Effect of different surface treatments on the hydrothermal degradation of a 3Y-TZP ceramic for dental implants

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Reference

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Abstract

Objectives. Implant surface modifications are intended to enhance bone integration. The objective of this study was to assess the effect of different surface treatments on the resistance to hydrothermal degradation, hardness and elastic modulus of a 3Y-TZP ceramic used for dental implants.

Methods. Samples grouped according to their surface morphologies (AS, as-sintered; C, coated; P, dry-polished; R, roughened; PA, polished and annealed; RA, roughened and annealed) were subjected to accelerated hydrothermal degradation (LTD) by exposure to water steam (134 °C, 2 bars) for 100 h. The t→m phase transformation was quantified by grazing incidence X-ray diffraction (GIXRD) and by combined focused ion beam and scanning electron microscopy (FIB-SEM). Elastic modulus and hardness before and after prolonged aging (100 h) were assessed by nanoindentation.

Results. AS and C specimens presented a better resistance to hydrothermal degradation than P and R samples. After prolonged aging, the depth of the monoclinic transformed layer ranged from 11 μm to 14 μm. Hydrothermal degradation led to a significant decrease of elastic modulus and hardness.

Significance. Surface treatments affected the resistance to hydrothermal degradation of the 3Y-TZP ceramic. Dry mechanical surface modifications should be avoided since a high t→m transformation rate associated to the initial monoclinic content was observed. Annealing was useful to reverse the initial t→m transformation, but did not improve the resistance to hydrothermal degradation.

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1. Introduction

Since the inception of modern dental implantology, titanium has been used as prime implant material due to its excellent osseointegration and favorable mechanical properties [1]. In recent years though, ceramic implants were developed as part of a strategy aimed at avoiding any intraoral metal. Such implants are made of zirconium oxide polycrystals which are stabilized in their tetragonal form by 3 mol% yttrium oxide and hence referred to as 3Y-TZP. Compared to other oxide ceramics, 3Y-TZP is considered a “high performance ceramic” due to its superior flexural strength and fracture toughness. Moreover, zirconia may be accurately processed to complex geometries using CAD–CAM [2–5] or low-pressure injection molding [6] and therefore is applicable to dental implantology [7–9].

Research on zirconia implants typically focuses on their mechanical properties, fatigue resistance and surface modifications which may enhance bone integration. As to the latter, a number of methods were developed to texture the surface and produce micro-porosity. For instance, the surfaces were roughened by sandblasting the implants with Al₂O₃ powders of various granularities [4,10–12], which some researchers complemented with hydrofluoric acid etching [11,13] or alkaline salt treatment [12]. In other works, a micro-porous structure was created by coating the implants’ surface with a porous layer of zirconia [9]. More recently, a femtosecond laser technique was used to generate micro-pores or microgrooves at the surface and thus create a controlled surface texture [14].

Proportionally, while it positively affects osseointegration [15–17] surface texturing also alters the implants’ mechanical strength and fatigue resistance as the surface treatments might trigger the t–m transformation, build-up residual stresses and/or create critical-size defects [18–21].

As an additional limitation, 3Y-TZP ceramics are vulnerable to hydrothermal degradation, also known as low temperature degradation (LTD) [22–25]. A phenomenon in which, due to the presence of water, the t–m phase transformation is triggered at the ceramic surface. It results in a volume expansion of the grains, inducing surface roughening, micro-cracking and possibly loss of strength [23,24,26]. Hydrothermal degradation is time- and temperature dependent and does occur at 37°C during the lifetime of the implanted device, as reported for explanted hip implants [27–30]. However, clinical hydrothermal degradation has not yet been documented for dental implants. This may be due either to differences in environmental conditions and applied forces or lack of studies addressing this particular issue. Moreover, it is well established that surface treatments such as polishing, grinding or sandblasting may affect the susceptibility of 3Y-TZP ceramics toward hydrothermal degradation [31–34].

The present study aimed at evaluating the resistance to hydrothermal degradation of a 3Y-TZP ceramic for dental implants. More specifically, the objectives were

1. to determine the influence of selected surface treatments on the kinetics of hydrothermal degradation and
2. to assess the elastic modulus and hardness of the 3Y-TZP before- and after accelerated aging.

