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Characterization of a Diamond Ground Y-TZP and Reversion of the Tetragonal to Monoclinic Transformation

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Clinical Relevance

Surface characterization of Y-TZP frameworks provides a better understanding of why adjustments can weaken the interface between such structures and veneering porcelain. A heat treatment after grinding can reverse the transformation and potentially restore the protective toughening of the restoration.

SUMMARY

Purpose: To characterize the surface of an yttria-stabilized zirconia (Y-TZP) ceramic after diamond grinding in terms of its crystalline phase, morphology, mean roughness (*Ra*), and wettability as well as to determine a thermal treatment to reverse the resulting tetragonal to monoclinic (*t-m*) transformation.

Methods and Materials: Y-TZP specimens were distributed into different groups according to the actions (or no action) of grinding and irrigation. Grinding was accomplished using a diamond stone at a low speed. The samples were characterized by x-ray diffraction (XRD), scanning electron microscopy, goniometry, and profilometry. *In situ* high-temperature XRD was used to determine an annealing temperature to reverse the *t-m* transformation. *Ra* was submitted to the Kruskal-Wallis test, followed by the Dunn test (α=0.05). The volume fraction of the monoclinic phase and contact angle were submitted to one-way analysis of variance, followed by the Tukey test (α=0.05).

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Results: Monoclinic zirconia was observed on the surface of samples after dry and wet grinding with a diamond stone. The volume fraction of the monoclinic phase was smaller on the dry ground samples (3.6%±0.3%) than on the wet ground samples (5.6%±0.3%). High-temperature XRD showed reversion of the *t-m* phase transformation, which started at 700°C and completed at 800°C in a conventional oven.

Conclusions: Grinding with a diamond stone partially transformed the crystalline phase on the surface of a Y-TZP ceramic from tetragonal to monoclinic zirconia while simultaneously increasing the surface roughness and wettability. The *t-m* transformation could be reversed by heat treatment at 800°C or 900°C for 60 minutes or 1000°C for 30 minutes.

INTRODUCTION

Yttria-stabilized tetragonal zirconia polycrystal (Y-TZP) is a polycrystalline material composed of the following three polymorphic phases: monoclinic (*m*), tetragonal (*t*), and cubic (*c*) zirconia; the proportions of these phases can vary by thermomechanical factors, rendering the material tougher. However, if the phase transformation is triggered during processing, the transformation might not result in beneficial properties.[1,2] In dentistry, Y-TZP has been widely used as a framework for metal-free crowns and fixed partial dentures, implants, abutments, and orthodontic brackets[1-6] because of its interesting optical and esthetic properties, high hardness, wear resistance, high flexural strength, and high resistance to fracture, inherent to the toughening process due to the tetragonal to monoclinic (*t-m*) transformation.[1-3,7]

However, aging, delamination, and chipping of veneering porcelain are problems often reported in the literature[4,5,8-11] associated with this type of material. Aging is connected to prolonged contact with an aqueous medium, which favors a slow phase *t-m* transformation on the material surface, which causes the loss of grains, increases in roughness, and the formation of microcracks as well as decreases in the hardness and strength of the material.[5,8] Delamination and chipping occur through different mechanisms, such as the mismatching of thermal expansion coefficients between the framework and the veneer ceramic, microstructural defects in the porcelain, porosity, surface defects, improper support frameworks, overload, fatigue, and low fracture resistance of the veneer ceramic.[4,10-13] While chipping results from the cohesive failure of the veneering porcelain, delamination arises from the adhesive failure between the zirconia framework and porcelain coverage.[4,11]

Attempts to improve the adhesion at the interface between zirconia and veneering porcelain have been undertaken. Different surface treatments, such as sandblasting, liner applying, polishing, grinding, etching, laser etching, and silicatization,[13-17] have been used to change the zirconia surface, increasing its roughness or its surface energy to improve wettability and, thus, favor adhesion.[13,16,17]

Special attention must be paid to grinding because, although it has been studied as a method to improve adhesion, it is often necessary during clinical trials to modify and adapt the sintered frameworks,[14,18-20] which can induce stresses promoting *t-m* transformation.[1,14,21,22] This transformation momentarily toughens the zirconia by local expansion and crack closing because the specific volume of the monoclinic phase is greater than the tetragonal phase; however, it can have a negative impact on the mechanical stability of fixed prostheses over time. After the *t-m* transformation, the material presents total or partial loss of the ability to prevent or to retard the propagation of cracks, and it can become critically friable.[14,23-26]

Given these contradictory results,[14,18,21,22,25,27-31] some authors have emphasized the importance of studying the effects of grinding with different types of instruments at high and low speeds.[1,20,30,32] Regardless of the method used for grinding, changes in the material surface can increase the surface roughness, induce defects, and activate the *t-m* transformation,[14,18,21,22,27,29-31] thereby increasing the volume percentage of monoclinic zirconia. Such phase transformation depends on the metastability of the conversion, the grinding severity, and the temperature at the site.[14,25,29,30] A higher content of monoclinic zirconia, together with greater roughness and a higher concentration of surface defects, renders the material more susceptible to long-term degradation and loss of mechanical strength.[3,5,8,21,23,26,30,33] Different grinding procedures have been studied in the literature,[19,22,24,25,32] but to the best of our knowledge, no one has examined whether grinding with a diamond stone is a less harmful technique for Y-TZP.

