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Silica infiltration as a strategy to overcome zirconia degradation

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Abstract

The excellent clinical performance of yttria-partially stabilized zirconias (Y-SZs) makes them promising materials for indirect restorations. However, the Y-SZ phase stability is a concern, and infiltrating Y-SZs with a silica nanofilm may delay their degradation processes. In this study, we analyzed stabilities of silica-infiltrated zirconia surfaces after exposure to artificial aging (AA).

Four zirconia materials with different translucencies ($n=40$) were used, including low translucency 3 mol% Y-SZ (3Y-LT, Ceramill ZI, Amann Girschbach); high translucency 4 mol% Y-SZ (4Y-HT, Ceramill Zolid); and two high translucency 5 mol% Y-SZs (5Y-HT, Lava Esthetic, 3M and 5Y-SHT, Ceramill Zolid, FX white). Sintered specimens were exposed to 40 cycles of silica (SiO₂) through room temperature atomic layer deposition (RT-ALD) using tetramethoxysilane (TMOS) and ammonium hydroxide (NH₄OH). AA was applied for 15 h in an autoclave (134°C, 2 bar pressure). Stabilities of zirconia-silica surfaces were characterized in terms of hardness and Young's modulus using nanoindentation techniques and crystalline contents using x-ray diffraction (XRD) analyses. Silica deposition was also characterized by X-ray photoelectron spectroscopy (XPS).

There was a significant effect of the interaction of materials and surface treatments on the hardness and Young's modulus values of zirconia-silica surfaces ($p < 0.001$). Silica deposition on zirconia surfaces improved the material resistance to degradation by AA.

Keywords Degradation, Dental zirconia materials, Hardness, Modulus, Surface treatment

Introduction

Zirconia-based dental ceramics are promising materials in dentistry, medicine and engineering due to their tooth-like appearance, biocompatibility and excellent mechanical properties such as high strength, hardness, and wear resistance (Elnayef et al. 2017; Malkondu et al. 2016; Yoshinari 2020). The transformation-toughening mechanism of yttria-partially stabilized zirconia (Y-SZ) results in higher strength and toughness in comparison with other ceramic materials due to its inner capacity to delay crack propagation (Bethke et al. 2020; Hannink et al. 2000; Kohal et al. 2020). However, zirconia is a polycrystalline ceramic material that is temperature-dependent and can exist in three different forms: monoclinic (m), tetragonal (t), and cubic (c) (Chevalier et al. 2009). Crystalline stability is a concern since those forms are

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metastable when exposed to specific conditions such as stress and humidity.

Low temperature degradation (LTD) has been reported as an unavoidable process that happens when Y-SZ is exposed to localized stresses in the presence of humidity at low temperatures (Amaral et al. 2013; Ban et al. 2008; Kim et al. 2010; Lughy and Sergio 2010). The crystalline *t-m* transformation begins at localized spots. This transformation is associated with generalized granular volume increase. It leads to compressive stresses, inducing a cascade of events that lead to development of a surface and sub-surface *t-m* layer that affect the surface and bulk properties of Y-SZ by changing the surface roughness and reducing the overall strength of the material (De Souza et al. 2017; Flinn et al. 2017; Monzavi et al. 2020; Pinto et al. 2016). Our previous studies have indicated that nanospaces at grain boundaries may be used for the infiltration of materials (Alfrisyany et al. 2022; Bastos-Bitencourt et al. 2021) to minimize LTD of zirconia materials.

To increase the resistance of Y-SZ to LTD, a variety of techniques have been previously described (Aboushelib et al. 2009; Cakir-Omur et al. 2019; Hübsch et al. 2015; Kohorst et al. 2012; Nakamura et al. 2011), including the infiltration of zirconia with glass-ceramics and silica (SiO₂) film coating (Cakir-Omur et al. 2019; Chen et al. 2012). However, drawbacks have been reported for each technique, which limit their applicability (Devi 2013; Muñoz-Rojas et al. 2019; Zaera 2012). The use of silica physical vapor deposition (PVD) to zirconia surfaces has shown mixed results on Y-SZ degradation as a function of the level of finishing of the substrate (Cakir-Omur et al. 2019). For example, a previous study on the usage of PVD for coating zirconia materials with silica have showed no effect of silica coating on the LTD of the aged zirconia specimens. However, silica coating increased the resistance of ground zirconia to LTD and thus the *t-m* transformation was inhibited (Cakir-Omur et al. 2019).

Atomic layer deposition (ALD) is a form of chemical vapor deposition (CVD) to deposit inorganic thin films, commonly used for microelectronics fabrication. It has also been used for the infiltration of nano-scale thin films in a wide range of fields (Bakke et al. 2011; Bishop 2011; Leskelä and Ritala 2002; Meng et al. 2012). The technique depends on self-limiting vapor-solid reactive precursors (Xie et al. 2014), and enables the deposition of a series of nano-scale thin layers of oxides with controlled thicknesses on different substrates such as polycrystalline and amorphous materials (Ferguson et al. 2000; Ritala et al. 1997, 1993). However, ALD presents some limitations, such as restricted options for the chemical precursors that can be used, and the necessity of vacuum conditions (Devi 2013; Muñoz-Rojas et al. 2019; Zaera 2012). Further, ALD precursors are required to be highly

reactive and robust enough to avoid thermal decomposition (Devi 2013; Zaera 2012). Meanwhile, ALD requires a vacuum condition, demanding specialized equipment and increasing its operational costs (Muñoz-Rojas et al. 2019). Thus, the understanding of the usage of ALD for the deposition of SiO₂ thin films on dental zirconia is very limited, so this adds a gap in the knowledge of the applicability of this technique to dental materials (Yan et al., 2021).

Room temperature atomic layer deposition (RT-ALD) is an alternative technique that enables the deposition of silica (SiO₂) thin films on zirconia substrates (Bastos-Bitencourt et al. 2021), by the sequential exposure of specimens to tetramethoxysilane (TMOS) and ammonium hydroxide (NH₄OH) (Hatton et al. 2010; Klaus and George 2000; Klaus et al. 1997). With this process, thin layers of silica films have been previously deposited at rates of 4–5 nm per cycle at room temperature and ambient conditions (Hatton et al. 2010). In a previous study, the infiltration of 3Y-SZ with silica was demonstrated in a depth of approximately 900 nm when the *t-m* microcracked layer was developed by controlled hydrothermal treatment (Alfrisyany et al. 2022). However, the effect of silica nano-oxide deposition via RT-ALD on the degradation resistance of zirconia-based materials remains unknown. Therefore, this study aimed to analyze stabilities of hybrid silica-zirconia surfaces after exposure to artificial aging. Hydrothermal treatment (HTT) was used prior to RT-ALD as a way to develop a *t-m* microcracked layer to develop nanospaces to be infiltrated by the silica vapor. The null hypotheses to be tested were (1) Silica deposition/infiltration has no effect on the crystalline stability or the surface mechanical properties of zirconia-based materials; and (2) Zirconia composition has no effect on the crystalline stability or the surface mechanical properties of zirconia-based materials.