2. Materials and methods

The material studied is a 3Y-TZP ceramic processed by hot isostatic pressing and sintering and used to produce a recently marketed implant system (Axis Biodental, Les Bois, Switzerland). Bar-shaped samples (13 mm × 5 mm × 3 mm) were provided by the manufacturer and assigned to four different groups according to their surface morphologies. Specifically, the first group contained ‘as-sintered’ specimens without additional treatment (AS, n = 3). After sintering, a 3Y-TZP coating was deposited on top of the surface (C, n = 3), using a proprietary method (EP 1 924 300). The ‘polished’ group (P, n = 3) was obtained after mechanical dry-polishing the ‘as-sintered’ surface with a diamond disk of grit size between 1 and 3 µm. The ‘rough’ group (R, n = 3) was obtained after mechanical-dry-mechanical treatment of the ‘as-sintered’ surface, using a 20 µm grit diamond wheel. These two specific surfaces were added for a comparative purpose. Moreover, two ‘polished-annealed’ (PA group) and two ‘rough-annealed’ (RA group) specimens were obtained by annealing at 1050°C for 15 min (Programat P500, Ivoclar-Vivadent, Schann, Liechtenstein) two polished respectively rough specimens.

Prior to proceeding to the tests, all specimens were ultrasonically cleaned in ethanol for 20 min (45–90 kHz, 320W, Fisa Compact, FISA, France).

2.1. Surface characterization

Surface roughness was measured using an electro-mechanical profilometer (M1, Mahr, Göttingen, Germany) featuring a drive unit (PGK, Mahr) and a measuring sensor with a 40 nm z-resolution (MFW-250, Mahr). The specimens were mounted on an X-Y cross-slide table. They were scanned using a 2 µm radius diamond stylus at a force of 0.5 mN and a traveling speed of 0.5 mm s⁻¹. The profilometer generated frames of 21 line profiles with an interdistance of 140 µm. Rₚ was calculated using a Gaussian profile filter (ISO 11562:1996) [35] with the cut-off wavelength set at λc = 0.8 mm and the evaluation length at lₑ = 5.6 mm.

Images of the surface were obtained using a scanning electron microscope (XL 20, Philips, Eindhoven, Netherlands).

2.2. Hydrothermal degradation (LTD)

The samples were aged for selected times between 1 and 100 h in an autoclave at 134°C under 2 bars of water pressure. Tetragonal-to-monoclinic surface phase transformations consecutive to aging were measured using the grazing incidence X-ray diffraction technique (GIXRD) with a fixed incidence angle of 2° to ensure the analysis of the outermost surface layer (D500, Bruker AXS, Karlsruhe, Germany). Under these conditions, the X-ray penetration depth is 1.2 µm (as determined by the AbsorDX software, DIFFRACplus BASIC Evaluation Package, Bruker, Karlsruhe, Germany). XRD profiles were generated in a range of 26°–33° 2θ with a step size of 0.01° and a counting time of 5 s/step. The integrated intensity ratio (Iₐ/Iₘ) and the volume fraction of the monoclinic phase (fₚ) were determined from the X-ray diffraction patterns using Garvie and Nicholson’s [36] and Toraya et al.’s [37] equations.
Hydrothermal degradation kinetics were calculated from Mehl-Avrani-Johnson's (MAJ) equation [38]:

\[ f = f_{\text{min}} + \left( f_{\text{max}} - f_{\text{min}} \right) \left[ 1 - \exp\left(-ht^{\nu}\right) \right] \]  

(1)

where \( f \) is the volume fraction of the monoclinic phase, \( f_{\text{max}} \) and \( f_{\text{min}} \) are the maximum and initial volume fractions, \( n \) is a constant describing the nucleation and growth mechanism, \( h \) depends on temperature and is related to the apparent activation energy of the t-m transformation and \( t \) is the time.

2.3. Depth profiles of the monoclinic phase

Assuming an exponential decrease of the volume of monoclinic fraction \( f_0 \) with depth \( D \), depth profiles were generated from diffraction data obtained with the GIXRD technique at selected fixed incidence angles. To begin with, the monoclinic fractions \( f_0 \) acquired experimentally were reported as a function of the X-ray penetration depth. They were subsequently fitted with the Laplace transform of the exponential function, to take into account the X-rays' penetration profile into the material. The monoclinic fraction at the surface \( f_0 \) and the depth of the transformed layer \( z \) were taken as variables. Finally, the depth profiles of the monoclinic phase were calculated using the \( f_0 \) and \( z \) fitted values. For a rationale of the method, see Gremillard et al. [39].

