

# Effects of Silica Coating by Physical Vapor Deposition and Repeated Firing on the Low-Temperature Degradation and Flexural Strength of a Zirconia Ceramic

Tutku Cakir-Omur, DDS, Rifat Gozneli, PhD, DDS, & Yasemin Ozkan, PhD, DDS

Department of Prosthodontics, Faculty of Dentistry, Marmara University, Basibuyuk, Istanbul, Turkey

## Keywords

Grinding; heat treatment; hydrothermal aging; silica; strength; zirconia.

## Correspondence

Tutku Cakir-Omur, Marmara University,  
Faculty of Dentistry, Basibuyuk Mah, No:9/3,  
34854 Maltepe/Istanbul, Turkey.  
E-mail: tburcucakir@hotmail.com

*This study was supported in part by a research grant from the Scientific Research Projects Committee of Marmara University, Istanbul (Project no: SAG-C-DRP-110915-0418).*

*The authors declare that they have no conflict of interest.*

Accepted January 25, 2017

doi: 10.1111/jopr.12618

## Abstract

**Purpose:** To examine the application of physical vapor deposition (PVD) silica coating as an approach to retard low temperature degradation (LTD) for dental applications. Accelerated aging characteristics of heat- and surface-treated zirconia material were also investigated by exposing specimens to hydrothermal treatment.

**Materials and Methods:** The specimens (90 disc-shaped specimens [15 mm × 1.2 mm]) were divided into 9 groups (n = 10) according to the test protocol: Ctrl, control (no surface treatment); Ag, autoclave aging; GrAg, grinding + aging; SiAg, silica coating + aging; GrSiAg, grinding + silica coating + aging; 3FAg, 3-time firing + aging; Gr3FAg, grinding + 3-time firing + aging; 5FAg, 5-time firing + aging; Gr5FAg, grinding + 5-time firing + aging. Accelerated aging was performed in a steam autoclave (134°C, 2 bars) for 12 hours. Following each treatment protocol, X-ray diffraction (XRD) analysis was used to estimate the relative amount of monoclinic phase and corresponding transformed zone depth (TZD). Additionally, a biaxial flexure test was used to calculate the flexural strength. Statistical analysis was conducted with one-way ANOVA and Fisher's LSD test ( $p < 0.05$ ).

**Results:** The tetragonal-to-monoclinic transformation was retarded by PVD silica coating only on ground surfaces. Ground and heat-treated specimens exhibited the lowest monoclinic content after aging. The biaxial flexural strength value of the GrAg group was significantly higher than the values in all of the other groups except the SiAg group. The flexural strength value of the GrSiAg group was significantly higher than that of the 3FAg group. There was no statistically significant difference between the other groups ( $p > 0.05$ ).

**Conclusions:** Grinding decreased the susceptibility of zirconia to LTD and increased the flexural strength. PVD silica coating and repeated firing decreased the monoclinic content only in ground specimens during aging.

The increasing demand for improved esthetics has driven the search for metal-free restorative materials. A major problem with all-ceramic restorations is low fracture resistance.<sup>1</sup> The introduction of CAD/CAM technology in dentistry has led to the production of stronger ceramics as an alternative to conventional feldspathic ceramic systems. The use of stabilized zirconium oxide (ZrO<sub>2</sub>) as an esthetically favorable material provides the highest mechanical properties due to the combination of high strength and toughness. These structural advantages of zirconia make this material one of the best options to produce all-ceramic fixed dental prostheses.<sup>2</sup>

Zirconia is a polymorphic material with three crystal line forms: cubic (*c*), tetragonal (*t*), and monoclinic (*m*). Pure zirconia is stable in its monoclinic crystalline form at room temperature. It transforms into the tetragonal structure above 1170°C

and into the cubic form above 2370°C. After sintering, the tetragonal crystals transform to the monoclinic form during the cooling process, causing a volumetric expansion of ~4% that generates stress and cracks in the structure of the ceramic material. Therefore, 3% mol of yttrium oxide is added to pure zirconia (producing zirconia stabilized by yttria, Y-TZP) to stabilize high-temperature tetragonal zirconia at room temperature.<sup>3</sup>

Zirconia ceramic has the ability to change its microstructure when subjected to external stress, improving its mechanical performance.<sup>4</sup> When zirconia is subjected to an external stress and the resulting crack propagation, metastable tetragonal crystals at the crack tip spontaneously transform into the monoclinic phase, causing a volumetric expansion of approximately 3% to 5%. This volumetric expansion of the transformed grains induces compressive stresses that resist crack propagation.<sup>5</sup> This

effect is referred to as a “transformation toughening mechanism” and is responsible for the high strength and toughness of Y-TZP.<sup>6,7</sup> In this toughening process, the crystalline structure of the material changes, and the macroscopic modification of the processed areas resulting from spontaneous atomic movement improves the strength of the zirconia.<sup>8</sup> However, when the volumetric expansion exceeds the elastic limits of the zirconia, crack propagation is promoted, causing the formation of new cracks, and potentially catastrophic failure. This mechanism is influenced by several factors, such as the size, shape, and location of grains, the presence of defects in the structure, the fabrication technique, the applied stress, and the magnitude of temperature variations.<sup>9</sup> A key concept to understanding transformation toughening is that the development of the transformation zone is associated with the crack tip. The formation of the transformation zone is hypothesized to be responsible for the increase in zirconia reliability.<sup>2</sup> The strengthening of toughened zirconia ceramics depends on the amount of transformed zirconia in the deepest region of the compressive surface layer.<sup>4</sup>

The tetragonal-to-monoclinic transformation may also occur at low temperatures in the presence of water.<sup>2,10</sup> In the late 1980s, zirconia was used as an orthopedic femoral head prosthesis material.<sup>11</sup> However, a large number of failures in a short period were reported, generating major medical device concerns. In the search for the failures’ origins, it was observed that zirconia is destabilized in the presence of water or water vapor and that moisture induces the *t-m* transformation and increases the surface roughness of the material.<sup>11,12</sup> Based on medical device studies, this mechanism has been attributed to aging or low-temperature degradation (LTD).<sup>12,13</sup> In dentistry, the humid environment of the oral cavity renders the zirconia susceptible to LTD.<sup>14</sup> In the oral cavity, water is absorbed by zirconia and initiates the *t-m* transformation from the material’s surface grains. This aging process spreads along the surface and proceeds into the bulk material, leading to a degradation in mechanical properties.<sup>10,15</sup>

