. The sigmoid shape of the curve is characteristic of a nucleation-and-growth (N–G) process. Consequently the LTD kinetics can be described using Mehl–Avrami–Johnson’s law:

$$X_m = 1 - \exp[-(bt)^n]$$

where $X_m$ is the monoclinic fraction and $t$ the aging time, $b$ and $n$ are parameters describing the apparent activation energy and the nucleation-and-growth mechanisms. From this equation, values of $n = 1.5 \pm 0.2$ and $b = 0.01 \pm 0.006$ were obtained by plotting $\ln \left( \frac{\ln (\frac{X}{X_0})}{\ln (\frac{1}{X_0})} \right)$ as a function of $\ln(t)$. Moreover, $n$ was not constant as it varied between 1 and 2 over the entire interval of hydrothermal aging. Typically $n$ initially increased, then reached a plateau and eventually decreased at the end of the transformation process.

A Rietveld analysis conducted on the $\theta$–2$\theta$ XRD diffraction data of the samples aged for 168 h yield fractions of $48 \pm 1 \text{wt.\%}$ for the monoclinic phase and a total of $52 \pm 1 \text{wt.\%}$ for the tetragonal and cubic phases.

Quantitative information about the thickness of the transformed layer and the distribution of the monoclinic phase below the surface was obtained from XRD data at fixed incidence angles. Both the experimental ($X_m$) and the real ($f_m$) depth profiles of the monoclinic fraction are depicted in Fig. 2b for a specimen aged for 168 h. The monoclinic fraction $f_m$ was deducted from an inverse Laplace transform of an exponential fit of $X_m$. The monoclinic fraction $f_m$ at the surface was 77% and decreased exponentially within the first 6 µm.

### 3.2. Surface topography

A typical AFM view of a native specimen is displayed in Fig. 3a. The grain boundaries were clearly visible. The grains were equiaxial in shape and presented a smooth surface devoid of any noticeable texture. Different grain sizes were observable ranging between 270 ± 30 nm and 800 ± 40 nm. After 24 h of hydrothermal aging, the t–m transformation was clearly visible with typical self-accommodating martensitic variants and associated surface uplifts appearing on the ceramics’ grains (Fig. 3b). A Sobel algorithm was applied to the topographical mappings to improve edge detection (Fig. 3c and e). Smaller martensitic plates were also observed along the grain boundaries (Fig. 3c). With increasing aging time, the transformation process proceeded predominantly along the grain boundaries, thereby leading to an apparent coalescence of the grains (Fig. 3d and e).

An SEM view of a sample aged for 168 h is shown in Fig. 4. The grains’ surfaces appeared as textured due to the preferential crystallographic orientations of the monoclinic phase.

### 3.3. Surface mechanical properties

Typical loading–unloading curves prior to and after 168 h of hydrothermal aging are displayed in Fig. 5. LTD has an obvious effect on the load–penetration response. Indeed, for identical loads, a greater penetration was observed after hydrothermal aging. No

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**Fig. 1.** GIXRD diffraction patterns obtained with a fixed incidence angle of $2\theta$ before and after 168 h low temperature degradation at 140 °C.

**Fig. 2.** (a) Monoclinic fraction $X_m$ measured by GIXRD with a fixed incidence angle of $2\theta$ as a function of hydrothermal aging time. (b) $X_m$ and $f_m$ monoclinic fractions represented as a function of the X-ray penetration depth.
discontinuities due to “pop-in” or “pop-out” effects were detected on the loading–unloading paths. Fig. 6 illustrates the variation of Young’s modulus (a) and hardness (b) of the ceramic before and after LDT as a function of penetration depth. A slight decrease in hardness with increasing indentation depth is noticeable in Fig. 6b. This can be attributed to the indentation size effect (ISE), which is often observed in the hardness response of hard brittle materials such as ceramics. Note that at higher indentation depths, hardness values became constant. Before aging, a Young’s modulus of 237 ± 22 GPa and a hardness of 18.8 ± 1.1 GPa were obtained at a penetration depth of 800 nm. After aging, both Young’s modulus and hardness values decreased. The decline in properties was more
pronounced as hydrothermal aging progressed, reaching a plateau after 96 h. After 168 h of aging time, values of 163 ± 47 GPa for Young’s modulus and 12.5 ± 1.8 GPa for hardness were obtained at 800 nm depth.

Significant differences in mechanical properties registered at 400, 600 and 800 nm were found after hydrothermal degradation (Table 2). With respect to the native material, the decrease of Young’s modulus and hardness after hydrothermal degradation were significant. Increasing aging time beyond 96 h did not degrade the ceramic further.