Statistical differences between \( f_0 \) and \( z \) values were evaluated by analysis of variance followed by Fisher's LSD multiple comparison test at 95% level of significance. Percentage values of \( f_0 \) were transformed prior to statistical analysis with arcsin(\( \frac{f_0}{100} \)).

2.4. Direct determination of the transformed depth by FIB-SEM technique

To gain direct access to the microstructural features of the transformed layer below the surface, Dual Focus Ion Beam (FIB) – Scanning Electron Microscopy (SEM) was applied to some samples before and after aging. FIB-SEM imaging was performed using a FIB-SEM workstation (NVision 40; Carl Zeiss Microscopy GmbH, Oberkochen, Germany) combining a SiNIT zeta FIB column (Seiko Instruments Inc. NanoTechnology, Japan) with a Gemini column.

In brief, the FIB uses a liquid metal ion source of Ga+ ions accelerated to 2–30 keV which are focused onto one spot of the surface to cut slices of material. SEM images are generated simultaneously with the electron beam. FIB-SEM is a powerful tool for producing sets of 2D images where the crystallographic orientation contrasts are apparent. In the present experiment, FIB-SEM was used to obtain images of the undamaged t-m transformation zone. Indeed traditional techniques require a mechanical sectioning and polishing of bulk samples for SEM inspection – a procedure which leads to extraneous t-m transformation due to the mechanical work on the slice.

2.5. Elastic modulus and hardness

Elastic modulus and hardness were assessed by nanindentation. An NHT nanoindenter (GSM Instruments, Peseux, Switzerland) was used. A load of up to 300 mN was applied at a constant strain rate of 0.05 s\(^{-1}\). The Berkovich diamond tip was calibrated using a fused silica standard provided by the manufacturer. Hardness (H) and E-moduli (E) were calculated from the unloading portion of the indentation curves using Oliver and Pharr's method [40]. The mechanical properties thus determined characterized the volume of material in the immediate vicinity of the indenter at the maximum penetration depth. Ten indentations were placed for each specimen before- and after an aging time of 100 h. To compute the E-moduli, Poisson's ratio was taken as 0.32 [41].

Data on E-moduli and hardness before- and after aging were evaluated by analysis of variance followed by Fisher's LSD multiple comparison test at 95% level of significance.

3. Results

3.1. Surface characterization of the 'as-received' specimens

Representative SEM views of the different specimens' surfaces are shown in Fig. 1. AS specimens (Fig. 1a) were characterized by a grainy, rough surface with humps and hollows. On C samples (Fig. 1b), large open porosities (ca.50 μm) were observed along with cracks. P samples (Fig. 1c) presented a rather smooth surface. R samples (Fig. 1d) were characterized by large parallel grooves, together with 1–2 μm debris. These were probably caused by chipping or fragmentation of the ceramic during the dry-polishing process.

The specimens' mean surface roughness \( R_a \) is tabulated in Table 1. The \( R_a \) of AS specimens was 1.5 ± 0.3 μm. Quite logically, the coarse castings substantially increased roughness whereas polishing produced smoother surfaces.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( R_a ) (μm)</th>
<th>( f_m ) (%)</th>
<th>( 2r_{TB} ) (μm)</th>
<th>( f_0 ) (%)</th>
<th>( z ) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>1.5 (0.3)</td>
<td>2.6 (1.6)</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>C</td>
<td>11.0 (2.0)</td>
<td>0 (0)</td>
<td>0</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>P</td>
<td>0.01 (0.00)</td>
<td>49 (2)</td>
<td>&lt;1</td>
<td>57 (1)</td>
<td>0.5 (0.1)</td>
</tr>
<tr>
<td>R</td>
<td>0.06 (0.01)</td>
<td>48 (1)</td>
<td>1</td>
<td>99 (1)</td>
<td>0.5 (0.1)</td>
</tr>
<tr>
<td>FA</td>
<td>–</td>
<td>0 (0)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>RA</td>
<td>–</td>
<td>0 (0)</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Only a minor amount (<3%) of monoclinic fraction was measured in the AS samples and no monoclinic phase was detected in C specimens.