Considering the phase transformation and superficial defects induced by grinding, a heat treatment can be performed before application of a veneering porcelain.[5,19,32] It was suggested that the applied heat acts as a regenerative treatment,[13] reversing

Table 1: *Distribution of the Experimental Groups*

Group	Condition
C	Sintered without grinding, control
DG	Sintered and dry ground
WG	Sintered and wet ground

the monoclinic zirconia to the tetragonal phase, and thus returning the zirconia to a metastable tetragonal phase.[5,19] In addition to the reversing transformation, such regenerative thermal treatment is very interesting because it could also act to close the surface microcracks caused by grinding.[13] Such treatment would then reduce all of the aforementioned problems, making it extremely important for the durability of a prosthesis.[5,19,32]

In combination with a less invasive grinding technique, a protocol of heat treatment with appropriate parameters could render the prosthesis material more stable against fracture and degradation. Although several authors have studied the application of heat treatment after the grinding procedure,[5,13,14,19,23,28,32] there is still no consensus in the literature on whether [5,19,32] or not[13,14,23,28] such a treatment should be performed, which could be related to the use of inappropriate parameters of temperature and time. It is essential to determine the effect of stone grinding and to elaborate a protocol of regenerative heat treatment for Y-TZP.

Thus, the aims of the present study were to characterize the crystalline phases, surface morphology, roughness, and wettability of the surfaces of Y-TZP specimens after grinding with a diamond stone with or without irrigation and to determine the time and temperature to reverse the *t-m* transformation to establish a protocol for regenerative heat treatment (annealing) of ground Y-TZP. The null hypothesis was that grinding with a diamond stone would not change the crystallographic phases, morphology, roughness, or wettability of the surface of a Y-TZP ceramic.

METHODS AND MATERIALS

Specimen Preparation

Blocks of Y-TZP zirconia (Lava Frame Zirconia, 3M ESPE AG, Seefeld, Germany) were sectioned into pre-sintered specimens using a high precision cutoff machine (ISOMET 1000, Buehler, Lake Bluff, IL, USA) with a diamond disc (Series Diamond 15LC, Buehler) under water irrigation. The samples were cut into two different sizes as follows: 10 mm × 10 mm × 1.5 mm for non-ground specimens and 10 mm × 10 mm × 1.9 mm for ground specimens.

Irregularities at the specimen edges were removed with silicone tips (Exa-cerapol, Edenta, Labordental, Hauptstrasse, Switzerland). The upper surfaces of the specimens were sequentially polished with #1200, #1500, and #2000 silicon carbide sandpaper (401Q, 3M ESPE, Sumaré, Brazil). The final dimensions were measured using digital calipers (500-144B, Mitutoyo Sul Americana, Suzano, Brazil). Sintering was accomplished with a heat treatment program of 8 hours at a maximum temperature of 1500°C, following the manufacturer's instructions (Lava Furnace 200, Dekema Dental-Keramiköfen, Freilassing, Germany). The specimens were divided into three groups according to the experimental procedures (Table 1).

Zirconia Grinding

A homemade device (Figure 1a) was developed at the Araraquara Dental School, UNESP, to standardize the amount of longitudinal grinding. It was used to remove 0.3 mm from the surfaces of zirconia samples with and without irrigation (groups WG and DG, respectively). The sample grinding was performed with a diamond stone (MasterCeram, MCE 133 104, Eurodental Commercial Importer Ltd, São Paulo, Brazil) in a low-speed electric handpiece (Micro Electric Motor Bench for Prosthetics LB 100, Beltec, Araraquara, Brazil) at 20,000 rpm. During grinding, the long axis of the diamond stone was set parallel to the long axis of the sample (Figure 1b), which remained static while the electric low-speed handpiece moved with the aid of a tailstock. The WG specimens were ground under water flowing from a triple syringe (Figure 1c).

Surface Properties

X-Ray Diffraction (XRD)—XRD was used to identify the Y-TZP crystalline phases with an x-ray diffractometer D8 Advance (Bruker, Karlsruhe, Germany) using the following settings: a Cu $K\alpha_1$ wavelength = 1.5406 Å and a $K\alpha_2$ wavelength = 1.5444 Å, an intensity ratio of $I_{k\alpha 2}/I_{k\alpha 1} = 0.5$, 2θ between 20° to 80°, an angular step of 0.02°, the use of continuous mode, a step time of 3 seconds, and a sample size of n = 3. The monoclinic and tetragonal phases were identified by comparison with the crystal structures described in Gualtieri and others[34] and Bondars and others.[35]

Scanning Electron Microscopy (SEM)—Specimens (n=2) were covered with carbon, and their surfaces

Figure 1. *(a): Grinding device. (b): Dry grinding. (c): Wet grinding.*

were examined using a scanning electron microscope (Inspect F50, FEI, Achtseweg Noord 5, Eindhoven, Netherlands).

Mean Roughness—The mean roughness of specimens (*Ra*, μm; n=10) was measured using a profilometer (Mitutoyo SJ 400, Mitutoyo Corporation, Yokohama, Japan) with a reading accuracy of 0.01 μm, a read length of 2.5 mm, an active tip speed of 0.5 mm/s, and an active tip radius of 5 μm. Three measurements were obtained for each surface, and the average was calculated. For the G groups, the measurements were performed in the opposite direction of the grinding lines.

Wettability—Wettability (n=5) was determined by measuring the static contact angle of a sessile drop of distilled water in an automatic goniometer (Dataphysics, OCA20, Filderstadt, Baden-Württemberg, Germany). The wettability measurement was performed at a controlled temperature (20°C) and after a settling time of 20 seconds for a distilled water drop (15 μL). The average contact angle was calculated from three readings performed on the surface of each sample.