Materials and methods

Experimental groups

Dental zirconia materials with different translucencies were used (Table 1). Specimens were sintered following the manufacturers' recommendations, obtaining the final dimensions of 14 mm × 4 mm × 2 mm (±0.2 mm) (*n*=10 per group/material). Specimens were ground and wet-polished and then heat-treated in a laboratory chamber furnace (CWF1300, Carbolite, Hope valley, UK) to remove any compressive strains generated by the polishing procedure (Ho et al. 2009). The annealing cycle commenced the heating of the specimens at a heating rate of 5 °C/min to 1200 °C, holding the temperature for 2 h, then cooling at a cooling rate of 1 °C/min to room temperature. Specimens from each material were then randomly distributed into six experimental groups to

Table 1 Characteristics of zirconia-based materials

Material description/Batch number	Composition (wt. %)				
	ZrO ₂ + HfO ₂ + Y ₂ O ₃	Y ₂ O ₃	HfO ₂	Al ₂ O ₃	Other oxides
Ceramill Zi-low translucency, Amann Girrbach (3Y-LT) LOT#1807000	≥ 99.0	4.5–5.6	≤ 5	≤ 0.5	≤ 1
Ceramill Zolid, Amann Girrbach, (4Y-HT) LOT#1806002	≥ 99.0	6.7–7.2	≤ 5	≤ 0.5	≤ 1
Lava Esthetic Fluorescent, 3M ESPE (5Y-HT) LOT#3584272	≥ 99.0	9	≤ 5	≤ 0.1	≤ 1
Ceramill Zolid fx, Amann Girrbach (5Y-SHT) LOT#1701000	≥ 99.0	9.15–9.55	≤ 5	≤ 0.5	≤ 1

ZrO₂ Zirconium dioxide, HfO₂ Hafnium dioxide, Y₂O₃ Yttrium oxide, Al₂O₃ Aluminium oxide

undergo surface treatment and artificial aging processes (Table 2). Untreated groups as control (C) specimens were stored in deionized water (~22 °C) until analyses were performed.

Hydrothermal treatment (HTT)

To expedite the development of a transformed (microcracked) layer in a zirconia surface, specimens were placed in autoclave (Mid Mark M9—Ultraclave, Midmark, Versailles, OH, USA) following the International Organization for Standardization (ISO) protocol (ISO-13356, 2015) at 134 °C and 2 bar pressure for 15 h. HTT parameters were based on the findings of previous studies that characterized properties of the *t-m* transformed layer (Alfrisany and De Souza 2022; Pereira et al. 2015; Xiao et al. 2012).

Silica (SiO₂) deposition (RT-ALD)

To improve the wettability of zirconia, a thin layer of a silane-based primer of 3-trimethoxysilylpropylmethacrylate (MPS, RelyX ceramic primer, 3M ESPE—Saint Paul, MN, USA) was applied to a zirconia surface with a micro brush and air-dried (Lima et al. 2019). Silica

deposition using RT-ALD was carried out in a fume hood at room temperature. Specimens were placed on a metallic mesh that was elevated over conical centrifuge tubes containing either tetramethoxysilane orthosilicate (TMOS-Sigma-Aldrich, 98%) or ammonium hydroxide (NH₄OH-Sigma-Aldrich, 30 wt. % solution) for 1 min and 10 min, respectively (Hatton et al. 2010). To ensure full coverage of the Y-SZ substrate with silica, 40 cycles were applied.

Artificial aging (AA)

To investigate the effect of silica deposition on the resistance of zirconia to degradation during aging, an accelerated artificial aging (AA) was performed by applying a second HTT procedure, following the ISO protocol (ISO-13356, 2015) for 15 h, as previously described.

Nanoindentation

Nanoindentation was carried out on the zirconia specimens to evaluate their hardness and Young's modulus. Prior to the indentation testing, all specimens were cleaned in acetone in an ultrasonic bath for 10 min and thoroughly dried in air. Using a progressive loading

Table 2 Experimental groups according to surface treatment

Experimental groups	Surface treatment
Control (C)	No surface treatment
Hydrothermal treatment (HTT)	Hydrothermal treatment in autoclave for 15h at 134 °C, 2 bars
Room temperature atomic layer deposition (RT-ALD)	Silica deposition using subsequent vapor exposure to tetramethoxysilane orthosilicate (TMOS) (1 min) and ammonium hydroxide (NH ₄ OH) (10 min) for 40 cycles
Hydrothermal treatment (HTT) + RT-ALD (HTT-RT-ALD)	HTT was applied followed by silica deposition by RT-ALD
RT-ALD + Artificial aging (AA) (RT-ALD-AA)	RT-ALD treated specimens (RT-ALD) were exposed to AA for 15 h using the same HTT parameters previously described
HTT + RT-ALD + AA	15 h of AA was applied on HTT-RT-ALD specimens

and partial unloading multicycle mode, a nanoindenter (NHT³—Anton Paar GmbH, Austria) equipped with a 50 nm radius Berkovich diamond tip was used to perform 35 indentations on each specimen with a distance of 20 μm between indentations. The maximum load of 100 mN, a penetration depth of 800 nm, and a loading/unloading rate of 200 mN/min were applied. The hardness and Young's modulus values were calculated according to the maximum load and the maximum penetration depth using the Oliver and Pharr method (Oliver and Pharr 1992).

Crystalline phase quantification

Crystalline phase compositions of specimens were analyzed using x-ray diffraction (XRD). The XRD patterns were collected with a diffractometer (Bruker D8 DISCOVER with DAVINCI design) equipped with a cobalt sealed tube source (λ avg = 1.79026 Å) and an area detector (Vantec 500, MiKroGap—TM technology). Three frame exposures of 900 s/frame and detector distance of 20 cm were collected between 20–80° diffraction angles. 2D frames were also collected using software (Version 7.5, DIFFRAC.Measurement Centre) and integrated to 1D ones using software (Version 5.2, DIFFRAC.EVA) and displayed and analyzed using Topas software (Version 5, Bruker AXS). The quantitative analysis was performed using the whole pattern fitting approach with the Rietveld method (Young 1993).

X-ray photoelectron spectroscopy (XPS) analysis

3Y-LT and 5Y-HT specimens were analyzed using X-ray photoelectron spectroscopy (XPS, Escalab 250Xi Thermo Fisher Scientific—E. Grinstead, UK) to characterize their outermost Y-SZ surface compositions as a result of RT-ALD. All data was processed using the software supplied with the system (Avantage 5.957). Relative atomic percentage (Rel. At. %) compositions were obtained from individual region spectra by subtracting a modified Shirley-type background (designated "Smart" in the software) and applying the supplied sensitivity factors (Shirley 1972). For very weak peaks, a linear background was used.

Hardness and Young's modulus data analyses

The hardness and Young's modulus results were calculated to obtain their mean and standard deviation values for each experimental group. Two-way analysis of variance (ANOVA) and Tukey Honest Significance Difference (HSD) at 5% significant level ($p=0.05$) were used to determine the effects of materials and surface treatments on the surface hardness and Young's modulus. The independent factors were zirconia compositions (four levels) and surface treatments (six levels). In the case of a

significant interaction effect, one way ANOVA and Tukey HSD tests at 5% significant level ($p=0.05$) were used for post hoc comparisons. When the test of homogeneity of variances was significant in Young's modulus, Games-Howell test at 5% significant level ($p=0.05$) was used for post-hoc comparisons.