LTD of zirconia is a structural degradation phenomenon related to the transformability of the tetragonal phase that initiates at the zirconia surface. This surface transformation, which is slow, spontaneous, and progressive, proceeds more rapidly in the presence of water, hot water vapor, or body fluids such as saliva; the critical temperature range is 200°C to 300°C.<sup>16</sup> This transformation induces local volumetric expansion and stress on neighboring grains.<sup>17</sup> Due to this stress, the *t-m* transformation also occurs in the neighboring grains, and the result is the formation of a region that enables the penetration of water molecules and the propagation of grain transformation deeper in the bulk of the material,<sup>18</sup> along with micro- and macrocracking of the zirconia.<sup>19</sup>

Zirconia ceramics are fabricated by machining Y-TZP blocks in high-precision CAD/CAM systems, providing frameworks with optimum marginal and internal fit.<sup>20</sup> However, clinicians sometimes need to apply subsequent grinding to adjust the final form before placement.<sup>21</sup> Grinding of the zirconia surface generates various types of surface defects, such as scratches and cracks of various depths and widespread phase transformation.<sup>22-24</sup> These defects can affect the LTD and strength of the material.<sup>25</sup>

Some investigations have focused on mitigating the LTD phenomenon.<sup>26-28</sup> To shield the zirconia surface and prevent its contact with water vapor, the use of ceramic infiltration with glass ceramic having a thermal expansion coefficient similar to that of zirconia has also been recommended.<sup>29</sup> Silica can also be used as an interlayer material on zirconia to reduce the negative effect of liquids in the slurry on the Y-TZP grains.<sup>21</sup> The physical vapor deposition (PVD) technique enables conformal silicate surface modification without the use of an aggressive physical process that might result in damage to the coping surface.<sup>30</sup> It is a vacuum deposition process in which the coating material is evaporated by one of several possible mechanisms (resistance heating, high-energy ionized gas bombardment, or electron gun) under vacuum, followed by vapor phase transportation to the substrate to deposit a coating.<sup>31</sup> The PVD coating process takes place between temperatures of 100°C to 600°C and features multiple advantageous properties, such as high deposition rates, dense coatings, composition control, low contamination, and high thermal efficiency. Uniform coatings with favorable surface finish can be obtained by PVD. The microstructure and composition of the coating can be easily altered by manipulating the process parameters. Thus, multilayered ceramic/metallic coatings can be readily formed, and various metallic and ceramic coatings (oxides, carbides, and nitrides) can be deposited at relatively low temperatures.<sup>31</sup> Due to the lack of silica in zirconia, “PVD-silica-coated zirconia” studies have generally relied on the chemical bonding provided by silanization, and core-resin cement and core-veneer porcelain bond strength have been investigated.<sup>32,33</sup> The effect of PVD silica coating on the LTD of zirconia has not yet been investigated, however.

The *t-m* phase transformation induced by aging or grinding may be reversed by heat treatment at sufficiently high temperatures. It has been reported that under heat treatment in the range of 350°C to 550°C, the reverse phase transformation from monoclinic to tetragonal occurs.<sup>34</sup> Because zirconia restorations are exposed to a humid environment coupled with cyclic loading in the oral cavity, evaluation of the additive effect of grinding on the LTD of zirconia ceramics is likely essential for the successful application of zirconia in dentistry. The aim of this study was to investigate the effect of grinding on LTD susceptibility by autoclaving zirconia ceramics and determining the protective effect of a PVD silica coating on the LTD and the effect of repeated firing on the reverse phase transformation of both ground and unground zirconia. The flexural strength and phase changes of zirconia were investigated for this purpose. The null hypothesis was that (1) grinding would decrease the LTD susceptibility of zirconia ceramic and that (2) PVD silica coating and (3) repeated firing would suppress the monoclinic content of ground and unground zirconia specimens during autoclave aging without decreasing their flexural strength.

## Materials and methods

### Sample size and power calculation

With a sample size of 90 (10 per group) 92% power was achieved to detect a difference among the groups. Statistical software (PASS Software; NCSS, LLC, Kaysville, UT)

**Table 1** Firing processes recommended by the manufacturer

Firing	Start temp. (°C)	Drying time (min)	t under vacuum (°C/min)	Final temp. (°C)	Hold time under vacuum (min)	Hold time without vacuum (min)
1st	450	4	45	840	1	–
2nd	450	4	45	830	1	–
3rd	450	6	45	810	1	–
4th	450	6	45	800	1	–
5th	480	2	–	790	–	1

was used to calculate the sample size required to achieve an  $\alpha = 0.05$ .

### Specimen preparation

Disc-shaped specimens ( $N = 90$ ) were manufactured from pre-sintered blocks of YZ (LAVA Frame Multi; 3M ESPE, Seefeld, Germany) according to ISO 6872.<sup>35</sup> After sintering (LAVA Furnace 200; 3M ESPE) at temperature of 1530°C, discs with final dimensions of 15 mm × 1.2 mm were obtained.

The specimens were divided according to surface treatment conditions (9 levels) as follows ( $n = 10$ ): **Ctrl**, control (no surface treatment); **Ag**, autoclave aging; **GrAg**, grinding with 150 grit diamond bur + aging; **SiAg**, silica coating + aging; **GrSiAg**, grinding + silica coating + aging; **3FAg**, 3-time firing + aging; **Gr3FAg**, grinding + 3-time firing + aging; **5FAg**, 5-time firing + aging; **Gr5FAg**, grinding + 5-time firing + aging.

### Grinding procedure

Grinding was standardized with the assistance of a specific device. The specimens were prepared with 150-grit diamond burs for low-speed straight hand grinding (Kavo Typ960; KaVo Dental GmbH, Riss, Germany) at a rotational speed of 20,000 rpm. Zirconia discs were marked with permanent pen and were ground with continuous grinding to achieve a reduction of 0.1 mm.

### PVD process

A thin silica layer (~570 nm) was deposited on the surface of 20 specimens (10: silica coated, 10: ground + silica coated) of zirconia discs. Deposition was performed using an electron beam physical vapor deposition (EB-PVD) system in a cylindrical vacuum chamber evacuated to a base pressure of  $7.5 \times 10^{-4}$  Torr. The cathode voltage and electric current were kept constant at 6.70 kV and 0.015 A, respectively. The mean coating rate was 3.4 Å/s. Pure sintered silica particles were used as target materials. The thickness of the coating was measured by SEM analysis of a witness sample. Prior to coating, the specimens were cleaned for 10 minutes in an ultrasonic bath containing distilled water.