High-Temperature In Situ XRD—To set the parameters for establishing a protocol for regenerative heat treatment (annealing), the specimen that presented the largest fraction of monoclinic phase identified by room temperature XRD (group WG) was submitted to an *in situ* high-temperature XRD analysis (n=3). For this analysis, a heating chamber was coupled to the same XRD equipment described previously. The XRD patterns were measured at a step size of 2.7° and a step time of 0.5 seconds in continuous mode at temperatures of 25°C, 100°C, 200°C, 300°C, 400°C, 500°C, 600°C, 700°C, 800°C, and 900°C. The sample was heated at 10°C/min up to the set temperatures, and the temperature was maintained for 5 minutes for stabilization before each analysis. The analyses were performed in a unique sequence, and it took 10 minutes to complete the analysis at each temperature step.

Annealing—The specimens with the highest amount of monoclinic zirconia after grinding (group WG) were heat treated at different temperatures and for different time periods to study the possibility of reversion of the *t-m* transformation. Isothermal heat treatments were performed in a lab furnace (AluminiPress, EDG Equipamentos e Controles Ltda, São Carlos, Brazil) at 700°C, 800°C, 900°C, and 1000°C for 30 and 60 minutes (N=8, one specimen per temperature and time). The samples were placed in the preheated furnace, which was already at the treatment temperature. After heat treatment, the specimens were removed from the furnace and cooled to room temperature. The crystalline phases on the previously ground and annealed surfaces were then characterized by conventional XRD.

Statistical Analysis

The SEM results were submitted to descriptive analysis, and the conventional and high-temperature XRD patterns were analyzed using the Rietveld method. The normality of the mean roughness (*Ra*), contact angle, and amount of monoclinic phase

Table 2: *Average Volume Fraction (%) and Standard Deviations of the Monoclinic Phase in Y-TZP*

Group	Monoclinic Fraction (%)*
C	0.0 ± 0.0[a]
DG	3.6 ± 0.3[b]
WG	5.6 ± 0.3[c]

** Different superscript letters indicate statistical difference ($p<0.01$).*

obtained by conventional XRD was verified by the Shapiro-Wilk test ($\alpha=0.05$). *Ra* was submitted to the Kruskal-Wallis test followed by the Dunn test ($\alpha=0.05$). The contact angle and amount of monoclinic phase were submitted to one-way analysis of variance, followed by the Tukey test ($\alpha=0.05$).

RESULTS

X-Ray Diffraction

The results of XRD are shown in Table 2. The presence of monoclinic zirconia was observed in both G groups (DG and WG). The volume fraction of monoclinic zirconia in the group ground with irrigation (WG, 5.6%±0.3%) was statistically higher ($p<0.01$) than that in the DG group (3.6%±0.3%).

Scanning Electron Microscopy

Figures 2 through 5 show SEM micrographs of the specimens in which one can observe the grinding effects on the material surface. For groups DG (Figure 3) and WG (Figure 4), grinding produced scratches, which were parallel to the direction of longitudinal movement of the diamond stone. After roughening the sample surface with a diamond stone, the heterogeneous wear hid the grain microstructure under the microscope. By observing the

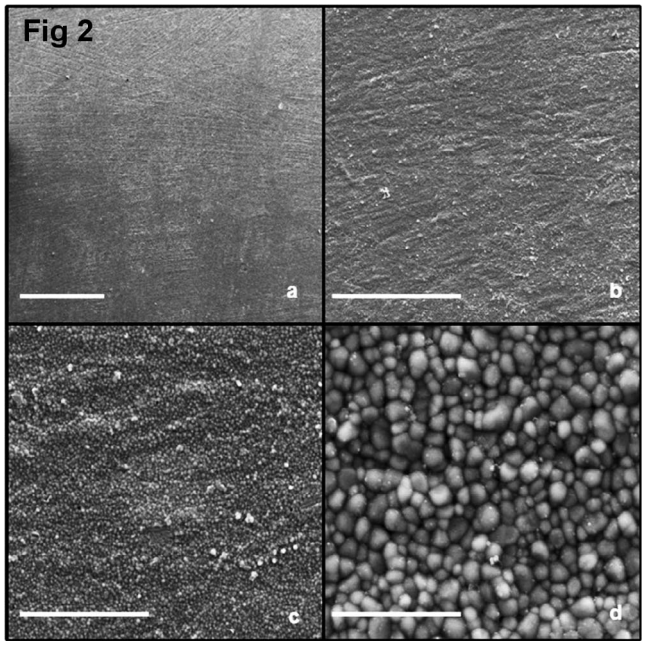

Figure 2. *Surface topography of sintered Y-TZP (C) without grinding at different magnifications. Scale bars correspond to (a): 500 μm, (b): 100 μm, (c): 20 μm and (d): 4 μm.*

