A PROPOSAL OF THERMAL ETCHING PROTOCOL ON INTERGRANULAR REGIONS OF DENTAL ZIRCONIA

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ABSTRACT

Objective: To analyze the topography and microstructure surface parameters of 3Y-TZP after different thermal treatments that aims to reach a zirconia grain boundary as close as possible to its thermodynamic equilibrium geometry, with higher surface energy state. **Methods:** 3Y-TZP surface was polished and then thermally treated at 1350°C for 10 minutes, as a means of standardizing the roughness. After this, different thermal treatments were carried out. The control group (G1) received no further treatment, Group 2 (G2) was submitted to 750°C for 3 minutes and Group 3 (G3) at 1350°C for one hour. After the treatments, the zirconia surface was analyzed by Atomic Force Microscopy (AFM) and X-ray diffraction (XRD). **Results:** G3 was the only that promoted increase in surface roughness by enlargement of the groove region. No heat treatment resulted in phase transformation —all samples remained with the same monoclinic phase content (around 4% by weight)— or grain size increase (average grain size ~ 300 nm). **Conclusions:** The present study demonstrated that G3 treatment is best suited to achieve thermal equilibrium geometry. With the addition of G3, the zirconia reached the higher surface energy state with the intergranular regions more evidenced. That is the ideal surface for future studies that aim to chemically or physically alter 3Y-TZP and promote adhesion to dental resin cements. Additionally, the results confirm that the temperature (750°C) used for the application of glazes and porcelain do not alter the topography and microstructure parameters of the 3Y-TZP surface.

KEYWORDS: Ceramics. Microscopy, atomic force. Thermic treatment. X-ray diffraction. Dental materials.

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INTRODUCTION

The use of ceramics as materials for fixed prosthesis is widespread in dentistry. This is because they are not only aesthetic materials, but also have chemical stability, biocompatibility and excellent mechanical properties.[1,2]

Among all dental ceramics, the yttria-stabilized zirconium oxide (Y-TZP) with its excellent mechanical properties, should be highlighted. The Y-TZP modulus of elasticity is around 200 GPa, accompanied by a very high melting temperature, above 2370 °C, flexural strength in the range of 700-1200 Mpa[3] and its fracture toughness is in the range of 7-10 MPa.m.½ Such properties guided the use of zirconia as core in restorations of metal-free ceramics and recently as a monolithic restoration since the advance of translucent zirconia.[4] Polycrystalline tetragonal zirconia has improved mechanical strength compared to other dental ceramics due to its ability to undergo martensitic type transformation when submitted to mechanical and/or thermal stresses. This phase transformation (tetragonal to monoclinic) is accompanied by volumetric expansion around 4% and a very large shear strain (16%) which generates a field of compressive tensions, around the transformed grains, resulting in fracture toughness increase.[5]

One of the major challenges in the dental use of Yttria-stabilized Polycrystalline tTtragonal Zirconia (Y-TZP) is its effective bonding with dental resin cement and porcelain.[6,7] Several methods have been studied and tested in the literature[2] to improve the bond strength of resin cements and the zirconia surface, such as increasing surface roughness[8], silica layer deposition, use of silane bonding agents and/or plasma.[9-11]

The intergranular region is the site at zirconia surface most susceptible to be chemically or morphologically modify to promote adhesion. This occurs because the intergranular region has higher surface energy, lower atomic density and is the site of concentration of dopants, second phase and impurities.[12]

The Heat Induced Maturation (HIM) with Selective Infiltration Etching (SIE), was proposed, as a form of dental zirconia surface treatment which alter the grain contour region in a research study.[11] The SIE method assumes that by chemically altering the grain contour region, it would be possible to intensify the groove on zirconia surface to the point of imparting a greater roughness in relation to untreated surfaces.[11] According to the results of microtensile bond strength (μTBS) obtained by such authors, the SIE treatment increased the bond strength compared to the use of other methods.

A recent study verified the influence of different Y-TZP surface treatments on topography and ceramic/resin cement interfacial fracture toughness[8]. The treatments proposed were SIE, hydrofluoridric acid etching, airborne-particle abrasion and the heat treated at 750 °C. The effect of Heat Induced Maturation (HIM) at 750 °C for 3 min. performed didn't improve the ceramic/res-

in cement interfacial fracture toughness, but it does show a slight and statistical significant increase in nano roughness (R_a) without monoclinic phase transformation.[8]

Because it is a polycrystalline ceramic, the surface of 3Y-TZP is formed by the union of several grains, each grain is defined as a region with given crystallographic orientation and the interface between these crystals is called grain boundary (GB). When the grain boundary is on the surface a recess (groove) is formed at that location.