Results

Surface hardness and Young's modulus

The results of the two-way ANOVA indicated a significant interaction effect (material and surface treatment) on zirconia surface hardness ($p<0.001$) (Fig. 1). For 3Y-LT, the control group specimens were significantly harder than all other groups, except RT-ALD treated specimens, which are as hard as the control group. Artificial aging significantly decreased hardness values for 3Y-LT and did not affect those for HTT and HTT-RT-ALD groups. For 4Y-HT, the control, and HTT, RT-ALD-AA, and HTT-RT-ALD-AA treated groups had similar hardness, which are significantly higher than RT-ALD and HTT-RT-ALD treated groups ($p\leq0.05$). For 5Y-HT and 5Y-SHT materials, all hardness values were not significantly affected by the different treatment ($p>0.05$).

There was a significant interaction effect (material and surface treatment) ($p<0.001$) on zirconia Young's modulus (Fig. 2). The highest Young's modulus of 241.98 ± 9.00 GPa were measured for 5Y-SHT after RT-ALD while the lowest values of 175.95 ± 5.78 GPa were found for 3Y-LT zirconia after HTT. The moduli of artificially aged 3Y-LT showed a significant decrease when compared to the control and RT-ALD groups, but they were comparable to HTT and HTT-RT-ALD groups.

Crystalline phase quantification

The Rietveld quantification of XRD analysis showed no or a small amount of monoclinic phase, less than 5 vol %, in all control groups tested (Fig. 3). The HTT treatment resulted in an increase in the *m* content by 68.6 vol % in 3Y-LT specimens, which is higher than 58.7 vol % processed by RT-ALD-AA but lower than 78.1 vol % treated by HTT-RT-ALD-AA. As expected, all groups of high translucency zirconia materials (4Y-HT, 5Y-HT, and 5Y-SHT) had higher crystalline stabilities than 3Y-LT, regardless of the surface treatment employed.

XPS

The XPS analysis showed an example of effective silica depositions on both 3Y-LT and 5Y-HT processed (Fig. 4), both revealing an increase in Si content and a decrease in Zr content after RT-ALD. For 3Y-LT, the atomic ratios of Si in RT-ALD groups were higher than those of the groups with and without previous HTT exposure (e.g., 30.9 vol % for HTT-RT-ALD versus 29.6 vol

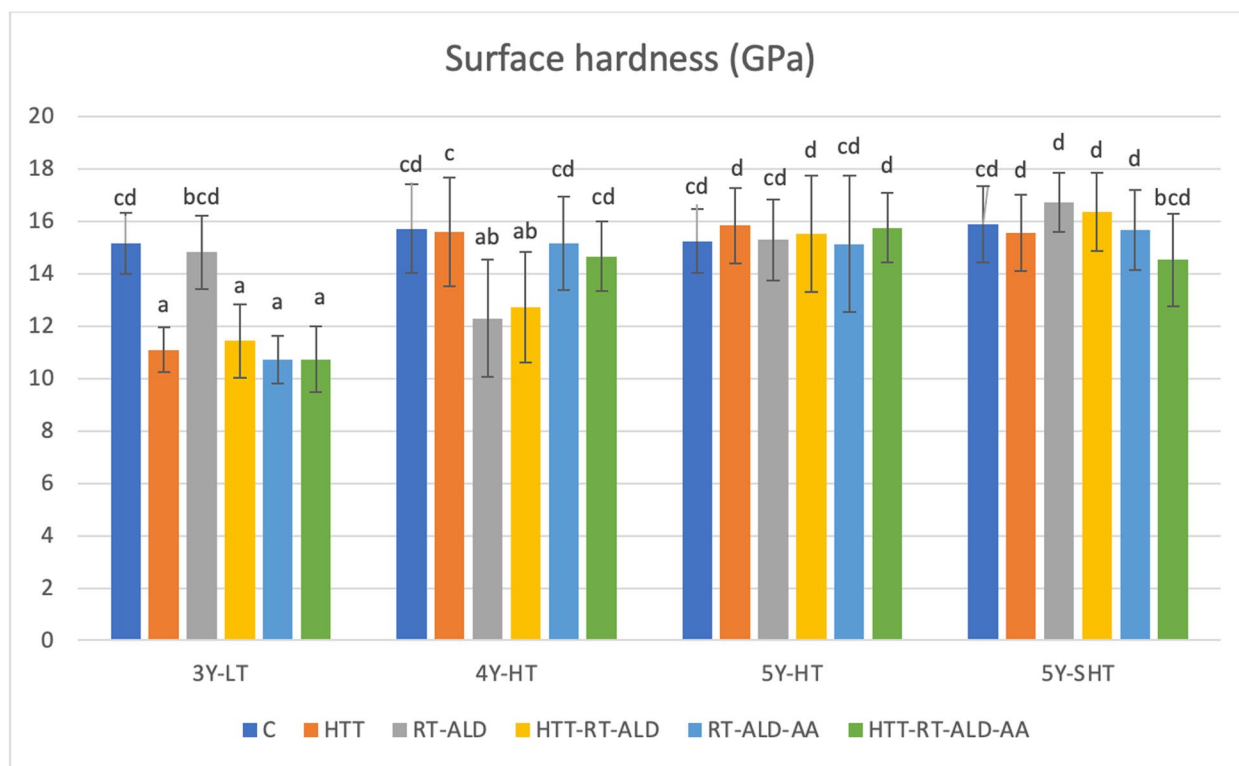


Fig. 1 Surface hardness of zirconia as a function of the interaction (material and treatment). *Dissimilar letters indicate significant differences ($p < 0.001$)

% for RT-ALD groups). A decrease in silica content was observed as a result of artificial aging (AA), with higher residual amounts being detected for HTT-treated specimens (HTT-RT-ALD-AA group with 12.9 vol %). 5Y-HT also showed an increase in silica on the surface with a decrease in Zr atomic ratio after RT-ALD exposure. Artificial aging resulted in a decrease in the silica content on the surface of RT-ALD groups. Surprisingly, HTT-RT-ALD group of 5Y-HT material showed an increase in silica content after AA.

Discussion

In the present study, the stability of zirconia materials exposed to silica via RT-ALD was examined through accelerated artificial aging in autoclave. The 15 h duration of the artificial aging applied was based on previous investigations of the mechanical and bulk properties of zirconia materials, as well as preliminary data on depths of *t-m* transformed zones (Alfrisany and De Souza 2022; Pereira et al. 2015; Xiao et al. 2012). The International Organization for Standardization (ISO) defines that hydrothermal aging for 5 h in autoclave at 134 °C (ISO-13356, 2015) resulting in no more than 25 vol % of *m* phase in zirconia is considered appropriate for biomedical use (ISO-13356, 2015; Siarampi et al. 2014). However,

accelerated aging standards are currently missing to evaluate the stability of zirconia-based materials in dental application, in spite of various studies reporting significant changes in zirconia crystalline structure as a consequence of hydrothermal aging (Alfrisany and De Souza 2022; Chevalier et al. 1999, 2007; de Araújo-Júnior et al. 2020; Deville et al. 2005; Hajhamid et al. 2022; Kelesi et al. 2020; Kobayashi et al. 1981).