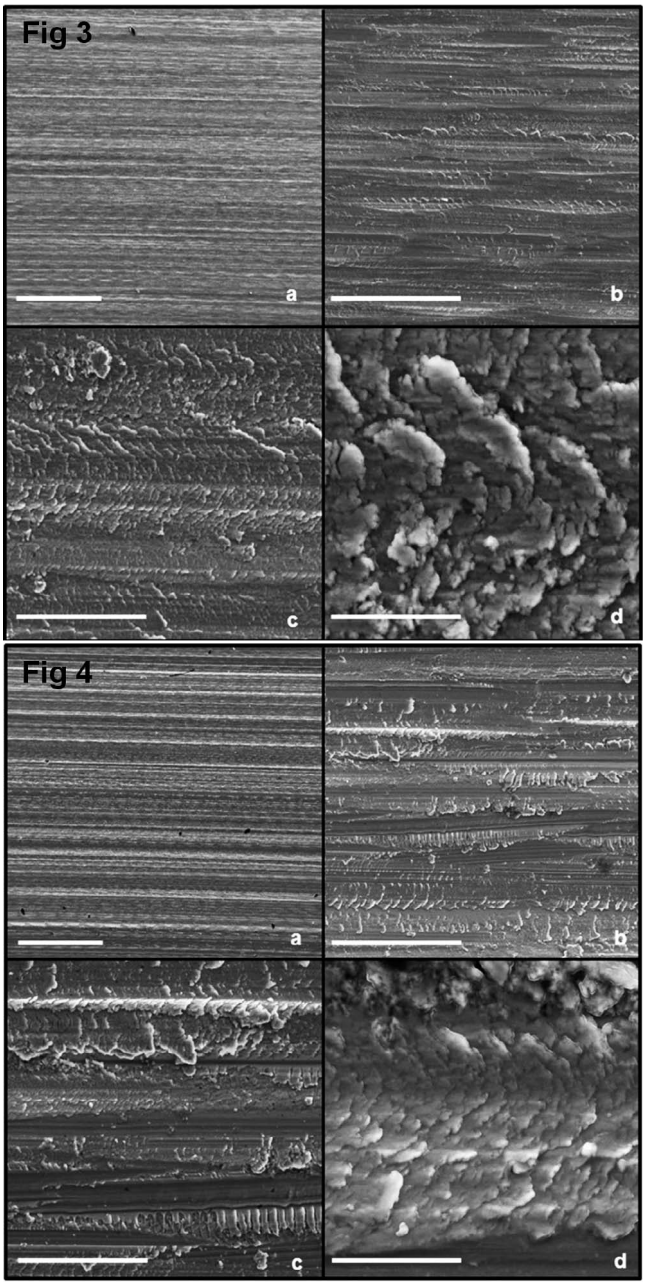

Figure 3. *Surface topography of sintered and dry ground Y-TZP (DG) at different magnifications. Scale bars correspond to (a): 500 μm, (b): 100 μm, (c): 20 μm, and (d): 4 μm.*

Figure 4. *Surface topography of sintered and wet ground zirconia (WG) at different magnifications. Scale bars correspond to (a): 500 μm, (b): 100 μm, (c): 20 μm, and (d): 4 μm.*

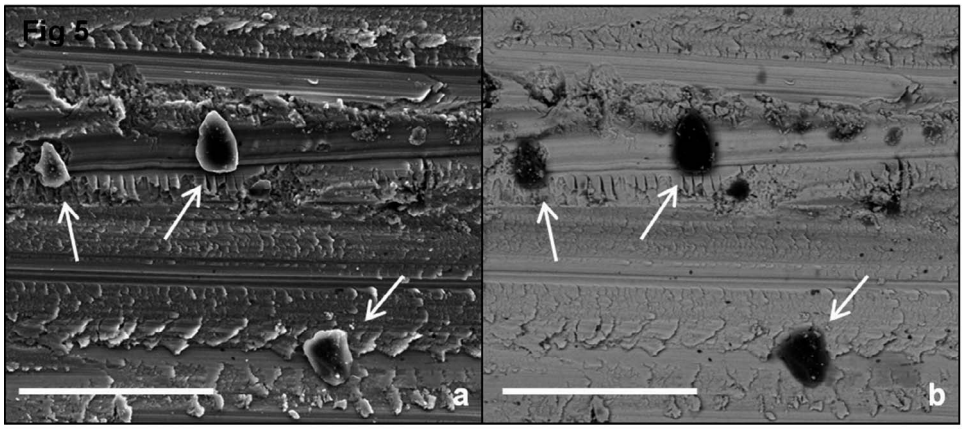

Figure 5. *Surface topography of a WG sample observed by SEM with (a): secondary electrons, and (b): backscattered electrons. Arrows indicate particles compatible with diamond stone. Bar corresponds to 20 μm.*

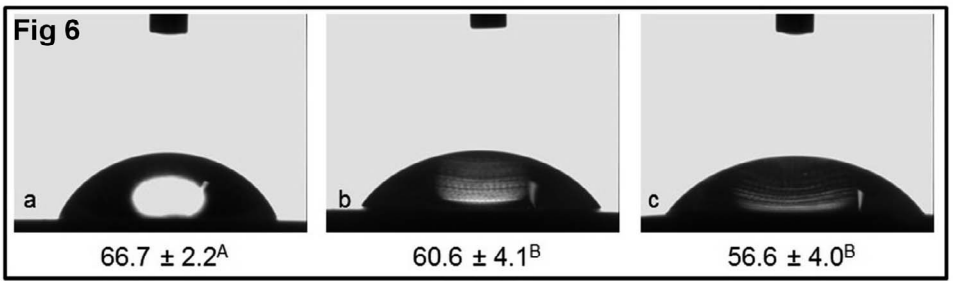

Figure 6. *Spreading of a distilled water drop with contact angle mean values and standard deviations. (a): C group, (b): DG group, and (c): WG group.*

grinding patterns at the same magnification in the SEM, one could observe that some grinding lines in Figure 4a were darker than those in Figure 3a, showing that the scratch valleys were deeper in group WG than in group DG (confirmed subsequently with profilometry), which, together with a more splintered surface, indicated that wet grinding was more severe. Figure 5 shows particles on the surface of one such sample after grinding. Using SEM/BSE (backscattered electrons), one could observe that these particles had a composition different from (lighter than) zirconia, likely because of the presence of fragments of diamond stone.