The GB are regions of higher surface energy and lower atomic density in relation to the crystal, and therefore are sites that concentrate the impurities, dopants and second phases. A physical effect of this higher surface energy is that the GB regions of a ceramic or metal are usually conditioned (etched) with acids for better visualization under a microscope, a common practice in physical metallurgy.[12] However, in Y-TZP, because of its high chemical stability, the chemical etching (by acids) of the zirconia grains is not satisfactory.

Another usual way of grain boundary evidence used in physical metallurgy is the thermal etching. During such heat treatment, the material is exposed to high temperatures which will allow the surface geometry of the GB to reach or approach its thermal equilibrium configuration.

Both forms of evidence of intergranular region cited (chemical and thermal) results in a variation in the profile of heights of surface relief where grooves will form recess regions, but there is no clear protocol in the scientific literature for procedures to achieve thermal equilibrium geometry of the surface grooves of dental zirconia, and several authors used to perform the thermal etching during 10 min at 100 °C below the sintering temperature, which for Y-TZP is 1350 °C.[8]

The AFM technique can be used to obtain information about the surface relief heights profile. From the images generated by such analysis it is possible to calculate - with the use of specific software such as Gwyddion - both the mean squared roughness (R_q) and other amplitude parameters.[13]

The present study aims to analyze topography and microstructure parameters of the Y-TZP surface after being subjected to different thermal treatments. Thus, it is intended to define the best protocol to not only evidence zirconia grains but also to allow the surface grooves of the zirconia reach its geometry of thermal equilibrium without occurring phase transformation or grain growth.

MATERIAL AND METHODS

The evaluated factor was the additional thermal treatment of the zirconia Y-TZP in 3 levels after polishing and thermal etching of grain disclosure. The first level was maintained without additional heat treatment (control), while the second level was treated at 750 °C for 3 min and the third level comprised treatment at 1350 °C for 1 h. In this way, 3 experimental groups were constituted. The response variables were quadratic surface roughness (R_q) in nanometers, grain size and mean increase of monoclinic content (wt%).

Pre-sintered ceramic blocks of Ceramill Zi yttrium zirconia (Amanngirrbach, Austria) whose composition is shown in Table 1 were used.

The specimens were machined in a Ceramill Motion model CAD-CAM machine (Amanngirrbach, Austria). After the complete sintering process, 3 samples of 10 mm high and 10 mm diameter discs were obtained for atomic force microscopy (AFM) and X-ray diffraction (XDR) analysis.

Final sintering was performed according to the manufacturer's instructions following Program 1. The total sintering time from heating to cooling was 10 hours. After sintering, the surface was polished to standardize the sample and provide minimum roughness avoiding damage to the AFM tip. For this, the specimens were polished with silicon carbide water sands in the granulations 220, 320, 400, 600 and 1200 under running water in a sander. The sample was then polished with 3, 1 and 0.5 µm diamond paste sequence on greased felt disc and cooled with ethanol.

Table 1:
Chemical composition of ceramic (Ceramill Zi). Data provided by the manufacturer.

COMPONENT	AMOUNT (WT%)
$ZrO_2 + HfO_2 + Y_2O_3$	99.9
Yttrium Oxide	4.5 - 5.6
Hafnium Oxide	5
Aluminum Oxide	0.5
Others	< 0.5

After the standard polishing procedure, each specimen was cleaned with an ultrasonic bath, immersed in alcohol for 10 minutes, and then dried with air jets free of dust and oils. Finally, after polishing and cleaning, a thermal etching was performed to evidence the grain boundaries of the zirconia surface.

The standardized thermal etching consisted of heating (rate 30 °C/min) of the samples in a ceramic furnace to a temperature of 1350 °C (100 °C below the sintering temperature), remaining at this maximum temperature for 10 minutes. This procedure was chosen because it promoted excellent "evidence" of grain boundaries without allowing intense atom diffusion or phase changes[8].After cleaning, the specimens were randomly divided into the 3 experimental groups, according to the additional heat treatment employed, as shown in Table 2.

