

Nanoscale physico-mechanical properties of an aging resistant ZTA composite

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ABSTRACT

Objective: To characterize the effects of aging on the nanomechanical properties and 3D surface topographical parameters of an experimental Zirconia Toughened Alumina (ZTA) composite compared to its respective individual counterpart materials.

Methods: Disk-shaped specimens comprised of three material groups were processed: 1) ZTA 70/30 (70% alumina reinforced with 30% second-generation 3Y-TZP); 2) Zpex (Second-generation 3Y-TZP), and; 3) Al₂O₃ (High purity Alumina) (n = 10/material, 12 × 1 mm). After synthesis, ceramic powders were pressed, the green-body samples were sintered and polished. Nanoindentation testing was performed to record elastic modulus (E) and hardness (H). Interferometry was utilized to assess 3D surface roughness parameters (S_a, S_q), while X-ray diffraction (XRD) and scanning electron microscope (SEM) assessed the crystalline content and microstructure. All tests were performed before and after simulated aging (134°C, 2.2 bar, 20 h). Statistical analyses were performed using linear mixed-model and least square difference pos-hoc tests (α = 5%).

Results: XRD spectra indicated increase of monoclinic peaks for Zpex (~18%) relative to ZTA 70/30 (~2.5%) after aging. Additionally, aging did not affect the surface roughness parameters of ZTA 70/30 and Al₂O₃, although a significant increase in S_a was recorded for Zpex following aging (~90 nm) (p < 0.001). Al₂O₃ yielded the highest H and E values (H:21 GPa, E: 254 GPa), followed by ZTA 70/30 (H: 13 GPa, E: 214 GPa) and Zpex (H:11 GPa, E: 167 GPa), all significantly different (p < 0.03).

Conclusion: ZTA 70/30 and Al₂O₃ presented high hydrothermal stability with respect to all evaluated variables, where artificial aging significantly increased the monoclinic content and surface roughness of Zpex.

1. Introduction

Yttrium-stabilized tetragonal zirconia polycrystals (3Y-TZP) has been introduced as a suitable alternative for esthetic dental restorations

due to its favorable combination of optical and mechanical properties relative to metal ceramics (Denry and Kelly, 2008). Zirconia's polymorphism yields this polycrystalline ceramic unique mechanical properties, such as high flexural strength (~1000 MPa) and fracture

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toughness (5–9 MPa·m^{1/2}) (Denry and Kelly, 2008; Garvie et al., 1975; Guess et al., 2011). Zirconia occurs naturally in three distinct temperature-dependent crystalline structures: monoclinic (*m*) stable at room temperature up to 1170°C, tetragonal (*t*) stable up to 2370°C, and cubic (*c*) stable from 2370°C up to the melting point (El-Ghany and Sherief, 2016; Chevalier et al., 1999, 2007; Hisbergues et al., 2009). The development of zirconia as a bioengineered ceramic commonly requires the stabilization of a predominant tetragonal matrix at room temperature through the addition of metallic oxides, with yttrium oxide (3 mol %) being the most frequent (Chevalier and Gremillard, 2009; Zhang and Lawn, 2018). Considering that the *t* phase remains metastable at room temperature, 3Y-TZP may undergo *t-m* phase transformation when exposed to tensile stresses with the exposure to humidity, mechanical loading, and low temperatures (Chevalier et al., 2007). The stress mediated transformation is the key to zirconia's high mechanical properties due to transformation toughening, where *t-m* transformation is accompanied by a volumetric expansion and shear strain, inducing compressive stresses that can potentially act in opposition to the stress field that promotes crack propagation (Garvie et al., 1975; Stevens and Evans, 1984). Nevertheless, *t* phase metastability also makes 3Y-TZP susceptible to low temperature degradation (LTD), a steady and continued *t-m* phase transformation due to the exposition to a moist environment in a relatively low temperature (Chevalier et al., 1999). LTD may be accompanied by grain growth, grain extrusions and eventually by grain pull-out, with the generation of microstructural defects that may alter the mechanical behavior of 3Y-TZP over time (Chevalier et al., 2007).

First generation 3Y-TZP, chief polycrystalline *t* matrix, was introduced as a core ceramic due to its high opacity inherent to the anisotropic *t* structure (Zhang, 2014; Krell and T. Klimke, 2007). However, chipping of the veneering porcelain has been reported as a recurrent complication, especially for long span fixed dental prostheses (Pieralli et al., 2018; Sailer et al., 2018a). Numerous studies have focused on investigating the reasons for the high incidence of porcelain fractures in 3Y-TZP prostheses (Quinn et al., 2010; Kim et al., 2018). The veneering process *per se* has shown to trigger *t-m* phase transformation at the porcelain/3Y-TZP interface due to the presence of moisture from the porcelain slurry and its subsequent heating in the furnace, increasing the presence of residual stresses at the porcelain and eventually compromising its strength (Tholey et al., 2009; Fukushima et al., 2014). Subsequently, a second generation 3Y-TZP was developed, where a reduction in the alumina (Al₂O₃) content, as well as alterations in the sintering parameters and reduced particle size, led to improved optical properties. Such improvement increased the range of indications of 3Y-TZP systems to monolithic restorations (Zhang and Lawn, 2017), which brought a larger exposure of 3Y-TZP to the oral environment and raised considerably the clinical concerns about the effects of LTD on prostheses longevity (Miragaya et al., 2017). Scientific evidence on 3Y-TZP oral degradation has demonstrated a significant *t-m* transformation accompanied by increased surface roughness, eventually affecting its mechanical properties after short periods (60–100 days *in situ*) (Miragaya et al., 2017; Borges et al., 2019). A progressive *t-m* phase transformation has also been associated with an increase in the 3Y-TZP translucency, which may alter prosthesis esthetic results in the short-term (Kim and Kim, 2018; Benalcázar Jalkh et al., 2020a, 2020b). *In vitro* researches have indicated that 3Y-TZP *t-m* transformation susceptibility was dependent on the microstructure, grain size, and manufacturing and processing methods, along with laboratory aging protocol (Pereira et al., 2015, 2016).

As an alternative to overcome stability issues of 3Y-TZP systems at room temperature, studies have proposed the combination of zirconia particles within an Al₂O₃ matrix (Chevalier, 2006a; Fabbri et al., 2014a). Zirconia toughened alumina (ZTA) composites are comprised by an Al₂O₃ matrix along with a secondary phase of disperse *t* 3Y-TZP grains, combining the advantageous properties of both materials through a trade-off between enhanced toughening by crack-shielding,

favorable tribochemical properties, and LTD resistance (Chevalier and Gremillard, 2009; Schneider et al., 2008; Sequeira et al., 2016; Zhao et al., 2013a, 2013b; Wang and Stevens, 1989). Considering that the *t-m* transformation spreads by a nucleation and growth mechanism, it has been suggested that the maximum 3Y-TZP fraction to limit the spread of transformation may be related to the interconnectedness of the zirconia phase, namely the percolation threshold (Kurtz et al., 2014). Studies have indicated that this fraction should be up to 16% of 3Y-TZP, where higher values could promote a continuous path for zirconia grains to transform without restraint (Pecharroman et al., 2003; Ueno, 2012).