Mean Roughness (Ra)

The medians and standard deviations of *Ra* from all of the groups are shown in Table 3. Statistically significant differences were observed among all of the groups ($p<0.01$). Group WG was rougher than the others.

Table 3: *Medians and Standard Deviations of* Ra *(μm) of Specimens From All of the Groups*

Group	*Ra**
C	0.14 ± 0.02^{a}
DG	1.44 ± 0.13^{b}
WG	3.24 ± 0.75^{c}

** Different superscript letters indicate statistical difference (p<0.01).*

Wettability

The images of the contact angles and the averages and standard deviations of the specimens are shown in Figure 6. Statistically significant differences were observed between the contact angles ($p<0.01$). The ground specimens presented average contact angles smaller than the controls ($p<0.01$), but there was no significant difference between the WG and DG groups.

In Situ High-Temperature XRD

Table 4 shows the percentages of tetragonal and monoclinic zirconia obtained by *in situ* high-temperature XRD. As shown in Table 4, one could observe that annealing at 700°C under the conditions of high-temperature XRD could totally reverse the monoclinic zirconia to the tetragonal phase.

Annealing

Table 5 shows the volume fraction of tetragonal and monoclinic zirconia as a function of the time and temperature of isothermal heat treatments. It could be observed that in the lab furnace the *m-t* transformation was complete after 800°C for 60 minutes. At 900°C, the entire transformation also occurred in 60 minutes, and at 1000°C, the monoclinic zirconia was totally eliminated in 30 minutes.

Table 4: *Volume Fraction of Tetragonal and Monoclinic Zirconia on the Specimen Surface Depending on Temperature in the* In Situ *High-Temperature X-Ray Diffraction*

Temperature	Tetragonal (%)	Monoclinic (%)
25°C	94.6 ± 0.3	5.4 ± 0.3
100°C	95.2 ± 1.7	4.8 ± 1.7
200°C	91.6 ± 4.0	8.4 ± 4.0
300°C	92.1 ± 2.4	7.9 ± 2.4
400°C	91.6 ± 2.0	8.4 ± 2.0
500°C	94.4 ± 1.5	5.6 ± 1.5
600°C	96.0 ± 0.4	4.0 ± 0.4
700°C	100.0 ± 0.0	0.0 ± 0.0
800°C	100.0 ± 0.0	0.0 ± 0.0
900°C	100.0 ± 0.0	0.0 ± 0.0

Table 5: *Volume Fraction of Tetragonal and Monoclinic Zirconia as a Function of Time and Temperature of the Heat Treatment*

Temperature	Time (min)	Tetragonal (%)	Monoclinic (%)
700°C	30	98.3	1.7
	60	99.2	0.8
800°C	30	99.0	1.0
	60	100.0	0.0
900°C	30	99.5	0.5
	60	100.0	0.0
1000°C	30	100.0	0.0
	60	100.0	0.0

DISCUSSION

Although zirconia frameworks are obtained using CAD-CAM (computer-aided design/computer-aided manufacturing) systems, there is often a need for grinding, whether in the clinic or prosthetic laboratory.[18,19] While most of the available studies have evaluated the effects of grinding with diamond burs,[22,24,27] other methods, such as diamond stones at low speed, have not been studied in the literature, but such grinding can cause different changes on the Y-TZP surface.

Therefore, the present study evaluated the effects of grinding the surface of a Y-TZP ceramic with a diamond stone, with and without water irrigation, by characterizing the resulting superficial crystalline phases, morphology, roughness, and wettability and by determining the time and temperature to reverse the *t-m* transformation to establish a protocol for a regenerative heat treatment (annealing) of diamond-ground Y-TZP. The null hypothesis (grinding with diamond stone would not change the crystallographic phases, roughness, or wettability of the surface of a Y-TZP ceramic) was not supported.

As observed in the present study, grinding with a diamond stone led to significant changes in the material. After grinding, one could observe changes in the surface amount of monoclinic and tetragonal zirconia, morphology, roughness, and wettability. In the literature,[19,22,24,26,27] factors such as the abrasive grain size, wear time, load pressure, tool efficiency, and temperature of grinding could cause changes in the material associated with the polymorphic transformation of the tetragonal zirconia to the monoclinic phase (*t-m*).

The *t-m* phase transformation produced a toughening effect in which zirconia grains increased in size by becoming monoclinic. Grinding, sandblasting, and/or chemical etching[24,25,32] induce crack nucleation and growth on the surface. In turn, this action causes pressure release in the microstructure around the metastable tetragonal grains, subsequently causing the tetragonal to monoclinic transformation and forcing cracks to close. This transformation can increase the flexural strength of the material,[19] but it can also cause the loss of the ability to prevent the spread of cracks,[30,36] it might favor long-term degradation,[8,5,14] and it can damage the adhesion of the veneering porcelain.[4,12,13,22,25]

Grinding with diamond stone with (WG) or without (DG) irrigation induced the *t-m* phase transformation, as evidenced in Table 2. Grinding under water (WG) produced larger amounts of transformation and monoclinic phase, which is in accordance with some authors' results showing that grinding led to higher monoclinic content.[19,24,25,32] However, in these studies, grinding was performed using diamond burs, while in the present study, it was conducted with a diamond stone at a lower speed.