In this study, the stability of RT-ALD treated zirconia substrates was characterized by the surface hardness, Young's modulus, crystalline compositions and surface chemical compositions. The measured hardness and Young's modulus values were similar to those reported in previous studies (Alfrisany and De Souza 2022; Cattani-Lorente et al. 2014; Gaillard et al. 2008). There was a significant interaction effect of material and surface treatment on hardness. For instance, without RT-ALD, HTT only affected the hardness of low translucency 3Y-LT. The detrimental impact of HTT on the properties of 3Y-LT may be associated with the development of microcracks and the higher monoclinic phase content confirmed by the XRD crystalline distribution (Fig. 3). This is in agreement with studies previously published (De Souza et al. 2017; Monzavi et al. 2020). The increased monoclinic content deteriorates the surface roughness and

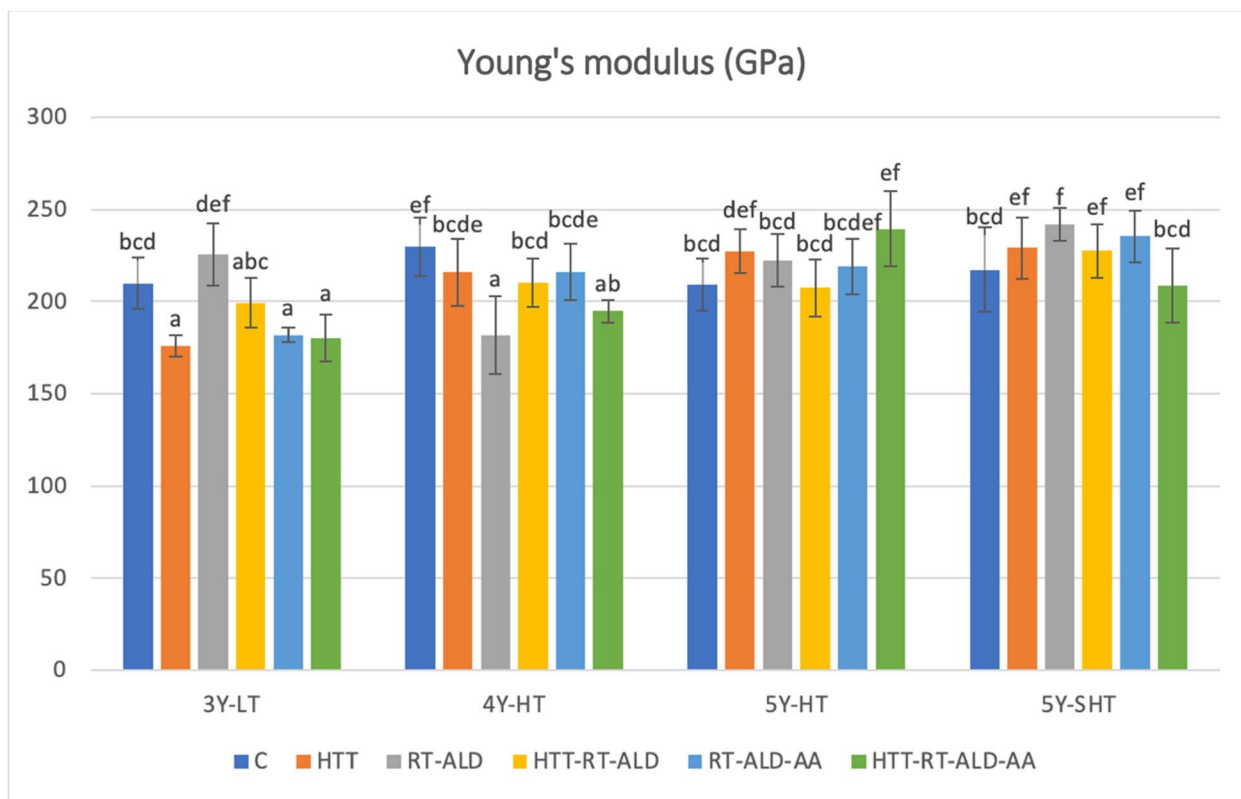


Fig. 2 Zirconia's Young's modulus as a function of the interaction (material and treatment). *Dissimilar letters indicate significant differences ($p < 0.001$)

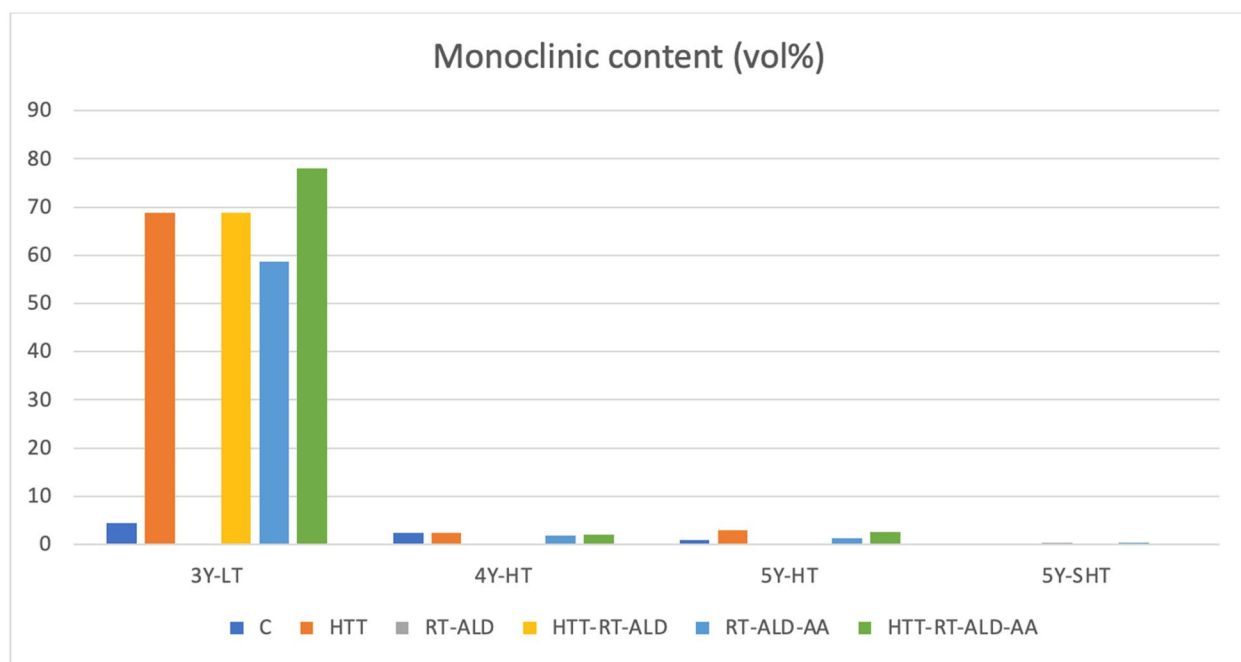


Fig. 3 Quantitative analysis of zirconia monoclinic phase (*m*-vol%) according to XRD results