In contrast, mechanical surface treatments resulted in notable t-m phase transformations (Table 1). The volume monoclinic fractions \( f_{\text{m}} \), as determined by GIXRD with a 2° fixed incidence angle, amounted to 49% and 48% for the P and R groups respectively. Moreover, the monoclinic grains were highly textured, as the ratio of the (1 1 1) to (1 1 1) was different from that inferred from powder diffraction (JCPDS No 70-2491), that is, in the order of 0.03-0.06 as compared to 0.68 from powder diffraction. Also worth noting, the t-m transformation was reversed by annealing at 1050°C.

Regarding the \( \theta-2\theta \) XRD patterns of the P and R specimens, a minor asymmetric broadening of the (1 1 1) tetragonal peak, but no intensity reversal of the (0 0 2) and (2 0 0) tetragonal peaks were observed (Fig. 2).

3.2 Hydrothermal degradation kinetics

Hydrothermal degradation in water steam at 134 °C resulted in a significant t-m phase transformation (Fig. 3). For all groups, the monoclinic content increased with time, reaching a maximum for aging times beyond 40 h. The data could be fitted with Mehl-Avrani-Johnson’s equation, that is, by plotting \( \ln(\ln((f_{\text{max}} - f_{\text{min}})/(f_{\text{max}} - f))) \) as a function of \( \ln(t) \). Low \( n \) values ranging from 0.6 to 1 were obtained. Parameter \( b \) varied from 0.07 to 0.37 (Table 2). The time \( \langle t \rangle \) required for a given degree of transformation \( P = (f - f_{\text{min}})/(f_{\text{max}} - f) \) to proceed...

Fig. 1 – SEM images of the (a) ‘as-sintered’ (AS), (b) coated (C), (c) polished (P) and (d) roughened (R) specimens showing the different surface morphologies (1600×).

Fig. 2 – \( \theta-2\theta \) X-ray diffraction patterns obtained for the AS, P, R and PA samples before hydrothermal degradation.
Table 2 – Characterization of the specimens after hydrothermal degradation. Parameters of the MAJ equation (\(a\) and \(b\)) describing the kinetics of hydrothermal degradation. Time required for 90% of the maximum transformation \(f_{0.9}\) to proceed. Depth of the transformed layer \(z_{f_{0.9}}\) obtained from FIB excavations at the surface. Volume monoclinic fraction at the surface \(f_{s}\) and depth of the transformed layer \(z\) calculated from GIXRD data after prolonged aging (100 h).

<table>
<thead>
<tr>
<th></th>
<th>(n)</th>
<th>(b)</th>
<th>(t_{0.9}) (h)</th>
<th>(z_{f_{0.9}}) ((\mu m))</th>
<th>(f_{s}) (%)</th>
<th>(z) ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS</td>
<td>0.7</td>
<td>0.08</td>
<td>40</td>
<td>14</td>
<td>87 (1) (^a)</td>
<td>15 (2) (^c)</td>
</tr>
<tr>
<td>C</td>
<td>0.9</td>
<td>0.07</td>
<td>36</td>
<td>13</td>
<td>88 (1) (^a)</td>
<td>10 (1) (^b)</td>
</tr>
<tr>
<td>P</td>
<td>1.0</td>
<td>0.10</td>
<td>22</td>
<td>11</td>
<td>90 (2) (^b)</td>
<td>10 (1) (^b)</td>
</tr>
<tr>
<td>R</td>
<td>0.6</td>
<td>0.16</td>
<td>23</td>
<td>11</td>
<td>95 (3) (^c)</td>
<td>8 (1) (^*)</td>
</tr>
<tr>
<td>PA</td>
<td>0.5</td>
<td>0.37</td>
<td>15</td>
<td>–</td>
<td>89 (1) (^b)</td>
<td>11 (1) (^b)</td>
</tr>
<tr>
<td>RA</td>
<td>0.6</td>
<td>0.20</td>
<td>22</td>
<td>–</td>
<td>93 (1) (^b)</td>
<td>9 (1) (^*)</td>
</tr>
</tbody>
</table>

Values marked with the same upper script letter denote no significant statistical differences (\(p < 0.05\)).

Near the surface, a few isolated transformed grains were observed before aging for the AS specimen (insert in Fig. 4a). In contrast, the R sample displayed a thin transformed layer of about 1 \(\mu m\) in thickness (Fig. 4b and Table 1). The transformed grains displayed the twinning features typical of the \(t\)-\(m\) transformation phase. Isolated horizontal cracks were visible near the surface on the R sample (see insert in Fig. 4b). Depth profiles of the volume monoclinic fraction \(f_{m}\) were also calculated from the experimental monoclinic fractions \(f_{s}\), assuming an exponential decrease with depth (Fig. 4c and Table 1).

