Degradation of dental ZrO₂-based materials after hydrothermal fatigue. Part I: XRD, XRF, and FESEM analyses

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The aim was to investigate the effect of simulated low-temperature degradation (s-LTD) and hydrothermal fatigue on the degradation of three ZrO₂-based dental materials. Lava, IPS, and NanoZr discs were randomly assigned to (1) Control-Storage in distilled water at 37°C; (2) Aging at 134°C for 5 h (s-LTD); (3) Thermocycling in saliva for 30,000 cycles (TF). XRD revealed that ZrO₂ *m* phase was identified in all groups but TF increased the *m* phase only for Lava. Under the FESEM, Lava showed no alterations under s-LTD, but displayed corrosion areas up to 60 µm wide after TF. We conclude that TF accelerated the degradation of Lava through an increase in the *m* phase and grain pull-out from the material surface.

Keywords: Zirconia, Electron microscopy, Thermal fatigue, Low-temperature degradation (LTD)

INTRODUCTION

The discovery of a transformation toughening phenomenon in ZrO₂ (zirconia) has led to a new class of strong, tough, relatively flaw-tolerant ceramics^{1,2}. Pure zirconia is polymorphic at ambient pressure, exhibiting cubic structure at high temperatures (>2,370°C), tetragonal structure at intermediate temperatures (1,200°C–2,370°C), and monoclinic structure at low temperatures (<950°C)³.

The high strength of zirconia is derived from a stress-induced transformation from the metastable tetragonal form to the stable monoclinic form (*t*→*m*)^{2,3}. The stress-induced transformation greatly enhances the mechanical properties of transformation-toughened ZrO₂ ceramics, where the crack resistance increases during the course of cracking propagation³. This *t*→*m* phase transformation can occur in the vicinity of a propagating crack¹⁻⁴, causing an increase in volume, which induces compressive stresses, thereby closing the crack tip and preventing further crack propagation⁴. The phase transformation can also be induced by environmental stresses, leading to accelerated ageing of the material⁵. Alloying pure zirconia with stabilizing oxides such as Y₂O₃ (yttria) or CeO₂ (ceria), allows the retention of the tetragonal structure at room temperature⁶, lowering the *t*→*m* transformation temperature and stabilizing the *t* phase^{6,7}. The amount of stabilizer has to be carefully controlled because it strongly influences the microstructure and mechanical properties of the final material³.

Tetragonal zirconia stabilized with 3 mol% yttria (or

3Y-TZP) is the material currently used for biomedical applications, including dentistry. In spite of being the golden standard in terms of strength and toughness⁶, 3Y-TZP may lack long-term stability, which has been a major issue for medical use and has led to the replacement of several zirconia femoral heads in orthopedic patients⁸. Low-temperature degradation (LTD) has been associated with several 3Y-TZP-based biomaterials⁹, but is difficult to simulate in the laboratory. Ageing occurs experimentally in zirconia, mostly in humid atmosphere or in water⁷. An accelerated ageing test using steam and pressure has been developed to simulate LTD¹⁰. No ceramics studied, including Y-TZP, have been found to be chemically inert in water^{11,12}. More recently, when 3Y-TZP disks were implanted in a denture and worn for 24 h/day for 1 year, the increase in the percentage of monoclinic phase was similar to that of zirconia aged in an autoclave at 134°C for 6 h¹³.

To overcome the potential degradation of 3Y-TZP, other zirconia-based materials have been recently developed. One of these new materials, NanoZr (Matsushita Electric Works, Shinbashi, Tokyo, Japan), uses ceria as the stabilizer (Ce-TZP) instead of yttria. Additionally, NanoZr contains a higher percentage of Al₂O₃ (alumina) that replaces part of the zirconia, as compared to the composition of 3Y-TZP materials. Initial tests with Ce-TZP/Al₂O₃ nanocomposite were very promising, however, other tests did not corroborate the initial data¹⁴⁻¹⁶.