4. Discussion

The purpose of this study was to assess the effect of LTD on the microstructure and mechanical properties of a Y-TZP dental ceramic. Clearly, the ceramic tested was affected by hydrothermal aging – AFM, SEM and GIRXD data analyses confirming the tetragonal-to-monoclinic phase transformation. These observations are in agreement with previous experiments which also demonstrated phase transformations in other biomedical grade Y-TZP ceramics after hydrothermal aging [8,9]. In addition, the present data also demonstrate a decrease in modulus of elasticity and hardness as determined by the continuous stiffness measurement method.

X-ray diffraction was used to identify and quantify the phases that prevailed on the surface of the dental ceramic prior to and after hydrothermal aging. GIXRD techniques were applied to generate the diffraction patterns from the subsurface layers. X-ray penetration was calculated in terms of the critical angle \( \alpha_{cr} \) for external reflexion for Cu K\( \alpha \), taken as

\[
D = \frac{2\alpha_{cr}}{\mu} \quad \text{with} \quad \gamma \gg \alpha_{cr},
\]

where \( \mu \) is the coefficient of linear absorption for the \( \text{ZrO}_2 \) substrate and was equal to 620 cm\(^{-1}\) and \( \gamma \) is the X-ray’s angle of incidence [45].

With an incidence of 2\( ^\circ \), the computed X-ray penetration was 1.1 \( \mu \)m. This value fell into the range of maximum penetration with the CSM method. Therefore, a fixed incidence angle of 2\( ^\circ \) was selected for subsequent GIXRD diffraction assays.

Low temperature degradation of the ceramic was time dependent. The sigmoïdal shape of the curve is characteristic of transformations proceeding via N–G kinetics [12,46,47]. The transformation mechanism can be derived from the “\( n \)” exponent of the MAJ equation. According to Chevalier et al. [12], a value approaching 4 indicates a constant nucleation and three-dimensional growth process during the LTD of 3Y-TZP. For lower “\( n \)” values, such as obtained in the present study, Gremillard et al. [25] suggested a different mechanism in which nucleation predominated and growth proceeded at slower rates, as it was hampered by rapid interactions between nuclei.

The monoclinic fraction did not increase further after 96 h of hydrothermal aging. This was due partly to the presence of the stable cubic phase (~13%) and partly to tetragonal zones which remained within the grains owing to stress buildups that prevented complete martensitic transformation. Compared to a similar 3Y-TZP [12], the dental ceramic is more resistant to hydrothermal aging, as the proportion of the monoclinic phase was 68% (as compared to 85% in Chevalier et al.’s study). Further,
the transformation proceeded at a slower pace. In this regard, LTD is mainly dependent on density and grain size which are both controlled by the conditions at the time of sintering [48]. Moreover, Y-TZP ceramics doped with oxides, such as Nb₂O₅ [49], CeO₂ [50] or MnO₂ [51] are less sensitive to hydrothermal aging. In the present situation, the high density of the dental ceramic and the presence of small amounts of oxides such as Al₂O₃, SiO₂ and Nb₂O₅ may possibly account for the greater resistance to degradation.

Quantification of the monoclinic fraction from the 0–2θ XRD patterns gave an apparent monoclinic content of 48% without any information about the transformation depth. By varying the GIXRD incidence angle, phase-depth profiles of the Xm and fm monoclinic fractions were obtained [44]. There is an obvious difference between these two fractions. Considering the Xm monoclinic fraction only would overestimate the depth of transformation (Fig. 2b). From the fm profile though, the transformed layer was 6 µm for the 168 h samples. This figure is in agreement with the value reported by Chowdhury et al. [33].

Prior to aging, AFM views of thermally etched zirconia displayed equiaxed smooth grains with no texture. According to the manufacturer, the typical grain size for this ceramic is ~300 nm, which was consistent with that of the smallest grains in the images. Hence, some grain growth during thermal etching cannot be excluded. After 24 h of hydrothermal aging, typical triangular shape reliefs indicative of martensitic transformation were visible in each area of interest. Martensitic transformation in TZP has been extensively investigated [46,52–56]. The surface-induced relief is due to the emergence of several martensitic self-accommodating variants pairs [52,53], which nucleated at grain boundaries (most likely at triple junctions), then proceeded within the grains and eventually propagated into the surrounding grains [46,53].

Some case studies on retrieved zirconia femoral heads describe damages of the zirconia implants that may be related to low temperature degradation. For instance, an increase of the surface roughness [57,58], a decrease in fracture toughness [58] and in surface hardness [59] was correlated with implantation time and prevalence of the monoclinic phase.