Atomic force microscopy (AFM) analysis was performed with POINTPROBE® NCSTR-10 silicon nitride probe (NanoWorld, Neuchâtel, Switzerland) with tip curvature = 8 nm in non-contact (intermittent contact) mode with frequency. The AFM technique aim was to evaluate, with greater reliability, variations in the nanometric range of zirconia surface relief values (Nano roughness) that would result after experimental treatments at the surface. For this, 4 images of 5 µm X 5 µm of each group were obtained (n=4).

Determination of the mean square roughness (R_q)

The mean surface roughness (R_q) values obtained by the AFM technique were estimated using the Statistical Quantities tool of the Gwyddion program[13] which follows the ASME B46.1-1995, ISO 4287-1997, ISO 4287 / 1- 1997 to calculate the average value of R_q according to Equation 1 below:

$$R_q = 1/N \sum_{i=1}^{N} r_i^2$$

Table 2:
Experimental groups.

GROUPS	TREATMENT
G1 (control)	Storage at room temperature.
G2	Thermal treatment (750 °C for 3 minutes with heating rate 30 °C / min).
G3	Thermal treatment (1350 °C for 60 minutes with heating rate 30 °C / min).

In Equation 1, R_q is the mean quadratic roughness value of the surface height values in relation to a midline in the profile, N is the number of points of different heights of the profile line and rj is the value of each point in the line from the profile.

Determination of Curtosis (R_{ku})

In addition to the parameter R_q, the Statistical Quantities tool of the Gwyddion[13] program, which follows ISO 4287 / 1-1997, uses Equation 2 to calculate the Curtosis (R_{ku}) of the profile obtained through the AFM image.

$$R_{Ku}=1/NR^4_q S_{i=1}{}^N r_i^4$$

In Equation 2, R_{ku} is the curtosis or flattening factor of the profile, N is the number of points in the profile line, R_q is the mean square deviation (square root of the mean of the squares of the profile heights) and rj is the variation between the height value in the profile line and its midline. Values of Curtosis equal to zero configure a low probability distribution of occurrence of grooves. Already values < 3, reveal predominance in the surface of valleys and recesses with greater width. Therefore, values > 3 indicate the predominance of narrow and thin valleys.

Grain Size

The average grain size was also obtained with the Gwyddion program using the Grain Statistics tool after image segmentation of the grains[13].

X-Ray Diffraction (XRD)

The 3Y-TZP crystallographic characterization used the Shimadzu X-ray diffractometer (XRD) model XED 6000 with radiation Monochromatic CuKa, (γ = 0.154 nm). A 10° to 80° scan was performed with a 0.02° step and a duration of 1.5 s per step. The diffractograms obtained by the XRD analysis were evaluated by comparing the values of the interplanar distance obtained with values and data of the crystal structure contained in the Inorganic Crystal Structure Data Base (ICSD). The quantitative analysis of monoclinic and tetragonal phases present was performed by the Rietveld[14-17] method using the TOPAS Academic program.

Statistical analysis (Non-parametric data)

The values of R_q were rejected in the hypothesis of being parametric (Kolmogorov-Smirnov and Levene). Therefore, a nonparametric analysis of Kruskal-Wallis that showed differences between the groups and Mann-Whitney's comparisons showed which groups presented statistically different values.

Table 3:

R_q, R_{ku}, mean grain size and monoclinic content values for each group.

	G1	G2	G3
R_q	5.59[b]	7.4[b]	13.6[a]
R_{ku}	4.070	0.403	0.056
Grain size	309.6 nm	313.7nm	310.7 nm
Monoclinic phase	4.2%	4.6%	4.1%

Groups with the same superscript lower letter represent, according to the Mann-Whitney statistical analysis, statistically same R_q values (α = 0.05).

RESULTS

The mean square root roughness (R_q) in nanometers, Curtosis, mean grain size and monoclinic content in percentage of mass for the experimental groups are presented in Table 3 The non-parametric analysis of Kruskal-Wallis for the parameter R_q - obtained by the AFM technique - showed difference between at least one R_q value of some experimental group in relation to the others at the level of significance of 95% (α = 0.05). However, the values of mean grain size and monoclinic content did not present statistical difference between the groups after Kruskal-Wallis non-parametric analysis.

The Mann-Whitney comparison test was then performed only for parameter R_q and pointed out, with 95 % Confidence that the mean R_q values of G1 and G2 were statistically similar.

Examples of 3D images with respective height profiles obtained by AFM for each experimental group are shown in Figure 1.