The aim of this project was to study the effect of s-LTD (simulated LTD) and thermal fatigue in artificial saliva on the chemical and structural stability of three zirconia-based dental materials. The null hypothesis was that s-LTD and thermal fatigue in artificial saliva

Table 1 Materials, experimental conditions, and V_m (monoclinic volume fraction²⁰⁾)

Material and batch numbers	Experimental conditions	V_m^{20} (%)
IPS e.maxZirCAD (IPS)	No treatment (control)	0.0
Lot: MO0/B40L–M37200	s-LTD (134°C under 2 bar for 5 h)	4.4
	Thermal fatigue for 30,000 thermal cycles in artificial saliva	2.4
Lava	No treatment (control)	1.5
Lot: 399620 and 392928	s-LTD (134°C under 2 bar for 5 h)	2.3
	Thermal fatigue for 30,000 thermal cycles in artificial saliva	6.4
NanoZr	No treatment (control)	*
Lot: DZFO/B40L–ZC147	s-LTD (134°C under 2 bar for 5 h)	*
	Thermal fatigue for 30,000 thermal cycles in artificial saliva	*

* For NanoZr, the monoclinic volume fraction (V_m) is not considered reliable due to the presence of high concentrations of alumina of unknown vol%.

do not trigger degradation of zirconia-based materials, as measured by the $t \rightarrow m$ transformation and alterations in the material ultra-structure.

MATERIALS AND METHODS

A total of 36 discs ($d=13.0$ mm; $h=1.2 \pm 0.2$ mm, as per ISO 6872¹⁷⁾) were obtained from three sintered zirconia-based materials: (1) IPS e.maxZirCAD (Ivoclar Vivadent, Schaan, Principality of Liechtenstein), a 3Y-TZP material (IPS); (2) Lava (3M ESPE, St. Paul, MN, USA), a 3Y-TZP material; (3) NanoZr (Matsushita Electric Works), a Ce-ZrO₂/Al₂O₃ material. The discs were polished under water for 15 min at 120 rpm, on a LaboPol-4 (Struers, Ballerup, Denmark), using 30 μ m and 15 μ m CarbiMet 2 paper (Buheler Ltd., Lake Bluff, IL, USA) following the ISO 6872 specifications¹⁷⁾. Twelve discs from each material were randomly assigned to one of three groups (Table 1): (1) Control: Discs were left in distilled water at 37°C for 5 h; (2) s-LTD: Discs were aged at 134°C under 2 bar for 5 h¹⁰⁾ in a SanoClavLas-3-13-MCS-J (SanoClav, Bad Überkingen-Hausen, Germany); (3) Thermal fatigue: Discs were fatigued in artificial saliva¹⁸⁾ for 30,000 thermal cycles between baths held at 5 and 55°C, with a dwell time of 30 s in a AraLab REFRI 200E (AraLab, Rio de Mouro, Portugal). One year of clinical use corresponds approximately to 10,000 thermal cycles¹⁹⁾. Disks were cleaned in a 75% ethanol ultra-sonic bath for 15 min (Elma Hans Schmidbauer GmbH & Co, Singen, Germany) to remove residual saliva.

XRD and XRF

Six specimens for each material (two specimens per experimental condition) were analyzed with XRD (X-ray diffraction) and XRF (X-ray Fluorescence). The XRD patterns were recorded on a Rigaku Dmax III-C 3 kW diffractometer (Rigaku Corporation, Tokyo, Japan), using Cu K α radiation at 40 kV and 30 mA settings in the 2θ range from 20° to 65°, an acquisition time of 1 s and 2θ increment of 0.04°. The areas of the peaks corresponding to the monoclinic phase ((-1 1 1), at

$2\theta=28.2^\circ$ and (1 1 1), at $2\theta=31.5^\circ$) and to the tetragonal phase ((1 0 1), at $2\theta=30.2^\circ$) were computed using a suitable software (EVA, Bruker AXS GmbH, Karlsruhe, Germany). The monoclinic volume fraction, V_m , was then calculated²⁰⁾. The crystalline phases were identified by comparing the peak positions and intensities with those listed in the software standard files (ICDD, Newtown Square, PA, USA). For XRF elemental analysis, a PANalytical XRF-WDS 4 kW AXIOS (PANalytical B.V., Almelo, The Netherlands) sequential spectrometer (Rh X-ray tube) under He flow was used. Standardless semi-quantitative analysis was performed with the SuperQ IQ+ software package (PANalytical B.V., Almelo, The Netherlands).