After 100 h of aging, the transformed layer with twinned grains had growth in both specimens (Fig. 5a and b). The depth of transformation was 14 and 11 \(\mu m\) for the AS and R samples respectively. It is worth noting that the depths of the transformed layers as assessed from the BSE-SEM images of the FIB cross-sections are consistent with the \(z\) values calculated from the GIXRD data (Fig. 5c and d and Table 2). In addition, phase transformation-induced parallel cracks were clearly visible at several grain boundaries (see inserts in Fig. 5). The transformation depths of C and P samples are also given in Table 2 (images not shown).

A strong texture (surface favored orientation) of the monoclinic phase was observed on the diffraction patterns of the AS, P and R specimens. In contrast, aging of C specimens resulted in a less textured monoclinic phase, as indicated by an increased intensity ratio of the \((1 1 1)_{m}\) vs. the \((-1 1 1)_{m}\) peaks, specifically 0.37 instead of 0.07.

3.3. Depth and features of the transformed layer

BSE-SEM views of the FIB cross-sections are presented in Figs. 4 and 5 for AS and R samples before- and after aging. The BSE mode was used to evidence the contrasts in crystallographic orientation of the grains.

3.4. Mechanical properties of the surface

Typical nanoindentation load-displacement curves of a polished surface obtained before- and after hydrothermal degradation. The hardness \(H\) and modulus of elasticity \(E\) of a material can be calculated using Eq. (2). Values of \(t_{0.9}\) are also given in Table 2.

\[
\tau_{r} = \frac{1}{b} \ln \frac{1}{1 - \tau_{r}^{1/m}}
\]

\(2\)

Table 3 – Modulus of elasticity \(E\) and hardness \(H\) obtained before and after prolonged hydrothermal degradation (100 h) from the unloading part of the nanoindentation load-displacement curves.

<table>
<thead>
<tr>
<th></th>
<th>AS</th>
<th>P</th>
<th>R</th>
<th>PA</th>
<th>RA</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E) (GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before-</td>
<td>263 (51) (^b)</td>
<td>234 (20) (^a)</td>
<td>257 (37) (^b)</td>
<td>226 (7) (^a)</td>
<td>225 (35) (^a)</td>
</tr>
<tr>
<td>After 100 h aging</td>
<td>125 (31) (^b)</td>
<td>162 (11) (^b)</td>
<td>103 (16) (^b)</td>
<td>170 (3) (^b)</td>
<td>134 (15) (^b)</td>
</tr>
<tr>
<td>(H) (GPa)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Before-</td>
<td>15 (4) (^b)</td>
<td>16 (1) (^b)</td>
<td>14 (2) (^b)</td>
<td>17 (1) (^b)</td>
<td>13 (1) (^b)</td>
</tr>
<tr>
<td>After 100 h aging</td>
<td>12 (3) (^b)</td>
<td>11 (1) (^b)</td>
<td>11 (1) (^b)</td>
<td>12 (2) (^b)</td>
<td>10 (2) (^b)</td>
</tr>
</tbody>
</table>

\(^a\) Statistically significant different values versus the control group (before aging).

Within the rows, values marked with the same upper script letter denote no significant statistical differences (\(p < 0.05\)).
Degradation are displayed in Fig. 6. Aging has an obvious effect on the load-penetration response as for the same load a greater penetration was observed after hydrothermal aging. The character of the curves was similar for the P and R specimens. The path was smooth and no discontinuities were observed. In contrast, in many instances, an "elbow" appeared in the unloading path of AS specimens—a discontinuity which may be associated with load-induced \( t-m \) phase transformation \([42]\) (see arrow in Fig. 6b). As to the coated samples, they presented large "pop-in" discontinuities in the loading portion of the curves. These disruptions were still observed after the maximum force applied was reduced to 20 mN (see arrows in Fig. 6c). It is likely that these "pop-in" effects were caused by subsurface cracks which were either present or had formed under loading \([43]\). In view of this behavior, nanindentation was considered inappropriate to determine the mechanical properties of the coating.

