Research Article

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Ageing of Zirconia Dedicated to Dental Prostheses for Bruxers Part 1: Influence of Accelerating Ageing for Surface Topography and Mechanical Properties

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Abstract: BACKGROUND: Zirconia is a commonly used ceramic for fixed full-ceramic restorations. Porcelain-fused-to-metal restorations applied for bruxers are often very quickly destroyed by this group of patients.

OBJECTIVE: The aim of this study was to investigate the influence of accelerated aging tests on BruxZir HT 2.0 zirconia.

METHODS: Zirconia samples were prepared with ISO 13356:2013 and ISO 14704:2008 protocol recommendations. The ageing conditions were times of 2.5, 5 and 10 hours, and pressure of 0.2 MPa and a temperature of 134°C.

RESULTS: The correlation between ageing time and mechanical properties, particularly hardness, was difficult to find, while correlations between hardness and the surface topography and fracturing were clear.

CONCLUSION: On the basis of the conducted research, it can be stated that BruxZir HT 2.0 zirconia meets the technical requirements for medical grade zirconia used in dental technology. Future investigations should include phase composition research.

Keywords: Accelerated ageing, low thermal degradation, bioceramics, zirconia

1 Introduction

The use of zirconia-based ceramics in dental technology has been gaining considerable interest within the dental community. From the mid-1970s, significant research has been carried out on this subject as a result of the discovery of the phase transformation toughening of ZrO_2 [1–3]. The mechanical properties of zirconia are reported to be the strongest of all ceramic materials [2]. At room temperature and pressure, the monoclinic (m) phase is the stable phase of pure unalloyed zirconia. Doping zirconia with stabilising agents can maintain the metastable phases (tetragonal (t) and cubic (c)) in standard environments [4–7]. In response to an external mechanical stress, a structural $t \rightarrow m$ phase martensitic-type transformation may take place at crack tips. As a result, volume expansion can lead to compressive stresses in opposition to crack propagation, thereby improving the fracture toughness [1, 8]. Fracture toughness is described as the capability of a material to withstand load in the presence of a pre-existing flaw [9]. Therefore, the use of zirconia, in particular, yttria-stabilized tetragonal zirconia (Y-TZP), has extended the application of all-ceramic restorations from single crowns in the front section of the teeth arch, through full arch restorations fixed on implants, implant abutments and implant screws [10–12].

Nevertheless, the mass-scale use of Y-TZP as a biomedical ceramic, with more than 600,000 femoral heads im-

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planted worldwide, as provided clear evidence of the limitations of this material [9, 10]. For example, the uncontrolled $t \rightarrow m$ martensitic-type transformation can be induced by environmental stresses, leading to degradation resulting from this aging phenomenon, causing surface roughening, microcrack development and zirconia grain pull-out in the human body [13–16]. Aging occurs due to a slow $t \rightarrow m$ transformation on any Y-TZP surface in contact with an electrolyte or body fluid environment [17]. A degradation process starts at the surface with the transformation of isolated grains, generating localised surface uplift. As a result, a 4–6% volume increase was observed in one grain, promoting compressive stresses at the neighbouring grains via a kind of autocatalytic process, leading to further transformation and microcracking, which is a straightforward way to enable water penetration [17–19]. The kinetics of the Low Thermal Degradation (LTD) process are affected by material characteristics, such as density, grain size and residual stresses [20, 21].

Even though the lack of zirconia stability leads to a significant decrease in its applications as a biomedical material, due to high mechanical properties, very high aesthetics and the development of CAD/CAM systems, the use of zirconia as pre-sinter blocks for the manufacturing of dental restorations as a replacement of porcelain-fused-to-metal all-ceramic restorations is now common [22, 23]. In spite of this, the use of zirconia in prosthetic dentistry has led to many issues, such as early cracking, chipping or debonding of the veneer material [24, 25]. This means that yttria-stabilised zirconia restorations are in direct contact with the oral environment variables, pH variations, mechanical loading as a source of external stress, wetness and in a critically low temperature for t -phase stability [26]. Based on these reports, it can be stated that the improvement of zirconia stability and the study of phenomenon LTD are still open issues.