### Firing procedure

Specimens were subjected to heat treatment in a ceramic oven (Vita-Zahnfabrik, Bad Sackingen, Germany) either three or five times to simulate the correction and glaze firing recommended by the manufacturer (Table 1).

### Aging procedure

The protective effect of the coatings and heat treatment was investigated by aging of the specimens in an autoclave (BES 40 × 60; Hangzhou Chincan Trading Co., Hangzhou Zhejiang, China) for 12 hours in water vapor at 134°C and 2 bar to induce *t-m* transformation and LTD.

### Phase Analysis by XRD

The progress of the *t-m* transformation due to accelerated aging was analyzed by XRD (D2 Phaser; Bruker, Billerica, MA) using Cu K $\alpha$  radiation with four specimens per group. The XRD analysis was conducted between 20 and 40° ( $2\theta$ ) with a step size of 0.02°. The monoclinic phase content (%) on the surfaces was determined using formulas introduced by Garvie and Nicholson.<sup>36</sup>

$$X_m = [I_m(-111) + I_m(111)] / [I_m(-111) + I_m(111) + I_t(101)]$$

$$V_m = 1.311 \times X_m / 1 + (0.311 \times X_m)$$

In the first formula,  $I_m(-111)$  and  $I_m(111)$  represent the integral intensity of the monoclinic peaks ( $2\theta = 28^\circ$  and  $2\theta = 31.2^\circ$ , respectively) and  $I_t(101)$  indicates the intensity of the tetragonal peak ( $2\theta = 30^\circ$ ). In the second formula,  $V_m$  represents the monoclinic volumetric content.

### TZD

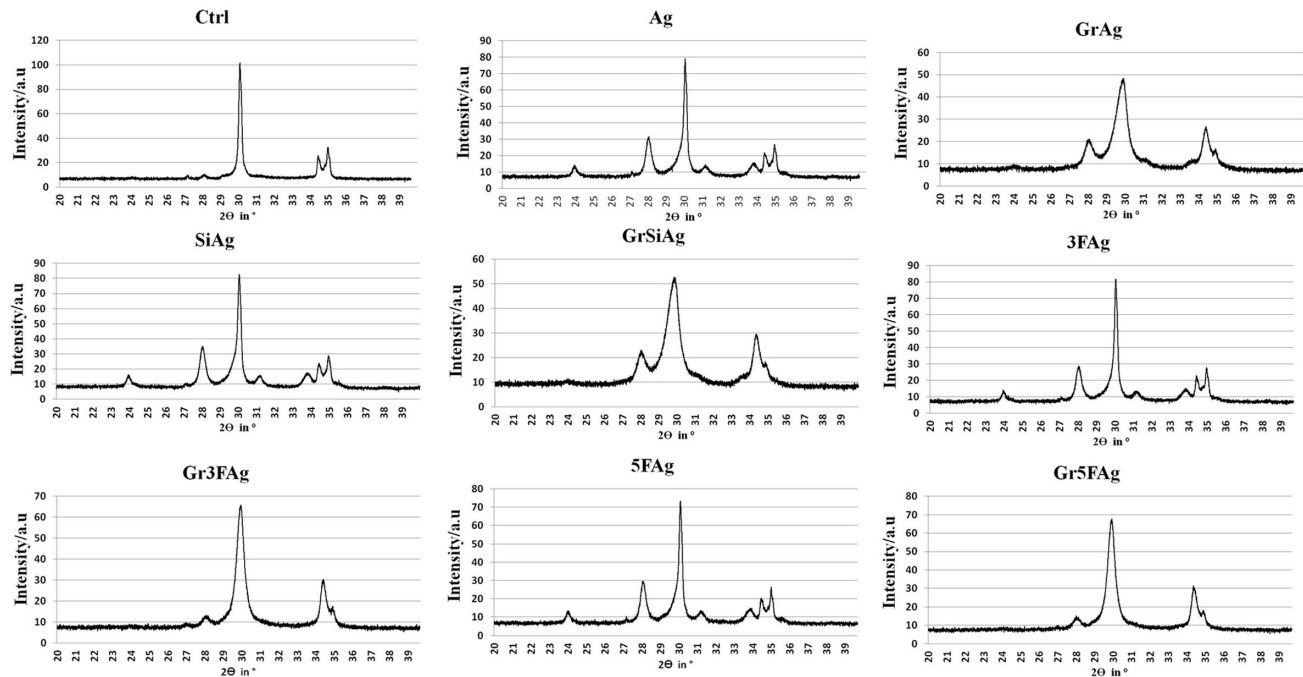
The thickness of the transformed surface layer (i.e., the TZD) of the specimens was calculated using the XRD method proposed by Kosmac et al<sup>37</sup> (assuming that within the transformed surface layer, all tetragonal grains were transformed into monoclinic grains):

$$TZD = \left( \frac{\sin\theta}{2\mu} \right) \ln \frac{1}{1 - XM}$$

where the angle of reflection = 15°, the absorption coefficient  $\mu = 0.0642$ , and  $XM$  is the relative monoclinic fraction obtained from XRD analysis.

### Biaxial flexure test

The disc-shaped specimens were subjected to biaxial flexure strength testing using the piston-on-three-ball test method as described in ISO 6872.<sup>35</sup> The test was performed with a universal testing machine (AG-5 kNG; Shimadzu, Tokyo, Japan).



**Figure 1** XRD patterns of tested groups.

Each specimen was positioned with the treated surface turned down on three steel balls with a diameter of 4 mm and positioned 120° apart on a 10-mm diameter support circle. A flat circular tungsten piston with a diameter of 1.6 mm was used to apply a load at a constant speed of 1 mm/min until fracture of the specimen. The biaxial flexural strength was calculated with the equation listed in the standard, using a Poisson's ratio for zirconia of 0.25:

$$S = -0.2387 \frac{P(X - Y)}{d^2}$$

where  $S$  is the maximum tensile stress (MPa),  $P$  is the load at fracture (N), and  $d$  is the specimen thickness at the origin of the fracture (mm);  $X$  and  $Y$  were calculated as follows:

$$X = (1 + \nu) \ln \left( \frac{r_2}{r_3} \right)^2 + \left[ \frac{(1 - \nu)}{2} \right] \left( \frac{r_3}{r_3} \right)^2$$

$$Y = (1 + \nu) \left[ 1 + \ln \left( \frac{r_1}{r_3} \right)^2 \right] + (1 - \nu) \left( \frac{r_1}{r_3} \right)^2$$

where  $\nu$  is Poisson's ratio,  $r_1$  is the radius of the support circle (mm),  $r_2$  is the radius of the loaded area (mm), and  $r_3$  is the radius of the specimen (mm).