Only few reports exist as to the effects of hydrothermal degradation of dental Y-TZP on mechanical properties. Ardlin et al. [35] observed no change in flexural strength for “Denzir” (Ivoclar Viva- dent AG, Schaan, Liechtenstein) ceramic blocks after aging in 4% acetic acid at 80 °C for 168 h. Similar results were found for “In Ceram YZ” ceramic bars (Vita Zahnfabrik, Bad Säckingen, Germany) by Papanagiotou et al. [36]. In this instance, a slight improvement in flexural strength was even reported after 7 days of aging in boiling water. More recently, Borchers et al. [60] demonstrated no significant influence of hydrothermal degradation on biaxial flexural strength of two dental 3Y-TZP ceramics. In these studies, t–m transformation was observed after aging. Interestingly, quite the opposite was reported for biomedical grade 3Y-TZP zirconia by Kosmac et al. [37] and Ban et al. [61] as these experiments demonstrated both a decrease of the survival strength and of the biaxial strength after aging at 134 °C. This inconsistency can be explained by the residual stresses generated during the t–m transformation. At the beginning, compressive stresses are induced in the surface layer, which would raise flexural strength. Yet with progressing t–m transformation, the formation of microcracks and the build-up of tensile residual stresses could lead to a decrease in strength. Micro- and nano-indentation hardness testing is a straightforward technique when examining the mechanical properties of small volumes and was effectively used to characterize hydrothermally aged zirconia femoral heads [13,33]. For instance, Chowdhury et al. [33] confirmed that hardness decreased by 41% in a femoral head with a 78% content of monoclinic phase.

Since LTD is primarily a surface occurrence, the continuous stiffness measurement technique was also used to generate a continuous record of the mechanical properties as a function of depth [32,62]. In this regard, Catledge et al. [32] also found a strong correlation between increasing monoclinic transformation and diminution of the surface hardness in explanted femoral heads.

Continuous stiffness measurements were also used in the present study. Elasticity and hardness values were obtained at depths ranging between 0.3 and 1 µm. Hydrothermal aging resulted in a significant decrease in Young’s modulus and hardness. Further, the properties of aged samples at 1 µm penetration differed from those of native specimens thereby implying that LTD proceeded to depths in excess of 1 µm. The latter was also corroborated by the GIXRD data. After 96 h of aging, a limit was reached, that is, a 30% reduction in both elasticity and hardness. Prolonged degradation times beyond 96 h did not further affect mechanical properties. These figures are in accordance with Gaillard et al. [62], who also reported a similar degradation of mechanical properties in hydrothermally aged 3Y-TZP.

A strong linear correlation was found between the increase in monoclinic fraction and the decrease in Young’s modulus (r: −0.98536) and hardness (r: −0.99796). In this regard, it was demonstrated that the increase in volume resulting from the t–m transformation led to the development of micro-fissures [63]. Microcracking might be the mechanism responsible for the decrease in Young’s modulus and hardness [62,64].

In dental applications, zirconia contact oral fluids only intermittently. Susceptibility to LTD is thus limited to the following intraoral conditions: (a) when the bulk of an endosseous implant is made of zirconia; (b) when zirconia is used to fabricate crown or bridge abutments of which parts are left bare and not covered by a restoration, and (c) when the framework of fixed dental prostheses was machined out of zirconia and was not coated with veneering ceramic, when the veneer was either ground off during occlusal adjustments or fractured under occlusal loads.

Besides, LTD proceeds at a slow pace. To these authors’ knowledge, no data are currently available on LTD at body temperature. Lifetime predictions at 37 °C are based on accelerated aging tests. However, because of the uncertainty in determining the activation energy of the t–m transformation [10], data from such tests may be extrapolated to anywhere between 1 and 12 years. Chevalier et al. [9] suggested that 5 h of steam sterilization at 134 °C simulated 15–20 years’ degradation at 37 °C. Assuming comparable time-temperature equivalences, less than 25% t–m transformation should be expected for the dental ceramic after this time interval which thus remains below the acceptable amount according to ISO standard 13356:2008. Another parameter to consider is the

![Diagram](image-url)

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<td>Statistical correlations between native samples and hydrothermally aged samples taken at (a) depths of 400 and 600 nm and (b) a depth of 800 nm.</td>
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<th>24h</th>
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E: Young’s modulus and H: hardness. ** Significant differences with p < 0.05.
depth of the transformation zone – 6 μm in the present study. Recently, Borchers et al. [60] estimated the crack length required to significantly decrease the strength of a Y-TZP ceramic to 11 μm.