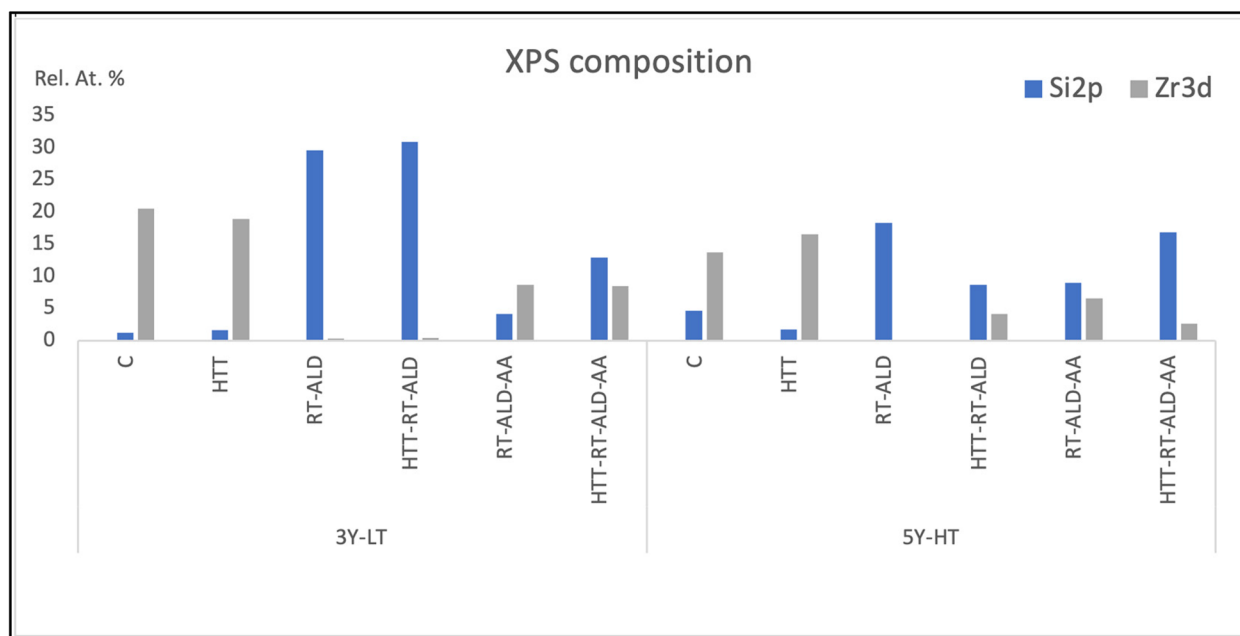


Fig. 4 Relative composition (Rel. At. %) of silica to zirconia as a function of treatment applied as taken from the XPS spectra

compromises its mechanical properties (Aldegeishem et al. 2015; Borchers et al. 2010; Cattani-Lorente et al. 2011; De Souza et al. 2017; Gaillard et al. 2008; Monzavi et al. 2020). When artificial aging was applied, surface hardness of RT-ALD treated 3Y-LT specimens decreased in comparison to the non-aged control groups. However, when 3Y-LT was hydrothermally treated and silica deposition was applied (HTT-RT-ALD), a stable performance of the material was observed, since the hardness was not significantly affected by artificial aging (HTT-RT-ALD-AA). This effect is possibly associated with the infiltration of silica into the *t-m* transformed layer of zirconia, sealing and protecting it against further microcrack-induced degradation by artificial aging. It is hypothesized that silica nanofilm may have surrounded some tetragonal crystals to prevent further degradation.

HTT negatively affected the Young's modulus of untreated 3Y-LT (Fig. 2), which may be attributed to the increased monoclinic content after HTT and the development of surface microcracks as a result of surface crystalline changes (Matsui et al. 1986). Studies have reported the decreases of approximately 30% in Young's moduli for 3Y-SZ materials, depending on the temperatures and the durations of artificial aging processes (Cattani-Lorente et al. 2011; Chowdhury et al. 2007; Ramesh et al. 2018). As *t-m* transformation starts from the surface and progresses into the bulk of the material (Chevalier et al. 2007), a constant increase in the *m* phase was expected. However, the progress of *t-m* transformation in this study could not be detected due to the limitations of the X-ray

diffraction technique applied. When RT-ALD treated 3Y-LT specimens were exposed to artificial aging without prior HTT (RT-ALD-AA), the Young's modulus values were also negatively affected. Similar to the hardness results, when 3Y-LT specimens were exposed to HTT followed by RT-ALD (HTT-RT-ALD), the subsequent artificial aging (HTT-RT-ALD-AA) did not significantly affect the Young's modulus. The successful silica infiltration to transformed zirconia layers may have helped to maintain the surface Young's modulus. Nonetheless, the penetration depths of the nanoindentation test were set to be approximately 800 nm, which might have exceeded the thicknesses of silica deposition layers tested. Based on a previous investigation (Alfrisany et al. 2022), the silica deposition depths range from 10 to 1300 nm depending on zirconia composition and the presence or the absence of the *t-m* transformed layer. This might influence the nanoindentation data obtained in the current study, and a further investigation of the actual silica layer thicknesses will be conducted in the future.

All high translucency materials were relatively stable (Fig. 3), revealing less than 5 vol % of monoclinic phase after all of the surface treatments assessed. Only 3Y-LT group had noticeable changes in the *m* contents due to both HTT and AA. The former resulted in 68.8 vol % *m* content in 3Y-LT. When the specimens were treated with RT-ALD and exposed to artificial aging, the *m* content reduced to 58.7 vol %, indicating that RT-ALD exerted some protective effect over the degradation. However, when the specimens were exposed to hydrothermal

treatment, silica deposition, and artificial aging (HTT-RT-ALD-AA), a higher *m* content of 78.1 vol % was measured. The explanation for the slower progression of the *t-m* transformation may be twofold: either the silica film exerted a protective effect or the crystalline changes had reached a point where the transformation rate reduced with the silica deposition depth due to the protective effect on the transformed layer.

As expected, silica contents were increased in both 3Y-LT and 5Y-HT materials investigated (Fig. 4) after RT-ALD. However, the amount of silica deposited on 5Y-HT was noticeably lower than on 3Y-LT, especially for the hydrothermally treated specimens. This could be explained by the differences in the crystalline structure/orientation of the two materials. As previously mentioned, *t-m* transformation is associated with the creation of a layer that is porous and microcracked to enable the penetration of the silica vapor. Upon artificial aging, the amounts of silica deposited on 3Y-LT zirconia surfaces were greatly reduced compared to the non-aged RT-ALD treated specimens. This is consistent with the further penetration of silica into the bulk material, making it difficult to be detected by XPS.

Based on the findings of the current study, the first null hypothesis was rejected. This means that silica deposition does affect the crystalline stability and surface mechanical properties of zirconia-based materials. After artificial aging, RT-ALD treated 3Y-LT specimens showed a lower *t-m* transformation rate than non-RT-ALD-treated specimens, which might indicate improved resistance to degradation. Besides, none of the high translucency materials showed changes on *t-m* transformation rate as a result of RT-ALD. The second null hypothesis was also rejected. This indicates that zirconia composition does affect its crystalline stability and surface mechanical properties because zirconia materials with different compositions showed differences in *m* content after aging.