FESEM

Six specimens for each material (two specimens per experimental condition) were processed for Field-Emission Scanning Electron Microscopy (FESEM). Specimens were ultra-sonicated for 5 min in 95% ethanol, thoroughly dried, mounted on aluminum stubs (Ted Pella, Inc., Redding, CA, USA) with graphite tape and silver paint, and sputter coated with Au-Pd by means of an E-5100 sputter-coater (Polaron Ltd., Denton Vacuum, Moorestown, NJ, USA) at 20 mA for 90 s. Observations were carried out in Hitachi S4700 Field-Emission Scanning Electron Microscope (Hitachi High Technologies America, Inc, Pleasanton, CA, USA) at 5 kV, WD=13.0 mm, and standard magnifications from of $\times 1,000$ – $\times 35,000$.

RESULTS

XRD and XRF

The XRD peak ((-1 1 1) appearing at around 28.2° (2θ) is specific of the zirconia monoclinic phase (m phase). It was present in all specimens regardless of the treatment (Fig. 1). For each material, the intensity of the peak characteristic of the m phase increased from the control specimens to the s-LTD specimens, as observed in the XRD patterns in 27.5 – 30.0° (2θ) range shown in Figs. 1 and 2.

Fig. 1 XRD patterns for control, LTD, and thermocycled specimens.

Table 2 Chemical analysis (wt%) of the different specimens in terms of oxides as measured by XRF

Specimen	ZrO ₂	Y ₂ O ₃	Al ₂ O ₃	HfO ₂	SO ₃	CeO ₂	P ₂ O ₅	CaO	K ₂ O
IPS–Control	94	4	0.4	0.9	0.2	n.d.	n.d.	n.d.	n.d.
IPS–s-LTD	94	4	0.4	0.7	0.2	n.d.	n.d.	n.d.	n.d.
IPS–Thermocycled in artificial saliva	74	4	0.3	0.8	n.d.	n.d.	9	7	2
Lava–Control	94	5	0.09–0.3	0.8–0.9	0.0–0.2	n.d.	n.d.	n.d.	n.d.
Lava–s-LTD	94	4–5	0.05–0.3	0.8–0.9	0.0–0.1	n.d.	n.d.	n.d.	n.d.
Lava–Thermocycled in artificial saliva	77	4	0.2	0.7	n.d.	n.d.	7	6	1
NanoZr–Control	65	n.d.	22	0.6	0.0–0.1	13	n.d.	n.d.	n.d.
NanoZr–s-LTD	64	n.d.	23	0.6–0.7	0.0–0.1	13–14	n.d.	n.d.	n.d.
NanoZr–Thermocycled in artificial saliva	53	n.d.	12	0.5	n.d.	11	11	7	2

Alumina was detected by XRD in NanoZr specimens and quantified in a range from 12–23 wt% by XRF analysis (Table 2). Although alumina was not identified by XRD in IPS or in Lava specimens, the respective XRF analysis detected alumina as a trace component (Table 2). XRF analysis measured 11–13 wt% ceria in NanoZr specimens. However, XRD did not detect cerium oxide as a crystalline phase in NanoZr.

For the specimens subjected to s-LTD, the calculation

of the monoclinic volume fraction (V_m , Table 1) depicted an increase for IPS from 0.0% (control) to 4.4%, whereas the V_m for Lava increased from 1.5% to 2.3%. The elemental composition after s-LTD, as measured by XRF, (Table 2) remained stable for the three materials.

For specimens subjected to thermal fatigue in artificial saliva, XRD results (Fig. 3) showed that the intensity of the peak corresponding to the m phase was higher in Lava specimens than in either IPS or NanoZr

Fig. 2 XRD patterns in the 2θ range 20° – 65° for each material: (A) Lava specimens; (B) IPS specimens; and (C) NanoZr specimens. There is an increase in the $(-1\ 1\ 1)$ peak (close to 28.2°) of the monoclinic phase. Graphic C shows that the intensity peaks for all three experimental conditions are very similar. In the range corresponding to the monoclinic phase, the peaks are also very similar. Control: red line; LTD: green line; Thermocycled: blue line.

specimens, suggesting that such treatment resulted in an increased m phase for Lava specimens. Calculations of the V_m indicated an increase from 1.5% (control) to 6.4% for Lava specimens (Table 1).

