

Recovery of Tetragonal Phase from Previously Transformed Y-TZP

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ZrO₂(Y₂O₃)-based ceramics are widely used as biomaterials due to high fracture toughness, resulting from the tetragonal-monoclinic phase transformation in which the ceramic is submitted during crack propagation. In this context, studies involving the possibility of optimization of the tetragonal phase are important for the properties improvement of this ceramic. This study investigated the recovery of tetragonal phase from a previously transformed ZrO₂(3 mol% Y₂O₃) ceramic. Zirconia samples were sintered at 1450 °C, at 1530 °C - 2 h and at 1600 °C - 4 h, in order to obtain materials with distinct microstructural features. The sintered samples were characterized by relative density, X-ray diffraction and scanning electron microscopy. Samples sintered at 1450 °C, 1530 °C - 2 h and 1600 °C - 4 h, presented relative densities of 94.2, 99.6 and 99.7% with grains size averages of 0.28, 0.49 and 1.31 μm, respectively. All samples were submitted to milling to induce the tetragonal→monoclinic phase transformation presenting 5, 50 and 65 vol% of monoclinic phase. Subsequently, heat treatments between 400 °C and 1200 °C were conducted to retransform monoclinic in tetragonal phase. It has been found that the smaller the grain size after sintering, the lower the necessary annealing temperatures for fully recovering of tetragonal phase. Annealing temperatures of 950, 1100 and 1200 °C were sufficient to recover almost fully the tetragonal phase.

Keywords: ZrO₂(Y₂O₃) ceramics, sintering, phase transformation, microstructure

1. Introduction

Ytria-stabilized tetragonal zirconia polycrystalline, Y-TZP, exhibits excellent mechanical properties due to the martensitic (tetragonal-monoclinic, t→m) phase transformation, accompanied by 3 to 5% volume change, which results in the well-known transformation toughening mechanism. In this way, it is possible to obtain a high strength and high toughness ceramic material^{1,2}. Because of its excellent mechanical properties, biocompatibility and aesthetical appearance, Y-TZP has been widely used for fixed dental prostheses³.

During the fabrication of indirect zirconia-based restorations, small adjustments of the zirconia may be necessary to guarantee its perfect adaption to the patient's teeth. These adjustments by grinding may induce prematurely the t→m phase transformation, thus reducing its mechanical properties^{4,5}.

Mochales et al.⁴ demonstrated that tetragonal-monoclinic transformation occurs on the surface layers of Y-TZP during grinding. Furthermore, Borchers et al.⁵ evaluated

the influence of different environments and loads on the phase transformation and showed that up to 10% conversion occurs in Y-TZP sintered at 1500 °C and stored in distilled water at 80 °C for 64 h.

Denry et al.⁶ presented possible factors which leads to precocity on tetragonal-monoclinic phase transformation. Based on consideration that zirconia-based dental restorations consist of a zirconia core (3Y-TZP) layered with veneering porcelain to render clinically acceptable esthetics, they cite that veneering porcelain is sintered through a short baking cycle in the temperature range 800 - 900 °C. Furthermore, occasionally, the restoration core can be adjusted by grinding and dental implant abutments also frequently require grinding before placement⁷⁻⁹. Another important factor related to tetragonal-monoclinic phase transformation is the hydrothermal degradation¹⁰.

The purpose of this study was to investigate the effect of heat treatment on the reversibility of t-m transformation in 3Y-TZP, correlating the grain size of the sintered samples with this phenomenon.

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2. Material and Methods

2.1. Processing and measurements

Commercial pre-sintered Y-TZP($ZrO_2 - 3 \text{ mol\% } Y_2O_3$) blocks with 100 mm diameter and 10 mm height (ProfMat Advanced Materials - Brazil) were used in this study. 30 samples of $10 \times 10 \times 10 \text{ mm}^3$ were prepared and sintered (heating and cooling rate of $10 \text{ }^\circ\text{C}/\text{min}$) under three different temperatures: $1450 \text{ }^\circ\text{C}$, $1530 \text{ }^\circ\text{C}$ with an isothermal holding time of 2 h (sintering parameters recommended by the manufacturer to achieve better densification results) and at $1600 \text{ }^\circ\text{C}$ with isothermal of 4 h.