Nonetheless, scientific evidence on the orthopedic field has also indicated favorable mechanical properties when 15–30% of 3Y-TZP particles were uniformly dispersed within an Al₂O₃ matrix (Casellas et al., 1999; Pezzotti et al., 2010; Tang et al., 2012), as well as favorable resistance to *t-m* phase transformation after hydrothermal aging (Pezzotti et al., 2010; Lopes et al., 2019a). Our group's previous studies have described successful results for the development of aging-resistant ZTA composites with high 3Y-TZP content presenting promising mechanical properties for dental applications (Benalcázar Jalkh et al., 2020a, 2020b; Lopes et al., 2019b, 2020). Therefore, this work aimed to analyze the effect of aging on the nanomechanical properties as well as the 3D topography of an experimental ZTA composite composed of 70% of a high-purity Al₂O₃ (350 nm) and 30% of a second generation 3Y-TZP (40 nm), to be compared with its individual counterpart materials. We hypothesized that the ZTA composite would be resistant to hydrothermal degradation and the corresponding nanomechanical properties and topography would only be altered in the pure 3Y-TZP.

2. Materials and methods

2.1. Experimental ceramic materials synthesis and specimen fabrication

The study comprised the following groups: 1) ZTA 70/30: Zirconia Toughened Alumina synthesized with 70% alumina with a particle size of 350 nm (Al₂O₃, Baikalex Regular CR10, Baikowski, Poisy, France) and 30% of a second generation 3Y-TZP with a particle size of 40 nm (Zpex, Tosoh Corporation, Tokyo, Japan); 2) Zpex: second generation 3Y-TZP (Zpex, Tosoh Corporation); and 3) Al₂O₃: High purity alumina (Al₂O₃, Baikalex CR10, Baikowski, Malakoff, France). The synthesis of the experimental materials was achieved following the methodology previously described and briefly explained below (Benalcázar Jalkh et al., 2020a, 2020b; Lopes et al., 2019b, 2020).

Ethanol suspension of alumina and zirconia powders (Al₂O₃-70% vs ZrO₂-30%), and high purity alumina with 500 ppm of magnesium oxide, were prepared for the synthesis of the ZTA composite and pure alumina respectively. Using a friction mill with high purity alumina spheres, the suspensions were homogenized and mixed for 4 h. Subsequently, slurries were dried in rotary evaporator (801, Fisaton, São Paulo, Brazil) and granulated and sieved to yield the final powder.

Zpex, Al₂O₃, and experimental ZTA powders were uniaxially pressed (1148 Kg/cm² for 30 s) using a tungsten carbide matrix to obtain disc-shaped green body samples with 15 mm of diameter and 1.8 mm thickness. All samples were then double wrapped and sealed in vacuum sealer (Jumbo Plus, Globavac, Itajai, SC, Brazil) and subjected to isostatic pressing using a cold isostatic press (National Forge, Pennsylvania, USA) at room temperature at 2110 Kg/cm² for 30 s.

Samples were then sintered at 1500°C (Zpex) and 1600°C (Al₂O₃ and ZTA composite) for 1 h (Zyrcomat Furnace, Vita Zahnfabrik, Bad Säckingen, Germany) with heating and cooling rate of 4°C per minute. Polishing of the two flat surfaces was carried out using a semi-automatic polishing machine (Automet, 2000; Buehler, Illinois, USA) with 220, 120, 90, 40, 25, 15, 9, 6 and 1 μm granulated diamond disks (ALLIED High-Tech Products, California, USA) with diamond suspensions.

A total of ten disc-shaped specimens were prepared with dimensions of 12 mm of diameter and 1 mm thickness (ISO 6872:2015). Apparent density of all experimental ceramics was assessed using Archimedes'

principle and characterizations involved the evaluation of the crystalline structure, micromorphology, nanomechanical properties and 3D surface analysis before and after autoclave accelerated artificial aging.

2.2. Density

The relative density was obtained using the Archimedes principle. An analytical balance (XS64 Analytical balance, Mettler Toledo, Columbus, OH, USA) and the theoretical density kit accessory (Mettler Density Kit, Mettler Toledo, USA) were used to measure the relative density of all ceramic materials after sintering.

2.3. X-ray diffraction

Spectra were obtained for all experimental materials using X-ray diffraction (XRD, Miniflex, Rigaku, Tokyo, Japan). The scanning was performed on the Bragg θ - 2θ geometry, equipped with a graphite monochromator and Cu K α radiation ($\lambda = 1.5406\text{\AA}$), operating at a voltage of 40 kV and a current emission of 40 mA. Data were obtained in periods of 1.0 s and steps of 0.020 (2θ) of 10–80°. After baseline subtraction (HighScore Plus Software, Malvern Panalytical Ltd, Westborough, Massachusetts, USA), monoclinic and tetragonal peaks were identified, and peaks intensity were recorded for monoclinic phase calculation. The monoclinic phase content was quantified through formulas introduced by Toraya et al. (1984) (Toraya et al., 1984), considering the monoclinic peaks intensity at $2\theta = 28^\circ$ and $2\theta = 31.2^\circ$, and the intensity of the tetragonal peak at $2\theta = 30^\circ$.

2.4. Scanning electron microscope by field emission (SEM-FE)

Two polished samples per group were submitted to thermal treatment at 1520°C for Alumina and ZTA composites, and 1420°C for Y-TZP specimens during 1 h with heating and cooling rate of 4°C per minute (Zyromat Furnace, Germany). The micromorphology of the experimental materials was analyzed at high-resolution Scanning Electron Microscope by Field Emission Gun (SEM-FE) (Magellan 400L, FEI Company, Brno, Czech Republic) with a secondary electron (SE) detector, under magnification of 10,000X.

2.5. Nanoindentation

Nanoindentation testing was performed at room temperature ($\pm 23^\circ\text{C}$) with previous tip-to-optic and air calibrations. Imaging of each region of interest and indentation processes were performed using a Berkovich fluid cell diamond three-sided pyramid probe with a half angle of 65.27°, included angle of 142.30° and 100 nm tip radius, in a Nanoindenter (950 TI; Hysitron, Minneapolis, MN, USA) with fused quartz calibration and a loading profile with a peak load of 10000 μN achieved in 15s, followed by complete unloading in 2s. The test was conducted under dry condition in the center, top, bottom, left and right regions of the discs ($n = 3/\text{group}$). Each region of interest received ten nanoindentations separated by 5 μm horizontally and vertically. For the determination of the elastic modulus, the characteristics of the Berkovich indenter were considered in the equations following Oliver and Pharr (1992). Hardness values were obtained directly from the nanoindentation software.

2.6. Interferometry

3D surface topographical parameters were obtained using a 3D non-contact profilometer (Phase View 2.5, Palaiseau, France) and Zeiss Axio-Imager A.1 microscope (Zeiss, Oberkochen, Germany) ($n = 4/\text{group}$). S_a , which is the arithmetic mean deviation of a surface; and S_q , which is the root mean square deviation of a surface, were determined. The average values for surface roughness (S_a and S_q) were calculated over an area of $150 \times 150 \mu\text{m}$ using a magnification lens of 50X.

