Research Article

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Ageing of Zirconia Dedicated to Dental Prostheses for Bruxers Part 2: Influence of Heat Treatment for Surface Morphology, Phase Composition and Mechanical Properties

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Abstract: Purpose: This part of the study focuses on the influence of zirconia heat treatment for surface morphology, phase composition and mechanical properties
Methods: Zirconia samples was prepared with ISO 13356:2013 and ISO 14704:2008 recommendations. X-ray diffraction, observations (SEM) and (AFM), microhardness (Olivera & Phara method), and static bending test (4PBT) were taken.
Results: characterization of YSZ and high temperature heat treatment has clearly shown that the aging process influences the change in phase composition of the material, significantly worsening the topography. In turn, re-treatment of the high temperature made after the artificial aging process results in reverse transformation of the desired tetragonal phase, but does not affect the improvement of surface morphology.
Conclusions: The research made it possible to assess the negative impact of the zirconium oxide aging simulation process. Because of the failure to achieve the intended results, it was also proved that the high-temperature reprocessing was not appropriate.

Keywords: heat treatment, accelerating ageing, bioceramics, zirconia, phase composition

1 Introduction

At the beginning of the 90's, zirconia was used to make coronal and root canals, while the technology of making individual prosthetic restorations was not developed until the late 90's. Currently, zirconium ceramics slowly supplant other types of implant materials due to their properties that meet both aesthetic and strength requirements. The ceramic base also provides color stability and biocompatibility. However, they are not devoid of defects resulting from the phases transforming itself spontaneously in the patient's oral environment, which in consequence leads to fractures of the framework or porcelain splinters. Several advantages of zirconium ceramics have been implicated in improving the technology of this type of restorations and the attempts to improve the material itself, supported by long-term clinical observations [1–3].

At ambient pressure, unalloyed zirconia can be found in three crystallographic forms depending on the temperature. At room temperature and upon heating up to 1170°C, it is monoclinic.

At temperature between 1170 and 2370°C it is tetragonal and above 2370°C and up to the melting point it is cubic. Upon cooling, the transformation from the tetragonal (β) phase to the monoclinic (α) phase is characterized by a substantial increase in volume (about 4.5%), sufficient to lead to catastrophic failure, sufficient to lead to catastrophic failure. This transformation begins at 950°C and is reversible [4, 5]. The transformation of the crystalline...
lattice between the tetragonal and monoclinic phases has the character of a non-fusion martensitic transformation, only coordinated displacement in the crystalline lattice depending on the transport of atoms. It generates an increase in the volume of particles, and because of the resulting stresses that may have a destructive effect on the material during thermal treatment [6]. Another disadvantageous occurrence in the electrolyte environment and accompanying martensitic transformation is low temperature degradation (LTD - low thermal degradation). It consists in the extrusion of surface particles by liquid penetration into the transforming grain boundaries. The effect of this phenomenon is uncontrolled martensitic transformation, and consequently, progressive microcracks and surface crumbling [7–9]. Unfortunately, the changes occurred in the electrolyte environment at elevated temperatures lead to the uncontrolled martensitic transformation with progressive degradation [10–12]. It should be noted that the mechanism of stabilization of metastable phases is still not clearly described [10, 11]. Thus, issues related to the improvement of the resistance of doped-ZrO$_2$ for low thermal degradation are still an open and very important issue. To the best of our current knowledge, the main factors that should be taken into consideration when discussing the issue of susceptibility of dental prostheses made from ZrO$_2$ for degradation changes in human mouth environment are [13–20]:

- grain size of ZrO$_2$ metastable phases, grains less than 0.3 μm are not prone to the spontaneous transformation and electrolyte degradation,
- type and concentration of the metastable-ZrO$_2$ stabilizer, higher concentrations of the stabilizing agent improve the stability of metastable phases in ambient conditions,
- the homogeneity of the dispersion of a stabilizer,
- the kind of the heat treatment of prepared dentures, low cooling rates and multi-stage heating-cooling cycles, favors nucleation and growth of the α-ZrO$_2$ grains.

These issues are directly related to the method of manufacturing powders, the preparation of ceramic discs, the machining and sintering processes [19–22]. For these reasons, the phase composition, heat treatment method and thermal stability of ZrO$_2$ are key factors that should be considered when during the machining and material development, synthesis technique and quality control [23, 24]. Based on the kinetics of one YSZ material, it was stated that 1 h of hydrothermal aging being equivalent to 1 year of in-vivo aging for grounded samples [2]. Therefore, the aim of this study is to evaluate the aging characteristics of BruxZir Y-TZP, dedicated especially for bruxing patients or for CAD/CAM systems in terms of mechanical properties and surface topography.

Current research is the second part of the investigations regarding the influence of low-temperature degradation on the behavior of zirconium oxide in the oral environment [25].