The differences relative to the amount of change measured in the DG and WG groups could be attributed to the cutting power of the diamond stone in these different situations because the grinding severity was directly related to the amount of *t-m* transformation.[1,29] It was observed during grinding with irrigation that water served as a cleaning agent, removing the stone powder, increasing the cutting capacity, and therefore providing more severe grinding. According to Wang and others,[37] grinding power increases due to irrigation, making

the cutting instrument more efficient. Moreover, the lack of lubrication of the stone during dry grinding (DG group) contributed to the impregnation of zirconia powder in the tool, a phenomenon described as "slurrying" in engineering,[38] and in this case, the diamond stone produced less severe grinding, resulting in a polished surface.

The effect of grinding on the ceramic material's surface was demonstrated by SEM images. It was observed for groups DG and WG that grinding produced scratches parallel to the direction of longitudinal movement of the diamond stone on the ceramic surface and a more irregular structure, with the presence of chips and concealment of the structure of the grains (Figures 3 and 4). In group WG, the wear valleys (Figure 4) were deeper than in group DG, and particles that had possibly detached from the diamond stone (Figure 5) were observed on the worn surface. BSE SEM showed that the composition of these fragments was lower in atomic weight than that of zirconia because of the darker glow.

The results of roughness (Table 3) were in agreement with the SEM images. The samples ground under irrigation showed higher *Ra* values ($p<0.05$). These results corroborated the micrograph results, which showed the influence of the deep valleys and particle deposition from the diamond stone on this surface. Grinding without irrigation yielded a less uneven surface and a lower phase transformation due to polishing afforded by the cutting tool, as described previously. The function of the polishing tool used in this study was studied by Chavali and others,[39] who observed a good polishing effect with the stone at a rotation of approximately 15,000 rpm with no irrigation.

Grinding increased the specimens' wettability (Figure 6) ($p<0.05$); however, there was no difference in the water drop spreading after grinding with and without irrigation, unlike what occurred with the roughness of the specimens. The *Ra* difference between the DG and WG groups was not sufficient to modify the wetting behavior of zirconia by water. This wettability difference between the worn groups, even with a major variation in roughness, might be related to the surface pattern and not only to the numerical value of *Ra*. Among the grinding groups, even at a larger value of *Ra*, the change in the surface pattern was smaller than the change observed between the ground groups and controls.

According to Noro and others,[40] in addition to surface morphology, the physical chemistry of the material also affects the wettability; therefore, beyond the standard roughness, the contamination of samples from the surfaces of the WG group by particles belonging to the diamond stone (Figure 5) and possibly the presence of natural hydrocarbons in the atmosphere[41] might have caused the drop spreading to be similar between the DG and WG groups. Even the samples cleaned by ultrasound had compounds that might have penetrated into the deepest valleys observed in group WG. It has been observed that chemical compounds consisting of carbon decrease the wettability of the surface of Y-TZP.[40,41]

As already mentioned, monoclinic grains can impair the long-term degradation of Y-TZP. Some manufacturers and researchers have suggested that an annealing process can reverse the *t-m* phase transformation caused by grinding. Such reverse transformation produces a tougher microstructure, minimizing the problems previously reported, which include degradation and the loss of adhesion of the veneering porcelain.[19,23,30]

The suggestion to heat-treat the material after grinding is not new. Denry and Holloway[23] fully reversed the phase transformation, that is, promoted the *m-t* reaction after heat treatment at 1000°C for 1 hour. However, various suggestions for treatment temperatures and times have emerged, with time periods varying between 15 minutes and 2 hour and temperatures between 500°C and 1200°C.[13,14,23,28,29]

In the present study, using high-temperature XRD, it was possible to more precisely observe the temperature at which the tetragonal to monoclinic phase transformation reversed in a commercial Y-TZP after grinding (Table 4). It was observed in specimens from the WG group that at temperatures greater than 700°C the *m-t* transformation occurred completely after the heat treatment schedule of the *in situ* high-temperature XRD, suggesting a temperature at this level for the reverse heat treatment. Thus, the temperature of 700°C served as a guide in the study of a heat treatment protocol.

Heat treatments were thus performed in a lab furnace at 700°C, 800°C, 900°C and 1000°C for 30 and 60 minutes. Table 5 shows that monoclinic zirconia remained on the surface of a WG sample after isothermal heat treatments at 700°C for 30 and 60 minutes. The ZrO_2-Y_2O_3 phase equilibrium diagram[42] shows a eutectoid reaction of $m+c \rightarrow t$ (by heating) at approximately 565°C and 2.5% Y_2O_3 (mole). At temperatures greater than ~565°C and with a typical molar composition of ZrO_2-3% Y_2O_3, the overall monoclinic phase vanishes, giving rise to

tetragonal and cubic zirconia when equilibrium is reached. In the cooling path, tetragonal zirconia can subsist in a metastable form, constrained by the neighboring cubic matrix. Thus, the reversal caused by annealing treatment must be suitable to convert the monoclinic to tetragonal zirconia at the same time that it retains the tetragonal form during cooling to room temperature. The nonexistence of the monoclinic phase after annealing at 700°C in the *in situ* high-temperature XRD could be explained by the longer heating time (~ 3 hours) and repetitive dwelling at different temperatures before reaching this temperature. In general, time periods longer than 1 hour would not be feasible for prosthetic preparation. In a conventional oven, with isothermal heat treatments, the total reversal of the monoclinic phase to tetragonal zirconia was obtained at 800°C after 60 minutes (Table 5), which was a lower temperature than those found in the literature.[13,14,23] At 900°C, the total reversal was observed in 60 minutes, corroborating the study of Kosmac and others.[14] This temperature level is less than that proposed by Denry and Holloway[23] and Fischer and others[13] of 1000°C for 15 minutes. For Denry and Holloway,[23] temperatures less than 1000°C were not sufficient to reverse the monoclinic to the tetragonal phase, whereas for Fischer and others,[13] the monoclinic phase could be transformed into the tetragonal at 1000°C, but microcracks in the material surface would not close, suggesting the need for further studies. The present study suggested that, together with the reversal of the *t-m* polymorphic transformation at temperatures greater than 800°C, a mechanism of crack healing must be active to constrain the transformed grains of t-ZrO_2 in the cubic matrix, retaining it in the metastable tetragonal form at room temperature. Nevertheless, further studies are necessary to confirm this hypothesis.