2.7. Simulated LTD aging

Low-temperature degradation (LTD) was simulated in an autoclave (Vitale Class CD, Cristofoli, Campo Mourão, PR, Brazil) at 134°C, under a 2.2 bar pressure, over a 20 consecutive hour period (Pereira et al., 2015).

2.8. Statistical analysis

Statistical analyses were performed using the linear mixed model and least square difference pos hoc tests to determine the influence of aging on all variables with significance level set at 5% (IBM SPSS 23, IBM Corp., Armonk, NY).

3. Results

The theoretical density values of the ZTA 70/30 (4.419 g/cm^3), Zpex (6.081 g/cm^3) and Al_2O_3 (3.98 g/cm^3) were calculated based on the mixture of the alumina and zirconia theoretical densities. A high density, on the order of 96–99% of the theoretical density, was obtained for all ceramic materials, as listed in Table 1.

The X-ray diffraction (XRD) spectra of all materials were plotted and typical Al_2O_3 and 3Y-TZP peaks could be identified, and the monoclinic crystalline content quantified, as demonstrated in Fig. 1 and Table 2. XRD spectra analyses indicated a slight percentage of monoclinic phase in the as-sintered Zpex and ZTA 70/30 groups (1.71 and 1.27%, respectively). However, an increased percentage of monoclinic phase could be observed after aging in the Zpex (23.5%), while monoclinic content remained stable in ZTA 70/30 (2.45%).

SEM-FE micrographs (Fig. 2) revealed a uniform distribution of zirconia grains within the alumina matrix and a dense surface for ZTA 70/30, which was similar to the control ceramics (Zpex and Al_2O_3). Zpex exhibited a similar grain growth in the pure and composite formulations. In the experimental ZTA composite, zirconia grains presented a mean size of $0.42 \pm 0.11 \mu\text{m}$, similar to the grain size measured in the pure formulation ($0.47 \pm 0.11 \mu\text{m}$). Conversely, Al_2O_3 showed a smaller particle size in the composite ($0.95 \pm 0.17 \mu\text{m}$) when compared with the pure formulation ($3.96 \pm 0.91 \mu\text{m}$), probably because of the interaction with the secondary zirconia phase. All ceramic groups presented few microstructural pores and defects distributed along the ceramic surface, which may be related to the ceramic processing.

Fig. 3 presents the estimated means and corresponding 95% confidence intervals (CI) for surface roughness parameters for each polycrystalline ceramic before and after aging. All polycrystalline ceramics demonstrated similar S_a and S_q after processing ($p > 0.07$). Aging did not affect the surface roughness (S_a and S_q) of the ZTA composite and Al_2O_3 ($p > 0.38$). However, *in vitro* induced low temperature degradation in autoclave significantly increased the S_a of pure translucent zirconia, Zpex ($p = 0.001$).

Fig. 4 represents the statistical summary of nanomechanical testing, including elastic modulus (E) and hardness (H) values. As expected, significantly lower H and E values were obtained for Zpex, intermediate values for ZTA 70/30 and higher values for Al_2O_3 , before and after aging ($p < 0.03$). Although a decrease in E and H was noticed for all groups after aging, values did not reach significance ($p > 0.32$).

Table 1

Density of the ceramics based on alumina and zirconia theoretical densities.

Material	Density (%)
ZTA 70/30	96.45 (± 0.15)
Zpex	99.13 (± 0.24)
Alumina	98.83 (± 0.33)

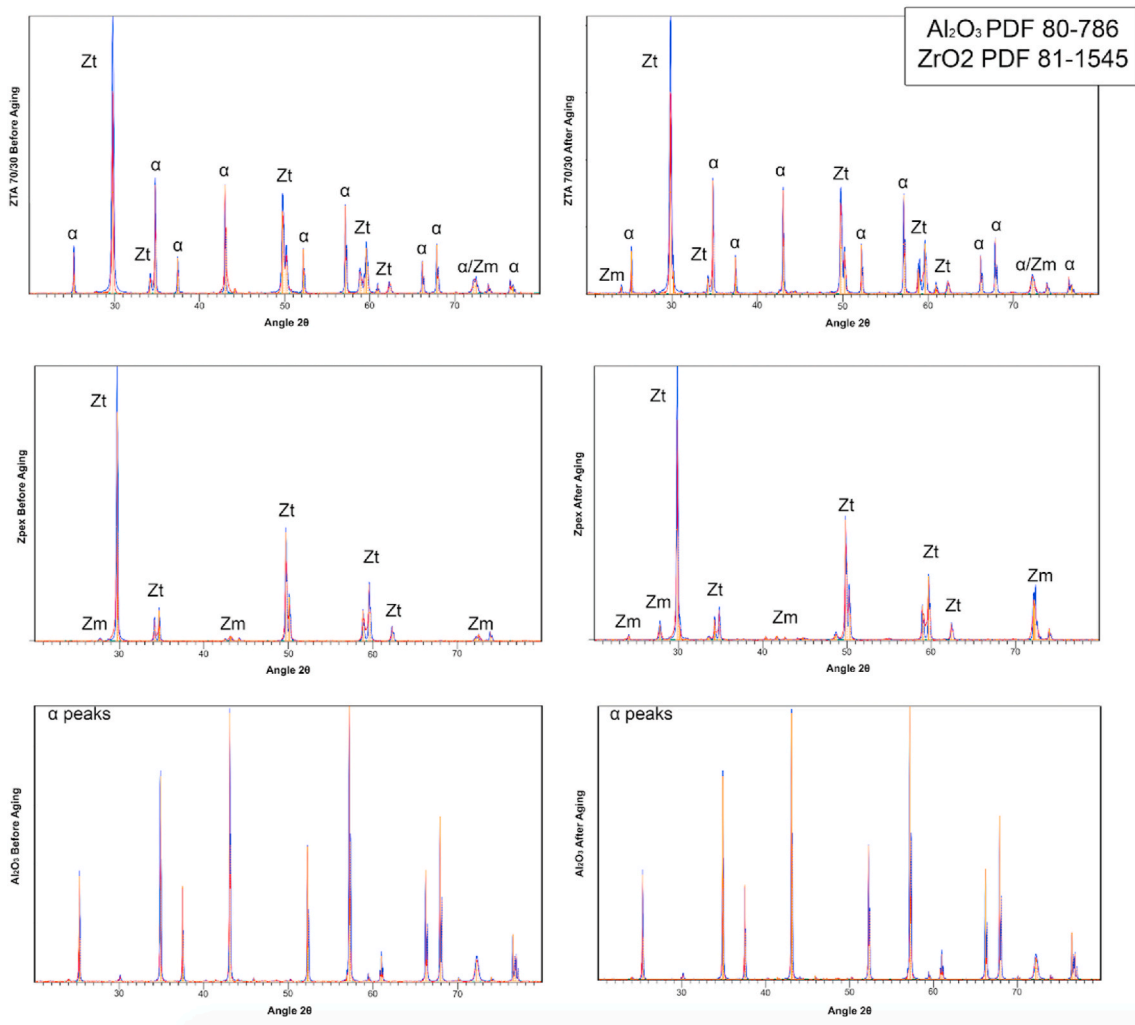


Fig. 1. XRD patterns of tested polycrystalline ceramics before and after aging.