The relative density of pre-sintered samples was evaluated by geometric method because of high open porosity of the samples. Relative density of the sintered samples was determined using the Archimedes principle. The microstructure of the sintered samples was analyzed by scanning electron microscopy, using a LEO 1450VP microscope. Polished surfaces were thermally etched at $1400 \text{ }^\circ\text{C}$ for 20 min, using a heating and cooling rate of $25 \text{ }^\circ\text{C}/\text{min}$. The average grain size of the samples was determined using image analyzer software, *ImageJ*, and measuring a grain population of more than 1000 grains.

2.2. Crushing of the sintered samples

In order to provide the largest possible amount of martensitic transformation, the sintered samples were crushed using agate-mortar, and sieved ($32 \text{ }\mu\text{m}$) to obtain a uniform particle size for different sintered samples.

2.3. Thermal treatments

The obtained powders were heat treated at temperatures of 400, 600, 800, 900, 950, 1000, 1100, 1150 and $1200 \text{ }^\circ\text{C}$, for 15 min, using a heating and cooling rate of $20 \text{ }^\circ\text{C}/\text{min}$.

2.4. Phase analysis

The phase composition of the pre-sintered blocks, sintered samples and crushed sintered samples, was analyzed by X-ray diffraction, Shimadzu XRD-6000, with $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) 2θ from 20° to 50° at an exposure time of 3 seconds per position and step size of 0.05° . The phases were identified by comparison of the peaks with the JCPDS files¹¹.

The amount of monoclinic phase was determined from the X-Ray powder pattern fitting technique, using model proposed by Toraya et al.¹² for $ZrO_2(Y_2O_3)$ samples: The monoclinic phase fraction (X_M) was estimated in integrated intensity ration between $(\bar{1}11)_M$ and $(111)_{M, \text{monoclinic}}$ phase peaks, and the $(101)_T$ tetragonal peak, according to Equation (1).

$$X_M = \frac{(\bar{1}11)_M + (111)_M}{(\bar{1}11)_M + (111)_M + (101)_T} \quad (1)$$

The volumetric fraction (V_M) of the monoclinic phase was then calculated by Equation (2) which is based on crystallographic correlations studied by Toraya et al.¹².

$$V_M = \frac{1.311X_M}{1 + 0.311X_M} \quad (2)$$

The depth of the X-ray penetration into the sample surface was calculated considering the absorption by the material, given by Equations (3) and (4)¹³:

$$h = -\frac{\sin\theta}{2\left(\frac{\mu}{\rho}\right)\rho} \left[\ln \frac{I}{I_0} \right] \quad (3)$$

with:

$$\left(\frac{\mu}{\rho}\right) = w_1\left(\frac{\mu}{\rho}\right)_1 + w_2\left(\frac{\mu}{\rho}\right)_2 + \dots \quad (4)$$

Where:

$\left(\frac{\mu}{\rho}\right)$ = mass absorption coefficient [cm^2/g] ($Zr = 143$; $O = 11.5$; $Y = 134$); h = penetration depth [μm]; θ = diffraction angle; I = intensity of the diffracted X-ray beam; I_0 = intensity of X-ray beam; μ = mass absorption; w = weight fraction of the element or component; ρ = density [g/cm^3] ($Zr=6.511$, $O=1.354$, $Y=4.472$, $ZrO_2 - 3 \text{ mol\% } Y_2O_3 = 6.051$).

3. Results and Discussion

3.1. Pre-sintered block characterization

The pre-sintered blocks present 80.2% of relative density aiming to facilitate the machining of dental parts. Figure 1 presents XRD pattern of the pre-sintered block. The result of the XRD analysis indicates the presence of tetragonal ZrO_2 as major crystalline phase, while 12 vol% of monoclinic phase is observed.