According to the manufacturer, the diamond stone used in the present work is recommended for use without irrigation, but it was tested here with irrigation in an attempt to promote a less aggressive procedure, following studies that suggested that refrigerated grinding caused fewer surface defects and produced an adequate compressive layer on the surface of Y-TZP.[1,14] However, in the present study, grinding with water caused greater damage to zirconia, with the MasterCeram diamond stone indicated for grinding without irrigation at approximately 20,000 rpm. Furthermore, to reverse the *t-m* transformation after diamond grinding, it is appropriate to perform a regenerative heat treatment at 800°C or 900°C for 60 minutes or 1000°C for 30 minutes.

CONCLUSIONS

Grinding with a diamond stone transformed part of the tetragonal crystallographic phase on the surface of Y-TZP ceramics into monoclinic zirconia and increased the surface roughness and wettability. Dry grinding with a diamond stone was less prejudicial to the zirconia. Heating at 800°C or 900°C for 60 minutes or at 1000°C for 30 minutes was an efficient treatment for the total reversion of the *t-m* phase transformation.

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Conflict of Interest

The authors of this manuscript certify that they have no proprietary, financial, or other personal interest of any nature or kind in any product, service, and/or company that is presented in this article.

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REFERENCES

1. Vagkopoulou T, Koutayas SO, Koidis P, & Strub JR (2009) Zirconia in dentistry: Part 1. Discovering the nature of an upcoming bioceramic *European Journal of Esthetic Dentistry* **4(2)** 130-151.
2. Piconi C, & Maccauro G (1999) Zirconia as a ceramic biomaterial *Biomaterials* **20(1)** 1-25.
3. Denry I, & Kelly JR (2008) State of the art of zirconia for dental applications *Dental Materials* **24(3)** 299-307.
4. Sailer I, Pjetursson BE, Zwahlen M, & Hämmerle CH (2007) A systematic review of the survival and complication rates of all-ceramic and metal-ceramic reconstructions after an observation period of at least 3 years. Part II: Fixed dental prostheses *Clinical Oral Implants Research* **18(3)** 86-96.
5. Lee TH, Lee SH, Her SB, Chang WG, & Lim BS (2012) Effects of surface treatments on the susceptibilities of low temperature degradation by autoclaving in zirconia *Journal of Biomedical Materials Research Part B Applied Biomaterials* **100(5)** 1334-1343.
6. Studart AR, Filser F, Kocher P, & Gauckler LJ (2007) In vitro lifetime of dental ceramics under cyclic loading in water *Biomaterials* **28(17)** 2695-2705.
7. Garvie RC, & Nicholson PS (1972) Structure and thermomechanical properties of partially stabilized zirconia in CaO-ZrO_2 system *Journal of the American Ceramic Society* **55** 152-157.