The moduli of elasticity and hardness are listed in Table 3. These values are obtained from the unloading part of the load-penetration curves and characterize the volume of the material in the immediate vicinity of the indenter at the maximum penetration depth (i.e. a half-sphere with an approximate radius of 30 \( \mu \)m). Slight differences were observed between the groups before and after aging. Independent of the original mechanical or thermal treatment, hydrothermal degradation led to a large decrease of both E-modulus and hardness.

4. Discussion

The surface of dental implants must be rough for the implant to integrate into osseous tissue. In the present work, 3Y-TZP ceramic specimens with different surface textures were exposed to steam pressure at 134 °C with the aim of investigating the effect of surface modifications on the \( t-m \) phase transformation of the ceramic.

In this study, a high initial content of monoclinic phase was found in all dry polished and roughened specimens, probably due to the temperature rise during the dry process. Dry grinding, as an alternate to wet grinding, might still be used on zirconia in order to obtain smoother surfaces devoid of large chippings \([44]\). The XRD pattern showed an asymmetrical broadening of the \((111)\) tetragonal peak. This alteration was typically associated with grinding and grit blasting and has been related either to (i) tetragonal lattice distortions \([45]\) or (ii) the appearance of a rhombohedral- \((46-48)\) or (iii) a cubic \([21]\) phase. No peak intensity reversals ((002) and (200)) were observed, thereby indicating that ferroelastic domain switching \([49]\) — another deformation mechanism associated with mechanical machining — did not occur in the present instance.

4.1. Hydrothermal degradation

Hydrothermal \( t-m \) phase transformation occurs by "nucleation and growth" (N-G) — a mechanism that is controlled by the diffusion of water species through the zirconia lattice \([50,51]\). The water species fill oxygen vacancies and trigger the \( t-m \) transformation \([26,52-54]\). Nucleation preferentially occurs at the grain junctions with the formation of a first martensitic
variant. The transformation process then propagates through the grain and into its neighbors due to ever increasing tensile stresses at the grain boundaries [24].

The N-G kinetics of the t-m transformation is commonly described by Mehl-Avrami and Johnson's (MAJ) equation. The $n$ exponent is of particular interest, as in this particular case it characterizes the ratios of nucleation to growth rate [55]. In the present study, the $n$ values for the different groups were low, thereby indicating that nucleation was the predominant step of the t-m transformation.

From GIXRD assessments, it also appeared that the t-m transformation was not complete, most likely due to the presence of some cubic phase in the native 3Y-TZP ceramic [56].

As the t-m transformation rate depends both on $n$ and $b$ parameters, the time $t_{0.9}$ required for $90\%$ of the maximum transformation to proceed, was used to assess the effect of the surface treatment on the resistance to hydrothermal degradation. The process was faster in the polished, roughened and annealed samples ($t_{0.9}$ between 15 and 23 h) than in the 'as-sintered' and coated specimens ($t_{0.9}$ equal to 40 and 36 h respectively). More than likely, the inferior resistance of mechanically treated specimens to hydrothermal degradation is due to the large amount of monoclinic phase initially present at the surface and to residual tensile stresses around scratches acting as nucleation sites [34]. These specimens were annealed at 1050°C to suppress the initial monoclinic phase. Unexpected, the t-m transformation kinetics was affected by the annealing process with an increase of parameter $b$ and consequently of $t_{0.9}$. This effect is more noticeable on the polished specimens. A tentative explanation follows. Polishing or grinding a specimen creates zones of compressive stresses at the surface [57]. In these zones the t-m transformation is impeded. Conversely, the microstructural defects produced during mechanical treatments act as nucleation sites and thus favor the transformation. The aging rate is thus controlled by the balance between the uplift brought about by the increase in nucleation sites and the depression due to the residual compressive stresses [32,34,58]. After annealing, most residual stresses are released but the nucleation sites remain, thus resulting in the annealed specimens' lower resistance to hydrothermal degradation.

Worth noting, the monoclinic fraction values were determined in a limited volume corresponding to the penetration depth of the X-ray, that is, 1.2 μm in the conditions used in the present study. However, it has previously been shown that the transformed layer spreads deeper into the bulk of the specimens [59,60]. After prolonged aging (100 h), the progression of the t-m transformed phase into the depth of the sample was greater for the 'as-sintered' specimens. The lower propagation of the transformed layer of the roughened and polished samples was probably related to the initial amount of monoclinic phase emerging after mechanical treatments, which