### Statistical methods

In addition to calculation of the mean value and the standard deviation, one-way ANOVA test was used to examine the strength values of the materials. Statistically significant differences between the groups were evaluated with Fisher's LSD test at a 0.05 level of significance.

**Table 2** Relative amounts of monoclinic zirconia (%) and standard deviation (SD), verified by XRD and TZD of surface treated Y-TZP ceramic

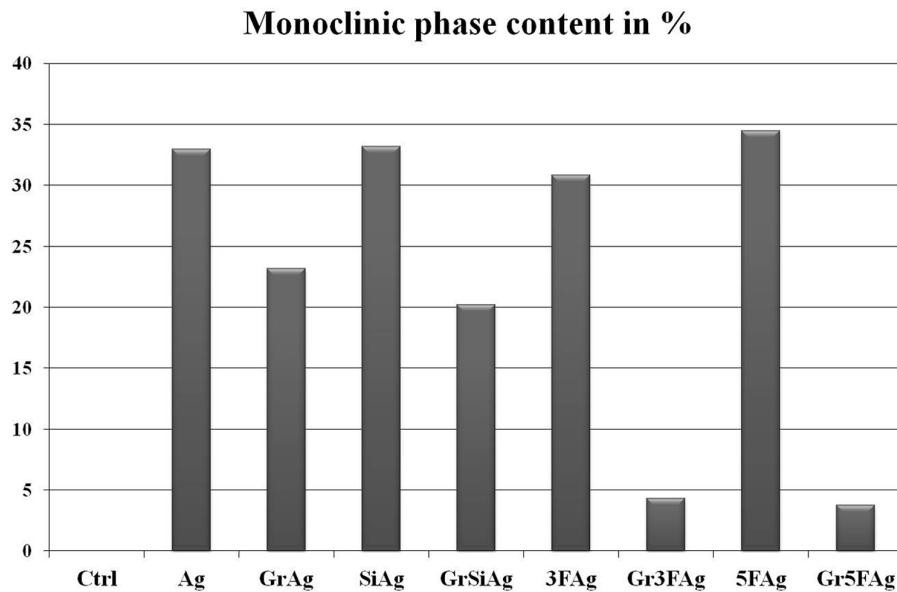
Group	Relative amount of monoclinic phase in % ± SD	Transformation zone depth TZD in μm ± SD
Ctrl	0 ± 0	0 ± 0
Ag	32.97 ± 1.44	0.80 ± 0.04
GrAg	23.15 ± 1.92	0.53 ± 0.05
SiAg	33.15 ± 2.17	0.81 ± 0.06
GrSiAg	20.2 ± 0.75	0.46 ± 0.02
3FAg	30.83 ± 2.1	0.74 ± 0.06
Gr3FAg	4.33 ± 0.64	0.09 ± 0.01
5FAg	34.48 ± 2.47	0.85 ± 0.08
Gr5FAg	3.75 ± 0.21	0.08 ± 0.004

### Results

The SEM image of the witness sample confirmed the existence of the silica layer. The silica layer exhibited thickness of ~570 nm.

XRD patterns for the experimental groups are shown in Figure 1. Control specimens exhibited only one peak, which represented the plane of the tetragonal phase. The results indicated no detectable monoclinic phase for the control group. The formation of monoclinic phase was detected in all of the groups except the control group.

The relative amounts of monoclinic zirconia detected by XRD on the treated surface of the specimens are listed in Table 2. Autoclave aging alone increased the formation of the monoclinic phase on the zirconia specimens. Based on the results, there were no differences in the diffraction patterns for the Ag and SiAg groups. The PVD silica coating did not



**Figure 2** Relative monoclinic content (%) of tested groups (Control value is zero).

protect against the LTD of unground zirconia specimens during autoclave aging: the specimens of SiAg group had a monoclinic content similar to the uncoated ones after aging. Grinding affected the material’s susceptibility to undergoing *t-m* phase transformation during autoclave aging: the monoclinic phase content was lower in the GrAg group than the Ag group.

Although the PVD silica coating did not exert any protective effect on monoclinic transformation of the unground specimens, it affected the susceptibility to *t-m* transformation of the ground specimens during autoclave aging. XRD results showed that the presence of the silica coating decreased the percentage of the monoclinic phase from 23.15% to 20.2% in the ground and aged surfaces.

According to the XRD results, repeated firing had different effects on the monoclinic contents of the specimens of different groups. Although specimens from the 3FAg group exhibited a slightly lower monoclinic phase content than the Ag group, the 5FAg group exhibited a slightly higher monoclinic content than the Ag and SiAg groups (Table 2). Repeated firing was associated with a substantially lower monoclinic content on the ground specimens exposed to autoclave aging (Fig 2). The monoclinic content of the Gr3FAg and Gr5FAg groups were  $4.33 \pm 0.64\%$  and  $3.75 \pm 0.21\%$ , respectively (Table 2).

The TZD values of the groups are also listed in Table 2. After autoclave aging, the TZD values of control specimens had increased from 0 to  $0.85 \mu\text{m}$ . Transformation at a greater depth was observed in group 5FAg.

The mean values of biaxial flexural strength (in MPa) and the respective standard deviation values are shown in Table 3. According to one-way ANOVA and Fisher’s LSD Test, the mean flexural strength of the specimens of GrAg group was statistically higher than that of all the other groups ( $p < 0.05$ ) except the GrSiAg group. The mean flexural strength of the GrSiAg group was significantly higher than that of the 3FAg

**Table 3** Mean flexural strength and standard deviation of all tested groups (MPa)

Group	Mean ± SD	Minimum	Maximum
Ctrl	1146.27 ± 130.23	917.66	1370.32
Ag	1178.31 ± 98.97	954.49	1292.94
GrAg	1283.21 ± 69.81	1201.67	1384.13
SiAg	1163.67 ± 103.98	976.33	1281.52
GrSiAg	1237.62 ± 98.2	1069.35	1390.81
3FAg	1135.17 ± 94.18	932.49	1286.53
Gr3FAg	1179.63 ± 154.09	939.25	1358.46
5FAg	1158.1 ± 104.32	998.07	1296.95
Gr5FAg	1183.14 ± 124.7	964.79	1351.04