Despite the lack of characterisation of Y-TZP as a dental material in clinical trials, different methodologies have been implemented to estimate the martensitic transformation in human body conditions. Isothermal accelerated aging tests can be performed in temperatures higher than 371°C, combining humidity, intermediate temperatures (134°C) and pressure [26]. Based on the kinetics of one YSZ material, it was stated that 1 h of hydrothermal accelerated aging in an autoclave in saturated water vapour is equivalent to 3–4 years in the human body [1, 8]. In other studies, it was stated that the degradation process may be more severe for full-monolithic YSZ, with 1 h of hydrothermal aging being equivalent to 1 year of *in-vivo* aging for grounded samples [1]. Therefore, the aim of this study is to evaluate the aging characteristics of BruxZir Y-TZP, ded-

icated especially for bruxing patients or for CAD/CAM systems in terms of mechanical properties and surface topography.

2 Materials and methods

2.1 Sample preparation

BruxZir HT 2.0 zirconia samples were prepared with ISO 13356:2013 and ISO 14704:2008 protocol recommendations for mechanical test evaluation. Zirconia CAD/CAM blocks were sintered in the following conditions: heating rate 10°C/min, final sintering temperature 1530°C, dwelling time 2 h and cooling rate 4°C/min. Sintered blocks were cut with a Struers Secotom 15 microcutter with a 0.05 mm/s table feed speed for a 45 mm width, 4.0 mm and 3.0 mm thickness. The cut samples were grinded and polished with a Struers Labopol 25 polisher with 1200 and 2000 grinding papers, as recommended for ceramics, and colloid diamond polishing liquid and diamond foil. As-polished samples were washed in an ultrasonic bath with deionised water and cleaned with cotton wool sticks immersed in absolute ethanol.

2.2 Characterisation

Cleaned samples were subjected to the accelerated ageing test in saturated steam in the following conditions: 134°C, 0.2 MPa pressure and three holding times of 2.5, 5 and 10 h. The accelerated degradation process was conducted in an HMC HMT 260 FA autoclave. Sample descriptions and characteristics are presented in Table 1. The surface topography was investigated with atomic force microscopy (AFM) using a PARK System X-E 100 microscope. The analysis was performed with a VIT_P needle-type probe analyser. The flexural strength was measured with a 4-point bending test (4PBT) using an MTS Criterion 45 testing machine. Vickers hardness measurements was conducted with a CSM Instruments Micro-Combi-Tester open platform system. The value of the loading force was 1000 mN. Slew rate the loading force and relieving was 2000 mN/min. The microstructures of the samples were investigated using scanning electron microscopy (SEM) with a FEI Inspekt S50 scanning electron microscope with a 2 kV accelerating voltage. The microscope was equipped with an Everhart–Thornley sensor. The laboratory stages are schematically shown in Figure 1.

Table 1: Sample description

Sample description	Ageing Time[h]
B.S.	0
I	2.5
II	5
III	10

Figure 1: Schematic of laboratory stages.

3 Results

3.1 Surface topography

Based on the AFM microphotographs of the aged samples, spherical changes were observed on the surface, as shown in Figure 2. On the basis of this observation and the available literature data [4, 5], it can be stated that the surface sample changes are connected to the accelerated $t \rightarrow m$ phase transformation. Additionally, grain pop-outs were observed in each sample group.

The largest amount of changes, both spherical-like and pop-outs, were observed in the samples that were aged for the longest period of time. The comparison between all samples is presented in Figure 3. In addition

Figure 2: Spherical changes on the surface of the accelerated aged samples (2.5 h ageing).**Table 2:** Measured surface roughness (R_A) of accelerating aged samples

Sample	R_A [nm]
I	64.76
II	87.83
III	57.74

to microtopography, the surface roughness (R_A) was measured (Table 2).

The SEM microstructure and fracture topography were also investigated. Figure 4 shows a comparison of all samples after accelerated aging and the blind samples. It is significant that with increasing aging time, an uplift of the surface and some pop-outs (uplift and loos of grains) were observed.