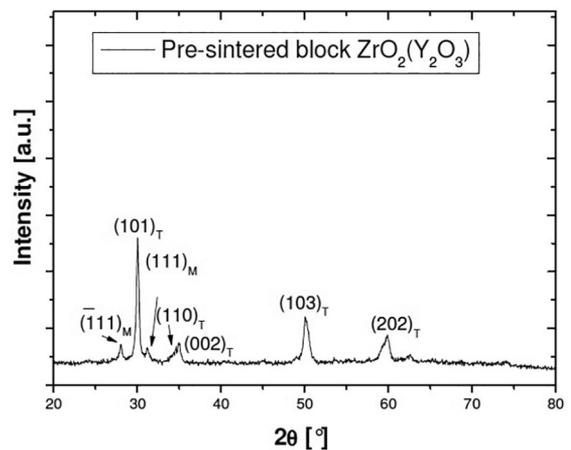


Figure 1: XRD pattern of the pre-sintered $ZrO_2(Y_2O_3)$ block.

3.2. Characterization of the sintered samples

Sintered samples exhibited relative density of $94.2 \pm 0.5\%$, $99.6 \pm 0.4\%$ and $99.7 \pm 0.3\%$ after sintering at 1450°C , $1530^\circ\text{C} - 2\text{ h}$ or $1600^\circ\text{C} - 4\text{ h}$, respectively. An increasing of densification is observed as function of sintering temperature increasing. Samples sintered at $1530^\circ\text{C} - 2\text{ h}$ and $1600^\circ\text{C} - 4\text{ h}$ lead to full densification, while samples sintered at 1450°C present 94.2% of relative density, indicating no complete pores elimination in this sintering condition.

Figure 2 presents X-ray diffraction of sintered samples. The results indicate only tetragonal ZrO_2 as crystalline phase in all cases. The results indicate that, after sintering, monoclinic phase present in pre-sintered samples, Figure 1, was integrally transformed in tetragonal phase.

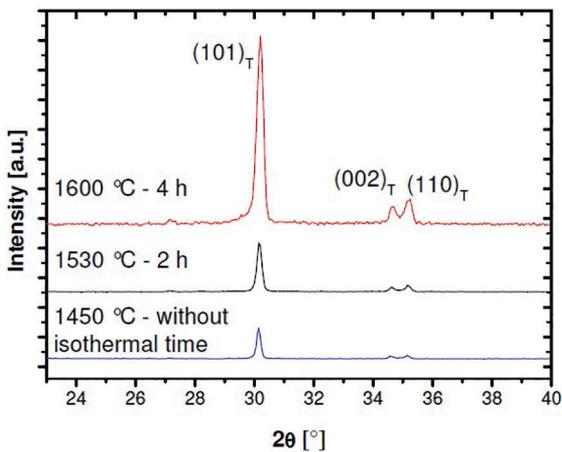


Figure 2: XRD patterns of the sintered samples.

Figure 3 shows SEM images of the sintered samples. Microstructural characterization indicated average grain sizes of 0.28 ± 0.08 , 0.49 ± 0.20 and $1.31 \pm 0.67 \mu\text{m}$ for samples sintered at 1450°C , $1530^\circ\text{C} - 2\text{ h}$ and at $1600^\circ\text{C} - 4\text{ h}$, respectively. As expected, considerable grain growth occurred with increasing sintering temperature and time.

3.3. Characterization of the crushed samples

Figure 4 presents representative XRD patterns of the crushed and heat-treated Y-TZP samples.

The fragmentation of the sintered samples allows simulating extreme conditions of phase transformation experienced by the material during application of mechanical stress. It can be observed that the increasing of heat treatment leads to a reduction of the monoclinic peak intensities in all sintering conditions experimented for zirconia samples.