In light of the above, LTD alone probably does not affect the bulk strength and the reliability of the “Lava” dental ceramic during the expected lifetime of a dental restoration. However, LTD as tested in the present project was entirely “passive” yet, in biomedical applications, Y-TZP ceramics are subjected to cyclic loading. Under these conditions, coalescence of initially harmless cracks becomes a distinct possibility. Besides, residual stresses due to thermal treatment or to surface grinding and grit blasting will affect LTD [38]. More work is needed regarding the combined effects of LTD, cyclic load application and residual stress generation on the long term stability of dental ceramics.

5. Conclusions

The Y-TZP Lava (3M-ESPE) dental ceramic was susceptible to hydrothermal degradation when exposed to water steam at 140 °C in vitro, despite the presence of Al2O3 in its composition.

The t–m transformation followed a nucleation-and-growth kinetic, with predominance of the nucleation process.

The transformation took place in a subsurface layer of 6 μm.

Hydrothermal degradation resulted in a deterioration of the mechanical properties, with a 30% reduction of Young’s modulus and hardness.

A strong correlation was found between the increasing monoclinic fraction and the decline in mechanical properties. Hence the emergence of the monoclinic phase and associated microcracking were the most likely cause for the degradation of mechanical properties.

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Appendix A

Hardness H and Young’s modulus E are extracted from the unloading portion of the load–displacement curves obtained by indentation techniques. These properties are given by Eqs. (1) and (2):

\[ H = \frac{P_{\text{max}}}{A(h_c)} \]  

where \( P_{\text{max}} \) is the maximum peak load and \( A(h_c) \) is the projected contact area.

\[ E_{\text{eff}} = \frac{E}{1 - \nu^2} - \frac{1}{\beta} \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A(h_c)}} \]

where \( \nu \) is the Poisson’s coefficient, \( S \) is the contact stiffness and \( \beta \) is equal to 1.034 for a Berkovich indenter.

Using the method of Oliver and Pharr [39], the contact stiffness \( S \) is given by the slope of the initial portion of the unloading curve; the contact depth \( h_c \) by solving Eq. (3) and can be estimated from the load–displacement data; the projected contact area \( A(h_c) \) depends on the geometry of the indenter and the contact depth. The area function is obtained by calibration.

\[ h_c = h_{\text{max}} - \frac{E_{\text{max}}}{S} \]  

where \( c \) is a parameter equal to 0.75 for a Berkovich indenter and \( h_{\text{max}} \) is the maximum penetration depth at the maximum peak load.

The contact stiffness can be alternatively measured during the loading portion of an indentation test using the continuous stiffness measurement CSM technique. A CSM is conducted by superimposing a small oscillating force onto the monotonically increasing load either in load-control (mN s\(^{-1}\)) or strain-control (s\(^{-1}\)) mode. The amplitude of the corresponding displacement is then measured. From the phase shift between applied force and actual displacement, several mechanical properties can be assessed as a continuous function of depth of penetration.

Considering a sinusoidal load \( p \) applied with a frequency \( \omega \) and an amplitude \( p_0 \), the resulting displacement \( \delta \) will oscillate with the same frequency but typically present a phase lag \( \phi \) relative to the original oscillation. The dynamic indentation testing system can be modeled as a mass (i.e., the indenter shaft) supported by two springs. From this model, a relationship between the applied sinusoidal load and the resulting displacement can be obtained (Eq. (4)). Moreover, the phase lag is given by Eq. (5):

\[ \frac{p_0}{\delta_0} = \sqrt{(S + K_s - m\omega^2)^2 + \omega^2 D^2} \]  

\[ \tan \phi = \frac{\omega D}{S + K_s - m\omega^2} \]

where \( m \) is the mass of the indenter shaft and \( S \) is the contact stiffness. \( K_s \) and \( D \) are instrument parameters, that is, the stiffness of the indenter shaft support springs \( (K_s) \) and the damping coefficient \( (D) \), respectively.

Hence, the contact stiffness and the damping coefficient can be calculated by solving Eqs. (4) and (5).

From the contact stiffness \( S \), the contact depth and the contact area can be obtained. In consequence, the hardness \( H \) and Young’s modulus can be calculated as a function of the penetration depth using Eqs. (1) and (2).

Appendix B. Figures with essential colour discrimination

Certain figures in this article, particularly Figs. 1, 3, and 5, are difficult to interpret in black and white. The full colour images can be found in the on-line version, at doi:10.1016/j.actbio.2010.09.020.

References