3.2 Mechanical properties

Mechanical tests were performed for all samples. All measurements were taken after three measurements for each sample. The results of a static sample for the 4PBT analysed materials are presented in Table 3. It was found that the obtained results are compatible with the ISO standards and exceed $\sigma_f = 800$ MPa, regardless of ageing time. More-

Figure 3: AFM microphotographs of accelerated aged samples: a) 2.5, b) 5 and c) 10 h.

over, the ageing time of 2.5 h caused an increase in flexural strength compared to the blind sample. In turn, for the 10 h aged sample, various bending strengths were found, which may be because of a strengthening of vari-

Figure 4: SEM microphotographs of samples: a) 10 h, b) 2.5 h, c) 5 h and d) blind sample.

Table 3: Results of the 4PBT

Sample	σ_f [MPa]
B.S.	850
I	1153
II	808
III	801

Table 4: Vickers hardness measurements

Repeat	Hardness HV1			
	B.S.	I	II	III
1	1588	1614	1449	1006
2	1561	1646	1573	745
3	1442	1680	1452	1272
4	1525	1666	1489	978
5	1501	1696	1499	1568
Average (arithmetic).	1523	1660	1492	1113

ous phases occurring in the ceramics. The Vickers hardness test results are presented in Table 4. Based on the obtained results, it can be observed that there is a strong dependence on the ageing time. A slight increase in hardness was found for the samples subjected to ageing for 2.5 h compared to the blind sample. For samples with 5 and 10 h of ageing, a reduction in the hardness occurred compared to the blind sample. Furthermore, the various results of hardness for 10 h of ageing may indicate the strengthening of various phases occurring in the ceramics.

4 Discussion

The obtained results give valuable information regarding the influence of accelerated ageing tests on the characteristics of the mechanical properties and surface topography of Y-TZP Glidewell BruxZir HT 2.0, dedicated specifically for bruxers, manufactured by CAD/CAM restorations. Accelerated aging tests were used to illustrate the impact of an environment simulating the effects of conditions in the stomatognathic system. On the basis of the results, it can be stated that the application of the external simulation environment can successfully reflect actual conditions [7]. The changes occurring during aging are characterised by the phase transformation of the diffusionless martensitic-type phases [7]. As a result of the transformation, the tetragonal phase changes to the stable monoclinic zirconia phase in an ambient atmosphere. Furthermore, the $t \rightarrow m$ transformation occurs with a volume expansion (when unconstrained) of approximately 5%, an uplift of the surface of a zirconium object, cracking on the surface and an increase in the hardness of the ceramic [4]. This investigation was concentrated on the description of correlations between ageing time and changes in the surface and mechanical properties.

Topographic studies were performed using AFM and SEM. On the basis of the observations and the available data [1, 7] on the surface of the analysed samples, we observed changes that may indicate a phase change of $t \rightarrow m$. On the samples from each series from I to III, we noted the characteristic efflorescence, indicating the increase of the volume of ZrO_2 grains and the uplift on the surface, which in turn indicates a change in the crystallographic orientation from tetragonal to monoclinic. By comparing the AFM studies of the $t \rightarrow m$ phase transformation, it can be stated that the analysed surface changes are significantly smaller [1, 7]. In addition, in each of the series, areas with significant grain losses were noted by grain pop-outs. The observed phenomenon is evidence for the volume of grains and the low-temperature degradation of ceramics, which occurs in a humid environment. Observed degradation changes are the result of the uncontrolled phase transformation. On the basis of the AFM studies, there was clear evidence for the relationship between aging time and the number of cavities in the surface of the samples (Figure 3(a)–(c)). A correlation between the aging time and surface roughness could not be found.

To determine the effect of aging conditions for the mechanical properties of samples, was flexural strength was measured with the 4PBT and hardness measurements with a Vickers penetrator (Oliver–Pharr method). The obtained

results confirm the deterioration of the strength properties as the aging of the material increases, but independently for the ageing time are consistent with the ISO standards. In addition, it was found that a 2.5 h sterilisation time causes an increase in flexural strength. Investigations after 10 h of ageing show that different bending strengths were obtained, which may indicate different phase transformations. For hardness measurements, the characteristics of the values obtained are similar to those for 4PBT. With aging time were observed more varied results of hardness measurements for an ageing time of 10 h. This also proves that the phases of the ceramics are different, which may affect the abrasive wear of prosthetic restorations.