Figure 5 shows the results of volume percentage of the monoclinic phase, determined by Equation (2), formed after crushing the samples (as milled) and after subsequent heat treatments from 400 up to 1200°C .

The results of the phase analysis of sintered and crushed samples indicate that the amount of monoclinic phase formed depends on the grain size of the samples and, therefore, on the sintering temperature. Lower sintering temperatures result in a smaller grain size of tetragonal phase, making

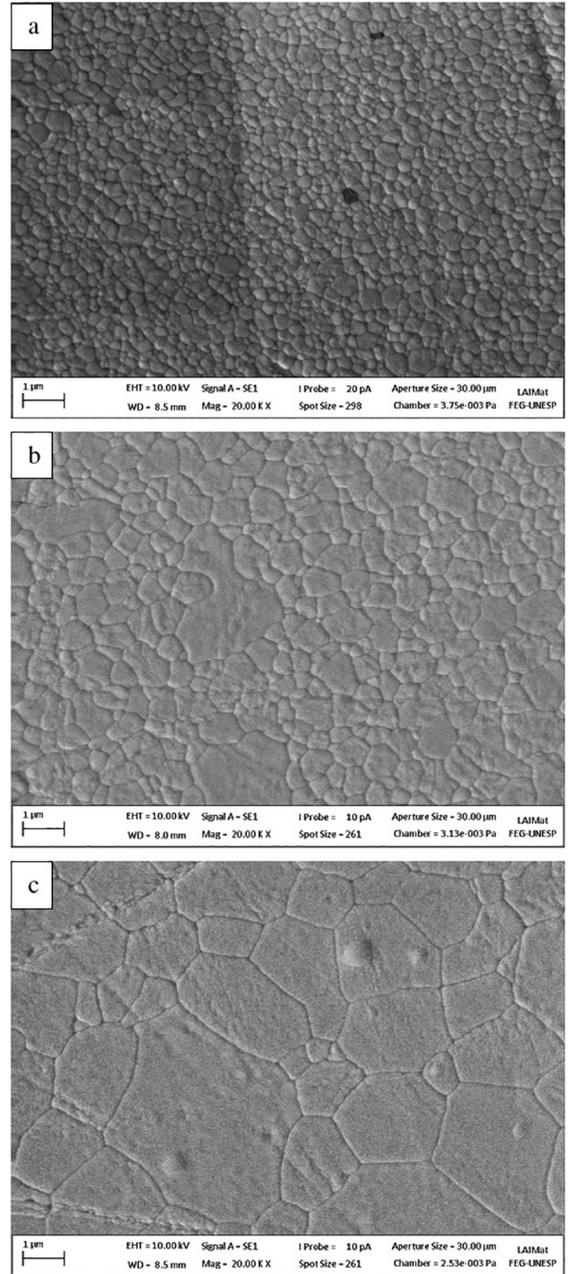


Figure 3: SEM micrographs showing different average grain size of samples sintered at: a) 1450°C , b) $1530^\circ\text{C} - 2\text{ h}$ and c) $1600^\circ\text{C} - 4\text{ h}$.

the $t \rightarrow m$ transformation difficult, because the actual grain size is much smaller than the critical size for spontaneous transformation².

The amount of recovery of tetragonal phase during the subsequent heat treatments also depends on the grain size achieved during sintering. While in the samples sintered at 1450°C a full recovery of tetragonal phase is observed at temperatures as low as 950°C , the same for samples sintered at 1530 or 1600°C is true only after treatments at 1100 and 1200°C .

The percentages of monoclinic phase shown in Figure 5 are based on the percentage of grains analyzed by X-ray diffraction at the sample surface and their peak intensity.