8. Chevalier J (2006) What future for zirconia as a biomaterial? *Biomaterials* **27(4)** 535-543.
9. Larsson C, & Wennerberg A (2014) The clinical success of zirconia-based crowns: A systematic review *International Journal of Prosthodontics* **27(1)** 33-43.
10. Sonza QN, Della Bona A, & Borba M (2014) Effect of the infrastructure material on the failure behavior of prosthetic crowns *Dental Materials* **30(5)** 578-585
11. Anusavice KJ (2012) Standardizing failure, success, and survival decisions in clinical studies of ceramic and metal-ceramic fixed dental prostheses *Dental Materials* **28(1)** 102-111.
12. Al-Amleh B, Neil Waddell J, Lyons K, & Swain MV (2014) Influence of veneering porcelain thickness and cooling rate on residual stresses in zirconia molar crowns *Dental Materials* **30(3)** 271-280.
13. Fischer J, Grohmann P, & Stawarczyk B (2008) Effect of zirconia surface treatments on the shear strength of zirconia/veneering ceramic composites *Dental Materials Journal* **27(3)** 448-454
14. Kosmac T, Oblak C, Jevnikar P, Funduk N, & Marion L (2000) Strength and reliability of surface treated Y-TZP dental ceramics *Journal of Biomedical Materials Research* **53(4)** 304-313.
15. Komine F, Fushiki R, Koizuka M, Taguchi K, Kamio S, & Matsumura H (2012) Effect of surface treatment on bond strength between an indirect composite material and a zirconia framework *Journal of Oral Science* **54(1)** 39-46.
16. Liu D, Matinlinna JP, Tsoi JK, Pow EH, Miyazaki T, Shibata Y, & Kan CW (2013) A new modified laser pretreatment for porcelain zirconia bonding *Dental Materials* **29(5)** 559-565.
17. Queiroz JR, Benetti P, Massi M, Junior LN, & Della Bona A (2012) Effect of multiple firing and silica deposition on the zirconia-porcelain interfacial bond strength *Dental Materials* **28(7)** 763-768.
18. Canneto JJ, Cattani-Lorente M, Durual S, Wiskott AH, & Scherrer SS (2016) Grinding damage assessment on four high-strength ceramics *Dental Materials* **32(2)** 171-182.
19. Ramos GF, Pereira GK, Amaral M, Valandro LF, & Bottino MA. (2016) Effect of grinding and heat treatment on the mechanical behavior of zirconia ceramic *Brazilian Oral Research* **30(1)** 1-8.
20. Nakamura K, Kanno T, Milleding P, & Ortengren U (2010) Zirconia as a dental implant abutment material: A systematic review *International Journal of Prosthodontics* **23(4)** 299-309.
21. Amaral M, Valandro LF, Bottino MA, & Souza RO (2013) Low-temperature degradation of a Y-TZP ceramic after surface treatments *Journal of Biomedical Materials Research Part B Applied Biomaterials* **101(8)**1387-1392.
22. Pereira GK, Amaral M, Simoneti R, Rocha GC, Cesar PF, & Valandro LF (2014) Effect of grinding with diamond-disc and -bur on the mechanical behavior of a Y-TZP ceramic *Journal of the Mechanical Behavior of Biomedical Materials* **37(September)** 133-134.
23. Denry IL, & Holloway JA (2006) Microstructural and crystallographic surface changes after grinding zirconia-based dental ceramics *Journal of Biomedical Materials Research Part B Applied Biomaterials* **76(2)** 440-448.
24. Güngör BM, Yılmaz H, Karakoca Nemli S, Turhan Bal B, & Aydın C (2015) Effect of surface treatments on the biaxial flexural strength, phase transformation, and surface roughness of bilayered porcelain/zirconia dental ceramics *Journal of Prosthetic Dentistry* **113(6)** 585-595.
25. Karakoca S, & Yilmaz H (2009) Influence of surface treatments on surface roughness, phase transformation, and biaxial flexural strength of Y-TZP ceramics *Journal of Biomedical Materials Research Part B Applied Biomaterials* **91(2)** 930-937.
26. Kim JW, Covel NS, Guess PC, Rekow ED, & Zhang Y (2010). Concerns of hydrothermal degradation in CAD/CAM zirconia *Journal of Dental Research* **89(1)** 91-95.
27. Aboushelib MN, & Wang H (2010) Effect of surface treatment on flexural strength of zirconia bars *Journal of Prosthetic Dentistry* **104(2)** 98-104.
28. Fonseca RG, Abi-Rached Fde O, da Silva FS, Henriques BA, & Pinelli LA (2014) Effect of surface and heat treatments on the biaxial flexural strength and phase transformation of a Y-TZP ceramic *Journal of Adhesive Dentistry* **16(5)** 451-458.
29. Guazzato M, Quach L, Albakry M, & Swain MV (2005) Influence of surface and heat treatments on the flexural strength of Y-TZP dental ceramic *Journal of Dentistry* **33(1)** 9-18.
30. Işeri U, Ozkurt Z, Yalnız A, & Kazazoğlu E (2012) Comparison of different grinding procedures on the flexural strength of zirconia *Journal of Prosthetic Dentistry* **107(5)** 309-315.
31. Qeblawi DM, Munoz CA, Brewer JD, & Monaco EA (2010) The effect of zirconia surface treatment on flexural strength and shear bond strength to a resin cement *Journal of Prosthetic Dentistry* **103(4)** 210-220.
32. Subaşı MG, Demir N, Kara Ö, Ozturk AN, & Özel F (2014) Mechanical properties of zirconia after different surface treatments and repeated firings *Journal of Advanced Prosthodontics* **6(6)** 462-467.
33. Monaco C, Tucci A, Esposito L, & Scotti R (2013) Microstructural changes produced by abrading Y-TZP in presintered and sintered conditions *Journal of Dentistry* **41(2)** 121-126.
34. Gualtieri A, Norby P, Hanson J, & Hriljac (1996) Rietveld refinement using synchrotron X-ray powder diffraction data collected in transmission geometry using an imaging-plate detector: application to standard m-ZrO_2 *Journal of Applied Crystallography* **29(6)** 707-713.
35. Bondars B, Heidemane G, & Grabis J (1995) Powder diffraction investigations of plasma sprayed zirconia *Journal of Materials Science* **30(6)** 1621-1625.
36. Preis V, Behr M, Hahnel S, Handel G, & Rosentritt M (2012) In vitro failure and fracture resistance of veneered and full-contour zirconia restorations *Journal of Dentistry* **40(11)** 921-928.
37. Wang Z, Willet P, Deaguiar PR, & Webster J (2001) Neural network detection of grinding burn from acoustic emission *International Journal of Machine Tools and Manufacture* **41(2)** 283-309.

38. Cameron A, Bauer R, & Warkentin A (2010) An investigation of the effects of wheel-cleaning parameters in creep-feed grinding *International Journal of Machine Tools and Manufacture* **50(1)** 126-130.

39. Chavali R, Lin CP, & Lawson NC (2015) Evaluation of different polishing systems and speeds for dental zirconia *Journal of Prosthodontics* epub ahead of print http://dx.doi.org/10.1111/jopr.12396.

40. Noro A, Kaneko M, Murata I, & Yoshinari M (2013) Influence of surface topography and surface physicochemistry on wettability of zirconia (tetragonal zirconia polycrystal) *Journal of Biomedical Materials Research Part B Applied Biomaterials* **101(2)** 355-63.

41. Rupp F, Scheideler L, Olshanska N, de Wild M, Wieland M, & Geis-Gerstorfer J (2006) Enhancing surface free energy and hydrophilicity through chemical modification of microstructured titanium implant surfaces *Journal of Biomedical Materials Research* **76(2)** 323-334.

42. Scott HG (1975) Phase relationships in the zirconia-yttria system *Journal of Materials Science* **10(9)** 1527-35.