In this study, silica nanofilm depositions on different dental zirconia materials via RT-ALD were investigated regardless of the ability of the materials to undergo *t-m* transformations after hydrothermal aging. The thicknesses of silica films deposited on the materials were not yet characterized and will be measured in the future studies. It is worth mentioning that the challenges present in the oral environment, such as mastication forces and temperature variations, can be even more detrimental to the crystalline stability of zirconia materials (Pinto et al. 2016) and were not reproduced in the current study. Lastly, regarding the apparent slower degradation in 3Y-LT, this study sheds light on a feasible technique for the production of functionally graded zirconia materials, which has been long needed in many areas of industry and medicine.

Conclusion

Based on the current study, the following conclusions can be drawn as follows:

1. The interaction of zirconia composition and surface treatment affected the hardness and Young's modulus of treated zirconia materials.
2. Low translucency zirconia showed a tendency to be affected by surface treatment in terms of the hardness and Young's modulus values but all high translucency zirconia materials did not.
3. The Young's modulus values of all RT-ALD treated zirconia-based materials were significantly affected by artificial aging (AA), particularly significantly decreased for 3Y-LT (without HTT) and 5Y-SHT (with HTT), and increased for 4Y-HT and 5Y-HT groups.
4. RT-ALD treated 3Y-LT group without HTT were more resistant to prolonged degradation by AA than the specimens not treated by RT-ALD.

Clinical relevance

In spite of their outstanding mechanical properties, yttria-stabilized zirconia materials are unstable and can undergo hydrothermal degradation when exposed to oral challenges such as humidity and mastication. The results of this study showed that with controlled crystalline changes and silica infiltration, zirconia-based materials can be more stable and predictable for dental applications.

Abbreviations

Y-SZs	Yttria-partially stabilized zirconias
AA	Artificial aging
3Y-LT	Low translucency 3 mol% yttria-partially stabilized zirconia
4Y-HT	High translucency 4 mol% yttria-partially stabilized zirconia
5Y-HT	5 Mol% yttria-partially stabilized zirconia
5Y-SHT	Super high translucency 5 mol% yttria-partially stabilized zirconia
RT-ALD	Room temperature atomic layer deposition
XRD	X-ray diffraction
XPS	X-ray photoelectron spectroscopy
LTD	Low temperature degradation
t	Tetragonal grains
m	Monoclinic grains
t-m)	Tetragonal to monoclinic transformation
PVD	Silica physical vapor deposition
ALD	Atomic layer deposition
CVD	Chemical vapor deposition
HTT	Hydrothermal treatment

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Authors' contributions

Najm Alfrisyany: Conceptualization, methodology, data curation, writing/original draft preparation, formal analysis, investigation, resources, funding acquisition and writing reviewing/editing. Eszter Somogyi-Ganss: Conceptualization and writing reviewing/editing. Laura Tam: Conceptualization and writing reviewing/editing. Benjamin Hatton: Conceptualization, methodology, and writing reviewing/editing. Rana Sodhi, Investigation, data curation, and writing reviewing/editing. Ling Yin; Validation and writing reviewing/editing. Grace De Souza: Conceptualization, investigation, methodology, data curation, supervision, validation, writing reviewing/editing, funding acquisition and project administration.

Availability of data and materials

The date of the current study will be made available from the corresponding author on reasonable request.