Table 2

Monoclinic phase content of experimental materials before and after aging.

Material	Monoclinic phase %	
	Before aging	After aging
ZTA 70/30	1.13 (± 0.26)	3.60 (± 0.35)
Zpex	2.45 (± 0.43)	21.13 (± 0.96)

4. Discussion

Considering that the long-term clinical success of biomedical ceramic prostheses is affected by hydrothermal stability, the development of high-strength and aging resistant polycrystalline ceramic systems has been deemed paramount (Chevalier et al., 2007; Chevalier and Gremillard, 2009; Chevalier, 2006b). Recently, zirconia toughened alumina (ZTA) polycrystalline composites synthesized and processed for dental purposes in different weight ratios of yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP), from 15% to 30%, have demonstrated favorable optical and mechanical properties, along with remarkably higher hydrothermal stability after artificial aging relative to first and second generation 3Y-TZPs, the most widely used polycrystalline ceramics in dentistry, yet susceptible to low temperature degradation (LTD) (Benalcázar Jalkh et al., 2020a, 2020b; Lopes et al., 2019b, 2020). Thus, the present study sought to provide a further characterization of a ZTA composite comprised by 70% alumina reinforced by 30% second

generation 3Y-TZP (ZTA 70/30) (Benalcázar Jalkh et al., 2020b) through nanoindentation to determine hardness and elastic modulus, as well as 3D non-contact profilometry to assess surface topography, and compare with the isolated counterparts, high-purity alumina (Al_2O_3) and second generation 3Y-TZP (Zpex), before and after laboratory aging.

The synthesis and processing methods were successful to provide dense polycrystalline ceramics, density superior to 96%, with a uniform microstructure and few pores and defects, as observed in the SEM images. The average grain size measured for Zpex in the present study is similar to grain sizes reported in previous literature (Tong et al., 2016; Kim et al., 2013) and were maintained in the composite material. Also, ZTA 70/30 presented a homogeneous distribution of the 3Y-TZP grains within the Al_2O_3 matrix, which is a favorable microstructure to restrain grains interconnectivity and tetragonal-to-monoclinic transformation (*t-m*), thus improving hydrothermal stability (Benalcázar Jalkh et al., 2020a; Chevalier et al., 2011). Moreover, crystalline, microstructural, topographical, and nanomechanical characterizations showed no significant alteration after autoclave simulated LTD for ZTA 70/30 and Al_2O_3 , while Zpex depicted an increased monoclinic content and surface roughness. Hence the postulated hypothesis of the present study that ZTA 70/30 would be resistant to hydrothermal degradation and that nanomechanical properties and topography would only be altered in the pure 3Y-TZP was accepted.

Extensive *t-m* phase transformation has been demonstrated for first and second generation 3Y-TZP after laboratory aging, simulating an extensive LTD, which compromised their optical and mechanical

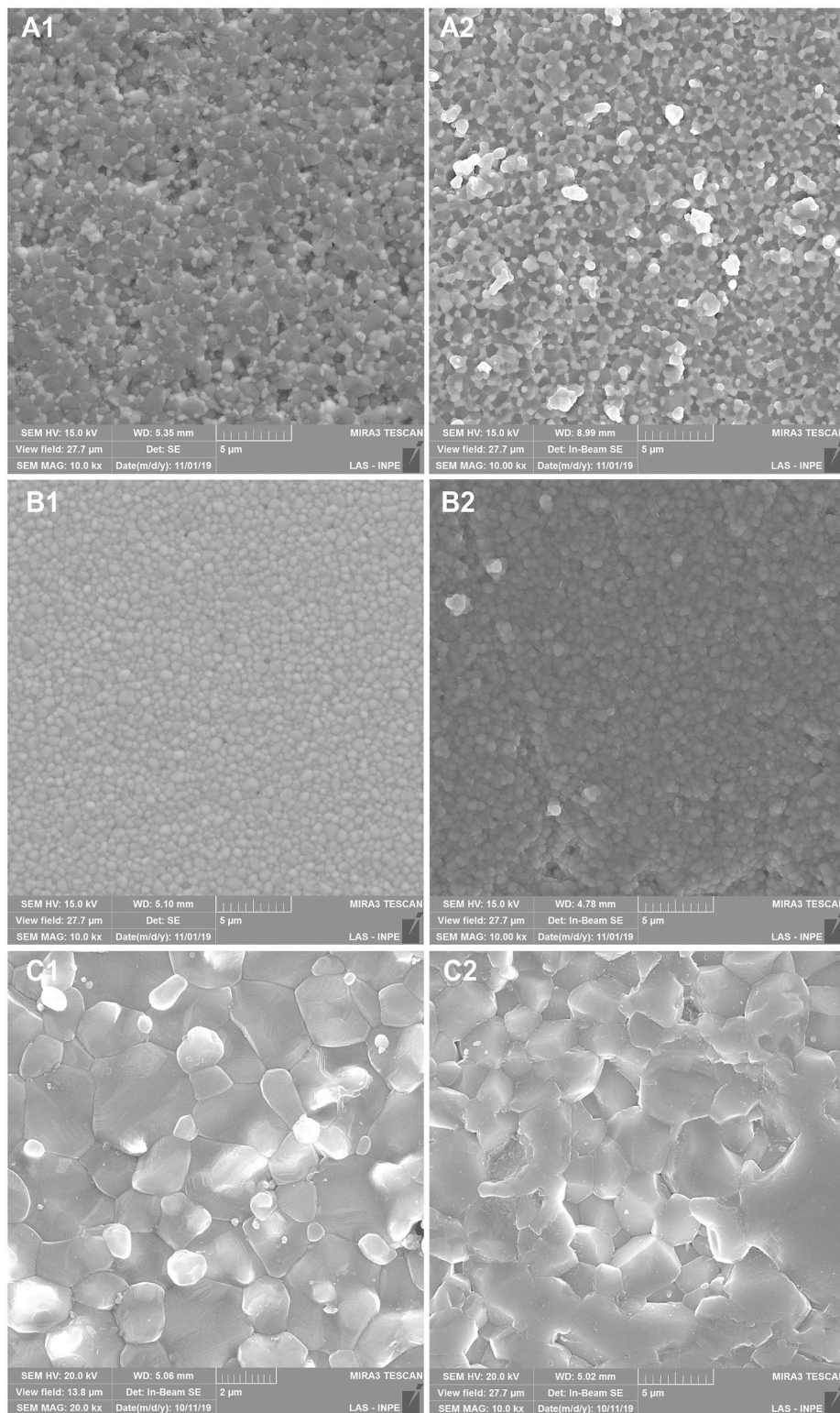


Fig. 2. SEM images of all ceramic groups represented by letters A) ZTA 70/30, B) Zpex and C) Al₂O₃. Numbers 1 and 2 represent the as sintered and aged conditions, respectively.