The purpose of the second part of the research was to determine the effect of reverse phase transformation of tetragonal zirconia to the monoclinic, determine mechanical properties and to describe changes in phase composition as a result of accelerated ageing. As a test material, was used zirconium oxide dedicated for the bruxers which was also selected for previous study [25].

### 2 Material and methods

#### 2.1 Samples preparation

Samples used in the study were obtained from a BruxZir™ Zirconia Milling Blanks – ZrO$_2$-Y$_2$O$_3$ blocks. Samples of Zirconia CAD/CAM blocks were divided in four groups. For first group was sintered only in high-temperature processing 1150°C. For two next groups was sintered in following conditions: final sintering temperature 1530°C, dwelling time 2.5 h for second group and 5 h for third group. The last group of BruxZir samples were sintering in temperature 1530°C, dwelling time 5 h and again sintering in temperature 1530°C. Zirconia samples (specimens for investigations were prepared with ISO 13356:2013 standard recommendation for mechanical test evaluation. Then sintered blocks were cut with Struers Secotom 15 microcutter with 0.035 mm/s table feed speed for 45 mm width 4.0 mm, and 3.0 mm thickness.

Prepared samples were subjected to accelerating ageing test in saturated steam in following conditions: 135°C, 0.2 MPa pressure and two holding times 2.5 and 5 hours. Accelerating degradation process was conducted in HMC HMT 260FA autoclave.

#### 2.2 Characterization

Identification of the phase transitions occurring during the process simulation and accelerating ageing and heat treat-
ment was investigated with X-ray diffractometer (XRD) by PANalytical X'Pert Pro with PIXcel 3D detector. Microstructure of the samples were investigated with FEI Inspect S50 scanning electron microscopy (SEM) with 2 kV accelerating voltage. The Scanning electron microscope was equipped with Everhart-Thornley sensor. Surface topography was investigated with atomic force microscopy (AFM) by PARK System X-E 100 microscope. Analysis was performed with VIT-P needle type probe analyzed. The hardness measurements were conducted by Oliver & Pharr method with Vickers-type. This measurements were performed on Micro-Combi-Tester open platform by CSM Instruments.

The loading force value was 1000 mN. Slew rate the loading force and relieving was 2000 mN/min. Flexural strength with 4-point bending test (4PBT) were executed with MTS Criterion 45 testing machine according with the ISO 13356:2013 standard [8].

3 Results

3.1 Phase composition

Based on the XRD diffractometer of the analyzed aged samples was allowed for the qualitative assessment of the phase composition. The obtained results of the study included the reflection angle $2\theta$, the unit cell parameters and the distance between the adjacent atomic planes. Figure 1 and Table 1-4 presents the result of diffraction patterns obtained for individual samples after various temperature treatment.

Table 1: Phase composition analysis of the reference sample

| $2\theta$ [°] | Phase   | hkl  | Wavelength K-Alpha1(Co) [Å] |
|--------------|---------|------|----------------------------|
| 27.845       | $\alpha$-ZrO$_2$ | 1 1  | 2.96065                     |
| 35.228       | $\beta$-ZrO$_2$ | 0 2  | 2.95601                     |
| 40.368       | $\beta$-ZrO$_2$ | 0 1  | 2.59250                     |
| 41.169       | $\beta$-ZrO$_2$ | 1 1  | 2.54417                     |
| 59.025       | $\beta$-ZrO$_2$ | 2 0  | 1.81585                     |
| 59.633       | $\beta$-ZrO$_2$ | 0 3  | 1.79900                     |
| 70.083       | $\beta$-ZrO$_2$ | 1 2  | 1.155791                    |
| 71.922       | $\beta$-ZrO$_2$ | 1 2  | 1.53677                     |
| 74.488       | $\beta$-ZrO$_2$ | 2 0  | 1.47800                     |
| 89.365       | $\beta$-ZrO$_2$ | 2 0  | 1.27209                     |
| 98.847       | $\beta$-ZrO$_2$ | 1 2  | 1.17769                     |

Table 2: Phase composition analysis of the sample after accelerated ageing $t=2.5$h

| $2\theta$ [°] | Phase   | hkl  | Wavelength K-Alpha1(Co) [Å] |
|--------------|---------|------|----------------------------|
| 32.691       | $\alpha$-ZrO$_2$ | 1 1  | 3.17849                     |
| 35.171       | $\gamma$-ZrO$_2$ | 1 1  | 2.96065                     |
| 40.368       | $\beta$-ZrO$_2$ | 0 0  | 2.59250                     |
| 41.169       | $\beta$-ZrO$_2$ | 1 1  | 2.54417                     |
| 59.126       | $\gamma$-ZrO$_2$ | 0 2  | 1.81302                     |
| 59.633       | $\beta$-ZrO$_2$ | 0 2  | 1.79900                     |
| 70.083       | $\beta$-ZrO$_2$ | 1 3  | 1.55791                     |
| 70.695       | $\gamma$-ZrO$_2$ | 1 1  | 1.54615                     |
| 74.352       | $\gamma$-ZrO$_2$ | 1 3  | 1.48033                     |
| 98.990       | $\gamma$-ZrO$_2$ | 1 3  | 1.17644                     |