**Table 4** Results of Fisher’s LSD test after one-way ANOVA

Group	Ctrl	Ag	GrAg	SiAg	GrSiAg	3FAg	Gr3FAg	5FAg
Ag	32.1	-	-	-	-	-	-	-
GrAg	137*	104.9*	-	-	-	-	-	-
SiAg	17.4	-14.7	-119.6*	-	-	-	-	-
GrSiAg	91.3	59.2	-45.7	73.9	-	-	-	-
3FAg	-11.2	-43.3	-148.2*	-28.6	-102.5*	-	-	-
Gr3FAg	33.3	1.2	-103.7*	73.9	-58	44.5	-	-
5FAg	11.8	-20.3	-125.2*	-5.6	-79.5	23	-21.5	-
Gr5FAg	36.8	4.7	-100.2*	19.4	-54.5	44.5	3.5	25

Values are the interval for column level mean minus row level mean; (\*) indicates groups with significant differences ( $p < 0.05$ ).

group (Table 4). There were no statistically significant differences between the other groups ( $p > 0.05$ ). The silica coating processes did not have a statistically significant influence on the flexural strength of the tested specimens.

## Discussion

Zirconia has been widely used in metal-free restorations. Its degradation in the oral environment, due to exposure to oral fluids and to subjection to mechanical stress for long periods, makes LTD of particular interest for dental zirconia.<sup>38</sup> Control of phase transformations in zirconia ceramics is important to maintain their mechanical properties and minimize the possibility of LTD. The main purpose of this study was to analyze the protective effect of a silica coating and the effect of repeated firing on the LTD of ground and nonground zirconia specimens after autoclave aging. Based on the results of this study, the hypothesis that grinding would decrease the LTD susceptibility of zirconia ceramic was confirmed, but the hypothesis that silica coating with PVD and repeated firing would decrease the monoclinic phase content of ground and unground zirconia specimens was partially rejected.

LTD mitigation of Y-TZP has been investigated in several studies.<sup>27,39,40</sup> Kohorst *et al*<sup>27</sup> reported that replacing yttrium oxide with cerium oxide suppressed LTD, but this modification also lowered the biaxial flexural strength of the material. Nogiwa-Valdez *et al*<sup>39</sup> reported that doping with aluminum oxide inhibited LTD by reducing the number of nucleation sites for the formation of monoclinic zirconia. Gremillard *et al*<sup>40</sup> reported adding silica to the structure mainly reduces the strain within the grains, which is important in impeding the nucleation and propagation of LTD. Samodurava *et al*<sup>41</sup> also reported that silica doping reduces the propagation of the transformation in to the bulk material via water penetration along the cracks. Some investigators studied protective coatings applied by the PVD technique. Hübsch *et al*<sup>28</sup> reported that extremely thin monolayers of titanium oxide and multilayers consisting of titanium oxide–alumina–titanium oxide coating suppressed LTD without affecting the mechanical strength of Y-TZP. In this study, it was expected that PVD-coated silica layer could reduce water penetration inside the material during the aging treatment and thus impede LTD. According to the XRD results of the current study, monoclinic phase formation was not inhibited in the SiAg group; in contrast, it was slightly increased relative to that in the Ag group; however, the silica-coated layer had a protective effect on the ground surfaces, and it altered the susceptibility of ground zirconia specimens to *t-m* phase transformation, as evidenced by the lower monoclinic content after autoclave aging for 12 hours (*m* phase of GrAg: 23%; GrSiAg: 20%). Thus, the second hypothesis was partially rejected.

Steam autoclave treatment at increased temperatures has been noted to serve as a good method for accelerated testing of LTD.<sup>17</sup> According to Chevalier *et al*,<sup>17</sup> an autoclave treatment of 1 hour at 134°C at 0.2 MPa pressure corresponds 3 to 4 years *in vivo*. The ISO recommendation is to perform autoclave aging at 134°C under 0.2 MPa pressure for 5 hours as an accelerated aging protocol for zirconia.<sup>35</sup> In most studies on accelerated aging, the employed temperature is 134°C,<sup>3,17,27,34</sup> and the duration of exposure varies between 1 and 960 hours.<sup>27,34</sup> In this study, zirconia specimens were subjected to a steam autoclave treatment at 134°C at 0.2 MPa pressure for 12 hours; with respect to the actual transformation kinetics, these conditions correspond to a period of 36 to 48 years at body temperature,

which is at least comparable to the expected lifetime of dental restorations.<sup>17</sup>

The present zirconia specimens were prepared with presintered Y-TZP blocks and the CAD/CAM milling stage induced compressive stresses and micro cracks at the surface. During the final sintering step, the reverse phase transformation (*m*→*t*) occurred, and microcracks derived from the machining stage were eliminated. Thus, the current XRD analyses revealed no detectable monoclinic phase content in the control specimens.

Zirconia grinding is a commonly performed surface treatment to achieve a better fit for dental applications. This process produces surface compressive stresses as well as microcracks, and may lead to increased susceptibility to LTD.<sup>2,10,42</sup> According to Deville *et al*,<sup>43</sup> the surface compressive stresses suppress the LTD process, while Chevalier *et al*<sup>17</sup> reported that microcracks provide passage for water and enhance LTD. According to Kim *et al*,<sup>10</sup> surface treatments (e.g., CAD/CAM machining, grinding, and grit blasting) have pronounced effects on the hydrothermal degradation behavior of Y-TZP. They reported that grit-blasted and ground Y-TZP surfaces had much lower monoclinic content than the control group after 20 hours of autoclave aging.<sup>10</sup> Additionally, Pereira *et al*'s study<sup>44</sup> found that grinding decreased the *t-m* phase transformation of zirconia during autoclave aging. In this study, which complements the studies of Pereira *et al* and Kim *et al*., it can be concluded that grinding decreased the susceptibility of zirconia to *t-m* phase transformation, as evidenced by the GrAg group exhibiting lower monoclinic content than the Ag group (23% vs. 33%). Thus, our first hypothesis was confirmed.