Declarations

Competing interests

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

- Aboushelib MN, Feilzer AJ, Kleverlaan CJ (2009) Bridging the gap between clinical failure and laboratory fracture strength tests using a fractographic approach. *Dent Mater* 25:383–391. <https://doi.org/10.1016/j.dental.2008.09.001>
- Aldegheshem A, Alfaer A, Brezavscek M, Vach K, Eliades G, Att W (2015) Wear behavior of zirconia substrates against different antagonist materials. *Int J Esthet Dent* 10:468–485
- Alfrisyany NM, De Souza GM (2022) Surface and bulk properties of zirconia as a function of composition and aging. *J Mech Behav Biomed Mater* 126:104994. <https://doi.org/10.1016/j.jmbbm.2021.104994>
- Alfrisyany NM, Somogyi-Ganss E, Tam L, Hatton BD, Sodhi RNS, De Souza GM (2022) Room-temperature atomic layer deposition of SiO₂ on microcracked ZrO₂ layers. *J Mech Behav Biomed Mater* 134:105410. <https://doi.org/10.1016/j.jmbbm.2022.105410>
- Amaral M, Valandro LF, Bottino MA, Souza RO (2013) Low-temperature degradation of a Y-TZP ceramic after surface treatments. *J Biomed Mater Res B Appl Biomater* 101:1387–1392. <https://doi.org/10.1002/jbm.b.32957>
- Bakke JR, Pickrahn KL, Brennan TP, Bent SF (2011) Nanoengineering and interfacial engineering of photovoltaics by atomic layer deposition. *Nanoscale* 3:3482–3508. <https://doi.org/10.1039/C1NR10349K>
- Ban S, Sato H, Suehiro Y, Nakanishi H, Nawa M (2008) Biaxial flexure strength and low temperature degradation of Ce-TZP/Al₂O₃ nanocomposite and Y-TZP as dental restoratives. *J Biomed Mater Res B Appl Biomater* 87:492–498. <https://doi.org/10.1002/jbm.b.31131>
- Bastos-Bitencourt NA, Soares Bombonatti JF, Bitencourt SB, Hatton BD, De Souza GM (2021) Mechanical performance of a hybrid zirconia developed through hydrothermal treatment and Room-Temperature Atomic Layer Deposition (RT-ALD). *J Mech Behav Biomed Mater* 123:104783. <https://doi.org/10.1016/j.jmbbm.2021.104783>
- Bethke A, Pieralli S, Kohal RJ, Burkhardt F, von Stein-Launsitz M, Vach K, Spies BC (2020) Fracture resistance of zirconia oral implants in vitro: a systematic review and meta-analysis. *Materials (Basel, Switzerland)* 13. <https://doi.org/10.3390/ma13030562>
- Bishop CA (2011) 19 - Atomic Layer Deposition, in: Bishop, C.A. (Ed.), *Vacuum Deposition onto Webs, Films and Foils* (Second Edition). William Andrew Publishing, Oxford, pp. 331–336. <https://doi.org/10.1016/B978-1-4377-7867-0.00019-2>
- Borchers L, Stiesch M, Bach FW, Buhl JC, Hubsch C, Kellner T, Kohorst P, Jendras M (2010) Influence of hydrothermal and mechanical conditions on the strength of zirconia. *Acta Biomater* 6:4547–4552. <https://doi.org/10.1016/j.actbio.2010.07.025>
- Cakir-Omur T, Gozneli R, Ozkan Y (2019) Effects of silica coating by physical vapor deposition and repeated firing on the low-temperature degradation and flexural strength of a Zirconia Ceramic. *J Prosthodont* 28:e186–e194. <https://doi.org/10.1111/jopr.12618>
- Cattani-Lorente M, Scherrer SS, Ammann P, Jobin M, Wiskott HW (2011) Low temperature degradation of a Y-TZP dental ceramic. *Acta Biomater* 7:858–865. <https://doi.org/10.1016/j.actbio.2010.09.020>
- Cattani-Lorente M, Scherrer S, Durual S, Sanon C, Douillard T, Gremillard L, Chevalier J, Wiskott A (2014) Effect of different surface treatments on the hydrothermal degradation of a 3Y-TZP ceramic for dental implants. *Dent Mater* 30:1136–1146. <https://doi.org/10.1016/j.dental.2014.07.004>
- Chen C, Kleverlaan CJ, Feilzer AJ (2012) Effect of an experimental zirconia-silica coating technique on micro tensile bond strength of zirconia in different priming conditions. *Dent Mater* 28:e127–e134. <https://doi.org/10.1016/j.dental.2012.04.020>
- Chevalier J, Cales B, Drouin JM (1999) Low-temperature aging of Y-TZP ceramics. *J Am Ceram Soc* 82:2150–2154. <https://doi.org/10.1111/j.1151-2916.1999.tb02055.x>
- Chevalier J, Gremillard L, Deville S (2007) Low-temperature degradation of zirconia and implications for biomedical implants. *Annu Rev Mater Res* 37:1–32. <https://doi.org/10.1146/annurev.matsci.37.052506.084250>
- Chevalier J, Gremillard L, Virkar AV, Clarke DR (2009) The tetragonal-monoclinic transformation in zirconia: lessons learned and future trends. *J Am Ceram Soc* 92:1901–1920. <https://doi.org/10.1111/j.1551-2916.2009.03278.x>
- Chowdhury S, Vohra YK, Lemons JE, Ueno M, Ikeda J (2007) Accelerating aging of zirconia femoral head implants: Change of surface structure and mechanical properties. *J Biomed Mater Res B Appl Biomater* 81B:486–492. <https://doi.org/10.1002/jbm.b.30688>
- de Araújo-Júnior ENS, Bergamo ETP, Campos TMB, Benalcázar Jalkh EB, Lopes ACO, Monteiro KN, Cesar PF, Tognolo FC, Tanaka R, Bonfante EA (2020) Hydrothermal degradation methods affect the properties and phase transformation depth of translucent zirconia. *J Mech Behav Biomed Mater* 112:104021. <https://doi.org/10.1016/j.jmbbm.2020.104021>
- De Souza GM, Zykyus A, Ghahnavyeh RR, Lawrence SK, Bahr DF (2017) Effect of accelerated aging on dental zirconia-based materials. *J Mech Behav Biomed Mater* 65:256–263. <https://doi.org/10.1016/j.jmbbm.2016.08.023>
- Devi A (2013) 'Old Chemistries' for new applications: Perspectives for development of precursors for MOCVD and ALD applications. *Coord Chem Rev* 257:3332–3384. <https://doi.org/10.1016/j.ccr.2013.07.025>
- Deville S, Gremillard L, Chevalier J, Fantozzi G (2005) A critical comparison of methods for the determination of the aging sensitivity in biomedical grade yttria-stabilized zirconia. *J Biomed Mater Res B Appl Biomater* 72:239–245. <https://doi.org/10.1002/jbm.b.30123>
- Elnayef B, Lázaro A, Suárez-López Del Amo F, Galindo-Moreno P, Wang HL, Gargallo-Albiol J, Hernández-Alfaro F (2017) Zirconia Implants as an Alternative to Titanium: a systematic review and meta-analysis. *Int J Oral Maxillofac Implants* 32:e125–e134. <https://doi.org/10.11607/jomi.5223>
- Ferguson JD, Weimer AW, George SM (2000) Atomic layer deposition of SiO₂ Films on BN Particles using sequential surface reactions. *Chem Mater* 12:3472–3480. <https://doi.org/10.1021/cm000313t>
- Flinn BD, Raigrodski AJ, Mancl LA, Toivola R, Kuykendall T (2017) Influence of aging on flexural strength of translucent zirconia for monolithic restorations. *J Prosthet Dent* 117:303–309. <https://doi.org/10.1016/j.prosdent.2016.06.010>
- Gaillard Y, Jiménez-Piqué E, Soldera F, Mücklich F, Anglada M (2008) Quantification of hydrothermal degradation in zirconia by nanoindentation. *Acta Mater* 56:4206–4216. <https://doi.org/10.1016/j.actamat.2008.04.050>
- Hajhamid B, Alfrisyany N, Somogyi-Ganss E (2022) The effect of accelerated aging on crystalline structures and optical properties of different monolithic zirconia: a qualitative systematic review. *Dent Mater* 38:569–586. <https://doi.org/10.1016/j.dental.2022.02.005>
- Hannink RH, Kelly PM, Muddle BC (2000) Transformation toughening in zirconia-containing ceramics. *J Am Ceram Soc* 83:461–487. <https://doi.org/10.1111/j.1151-2916.2000.tb01221.x>