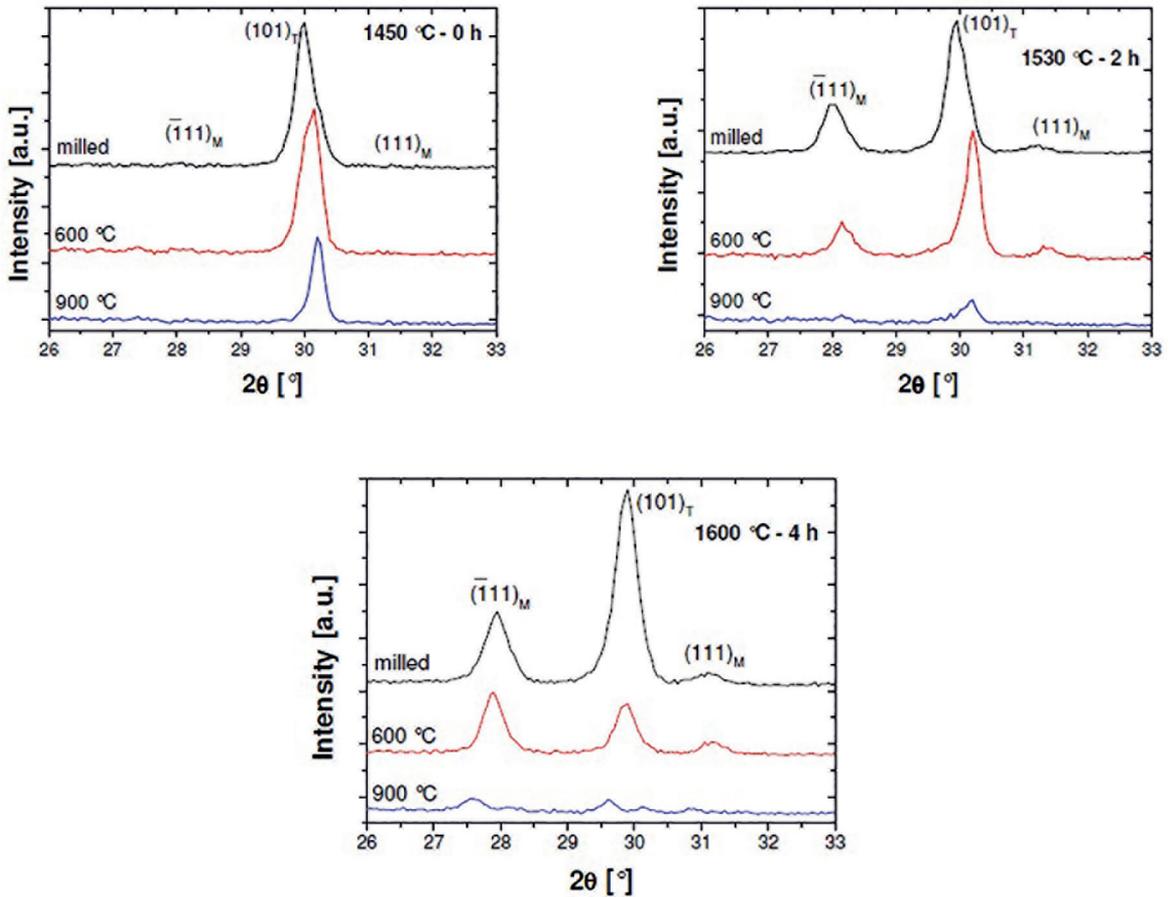


Figure 4: Representative XRD patterns of powder (crushed) samples before and after heat treatments.

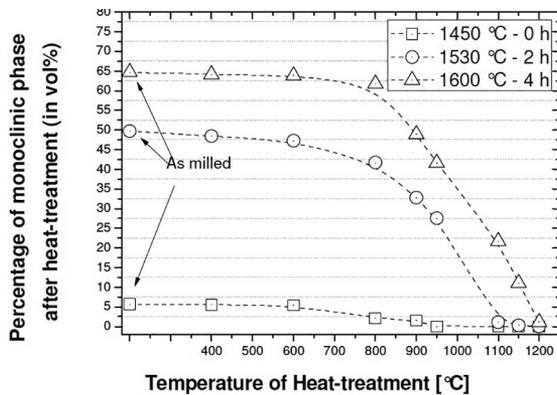


Figure 5. Amount of monoclinic phase formed after crushing the sintered samples (as milled) and after subsequent heat treatments.