The mean grain size remained unchanged around of 300 nm, in spite of the thermal treatment and the flatness factor (kurtosis) of the height profiles of the three groups indicated enlargement of the recesses with the G3 treatment, as shown in Table 3. X-ray diffraction (XRD) The diffractograms of each experimental group are presented in Figure 2.

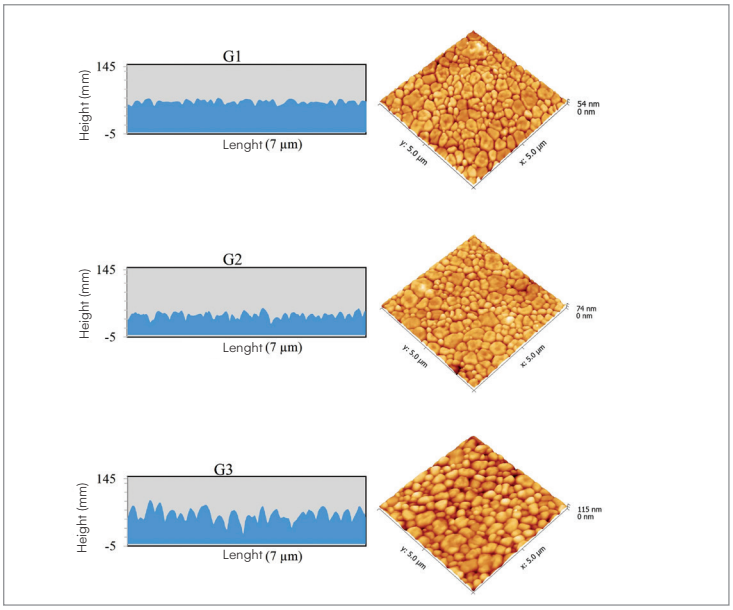

Figure 1:
Height profiles and 3D images obtained by atomic force microscopy for each experimental group in line.

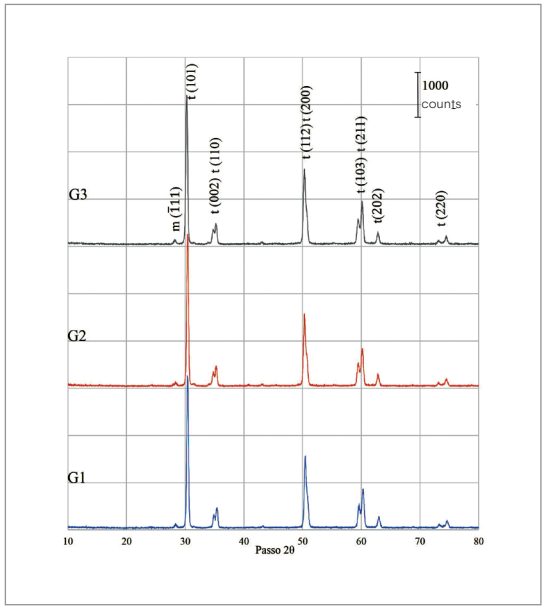

Figure 2:
Diffractograms of each experimental group.

Analysis of the monoclinic phase content by the Rietveld method showed that the thermal treatments did not cause phase change on the surface of the Y-TZP because the percentage found in the G2 and G3 groups was very close to the percentage found in the G1 control group, on a 4% wt.

DISCUSSION

The group 2 roughness data are much lower than those found in the literature for 3Y-TZP surface after SIE technique[8] despite both treatments have subjected zirconia to the same temperature (750°C). Such increases in roughness values would, according to those authors, have relation with possible enlargements and deepening of grooves and would not be linked to phase transformation or grain growth.

The change in the zirconia relief generated by SIE treatment would contribute to the creation of a rougher surface and receptive to the union with the resin cement.[11] However, despite the assumption of its existence, those authors did not directly prove by means of AFM or another method the existence of changes in grain boundaries as analyzed by atomic force microscopy in the present study.

The G2 thermal treatment was not able to change the roughness at the nanoscale with roughness values (7.4 nm) statistically similar to the roughness values of G1 (control), proving indirectly that in the case of SIE, temperature (750 °C) is not responsible for changes in surface topography found in the literature.

Before this study, bond strength of 3Y-TZP ceramics to the composite resin, bonded with resin cement was increased when the ceramic was treated with SIE[18]. The region of fracture after microtensile test was investigated and was concluded that, in the sample subjected to SIE treatment, there were changes indicative of increased roughness.