The XRF analysis of specimens subjected to thermal fatigue in artificial saliva revealed a reduction of the overall percentage of ZrO₂ on the specimens' surface (Table 2). Additionally, the XRF analysis of thermocycled

specimens depicted a surface accumulation of P₂O₅, CaO, and K₂O.

FESEM

The control specimens are shown in micrographs of Fig. 4. s-LTD (Fig. 5) did not cause any apparent surface morphological changes for any of the tested materials. Thermal fatigue in artificial saliva resulted in corrosion

Fig. 3 XRD patterns for specimens thermocycled in artificial saliva, showing the peaks corresponding to the monoclinic phase.

areas (up to 60 μm wide) and grain pullout in Lava specimens (Fig. 6A) while IPS resulted in very sporadic narrow areas of corrosion, 3–6 μm wide (Fig. 6B). NanoZr specimens did not show signs of surface corrosion with thermal fatigue (Fig. 6C).

DISCUSSION

Zirconia is unique among ceramic oxides as a result of its excellent properties^{21,22} such as dimensional and chemical stability, toughness, and elastic modulus in the same magnitude of that of stainless steel^{6,23}. These properties make the use of zirconia feasible as a ceramic biomaterial²³, as it can reach fracture strengths above 1 GPa and fracture toughness of 6–10 $\text{MPa}\cdot\text{m}^{1/2}$ ²⁴. Although standard Ce-TZP exhibits the largest crack resistance of oxide ceramics, it results in moderate mechanical strength and hardness compared to 3Y-TZP⁴.

Ceramic corrosion in aqueous environments occurs mainly through ion-exchange processes¹¹. The phase transformation is controlled by the chemical reaction between water and Zr-O-Zr bonds on the surface. On the basis of the corrosion mechanism, the reaction between water and Zr-O-Zr suggests that Zr-OH bonds are formed in the lattice of zirconia and it starts the phase transformation⁴.

Cerium found by XRF in the chemical composition of NanoZr specimens (11–13 wt%, Table 2) was not present

in the mineralogical composition of such specimens, as a crystalline phase containing cerium was not identified by XRD. This apparent paradox may be a result of the NanoZr being made of nanoparticles. Another possible explanation is that cerium is in solid solution, with Ce^{4+} ions substituting Zr^{4+} ions in the lattice of zirconia, thus not being detectable. Alumina was detected by XRD in NanoZr specimens, but not in any of the 3Y-TZP materials, which may have been a result of the very low concentration of aluminum in IPS and Lava, as shown with XRF. The reduction in the overall percentage of zirconia on the specimen surface after thermal fatigue may have been a result of both grain pull-out and adsorption of phosphates and calcium from artificial saliva. In contact with saliva or other organic fluids, biomaterials are instantly covered with organic films, the composition of which influences surface corrosion processes¹¹.

According to the XRD results, an increase in the intensity of the $(-1\ 1\ 1)$ peak was observed for Lava specimens after thermal fatigue (Fig. 2), which is likely associated to the increase in the *m* phase content in such specimens. The calculation of the respective monoclinic fraction volume (Table 1) resulted in $V_m=6.4\%$. For IPS specimens subjected to s-LTD, the respective V_m was calculated as 4.4%. Although both numbers represent an increase compared to the respective baseline V_m control (Table 1), it is known that XRD is not very precise for monoclinic contents lower than 5%⁶. Additionally, there was some background noise when calculating the peak areas, which may have caused lower peak definition. Therefore, while V_m values below 5% should be interpreted carefully, the $V_m=6.4\%$ calculated for Lava after thermal fatigue falls into a range that is relevant and deserves further consideration.