properties stability (Benalcázar Jalkh et al., 2020a, 2020b; Lopes et al., 2019b, 2020). Furthermore, recent studies evaluating the *in situ* oral degradation of 3Y-TZPs have shown a meaningful phase transformation, which increased their surface roughness and affected their flexural strength after only 60–100 days (Miragaya et al., 2017; Borges et al., 2019). Given the scientific evidence of the potential impact of 3Y-TZP

t-m phase transformation in clinical dentistry, the stability achieved by the experimental ZTA70/30 in the present study, approximately 2.5% *t-m* transformation and stable surface roughness, as well as the previously reported high and stable flexural strength when subjected to a similar aging protocol (immediate: 914 MPa/aged: 815 MPa) (Benalcázar Jalkh et al., 2020b), highly encourage subsequent testing for

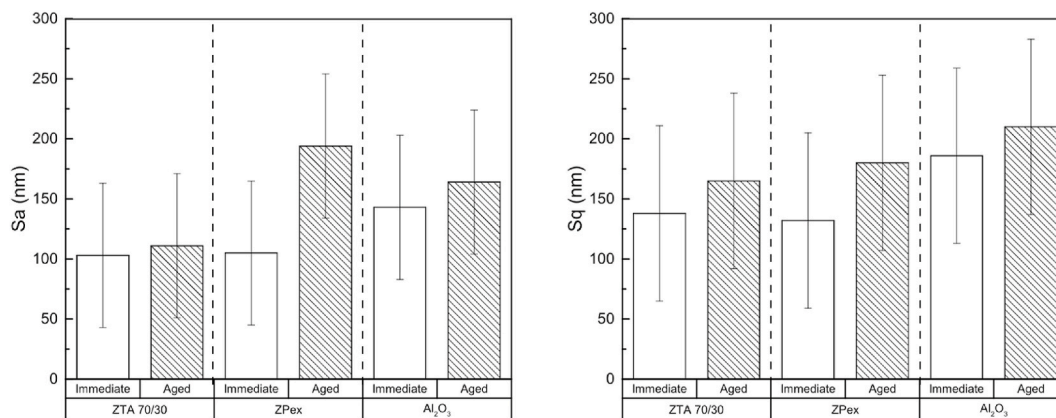


Fig. 3. Surface roughness estimated means and corresponding 95% confidence interval (CI) for all tested groups before and after aging.

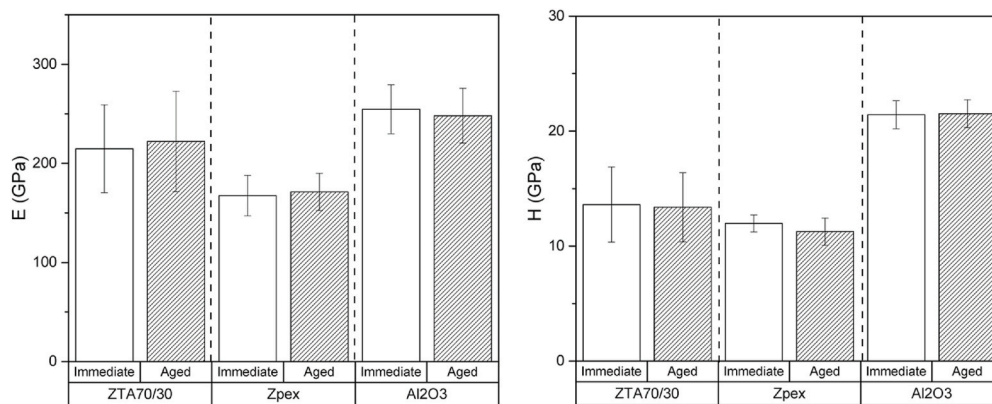


Fig. 4. Nanomechanical Properties (E and H) estimated means and correspondent standard deviation (SD) for all immediate and aged materials.

clinical experimentation.

It has been reported in the orthopedic field that an extensive *t-m* phase transformation due to LTD may lead to extrusion and pull-out of 3Y-TZP grains, increasing the surface roughness and having a detrimental effect on the long-term performance of hip prostheses (Haraguchi et al., 2001; Fernandez-Fairen et al., 2007). Furthermore, the examination of the surface properties of explanted zirconia femoral heads has revealed that an increase in the monoclinic content was associated with not only an increase in surface roughness, but also a decrease in hardness, which was positively correlated with time of implantation (Santos et al., 2004). Although nanomechanical testing in the present study has demonstrated no significant alterations either in the hardness or elastic modulus values of the 3Y-TZP after autoclave aging, the significant phase transformation (~18% monoclinic content increase), as well as the increase in surface roughness (~90 nm increase in the Sa parameter), raise concerns about the integrity of 3Y-TZP microstructure, increasing defect population, and its effects on the mechanical performance of monolithic prostheses. A previous study has shown a significant reduction (~200 MPa) in the flexural strength for a first generation 3Y-TZP under a similar aging protocol (Benalcázar Jalkh et al., 2020b). The absence of differences in hardness for all immediate and aged groups was reflected in the SEM micrographs where no major changes in microstructure, grain size, and densification, which affect materials surface properties (Prado et al., 2019; Camposilvan et al., 2018; Gaillard et al., 2009), were observed.

Nanoindentation test has been widely used to assess the mechanical properties of different materials at the nano/micro scale (Jin and Ebenstein, 2017). In the present study, the results of nanomechanical testing showed a higher hardness and elastic modulus for the experimental ZTA 70/30 composite when compared to the second generation

3Y-TZP, for both immediate and aged samples. As presented in Fig. 4, nanoindentation of the composite material resulted in larger standard deviation when compared to the nano-mechanical properties of pure zirconia. Such results were expected in light of the significant differences in the mechanical properties of the two ceramic phases, and the nanometric tip diameter of the Berkovich indenter. Moreover, it has been reported that ZTA composites hardness tends to proportionally decrease as the weight percentage of 3Y-TZP increase, as postulated by the rule of mixtures (Sequeira et al., 2016). Therefore, the significantly higher hardness of ZTA 70/30 relative to 3Y-TZP may lie on the Al₂O₃ content. The high hardness of the Al₂O₃ particles may also be responsible for the high hydrothermal stability of the ZTA 70/30, where the constraint that the matrix exerts on the Y-TZP particles maintains them in the metastable tetragonal state, thus acting as a mechanical stabilizer (Gutknecht et al., 2007; Fabbri et al., 2014b), and enhancing the energy threshold for *t-m* transformation in the vicinity zirconia grains (Zhao et al., 2013b). Additionally, the dense Al₂O₃ matrix limits the interconnectivity of tetragonal 3Y-TZP grains, restraining the nucleation and growth process related to LTD progression, as previously indicated (Chevalier et al., 2009).