Statically different mean values of R_q (α = 0.05) found between groups 1 (control) and group 3 show that the additional permanence of zirconia for one hour at a temperature of 1350 °C was able to statistically improve surface roughness of the sample, leading the groove to reach thermal equilibrium configuration geometry without promoting phase change or grain growth. Such results would point to G3 treatment as a more effective treatment for evidence of grain in zirconia. This would be especially important in future AFM studies, when it is intended to evaluate surface free energy through the zirconia surface grains geometry (dihedral angle).

However, only with the numerical R_q, it is not possible to evaluate completely and safely the existence of differences between the treatments etching patterns[12], that is, the average roughness alone is not enough to evaluate if the increase of the roughness observed and measured was originated mainly by the increase of groove width.

To provide more data for the evaluation and characterization of the surfaces studied, three-dimensional images of the zirconia surfaces of each group were obtained. The images of Figure 1 are representative of the surface of each treatment group and clearly show the difference between the average roughness obtained with the R_q parameter of G3 in relation to the others.

The treatment G3 effectively promoted a intergranular region deepening, as seen in Figure 1. The G3 image has a grain boundaries greater definition in relation to the images of groups G1 and G2 in which there is a less rough surface and with grooves clearly thinner as proven numerically by the value of kurtosis obtained.[13]

The G3 had its temperature set from literature data, using the value of 100 °C below the sintering temperature to arbitrate a temperature that should be used during the thermal etching in polycrystalline materials. In the case of zirconia used in this study, the sintering temperature (1450 °C) was used as the starting point for the determination of the heat treatment temperature (1450 °C – 100 °C = 1350 °C) which was associated with a time long enough to guarantee thermal groove (thermal equilibrium conformation of the surface grains) without increasing grain size and phase change.

The G3 group presented much higher values of surface roughness with < 3 kurtosis, which shows that the thermal treatment at 1350 °C for one hour caused greater roughness and enlargement of the groove in the zirconia (wider valleys).

In regardless of the changes in the intergranular region, the grain size remained unchanged, around 300 nm, revealing that, even after on hour, there was not enough time to present a significant amount of atomic diffusion. This ensures the reliability of the G3 treatment as greater alternative to evaluate the groove geometry and intergranular regions. Moreover, the G3 was most closely related to Y-TZP equilibrium configuration. The grain size remain is especially important when a translucent zirconia is being evaluated since a grain increase will compromiser the zirconia optical properties[4] and as future research, the effect of G3 treatment in translucent zirconia should be evaluated.

No treatment group evaluated had 100% tetragonal phase and detectable peaks of the monoclinic phase were observed for all specimens, including G1 (control). The results in Table 3 show that the monoclinic contents of the three groups were similar after the heat treatments. Thus, the additional thermal treatments performed in groups G2 and G3 did not result in zirconia phase change. It is important to note that the phase change in tetragonal zirconia will run under both mechanical stresses and thermal variations.[19]

XRD was used to verify the amount of monoclinic phase of the Y-PSZ ceramic after thermal treatments performed for different periods of time[20]. The authors concluded that there was no monoclinic content prior to heat treatments and that the longer the aging time of the sample, the greater the amount of monoclinic phase found, and it could reach 70% in longer aging times. However, the results of the present study show that the thermal treatment of G3, despite being used high temperature, was short enough to avoid the phase change that is known detrimental to the mechanical properties of zirconia.

changes in the surface of 3Y-TZP where evaluated used as orthopedic hip prostheses[21]. To reveal the microstructure, the sample was thermally etched at 1300 °C for 30 minutes and also, no phase changes were observed. The present study doubled the heat treatment time (G3), resulting excellent groove revelation without occurrence of phase change, thus contributing to the definition of thermal etching protocol in 3Y-TZP.

CONCLUSIONS

Heat treatment at 750 °C for 3 minutes (G2) did not increase surface roughness compared to the surface that did not undergo further heat treatment (G1). Therefore, G2 is not recommended by the authors as a method to increase the roughness of zirconia surfaces despite promoting groove region widening as demonstrated by its R_{ku} value, less than 3. G3 has already promoted increased surface roughness of zirconia and excellent evidence of the superficial groove, probably reaching the equilibrium geometry of the surface grains with maximum thermal groove without causing phase change or grain growth. Based on the evidence described above, the authors recommend G3 as a thermal etching protocol for optimum evidence of surface grooves.

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