The difference in the percentage of monoclinic fraction volume between Lava (6.4%) and IPS (2.4%) subjected to 30,000 thermal cycles in artificial saliva raises the issue of possible intrinsic structural differences in two identical commercial 3Y-TZP-based materials. This discrepancy associated with thermal fatigue behavior has not been reported in the literature. Apparently, the main difference between the two 3Y-TZP based materials used in this project (IPS and Lava) was the sintering schedule selected for processing these materials. According to the respective manufacturers' instructions, Lava recommended sintering temperature is 1,650°C in a single program of 4 h and 40 min, while IPS sintering temperature is 1,500°C in a program of 8 h divided in three cycles: (1) 90 min; (2) 2 h 45 min; (3) 3 h 30 min. This difference in sintering temperatures may be responsible for the lower sensitivity to ageing demonstrated by the IPS material compared to Lava. In fact, Rothbrust *et al.* found that the ageing process was more pronounced when 3Y-TZP materials were sintered at temperatures above 1,500°C²⁵. The optimal sintering process should be performed between 1,400°C and 1,500°C to allow the material to reach satisfactory mechanical characteristics²⁶. Also, the difference in sintering temperature may be responsible for different

Fig. 4 Original magnification: $\times 15,000$; A: FESEM micrograph of Lava, control group; B: FESEM micrograph of IPS, control group; C: FESEM micrograph of NanoZr, control group.

levels of yttrium and impurity segregation at the grain boundaries in Lava and IPS specimens. Hughes and Badwal²⁷ reported the segregation of yttrium and impurity phases at the grain boundaries of Y-TZP and they verified that the segregation layer increased with increasing annealing temperature.

Adding Ce to Y-TZP, as in NanoZr, increases the grain size^{28,29}, but improves aging resistance^{29,30}. An experimental material with similar composition has resulted in excellent aging resistance compared to biomedical grade yttria-stabilized zirconia¹⁴. In fact, the monoclinic phase remained relatively constant in NanoZr specimens (Fig. 1) regardless of the experimental condition. From Fig. 1 it is observed that for NanoZr specimens the intensity peak of the monoclinic phase is shifted to the left comparatively to Lava and IPS specimens. This is clearly shown in Fig. 3, where only the peaks for specimens that were submitted to thermal fatigue in artificial saliva are presented. The non-

coincidence of the peaks may be attributed to the existence of small-sized phases in NanoZr specimens³¹.

In Lava and IPS materials, only a monoclinic-tetragonal ZrO_2 system was present, and the calculation of the monoclinic volume fraction (V_m) was possible according to the method of Toraya *et al.*²⁰. However, the monoclinic volume fraction (or V_m) for NanoZr is not reported in Table 1 because the respective calculation is not reliable, due to the presence of high concentrations of alumina compared to the other two materials, and the lack of information of the exact vol% of alumina in NanoZr.

No morphological changes were found with NanoZr under the FESEM. In 3Y-TZP materials, the presence of numerous vacancies due to the trivalent character of Y_2O_3 makes the diffusion rate of species from the water higher than in CeO_2 -doped zirconia, such as NanoZr⁶. The areas of corrosion and grain pullout found in Lava specimens under the FESEM are very similar to

Fig. 5 Original magnification: $\times 15,000$. A: FESEM micrograph of Lava, LTD group; B: FESEM micrograph of IPS, LTD group; C: FESEM micrograph of NanoZr, LTD group.

morphological features that have been described in the literature as areas of increased monoclinic transformation^{6,32}. Transformation can be triggered by the action of water or by low temperature treatments³³. During $t \rightarrow m$ transformation, when a tetragonal grain transforms, the volume increase accompanying the phase transformation leads to stresses concentration in the surrounding zones and microcracking³². The stress rate formed could initiate the transformation in the neighboring grains, while microcracking allows entry of water with grain pullout³⁴. This transformation may lead to the formation of surface flaws that could be deleterious to *in vivo* performance of zirconia ceramics³⁴.

The discs of all specimens were polished following standard specifications¹⁷. It has been reported³⁵ that the polishing treatment has the potential to modify the sensitivity of zirconia to low temperature degradation and that the current ISO standards are not able to take these effects into account. According to the literature³⁵,

the scratches induced in the polishing stage, as observed in Lava specimens, may have acted as nucleation sites and, therefore, may have influenced the sensitivity of zirconia to ageing. However, not all the scratches would lead to $t \rightarrow m$ transformation in their surrounding areas, as only the deepest scratches have the most deleterious effect on transformation. Only the grains along the scratch edges, where the tensile stresses are located, may undergo transformation into m -phase³⁶.