The hydrothermal stability achieved by the ZTA 70/30 composite is also relevant when analyzing surface roughness parameters after aging. While 3Y-TZP submitted to laboratory LTD presented a significant increase in Sa parameter, ZTA 70/30 surface remained stable. Similar degradation behavior and increased surface roughness when submitted to simulated LTD have been reported for 3Y-TZP systems (Pinto et al., 2016; Amarante et al., 2020). Recently, a systematic review on the effect of aging on the surface roughness of 3Y-TZP based ceramics has concluded that LTD simulated in autoclave for 5 h did not affect their surface roughness (Yang et al., 2020); however, the data analyzed

presented high heterogeneity due to the significant variability in the commercial brands, aging protocols, and sample preparation methods, which may have a pivotal role on the aging behavior of 3Y-TZP ceramics (Pereira et al., 2015). Considering that second generation 3Y-TZPs are clinically indicated as a monolithic restorative material from single crowns to long-span fixed dental prostheses (FDP) (Zhang and Lawn, 2017), an increase in surface roughness when submitted to the oral environment is highly alarming, considering its potential impact on antagonist wear (Passos et al., 2014; Yang et al., 2019), biofilm adhesion (Ammar et al., 2015; Lee et al., 2019) and the potential effects on the long-term performance of these rehabilitations.

To date, there is a paucity of scientific information regarding survival rates on the long-term performance of monolithic 3Y-TZP FDP and implant abutments (Sailer et al., 2018b). The high rates of technical complications reported in systematic reviews for porcelain fused to zirconia (PFZ) FDP when compared to porcelain fused to metal restorations, especially for implant-supported reconstructions, have led to the conclusion that PFZ should not be considered as a first choice reconstruction for long-span FDP (Sailer et al., 2015, 2018b; Rabel et al., 2018). Moreover, despite the fact that chipping of the veneering ceramic has been reported as the most common technical complication, some clinical trials have demonstrated different problems as fatigue accumulates, including 3Y-TZP framework fractures (Taskonak et al., 2008; Sailer et al., 2018c). Currently, different approaches have been reported in the literature to overcome the problems associated with the hydrothermal instability of dental zirconia, including; formulations of Alumina-toughened Zirconia (ATZ) composites (Bergamo et al., 2021), Ceria-doped zirconia composites (Chevalier et al., 2020; Touaiher et al., 2018; Reveron et al., 2017), and sophisticated nanostructured zirconia-based materials (Arená et al., 2019). Although initial characterizations evidenced promising results for such materials, studies including fatigue characterization and/or clinical evaluation are warranted, as well as continued innovations in the synthesis of aging-resistant polycrystalline ceramics and processing methods to obtain blocks/discs for CAD/CAM use that would allow its use for large span reconstructions as an alternative to LTD susceptible 3Y-TZP systems that are still widely used in dentistry.

5. Conclusion

The proposed synthesis and processing protocols for the zirconia toughened alumina (ZTA 70/30) in a weight ratio of 70% pure alumina (Al_2O_3) and 30% second generation 3Y-TZP (Zpex) successfully resulted in a high-density polycrystalline ceramic, with the 3Y-TZP particles homogeneously distributed in the Al_2O_3 matrix. The physical-mechanical characterization demonstrated the high hydrothermal stability of the ZTA 70/30 and Al_2O_3 in all variables tested (crystalline content, 3D roughness parameters and elastic modulus and hardness), while artificial aging significantly increased the monoclinic content and surface roughness of Zpex.

CRedit authorship contribution statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References

- Amarante, J.E.V., Soares Pereira, M.V., De Souza, G.M., Pais Alves, M.F.R., Simba, B.G., Santos, C.D., 2020. Effect of hydrothermal aging on the properties of zirconia with different levels of translucency. *J Mech Behav Biomed Mater* 109, 103847.
- Ammar, Y., Swailes, D., Bridgens, B., Chen, J., 2015. Influence of surface roughness on the initial formation of biofilm. *Surf. Coating. Technol.* 284, 410–416.
- Arená, A., Prete, F., Rambaldi, E., Bignozzi, M.C., Monaco, C., Di Fiore, A., et al., 2019. Nanostructured zirconia-based ceramics and composites in dentistry: a state-of-the-art review. *Nanomaterials* (Basel) 9.
- Benalcázar Jalkh, E.B., Bergamo, E.T.P., Monteiro, K.N., Cesar, P.F., Genova, L.A., Lopes, A.C.O., et al., 2020a. Aging resistance of an experimental zirconia-toughened alumina composite for large span dental prostheses: optical and mechanical characterization. *J Mech Behav Biomed Mater* 104, 103659.
- Benalcázar Jalkh, E.B., Monteiro, K.N., Cesar, P.F., Genova, L.A., Bergamo, E.T.P., Lopes, A.C.O., et al., 2020b. Aging resistant ZTA composite for dental applications: microstructural, optical and mechanical characterization. *Dent. Mater.*
- Bergamo, E.T.P., Cardoso, K.B., Lino, L.F.O., Campos, T.M.B., Monteiro, K.N., Cesar, P.F., et al., 2021. Alumina-toughened zirconia for dental applications: physicochemical, mechanical, optical, and residual stress characterization after artificial aging. *J. Biomed. Mater. Res. B Appl. Biomater.* 109, 1135–1144.
- Borges, M.A.P., Alves, M.R., dos Santos, H.E.S., dos Anjos, M.J., Elias, C.N., 2019. Oral degradation of Y-TZP ceramics. *Ceram. Int.* 45, 9955–9961.
- Camposilvan, E., Leone, R., Gremillard, L., Sorrentino, R., Zarone, F., Ferrari, M., et al., 2018. Aging resistance, mechanical properties and translucency of different yttria-stabilized zirconia ceramics for monolithic dental crown applications. *Dent. Mater.* 34, 879–890.
- Casellas, D., Rafols, I., Llanes, L., Anglada, M., 1999. Fracture toughness of zirconia-alumina composites. *Int. J. Refract. Metals Hard Mater.* 17, 11–20.
- Chevalier, J., 2006a. What future for zirconia as a biomaterial? *Biomaterials* 27, 535–543.
- Chevalier, J., 2006b. What future for zirconia as a biomaterial? *Biomaterials* 27, 535–543.
- Chevalier, J., Gremillard, L., 2009. Ceramics for medical applications: a picture for the next 20 years. *J. Eur. Ceram. Soc.* 29, 1245–1255.
- Chevalier, J., Cales, B., Drouin, J.M., 1999. Low-temperature aging of Y-TZP ceramics. *J. Am. Ceram. Soc.* 82, 2150–2154.
- Chevalier, J., Gremillard, L., Deville, S., 2007. Low-temperature degradation of zirconia and implications for biomedical implants. *Annu. Rev. Mater. Res.* 37, 1–32.
- Chevalier, J., Grandjean, S., Kuntz, M., Pezzotti, G., 2009. On the kinetics and impact of tetragonal to monoclinic transformation in an alumina/zirconia composite for arthroplasty applications. *Biomaterials* 30, 5279–5282.
- Chevalier, J., Taddei, P., Gremillard, L., Deville, S., Fantozzi, G., Bartolome, J.F., et al., 2011. Reliability assessment in advanced nanocomposite materials for orthopaedic applications. *J Mech Behav Biomed Mater* 4, 303–314.
- Chevalier, J., Liens, A., Reveron, H., Zhang, F., Reynaud, P., Douillard, T., et al., 2020. Forty years after the promise of «ceramic steel?»: zirconia-based composites with a metal-like mechanical behavior. *J. Am. Ceram. Soc.* 103, 1482–1513.
- Denry, I., Kelly, J.R., 2008. State of the art of zirconia for dental applications. *Dent. Mater.* 24, 299–307.