Table 3: Phase composition analysis of the sample after accelerated ageing $t=5$h

| $2\theta$ [°] | Phase   | hkl  | Wavelength K-Alpha1(Co) [Å] |
|--------------|---------|------|----------------------------|
| 32.691       | $\alpha$-ZrO$_2$ | 1 1  | 3.17849                     |
| 35.171       | $\gamma$-ZrO$_2$ | 1 1  | 2.96065                     |
| 40.368       | $\beta$-ZrO$_2$ | 0 0  | 2.59250                     |
| 40.837       | $\beta$-ZrO$_2$ | 0 2  | 2.56400                     |
| 58.652       | $\alpha$-ZrO$_2$ | 2 0  | 1.82634                     |
| 70.083       | $\beta$-ZrO$_2$ | 1 3  | 1.55791                     |
| 70.695       | $\gamma$-ZrO$_2$ | 1 1  | 1.54615                     |
| 98.847       | $\beta$-ZrO$_2$ | 1 2  | 1.17769                     |

Table 4: Phase composition analysis of the sample after re-heat treatment

| $2\theta$ [°] | Phase   | hkl  | Wavelength K-Alpha1(Co) [Å] |
|--------------|---------|------|----------------------------|
| 35.228       | $\beta$-ZrO$_2$ | 0 1  | 2.95601                     |
| 40.368       | $\beta$-ZrO$_2$ | 0 0  | 2.59250                     |
| 41.169       | $\beta$-ZrO$_2$ | 1 1  | 2.54417                     |
| 59.025       | $\beta$-ZrO$_2$ | 1 1  | 1.81585                     |
| 59.633       | $\beta$-ZrO$_2$ | 0 2  | 1.79900                     |
| 98.847       | $\beta$-ZrO$_2$ | 1 2  | 1.17769                     |
Figure 1: Diffraction pattern of samples: (a) reference, (b) after ageing process $t = 2.5$ h, (c) after ageing process $t = 5$ h
accelerated aging process $t=5h$ revealed during the XRD tests were showed heterogeneity. In this case, all the varieties of allotropic zirconium oxide were found. The phases were visible: monoclinic $\alpha$-ZrO$_2$, tetragonal $\beta$-ZrO$_2$ and regular $\gamma$-ZrO$_2$. Analysis of phase composition of the last sample group (after re-heat treatment) uniquely, the homogeneous tetragonal structure $\beta$-ZrO$_2$ were showed.

3.2 Surface topography

Based on the AFM microphotographs of the aged samples on the surface was observed surface shape changes. Additionally, to microtopography the surface roughness $R_a$ was measured – Table 2. The lowest surface roughness was characterized by a reference samples ($R_a=32$ nm), while the higher roughness was found in the sample after the accelerated ageing process, $t=2.5h$ ($R_a=61$ nm).

The Figure 3 show the comparison of all samples after accelerating ageing and blind samples. Based on the SEM microphotographs of the aged references samples on the surface was observed the presence of layers formed by the thickening of the ceramic when pressing the liquid material. On the other hand, the visible hollows and protuberances on the surface of the samples were no visible. Significant is the fact that with increasing aging time of samples, it was observed increased of upheaval and hollows of the surface.

4 Mechanical properties

Mechanical tests treatment were performed for all samples. Table 5 presents the results of microhardness for all samples. The lowest value of microhardness obtained after re-heat treatment. The results of a static sample for a 4-point bending test (4PBT) analyzed materials are presented in Table 5:

| Sample                                      | $R_a$ [nm] |
|---------------------------------------------|------------|
| reference sample                            | 32         |
| after accelerated ageing, $t=2.5$ h         | 61         |
| after accelerated ageing, $t=5$ h           | 43         |
| re-heat treatment                            | 35         |
Figure 3: SEM microphotographs of samples: a) reference, mag. 2500x, b) 2.5 h, mag. 10000x, c) 5 h, mag. 10000x, d) b.s, mag. 10000x

Table 6: Vickers hardness measurements

| Samples                       | µHV [MPa] |  |  |  | Average [MPa] |
|-------------------------------|-----------|---|---|---|----------------|
|                               | 1         | 2 | 3 |  |                |
| reference sample              | 16965     | 17738 | 18629 | | 17777±833     |
| after accelerated ageing, t=2.5 h | 17233    | 17968 | 17435 | | 17545±379     |
| after accelerated ageing, t=5 h | 18235    | 17667 | 17981 | | 17961±29      |
| re-heat treatment             | 17098     | 17196 | 16727 | | 17007±247     |