Zirconia restorations are subjected to heat treatments during the firing of the veneering porcelain.<sup>45</sup> It has been reported that differences in the heat treatment process, heating rate, and final temperature may lead to different results concerning both *t-m* phase transformation and mechanical strength.<sup>38</sup> Song *et al*<sup>1</sup> reported that after heat treatment at 500°C to 1000°C for 15 minutes, the monoclinic phase transformed completely to the tetragonal phase, while Sato *et al*<sup>46</sup> reported that some monoclinic phase content remained on the surface after heat treatment at 500°C to 1200°C for 5 minutes. Several studies have indicated that when heat treatment in the temperature range of 900°C to 1000°C is applied after grinding, the reverse phase transformation (*m*→*t*) occurs, and the material strength decreases due to the relaxation of surface compressive stresses created by grinding.<sup>9,47</sup> According to Denry *et al*,<sup>34</sup> the reverse transformation in zirconia starts at temperatures as low as 350°C and is completed at 550°C. They also reported that no monoclinic phase was detected after a heat treatment at over 850°C, while minor amounts were found at 500°C, and heat treatment below 350°C did not alter the monoclinic phase. Therefore, firing of veneer porcelain is likely to lead to the reverse phase transformation. Thus, in this study, the veneer-firing instructions for Lava Frame zirconia material were applied as the heat treatment. The option for three or five firing cycles was selected to enable comparison based on the number of cycles.

Vatali *et al*<sup>38</sup> reported that applying a heat treatment accompanied by *in vitro* aging resulted in further *t-m* phase transformation than applying the heat treatment or *in vitro* aging alone. In this study, the 5FAG group exhibited higher monoclinic content (34.48%), while the 3FAG group exhibited lower

monoclinic content (30.83%) in comparison to the Ag group (32.97%).

Denry et al<sup>34</sup> reported that heat treatment applied after surface grinding led to recrystallization into significantly smaller grains and prevented the formation of the monoclinic phase after aging without significantly altering the flexural strength. This finding is also supported by this study: after 12 hours of aging, heat-treated ground surfaces (3.75-4.33%) exhibited remarkably lower monoclinic content than the nonheat-treated ground specimens (23.15%). Additionally, the Gr5FAG group exhibited lower monoclinic content than the Gr3FAG group (3.75%, 4.33%). Thus, it is possible to say that heat treatment decreases the susceptibility of ground specimens to the *t-m* phase transformation; thus, the third hypothesis was partially accepted.

The transformed layer depth is calculated by assuming that within the transformed surface layer, all the tetragonal grains have transformed into the monoclinic symmetry.<sup>37</sup> In this study, in every group, the higher the amount of the *m* phase, the deeper the transformed layer. Amaral et al<sup>2</sup> reported that TZD values of zirconia specimens increased from 0.07  $\mu\text{m}$  to 1.55  $\mu\text{m}$  after 12 hours of autoclave aging at 127°C and 1.5 bar pressure. The TZD value of the control group was 0  $\mu\text{m}$ ; after aging, it was detected that the Ag group had 0.8  $\mu\text{m}$  of transformed layer. TZD in the experimental groups varied from 0.08 to 0.85  $\mu\text{m}$ , with the highest values being found in the 5FAG group (0.85  $\mu\text{m}$ ).

Strength is an important parameter to determine the clinical success of a restoration. The flexural strength of Y-TZP is generally evaluated using either three-point tests,<sup>9,24</sup> four-point tests,<sup>3</sup> or biaxial flexural strength tests.<sup>28,48,49</sup> Kelly<sup>50</sup> reported that the fabrication of specimens suitable for three-point tests can introduce defects. According to Yilmaz et al,<sup>48</sup> it is almost impossible to remove all flaws in a ceramic during the production of specimens. Ozcan et al<sup>51</sup> reported that biaxial flexural strength testing, in contrast, does not involve edge chippings because this area is not subjected directly to the load. In this study, piston-on-three-ball testing was used to investigate the flexural strength of the specimens.

Amaral et al<sup>2</sup> reported that zirconia specimens subjected to steam autoclave treatment at 127°C and 1.5 bar for 12 hours exhibited significant increases in strength after aging. In this study, according to the biaxial flexural strength results, 12 hours of autoclave aging increased the mean strength values of the control specimens. This finding can be attributed to the substantial increase in monoclinic phase content (0-32.97%); however, this increase was not statistically significant ( $p > 0.05$ ).

Grinding has been recommended to increase the mean flexural strength of zirconia by developing a surface region of compressive stress.<sup>52,53</sup> Some reports have proposed that compressive stress initially increases the flexural strength of zirconia;<sup>15,16,54</sup> however, Chevalier reported that the progression of microcracks and formation of residual tensile stresses can lead to a decrease in strength.<sup>55</sup> It was also reported that the influence of grinding on the flexural strength of zirconia is related to the volumetric percentage of transformed zirconia.<sup>44</sup> Pereira et al<sup>44</sup> proposed that grinding increases the biaxial flexural strength of the control specimens before aging,

probably due to the compressive stress generated by the monoclinic phase transformation; however, they reported that grinding had a deleterious impact on the flexural strength of zirconia after 20 hours of aging, probably because the ground specimens had lower monoclinic content and a thinner transformed layer than the control specimens, and this layer was not sufficiently thick to prevent crack propagation.<sup>44</sup> In this study, grinding increased the strength of the specimens except in the GrSiAg group. In contrast to Pereira et al's study, the biaxial flexural strength values of the GrAg group were statistically significantly higher than the values of the Ag group, although the GrAg group specimens had lower monoclinic phase and lower TZD values than the Ag group specimens.

According to Kim et al<sup>10</sup> and Ban et al,<sup>22</sup> flexural strength is affected negatively only when the monoclinic phase content exceeds 50%. Kosmac et al<sup>56</sup> investigated the correlation between flexural strength and the relative monoclinic phase content after surface and heat treatments. They reported that heat treatment at 900°C for 1 hour decreased the monoclinic content and the mean flexural strength on surface-treated zirconia by releasing compressive stress due to reverse phase transformation. In this study, the mean flexural strength was statistically higher in the GrAg group (which contained  $23.15 \pm 1.9\%$  *m* phase) than in the Gr3FAG or Gr5FAG group, which had much less monoclinic content (4.33% and 3.75%, respectively). This finding can be explained by the reverse phase transformation releasing compressive stress from the ground surfaces due to the heat of repeated firing.

According to the statistical analysis, the hypothesis that neither PVD silica coating nor repeated firing would affect flexural strength was partially accepted. PVD silica coating did not have a deleterious impact on the flexural strength of the zirconia specimens. Moreover, after 12 hours of aging, although specimens ground and fired multiple times had statistically significantly lower flexural strength than the ground specimens, the ground and silica-coated specimens did not exhibit significant differences in mean strength values compared to the ground specimens.