- Hatton B, Kitaev V, Perovic D, Ozin G, Aizenberg J (2010) Low-temperature synthesis of nanoscale silica multilayers—atomic layer deposition in a test tube. *J Mater Chem* 20:6009–6013. <https://doi.org/10.1039/C0JM00696C>
- Ho C-J, Liu H-C, Tuan W-H (2009) Effect of abrasive grinding on the strength of Y-TZP. *J Eur Ceram Soc* 29:2665–2669. <https://doi.org/10.1016/j.jeurceramsoc.2009.02.011>
- Hübsch C, Dellinger P, Maier HJ, Stemme F, Bruns M, Stiesch M, Borchers L (2015) Protection of yttria-stabilized zirconia for dental applications by oxidic PVD coating. *Acta Biomater* 11:488–493. <https://doi.org/10.1016/j.actbio.2014.09.042>
- ISO-13356, 2015. International Organization for Standardization (ISO), 13356:2015-Implants for Surgery-Ceramic Materials Based on Yttria-Stabilized Tetragonal Zirconia (Y-TZP)
- Kelesi M, Kontonasaki E, Kantiranis N, Papadopoulou L, Zorba T, Paraskevopoulos KM, Koidis P (2020) The effect of different aging protocols on the flexural strength and phase transformations of two monolithic zirconia ceramics. *J Appl Biomater Funct Mater* 18:2280800020982677. <https://doi.org/10.1177/2280800020982677>
- Kim JW, Covell NS, Guess PC, Rewok ED, Zhang Y (2010) Concerns of hydrothermal degradation in CAD/CAM zirconia. *J Dent Res* 89:91–95. <https://doi.org/10.1177/0022034509354193>
- Klaus J, George S (2000) SiO₂ Chemical Vapor Deposition at Room Temperature Using SiCl₄ and H₂O with an NH₃ Catalyst. *J Electrochem Soc* 147:2658. <https://doi.org/10.1149/1.1393586>
- Klaus JW, Sneh O, George SM (1997) Growth of SiO₂ at room temperature with the use of catalyzed sequential half-reactions. *Science* 278:1934–1936. <https://doi.org/10.1126/science.278.5345.1934>
- Kobayashi K, Kuwajima H, Masaki T (1981) Phase change and mechanical properties of ZrO₂-Y₂O₃ solid electrolyte after ageing. *Solid State Ion* 3:489–493. [https://doi.org/10.1016/0167-2738\(81\)90138-7](https://doi.org/10.1016/0167-2738(81)90138-7)
- Kohal RJ, Spies BC, Vach K, Balmer M, Pieralli S (2020) A prospective clinical cohort investigation on zirconia implants: 5-year results. *J Clin Med* 9. <https://doi.org/10.3390/jcm9082585>
- Kohorst P, Borchers L, Strempe J, Stiesch M, Hassel T, Bach FW, Hübsch C (2012) Low-temperature degradation of different zirconia ceramics for dental applications. *Acta Biomater* 8:1213–1220. <https://doi.org/10.1016/j.actbio.2011.11.016>
- Leskelä M, Ritala M (2002) Atomic layer deposition (ALD): from precursors to thin film structures. *Thin Solid Films* 409:138–146. [https://doi.org/10.1016/S0040-6090\(02\)00117-7](https://doi.org/10.1016/S0040-6090(02)00117-7)
- Lima RBW, Barreto SC, Alfrisyany NM, Porto TS, De Souza GM, De Goes MF (2019) Effect of silane and MDP-based primers on physico-chemical properties of zirconia and its bond strength to resin cement. *Dent Mater* 35:1557–1567
- Lughi V, Sergio V (2010) Low temperature degradation-aging-of zirconia: a critical review of the relevant aspects in dentistry. *Dent Mater* 26:807–820. <https://doi.org/10.1016/j.dental.2010.04.006>
- Malkondu Ö, Tinastepe N, Akan E, Kazazoğlu E (2016) An overview of monolithic zirconia in dentistry. *Biotechnol Biotechnol Equip* 30:644–652. <https://doi.org/10.1080/13102818.2016.1177470>
- Matsui M, Soma T, Oda I (1986) Stress-Induced transformation and plastic deformation for Y₂O₃-containing tetragonal zirconia Polycrystals. *J Am Ceram Soc* 69:198–202. <https://doi.org/10.1111/j.1151-2916.1986.tb07406.x>
- Meng X, Yang X-Q, Sun X (2012) Emerging applications of atomic layer deposition for lithium-ion battery studies. *Adv Mater* 24:3589–3615. <https://doi.org/10.1002/adma.201200397>
- Monzavi M, Zhang F, Meille S, Douillard T, Adrien J, Noubbissi S, Nowzari H, Chevalier J (2020) Influence of artificial aging on mechanical properties of commercially and non-commercially available zirconia dental implants. *J Mech Behav Biomed Mater* 101:103423. <https://doi.org/10.1016/j.jmbbm.2019.103423>
- Muñoz-Rojas D, Maindrón T, Esteve A, Piallat F, Kools JCS, Decams JM (2019) Speeding up the unique assets of atomic layer deposition. *Mater Today Chem* 12:96–120. <https://doi.org/10.1016/j.mtchem.2018.11.013>
- Nakamura T, Usami H, Ohnishi H, Takeuchi M, Nishida H, Sekino T, Yatani H (2011) The effect of adding silica to zirconia to counteract zirconia's tendency to degrade at low temperatures. *Dent Mater J* 30:330–335. <https://doi.org/10.4012/dmj.2010-142>
- Oliver WC, Pharr GM (1992) An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments. *J Mater Res* 7:1564–1583. <https://doi.org/10.1557/JMR.1992.1564>
- Pereira GKR, Venturini AB, Silvestri T, Dapieve KS, Montagner AF, Soares FZM, Valandro LF (2015) Low-temperature degradation of Y-TZP ceramics: a systematic review and meta-analysis. *J Mech Behav Biomed Mater* 55:151–163. <https://doi.org/10.1016/j.jmbbm.2015.10.017>
- Pinto PA, Colas G, Filleter T, De Souza GM (2016) Surface and Mechanical Characterization of Dental Yttria-Stabilized Tetragonal Zirconia Polycrystals (3Y-TZP) After Different Aging Processes. *Microsc Microanal* 22:1179–1188. <https://doi.org/10.1017/S1431927616011843>
- Ramesh S, Sara Lee KY, Tan CY (2018) A review on the hydrothermal ageing behaviour of Y-TZP ceramics. *Ceram Int* 44:20620–20634. <https://doi.org/10.1016/j.ceramint.2018.08.216>
- Ritala M, Leskelä M, Nykänen E, Soininen P, Niinistö L (1993) Growth of titanium dioxide thin films by atomic layer epitaxy. *Thin Solid Films* 225:288–295. [https://doi.org/10.1016/0040-6090\(93\)90172-L](https://doi.org/10.1016/0040-6090(93)90172-L)
- Ritala M, Asikainen T, Leskelä M, Jokinen J, Lappalainen R, Utriainen M, Niinistö L, Ristolainen E (1997) Effects of intermediate zinc pulses on properties of TiN and NbN films deposited by atomic layer epitaxy. *Appl Surf Sci* 120:199–212. [https://doi.org/10.1016/S0169-4332\(97\)00387-5](https://doi.org/10.1016/S0169-4332(97)00387-5)
- Shirley DA (1972) High-Resolution X-Ray Photoemission Spectrum of the Valence Bands of Gold. *Phys Rev B* 5:4709–4714. <https://doi.org/10.1103/PhysRevB.5.4709>
- Siarampi E, Kontonasaki E, Andrikopoulos KS, Kantiranis N, Voyiatzis GA, Zorba T, Paraskevopoulos KM, Koidis P (2014) Effect of in vitro aging on the flexural strength and probability to fracture of Y-TZP zirconia ceramics for all-ceramic restorations. *Dent Mater* 30:e306–316. <https://doi.org/10.1016/j.dental.2014.05.033>
- Xiao R, Chu BF, Zhang L, Cao JK (2012) Aging performances for resisting low-temperature of three dental Yttria-stabilized zirconia ceramic core materials. *Chin Med J (Engl)* 125:1999–2003
- Xie L, Abliz D, Li D (2014) 7.07 - Thin Film Coating for Polymeric Micro Parts, in: Hashmi, S., Batalha, G.F., Van Tyne, C.J., Yilbas, B. (Eds.), *Comprehensive Materials Processing*. Elsevier, Oxford, pp. 157–170. <https://doi.org/10.1016/B978-0-08-096532-1.00713-5>
- Yan Y, Ji Y, Yan J, Hu X, Zhang Q, Liu M, Zhang F (2021) Atomic layer deposition SiO₂ films over dental ZrO₂ towards strong adhesive to resin. *J Mech Behav Biomed Mater* 114:104197. <https://doi.org/10.1016/j.jmbbm.2020.104197>
- Yoshinari M (2020) Future prospects of zirconia for oral implants -A review. *Dent Mater J* 39:37–45. <https://doi.org/10.4012/dmj.2019-151>
- Young RA (1993) *The rietveld method*. Oxford University Press, Oxford
- Zaera F (2012) The Surface chemistry of atomic layer depositions of solid thin films. *J Phys Chem Letters* 3:1301–1309. <https://doi.org/10.1021/jz300125f>

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