Because the depth of penetration of X-rays, estimated to be in the order of 4.5 μm , it is reasonable to assume that the materials with larger grain sizes, as the samples sintered at 1600 $^{\circ}\text{C}$ - 4 h (1.31 μm grain size) are much more influenced by the transformation at the fracture surface than samples with smaller grain sizes.

Therefore, volume fraction of monoclinic phase is a better representation of processing conditions experienced by the material within detection limit of about 4.5 μm depth of the

diffractometer. Analyzing this graph, the samples sintered at 1450 $^{\circ}\text{C}$ exhibit the lowest volumetric percentage transformed during crushing, about 6 vol%, which corresponds to approximately one tenth of the amount transformed in the material sintered at 1600 $^{\circ}\text{C}$ for 4 h. This difference is significant because a higher retention of tetragonal phase implies a higher life expectancy, especially when used in dental prostheses which are constantly under cyclic loading of mastication. A correlation between grain size and volume fraction of transformed monoclinic phase is showed in Figure 6.

It is possible to observe an increase of the amount of monoclinic phase with increasing grain size for different heat treatments used. In consequence, it becomes possible to predict the most appropriate heat treatment in function of the average grain size existing in the material to recover all or part of the tetragonal phase in zirconia. Based on these results, it is possible to propose heat treatments that minimize the transformation during processing. However, the results should be analyzed jointly with other properties evaluated, such as relative density, microstructural features, and especially mechanical properties of zirconia in order to optimize the performance of the ceramic material. Therefore, a special thermal treatment for each sintering temperature of zirconia after the grinding of zirconia-based restorations can be proposed to recover the tetragonal phase and improve their properties.

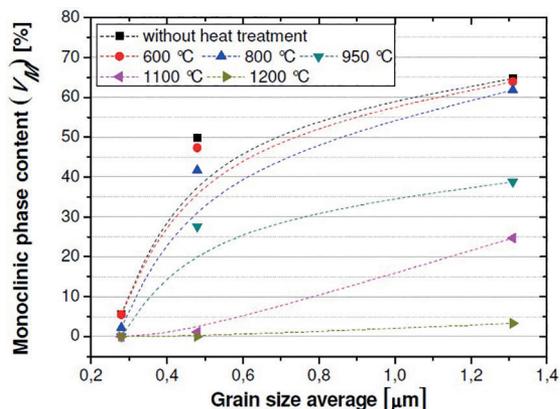


Figure 6: Volume fraction of monoclinic phase (V_M) as function of grain size for different heat treatments applied.

For the development of this procedure, the thermal treatments for which the zirconia will be submitted by the application of the porcelain veneer should be known. Thus, the following items should be considered:

The sintered material may be subject to machining using diamond drills to optimize the adaptation to the patient's teeth, which will cause localized martensitic transformation.

In case of fixed partial prosthesis, mechanical stress on the prosthesis is critical and it is essential to optimize the percentage of tetragonal phase.

All zirconia used for dental prosthesis are covered by a feldspathic porcelain layer which allows to mimetic the color of a tooth. This porcelain layer is applied in 2 to 5 steps involving thermal treatments at about 950 ± 50 °C.

3. Conclusion

The results indicated that sintering conditions of Y-TZP influenced tetragonal to monoclinic phase transformation due to the different microstructures. With the increasing sintering temperature and, therefore, the increasing grain size, the greater is the difficulty for the recovery of tetragonal phase. For a full recovery of the tetragonal for samples sintered at 1450 °C with an average grain size of 0.28 μm , heat treatment at 950 °C for 15 min is sufficient while heat treatments exceeding the martensitic transformation temperature of 1170 °C are required for samples sintered at 1600 °C for 4 h with an average grain size of 1.31 μm .

4. References

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