It has been reported that the safest way to predict clinical performance is to design tests that model the clinical conditions as closely as possible.<sup>50</sup> The current study has some limitations. Currently, there is no single in vitro test configuration that can exactly simulate the clinical environment. Furthermore, the specimens were not prepared in a crown shape and were not used with veneer ceramic material. The mean flexural strengths of the specimens of the current study far exceed stress achieved intraorally even after the surface treatments and aging; however, controlling the *t-m* transformation on surface-treated zirconia might be beneficial at reducing the risk of chipping. Zirconia-based specimens frequently exhibit tensile stress generated by the volume increase of zirconia grains at the interface that occurs due to a *t-m* phase transformation following the veneer firing process, and this stress increases the risk of chipping.<sup>57</sup> Finally, the in vitro aging step consisted of an accelerating aging test performed according to the Chevalier model. The amount of monoclinic zirconia phase detected in this study was obtained under static conditions where no loading was applied. It was reported that surface LTD even of few microns in depth could progress rapidly in the presence of mastication forces,

as even minor cracks may propagate far inside the bulk of the material leading to its failure.<sup>38</sup>

PVD system has advanced to being able to coat metal and nonmetal substrates at lower temperatures without the risk of damaged substrate. This broadens the applications and markets of PVD coating, and benefits manufacturers and users in various industries. In dentistry it needs further improvements to make it clinically applicable, however.

## Conclusions

Based on the results of this study, the following conclusions were drawn:

1. The PVD silica coating decreased the susceptibility of ground surfaces to LTD without producing deleterious effects on the flexural strength of the material. The *t-m* phase transformation of the zirconia ceramic was inhibited by the application of the PVD silica coating only on the ground surfaces during aging.
2. Repeated firing decreased the relative monoclinic content of the ground surfaces during aging, but after autoclave aging, the mean flexural strength of the ground and heated specimens was significantly lower than that of the ground specimens.
3. Grinding affected the susceptibility of zirconia to LTD by suppressing the *t-m* transformation during aging.
4. The biaxial flexural strength value of the GrAg group was significantly higher than that of all the other groups except the GrSiAg group.
5. There was no significant effect from PVD silica coating or repeated firing on the LTD of the unground zirconia specimens.

## References

1. Song JY, Park SW, Lee K, et al: Fracture strength and microstructure of Y-TZP zirconia after different surface treatments. *J Prosthet Dent* 2013;110:274-280
2. Amaral M, Valandro LF, Bottino MA, et al: Low-temperature degradation of a Y-TZP ceramic after surface treatments. *J Biomed Mater Res B Appl. Biomater* 2013;101:1387-1392
3. Flinn BD, Raigrodski AJ, Singh A, et al: Effect of hydrothermal degradation on three types of zirconias for dental application. *J Prosthet Dent* 2014;112:1377-1384
4. Kelly JR, Denry I: Stabilized zirconia as a structural ceramic: an overview. *Dent Mater* 2008; 24:289-298
5. Garvie RC, Hannink RHJ, Pascoe RT: Ceramic steel? *Nature* 1975;258:703-704
6. Pittayachawan P, McDonald A, Petrie A, et al: The biaxial flexural strength and fatigue property of Lava Y-TZP dental ceramic. *Dent Mater* 2007;23:1018-1029
7. Karakoca S, Yilmaz H: Influence of surface treatments on surface roughness, phase transformation, and biaxial flexural strength of Y-TZP ceramics. *J Biomed Mater Res B Appl Biomater* 2009;91:930-937
8. Kelly PM, Francis Rose LR: The martensitic transformation in ceramics-its role in transformation toughening. *Prog Mater Sci* 2002;47:463-557
9. Guazzato M, Albakry M, Quach L, et al: Influence of surface and heat treatments on the flexural strength of a glass-infiltrated alumina/zirconia reinforced dental ceramic. *Dent Mater* 2005;21:454-463
10. Kim HT, Han JS, Yang JH, et al: The effect of low temperature aging on the mechanical property & phase stability of YTZP ceramics. *J Adv Prosthodont* 2009;1:113-117
11. Piconi C, Burger W, Richter HG, et al: Y-TZP for artificial joint replacements. *Biomaterials* 1998;19:1489-1494
12. Chevalier J: What future for zirconia as a biomaterial? *Biomaterials* 2006;27:535-543
13. Chevalier J, Gremillard L, Virkar AV, et al: The tetragonal-monoclinic transformation in zirconia: lessons learned and future trends. *J Am Ceram Soc* 2009;92:1901-1920
14. Lughy V, Sergio V: Low temperature degradation-aging-of zirconia: a critical review of the relevant aspects in dentistry. *Dent Mater* 2010;26:807-820
15. Zhang Y, Lawn BR, Rekow ED, et al: Effect of sandblasting on the long-term performance of dental ceramics. *J Biomed Mater Res B Appl Biomater* 2006;71:381-386
16. Kobayashi K, Kuwajima H, Masak T: Phase change and mechanical properties of ZrO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub> solid electrolyte after aging. *Solid State Ionics* 1981;3-4:489-493
17. Chevalier J, Cales B, Drouin JM: Low temperature aging of Y-TZP ceramics. *J Am Ceram Soc* 1999;82:2150-2154
18. Deville S, Chevalier J: Martensitic relief observation by atomic force microscopy in yttria-stabilized zirconia. *J Am Ceram Soc* 2003;86:2225-2227
19. Yoshimura M, Noma T, Kawabata K, et al: Role of H<sub>2</sub>O on the degradation process of Y-TZP. *J Mater Sci* 1987;6:465-467
20. Pereira G, Amaral M, Cesar PF, et al: Effect of low-temperature aging on the mechanical behavior of ground Y-TZP. *J Mech Behav Biomed Mater* 2015;45:183-192
21. Aboushelib MN, Feilzer AJ, Kleverlaan CJ: Bridging the gap between clinical failure and laboratory fracture strength tests using a fractographic approach. *Dent Mater* 2009;25:383-391
22. Ban S, Sato H, Suehiro Y, et al: Biaxial flexure strength and low temperature degradation of Ce-TZP/Al<sub>2</sub>O<sub>3</sub> nanocomposite and Y-TZP as dental restoratives. *J Biomed Mater Res B Appl Biomater* 2008;87:492-498
23. Quinn GD, Ives LK, Jahanmir S: On the nature of machining cracks in ground ceramics. Part I: SRBSN strengths and fractographic analysis. *Machin Sci Technol* 2005;9:169-210
24. Papanagiotou HP, Morgano SM, Giordano RA, et al: In vitro evaluation of low-temperature aging effects and finishing procedures on the flexural strength and structural stability of Y-TZP dental ceramics. *J Prosthet Dent* 2006;96:154-164
25. Lee TH, Lee SH, Her SB, et al: Effects of surface treatments on the susceptibilities of low temperature degradation by autoclaving in zirconia. *J Biomed Mater Res B Appl Biomater* 2012;100:1334-1343
26. Nakamura T, Usami H, Ohnishi H, et al: The effect of adding silica to zirconia to counteract zirconia's tendency to degrade at low temperatures. *Dent Mat J* 2011;30:330-335
27. Kohorst P, Borchers L, Stempel J, et al: Low temperature degradation of different zirconia ceramics for dental applications. *Acta Biomater* 2012;8:1213-1220
28. Hübsch C, Dellinger P, Maier HJ, et al: Protection of yttria-stabilized zirconia for dental applications by oxidic PVD coating. *Acta Biomater* 2015;11:488-493
29. Zhang Y, Kim JW: Graded structures for damage resistant and aesthetic all-ceramic restorations. *Dent Mater* 2009;25:781-790