- El-Ghany, O.S.A., Sherief, A.H., 2016. Zirconia based ceramics, some clinical and biological aspects. *Future Dental Journal* 2, 55–64.
- Fabrizi, P., Piconi, C., Burresti, E., Magnani, G., Mazzanti, F., Mingazzini, C., 2014a. Lifetime estimation of a zirconia–alumina composite for biomedical applications. *Dent. Mater.* 30, 138–142.
- Fabrizi, P., Piconi, C., Burresti, E., Magnani, G., Mazzanti, F., Mingazzini, C., 2014b. Lifetime estimation of a zirconia–alumina composite for biomedical applications. *Dent. Mater.* 30, 138–142.
- Fernandez-Fairen, M., Blanco, A., Murcia, A., Sevilla, P., Gil, F.J., 2007. Aging of retrieved zirconia femoral heads. *Clin. Orthop. Relat. Res.* 462, 122–129.
- Fukushima, K.A., Sadoun, M.J., Cesar, P.F., Mainjot, A.K., 2014. Residual stress profiles in veneering ceramic on Y-TZP, alumina and ZTA frameworks: measurement by hole-drilling. *Dent. Mater.* 30, 105–111.
- Gaillard, Y., Anglada, M., Jiménez-Piqué, E., 2009. Nanoindentation of yttria-doped zirconia: effect of crystallographic structure on deformation mechanisms. *J. Mater. Res.* 24, 719–727.
- Garvie, R.C., Hannink, R.H., Pascoe, R.T., 1975. Ceramic steel? *Nature* 258, 703–704.
- Guess, P.C., Schultheis, S., Bonfante, E.A., Coelho, P.G., Ferencz, J.L., Silva, N.R., 2011. All-ceramic systems: laboratory and clinical performance. *Dent. Clin.* 55, 333–352 ix.
- Gutknecht, D., Chevalier, J., Garnier, V., Fantozzi, G., 2007. Key role of processing to avoid low temperature ageing in alumina zirconia composites for orthopaedic application. *J. Eur. Ceram. Soc.* 27, 1547–1552.
- Haraguchi, K., Sugano, N., Nishii, T., Miki, H., Oka, K., Yoshikawa, H., 2001. Phase transformation of a zirconia ceramic head after total hip arthroplasty. *J. Bone Joint Surg Br* 83, 996–1000.
- Hisbergues, M., Vendeville, S., Vendeville, P., 2009. Zirconia: established facts and perspectives for a biomaterial in dental implantology. *J. Biomed. Mater. Res. B Appl. Biomater.* 88, 519–529.
- Jin, C., Ebenstein, D.M., 2017. Nanoindentation of compliant materials using Berkovich tips and flat tips. *J. Mater. Res.* 32, 435.
- Kim, H.K., Kim, S.H., 2018. Effect of hydrothermal aging on the optical properties of precolored dental monolithic zirconia ceramics. *J. Prosthet. Dent.*
- Kim, M.J., Ahn, J.S., Kim, J.H., Kim, H.Y., Kim, W.C., 2013. Effects of the sintering conditions of dental zirconia ceramics on the grain size and translucency. *J. Adv. Prosthodont* 5, 161–166.
- Kim, J., Dhital, S., Zhivago, P., Kaizer, M.R., Zhang, Y., 2018. Viscoelastic finite element analysis of residual stresses in porcelain-veneered zirconia dental crowns. *J. Mech. Behav. Biomed. Mater.* 82, 202–209.
- Krell, A., Hutzler, T., Klimke, J., 2007. Transparent ceramics for structural applications: part 1. Physics of light transmission and technological consequences. *Ceram. Forum Int.* 84, 41–50.
- Kurtz, S.M., Kocagoz, S., Arnholt, C., Huet, R., Ueno, M., Walter, W.L., 2014. Advances in zirconia toughened alumina biomaterials for total joint replacement. *J. Mech. Behav. Biomed. Mater.* 31, 107–116.
- Lee, D.H., Mai, H.N., Thant, P.P., Hong, S.H., Kim, J., Jeong, S.M., et al., 2019. Effects of different surface finishing protocols for zirconia on surface roughness and bacterial biofilm formation. *J. Adv. Prosthodont* 11, 41–47.
- Lopes, A.C.O., Coelho, P.G., Witek, L., Jalkh, E.B.B., Génova, L.A., Monteiro, K.N., et al., 2019a. Nanomechanical and microstructural characterization of a zirconia-toughened alumina composite after aging. *Ceram. Int.*
- Lopes, A.C.O., Coelho, P., Witek, L., Jalkh, E.B., Génova, L., Monteiro, K., et al., 2019b. Nanomechanical and microstructural characterization of a zirconia-toughened alumina composite after aging. *Ceram. Int.* 45, 8840–8846.
- Lopes, A.C.O., Coelho, P.G., Witek, L., Benalcázar Jalkh, E.B., Genova, L.A., Monteiro, K.N., et al., 2020. Microstructural, mechanical, and optical characterization of an experimental aging-resistant zirconia-toughened alumina (ZTA) composite. *Dent. Mater.*
- Miragaya, L.M., Guimarães, R.B., Souza, R.O.A., Botelho, GdS., Guimarães, J.G.A., Silva, E.MdS., 2017. Effect of intra-oral aging on t–m phase transformation, microstructure, and mechanical properties of Y-TZP dental ceramics. *Journal of the Mechanical Behavior of Biomedical Materials* 72, 14–21.
- Oliver, W.C., Pharr, G.M., 1992. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J. Mater. Res.* 7, 1564–1583.
- Passos, S.P., Torrealba, Y., Major, P., Linke, B., Flores-Mir, C., Nychka, J.A., 2014. In vitro wear behavior of zirconia opposing enamel: a systematic review. *J. Prosthodont.* 23, 593–601.
- Pecharraman, C., Bartolomé, J.F., Requena, J., Moya, J.S., Deville, S., Chevalier, J., et al., 2003. Percolative mechanism of aging in zirconia-containing ceramics for medical applications. *Adv. Mater.* 15, 507–511.
- Pereira, G.K., Venturini, A.B., Silvestri, T., Dapieve, K.S., Montagner, A.F., Soares, F.Z., et al., 2015. Low-temperature degradation of Y-TZP ceramics: a systematic review and meta-analysis. *J. Mech. Behav. Biomed. Mater.* 55, 151–163.
- Pereira, G.K., Muller, C., Wandscher, V.F., Rippe, M.P., Kleverlaan, C.J., Valandro, L.F., 2016. Comparison of different low-temperature aging protocols: its effects on the mechanical behavior of Y-TZP ceramics. *J. Mech. Behav. Biomed. Mater.* 60, 324–330.
- Pezzotti, G., Saito, T., Padeletti, G., Cossari, P., Yamamoto, K., 2010. Nano-scale topography of bearing surface in advanced alumina/zirconia hip joint before and after severe exposure in water vapor environment. *J. Orthop. Res.* 28, 762–766.