Zirconia-based materials used for orthopedic surgery have been reported to undergo LTD in humid environments. The clinical failure events of 3Y-TZP femoral heads in 2000–2002 opened a controversial issue on the future of zirconia as a biomaterial^{37–39}. The femoral heads removed from patients showed signs of degradation with a very high content of monoclinic phase³⁹. The ISO standard s-LTD method, ISO 13356¹⁰, was developed as a result of the failures of zirconia hip joint heads in the early 2000's⁶. Classical sterilization for zirconia-based

Fig. 6 Original magnification: $\times 15,000$. A: FESEM micrograph of Lava, thermocycled group; B: FESEM micrograph of IPS, thermocycled group; C: FESEM micrograph of NanoZr, thermocycled group.

hip prostheses prior to orthopedic surgery has been carried out at 134°C in steam. Most of the s-LTD experiments involving biomedical grade zirconia materials usually rely on a similar aging method. Deville *et al.*³⁵⁾ estimated that ageing of zirconia for 20 min at 140°C under 3 bar pressure corresponded roughly to 1 year *in vivo*. This s-LTD method may be clinically relevant in Orthopedic Surgery, however zirconia is not usually sterilized in an autoclave prior to the fabrication of dental restorations. Thermal fatigue for 30,000 cycles is roughly equivalent to 3 years of clinical thermal cycling in the mouth¹⁹⁾. Therefore, thermal fatigue may be more clinically relevant for dental zirconia than s-LTD carried out in an autoclave. In fact, and in spite of the early reports of failures in orthopedic surgery, zirconia has been used in dentistry for a few years without any report of catastrophic failures of the zirconia

copings. The veneering feldspathic porcelain used in dental crowns, but not in other biomedical applications, might play a kind of protective role for the zirconia coping.

Several clinical studies have reported an incidence of chipping of the veneering porcelain as high as 10–15% at 3 years^{40,41)}. This failure has been attributed to a mismatch between the coefficient of thermal expansion of the 3Y-TZP material and that of the feldspathic porcelain used to veneer the coping. The present study did not take into consideration the veneering porcelain. A study evaluated the fracture resistance of 3Y-TZP bridge frameworks after mechanical fatigue, heat treatment similar to that used during veneering of the zirconia, or after veneering⁴²⁾. Veneering usually has to be carried out at a relatively high temperature (750–900°C), being the zirconia frameworks exposed to

moisture. The firing process is repeated two to five times⁴²⁾. Heat-treatment and veneering reduced fracture resistance of zirconia copings compared with those that were only subjected to cyclic loading⁴²⁾. These results suggested that multiple firings may induce a $t \rightarrow m$ transformation and affect the resistance of the framework to fracture and the adhesion of the veneering porcelain to the zirconia coping. However, the influence of the veneering porcelain firing cycles in the overall resistance of zirconia to LTD has not been documented.

As thermal fatigue in artificial saliva caused degradation (increase in the percentage of m phase and grain pull-out from the surface) of one of the 3Y-TZP materials in the present study, we have to reject the null hypothesis. In spite of threshold of 20% of monoclinic fraction volume that has been set as acceptable for aged specimens¹⁰⁾, the findings obtained in our study, that there is an increase of monoclinic phase and areas of corrosion in one of the 3Y-TZP materials after 30,000 thermal fatigue cycles, open a venue for future research on this topic. We hypothesize that the clinical failures associated with chipping of the veneering ceramic may be also related to the degradation of 3Y-TZP in the mouth. Consequently, future studies will include:

1. Testing the influence of firing the veneering porcelain on the resistance to s-LTD of the zirconia coping;
2. Analysis of the effect of fluoride in artificial saliva on the degradation of zirconia-based materials.

CONCLUSIONS

Within the limitations of this *in vitro* study, we conclude that thermal fatigue in artificial saliva for 30,000 cycles accelerated the degradation of Lava through an increase in the m phase and grain pull-out from the material surface.

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