30. Thompson JY, Stoner BR, Jeffrey PR, et al: Adhesion/cementation to zirconia and other non-silicate ceramics: where are we now? *Dent Mater* 2011;27:71-82
31. Singh J, Quli F, Wolfe DE, et al: An Overview: Electron Beam-Physical Vapor Deposition Technology- Present and Future Applications. Applied Research Laboratory, Pennsylvania State University, 1999.  
<http://infohouse.p2ric.org/ref/02/01162.pdf>. Accessed 12/22/16
32. Queiroz JRC, Duarte DA, Souza ROA, et al: Deposition of SiO<sub>x</sub> thin films by reactive magnetron sputtering: influence of plasma parameters on the adhesion properties between Y-TZP and resin cement for application in dental prosthesis. *Mater Res* 2011;14:212-216
33. Queiroz JR, Benetti P, Massi M: Effect of multiple firing and silica deposition on the zirconia-porcelain interfacial bond strength. *Dent Mater* 2012;28:763-768
34. Denry IL, Peacock JJ, Holloway JA: Effect of heat treatment after accelerated aging on phase transformation in 3Y-TZP. *J Biomed Mater Res B Appl Biomater* 2010;93:236-243
35. International Organization for Standardization. ISO-6872: 2008, Dental Ceramic. Geneva, ISO, 2008
36. Garvie RC, Nicholson PS: Phase analysis in zirconia systems. *J Am Ceram Soc* 1972;55:303-305
37. Kosmac T, Oblak C, Jevnikar P, et al: The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. *Dent Mater* 1999;15:426-433
38. Vatali A, Kontonasaki E, Kavouras P, et al: Effect of heat treatment and in vitro aging on the microstructure and mechanical properties of cold isostatic-pressed zirconia ceramics for dental restorations. *Dent Mater* 2014;30:272-282
39. Nogiwa-Valdez AA, Rainforth WM, Zeng P, et al: Deceleration of hydrothermal degradation of 3Y-TZP by alumina and lanthana codoping. *Acta Biomater* 2013;9:6226-6235
40. Gremillard L, Chevalier J, Epicier T, et al: Microstructural study of silica-doped zirconia ceramics. *Acta Mater* 2000;48:4647-4652
41. Samodurova A, Kocjan A, Swain MV, et al: The combined effect of alumina and silica co-doping on the ageing resistance of 3Y-TZP bioceramics. *Acta Biomater* 2014;11:477-487
42. Swain MV: Toughening mechanisms for ceramics. *Mater Sci Forum* 1989;13:237-253
43. Deville S, Gremillard L, Chevalier J, et al: Critical comparison of methods for the determination of the aging sensitivity in biomedical grade yttria-stabilized zirconia. *J Biomed Mater Res B: Appl Biomater* 2005;72:239-245
44. Pereira GK, Silvestri T, Camargo R, et al: Mechanical behavior of a Y-TZP ceramic for monolithic restorations: effect of grinding and low-temperature aging. *Mater Sci Eng C Mater Biol Appl* 2016;63:70-77
45. Subaşı MG, Demir N, Kara Ö, et al: Mechanical properties of zirconia after different surface treatments and repeated firings. *J Adv Prosthodont* 2014;6:462-467
46. Sato H, Yamada K, Pezzotti G, et al: Mechanical properties of dental zirconia ceramics changed with sandblasting and heat treatment. *Dent Mater J* 2008;27:408-414
47. Matsumoto RLK: Strength recovery in degraded yttria-doped tetragonal zirconia polycrystals. *J Am Ceram Soc* 1985;68:C213
48. Yilmaz H, Aydin C, Gul BE: Flexural strength and fracture toughness of dental core ceramics. *J Prosthet Dent* 2007;98:120-128
49. Souza RO, Valandro LF, Melo RM, et al: Air-particle abrasion on zirconia ceramic using different protocols: effects on biaxial flexural strength after cyclic loading, phase transformation and surface topography. *J Mech Behav Biomed Mater* 2013;26:155-163
50. Kelly JR: Perspectives on strength. *Dent Mater* 1995;11:103-110
51. Ozcan M, Melo RM, Souza RO, et al: Effect of air-particle abrasion protocols on the biaxial flexural strength, surface characteristics and phase transformation of zirconia after cyclic loading. *J Mech Behav Biomed Mater* 2013;20:19-28
52. Gupta PK: Strengthening by surface damage in metastable tetragonal zirconia. *J Am Ceram Soc* 1980;63:117-121
53. Green DJ: A technique for introducing surface compression into zirconia ceramics. *J Am Ceram Soc* 1983;66:C178-C179
54. Cattani-Lorente M, Scherrer SS, Ammann P, et al: Low temperature degradation of a Y-TZP dental ceramic. *Acta Biomater* 2011;7:858-865
55. Chevalier J, Gremillard L, Deville S: Low-temperature degradation of zirconia and implications for biomedical implants. *Ann Rev Mater Res* 2007;37:1-32
56. Kosmač T, Jevnikar P, Funduk N, et al: Strength and reliability of surface treated Y-TZP dental ceramics. *J Biomed Mater Res* 2000;53:304-313
57. Mainjot AK, Douillard T, Gremillard L, et al: 3D-characterization of the veneer-zirconia interface using FIB nano-tomography. *Dent Mater* 2013;29:157-165