- Pieralli, S., Kohal, R.J., Rabel, K., von Stein-Launsitz, M., Vach, K., Spies, B.C., 2018. Clinical outcomes of partial and full-arch all-ceramic implant-supported fixed dental prostheses. A systematic review and meta-analysis. *Clin. Oral Implants Res.* 29 (18), 224–236.
- Pinto, P.A., Colas, G., Filleter, T., De Souza, G.M., 2016. Surface and mechanical characterization of dental yttria-stabilized tetragonal zirconia polycrystals (3Y-TZP) after different aging processes. *Microsc. Microanal.* 22, 1179–1188.
- Prado, P., Monteiro, J.B., Campos, T.M.B., Thim, G.P., de Melo, R.M., 2019. Degradation kinetics of high-translucency dental zirconias: mechanical properties and in-depth analysis of phase transformation. *J. Mech. Behav. Biomed. Mater.* 102, 103482.
- Quinn, J.B., Quinn, G.D., Sundar, V., 2010. Fracture toughness of veneering ceramics for fused to metal (PFM) and zirconia dental restorative materials. *J. Res. Natl. Inst. Stand. Technol.* 115, 343–352.
- Rabel, K., Spies, B.C., Pieralli, S., Vach, K., Kohal, R.J., 2018. The clinical performance of all-ceramic implant-supported single crowns: a systematic review and meta-analysis. *Clin. Oral Implants Res.* 29 (18), 196–223.
- Reveron, H., Fornabaio, M., Palmero, P., Furderer, T., Adolfsson, E., Lugh, V., et al., 2017. Towards long lasting zirconia-based composites for dental implants: transformation induced plasticity and its consequence on ceramic reliability. *Acta Biomater.* 48, 423–432.
- Sailer, I., Makarov, N.A., Thoma, D.S., Zwahlen, M., Pjetursson, B.E., 2015. Corrigendum to "All-ceramic or metal-ceramic tooth-supported fixed dental prostheses (FDPs)? A systematic review of the survival and complication rates. Part I: single crowns (SCs). *Dent. Mater.* 31 (6), 603–623. *Dent. Mater.* 32 (2016) e389–e90.
- Sailer, I., Muhlemann, S., Kohal, R.J., Spies, B.C., Pjetursson, B.E., Lang, N.P., et al., 2018a. Reconstructive aspects: summary and consensus statements of group 3. The 5 (th) EAO Consensus Conference 2018. *Clin. Oral Implants Res.* 29 (18), 237–242.
- Sailer, I., Strassling, M., Valente, N.A., Zwahlen, M., Liu, S., Pjetursson, B.E., 2018b. A systematic review of the survival and complication rates of zirconia-ceramic and metal-ceramic multiple-unit fixed dental prostheses. *Clin. Oral Implants Res.* 29 (16), 184–198.
- Sailer, I., Balmer, M., Husler, J., Hammerle, C.H.F., Kanel, S., Thoma, D.S., 2018c. 10-year randomized trial (RCT) of zirconia-ceramic and metal-ceramic fixed dental prostheses. *J. Dent.*
- Santos, E.M., Vohra, S., Catledge, S.A., McClenny, M.D., Lemons, J., Moore, K.D., 2004. Examination of surface and material properties of explanted zirconia femoral heads. *J. Arthroplasty* 19, 30–34.
- Schneider, J., Begand, S., Kriegel, R., Kaps, C., Glien, W., Oberbachy, T., 2008. Low-temperature aging behavior of alumina-toughened zirconia. *J. Am. Ceram. Soc.* 11, 3613–3618.
- Sequeira, S., Fernandes, M.H., Neves, N., Almeida, M.M., 2016. Development and characterization of zirconia-alumina composites for orthopedic implants. *Ceram. Int.* 43, 693–703.
- Stevens, R., Evans, P., 1984. Transformation toughening by dispersed polycrystalline zirconia. *Trans. J. Br. Ceram. Soc.* 83, 28–31.
- Tang, D., Lim, H.-B., Lee, K.-J., Lee, C.-H., Cho, W.-S., 2012. Evaluation of mechanical reliability of zirconia-toughened alumina composites for dental implants. *Ceram. Int.* 38, 2429–2436.
- Taskonak, B., Yan, J., Mecholsky Jr., J.J., Sertgoz, A., Kocak, A., 2008. Fractographic analyses of zirconia-based fixed partial dentures. *Dent. Mater.* 24, 1077–1082.
- Tholey, M.J., Swain, M.V., Thiel, N., 2009. SEM observations of porcelain Y-TZP interface. *Dent. Mater.* 25, 857–862.
- Tong, H., Tanaka, C.B., Kaizer, M.R., Zhang, Y., 2016. Characterization of three commercial Y-TZP ceramics produced for their High-Translucency, High-Strength and High-Surface Area. *Ceram. Int.* 42, 1077–1085.
- Toraya, H., Yoshimura, M., Somya, S., 1984. Calibration curve for quantitative-analysis of the monoclinic-tetragonal ZrO₂ system by X-ray-diffraction. *J. Am. Ceram. Soc.* 67, C119–C121.
- Touaïher, I., Saïdaoui, M., Chevalier, J., Preiss, L., Reveron, H., 2018. Fracture behavior of Ce-TZP/alumina/aluminate composites with different amounts of transformation toughening. Influence of the testing methods. *J. Eur. Ceram. Soc.* 38, 1778–1789.
- Ueno, M., 2012. General Manager. Quality Assurance Corporate Division: Japan Medical Materials.
- Wang, J., Stevens, R., 1989. Zirconia-toughened alumina (ZTA) ceramics. *J. Mater. Sci.* 24, 3421–3440.
- Yang, S.W., Kim, J.E., Shin, Y., Shim, J.S., Kim, J.H., 2019. Enamel wear and aging of translucent zirconias: in vitro and clinical studies. *J. Prosthet. Dent.* 121, 417–425.
- Yang, H., Xu, Y.L., Hong, G., Yu, H., 2020. Effects of low-temperature degradation on the surface roughness of yttria-stabilized tetragonal zirconia polycrystal ceramics: a systematic review and meta-analysis. *J. Prosthet. Dent.*
- Zhang, Y., 2014. Making yttria-stabilized tetragonal zirconia translucent. *Dent. Mater.* 30, 1195–1203.
- Zhang, Y., Lawn, B.R., 2017. Novel zirconia materials in dentistry. *J. Dent. Res.* 22034517737483
- Zhang, Y., Lawn, B.R., 2018. Novel zirconia materials in dentistry. *J. Dent. Res.* 97, 140–147.
- Zhao, Y.J., Liao, L., Wang, Y., Lu, C., Zhang, J., Li, J., 2013a. Low temperature degradation of alumina toughened zirconia in artificial saliva. *W. J. Wuhan Univ. Technol.-Materials Sci. Ed.* 28, 844–848.
- Zhao, Y., Jiang, L., Liao, Y., Wang, C., Lu, J., Zhang, J., et al., 2013b. Low temperature degradation of alumina-toughened zirconia in artificial saliva. *J. Wuhan Univ. Technol.-Materials Sci. Ed.* 28, 844–848.