Table 7: Results of the 4PBT

| Samples                           | Young's modulus E [GPa] | Bending strength [MPa] | Max. force [kN] |
|-----------------------------------|-------------------------|------------------------|-----------------|
| reference sample                  | 57                      | 884                    | 1.40            |
| after accelerated ageing, t=2.5 h | 42                      | 852                    | 1.18            |
| after accelerated ageing, t=5 h   | 38                      | 760                    | 1.02            |
| re-heat treatment                 | 21                      | 603                    | 1.27            |

Table 6. It was found that the blind samples characterized the best bending strength.
5 Discussion and Conclusion

Accelerating ageing was intended to display the state of the simultaneous environment in the stomatognathic system. Zirconium oxide in such conditions is exposed to the change of the desired tetragonal phase into unfavorably monoclinic. The transitional phase transition is accompanied by a low temperature degradation process, which results in the uplift of individual grains produce desired results in falling out. In the first stage of the study, X-ray diffraction for phase composition analysis was performed. The results obtained during the study included the reflection angle 2θ, the unit cell parameters and the distance between the adjacent atomic planes. Analysis of the phase composition of the reference sample unequivocally indicates the homogeneous structure of the tetragonal phase. In turn, the sample after accelerating ageing t=2.5 h was characterized by heterogeneous structure with alternating occurrence of tetragonal β-ZrO₂ and regular γ-ZrO₂ phases. Whereas, the heterogeneity for the sample structure after the accelerating ageing t=5 h were showed. The phases such as: monoclinic α-ZrO₂, tetragonal β-ZrO₂ and regular γ-ZrO₂ were observed. On the other hand, analysis of the phase composition of the last group of samples (after re-heat treatment) a homogeneous tetragonal structure was showed. The study unequivocally confirmed the zirconia phase transition during accelerating aging and substantiated the use of thermal re-treatment.

In the next step, randomly selected micro-areas of samples from individual groups by scanning electron microscope to investigate surface topography were observed. The test area of the reference sample showed no damage of the surface. On the other hand, the surface images of the samples after accelerating aging (t=2.5 h), revealed the numerous uplift and hollows spread evenly over the whole surface were presented. In contrast, the accelerating aging t=5 h, an increase of the number hollows and overlaps were caused. Images examples of the samples surface after re-heat treatment are characterized by a relatively smooth surface, but observations were revealed uneven patches of chaotic material over the entire surface of the samples. This indicates a phenomenon of degradation of the aged material. As well as the lack of improvement of the samples surface due to the re-heat treatment.

The results of AFM were confirmed the diversity of the surface formation. The determined roughness coefficient $R_d$ was found for the smallest value (reference samples) and the largest value for samples after accelerating ageing t=2.5 h.

Table 6 present the results of microhardness tests of the samples. The smallest hardness values were obtained after re-treatment. However, the average hardness value was $H = 17007$ MPa. For the other group, the average hardness values were exceeded 17500 MPa, for reference samples $H = 17777$ MPa, for samples after accelerating ageing, such as $t=2.5$, $H=17545$ MPa and $t=5$ h, $H=17961$ MPa. The smallest hardness value of the sample after re-heat treatment indicate the lack of improvement of mechanical properties by reverse transformation.

Mechanical properties were also evaluated based on a static 4-point bend test. The results showed that the best bending strength was found in samples from the reference group. For this sample group, the average bending strength was $R_g=884$ MPa. The samples from the reference group also reached the highest value Young’s module $E=57$ GPa. In turn, the maximum value of the force causing the destruction of the sample was $F_g=1.40$ kN. In contrast, the strength of the fourth group of re-heat treated were the smallest. For this group of samples, it was found that the mean values were $R_g=603$ MPa, $E=21$ GPa and $F_g=1.27$ kN. However, for samples after accelerating ageing 2.5 h and 5h, results were obtained: $R_g=852$ MPa, $R_g=760$ MPa, $E=42$ GPa, $E=38$ GPa, $F_g=1.18$ kN, $F_g=1.02$ kN. The results obtained from the static bending test confirm the deterioration of the strength properties during ageing of the material.

The research on characterizing the properties of yttrium-stabilized zirconia (Y-TZP) after accelerating ageing and high-temperature heat treatment clearly showed that the ageing process affects for the composition of the phase change material, significantly impairing the topography of the samples surface’s and mechanical properties. In turn, high temperature retreating made after accelerating ageing process results in reverse transformation of the desired tetragonal phase. However, it does not improve for surface morphology and strength properties lost during ageing process.

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