5 Conclusions

Based on the strength tests of the BruxZir HT 2.0 zirconia ceramics, it can be concluded that the analysed materials reach the ISO standards for biomedical grade ceramics. There are some drawbacks in the topographic studies of the quantitative and qualitative share of the undesirable monoclinic ZrO_2 phase. Based on the obtained results, it can be clearly stated that structural studies, such as X-ray diffraction or micro-CT-SEM, could be desirable techniques for future studies.

References

- [1] J. Chevalier and L. Gremillard, *J. Europ. Ceram. Soc.*, 29 (2009) 1245–1255.
- [2] D. Nakonieczny, Z. Paszenda, S. Drewniak, T. Radko, and M. Lis, *ZrO₂-CeO₂, Acta Bioeng. and Biomech.*, 18(3) (2016) 53–61.
- [3] W. Rieger, *Medical applications of ceramics*. Academic Press, London (1989), pp. 1291–1328.
- [4] R. H. J. Richard, P. M. Kelly, and B. C. Muddle, *J. Am. Ceram. Soc.*, 83 (2000) 461–87.
- [5] D. Nakonieczny, W. Walke, J. Majewska, and Z. Paszenda, *Acta Bioeng and Biomech.*, 16 (2014) 99–106.
- [6] D. Nakonieczny, Z. Paszenda, S. Drewniak, T. Radko, J. Podwórny, W. Bogacz, et al., *Acta Bioeng and Biomech.*, 19(2) (2017) 21–30.
- [7] J. Chevalier, L. Gremillard, A. V. Virkar, and D. Clarke, *J. Am. Ceram. Soc.*, 92 (2009) 1901–1920.
- [8] L. Gremillard, S. Meille, J. Chevalier, J. Zhao, V. Fridrici, Ph. Kapsa, et al., Chapter 4 in *Degradation of implant materials*, edited by N. Eliaz, Springer, New York, (2012), pp. 195–240.
- [9] M. Ferrari, A. Vichi, and A. F. Zarone, *Dent Mater.*, 31 (2015) e63–e76.
- [10] T. Takeichi, S. Miura, S. Kasahara, H. Eguda, M. Hara, T. Sato, et al., *J. Prost. Res.*, 59 (2015) 81–93.
- [11] J. Chevalier, *Biomater.*, 27 (2006) 536–543.

- [12] S. Deville, J. Chevalier, and L. Gremillard, *Biomater.*, 27 (2006) 2186-2192.
- [13] V. Lughy and V. Sergo, *Dent Mater.*, 26 (2010) 807-820.
- [14] S. Deville and G. Guenin, *J. Acta Mater.*, 52 (2004) 5697-5707.
- [15] S. Somiya, M. Yoshimura, Z. Nakai, K. Hishuima, and T. Kumai, *Microstructure development of hydrothermal powders and ceramics* edited by J. A. Pask and A. G. Evans, *Ceramics microstructures*, Plenum Press, New York, (1987).
- [16] M. C. Aragon-Duarte, A. Navarez-Rascon, H. E. Esparza-Ponc, M. M. Nevarez-Rascos, R. P. Talamantes, C. Ornelas, et al., *Ceram. Inter.*, 43(5) (2017) 3931-3939.
- [17] I. G. Tredici, M. Sebastiani, F. Massimi, E. Bemporad, A. Resmini, G. Merlati, et al., *Ceram. Inter.*, 42(7) (2016) 8190-8197.
- [18] A. Perrichon, B. Reynard, L. Gremillard, J. Chevalier, F. Farzian, and J. Geringer, *J. Mech. Beh. Biomed. Mater.*, 65 (2017) 600-608.
- [19] H. Reveron, M. Fornabaio, P. Palermo, T. Furderer, E. Adolfsom, V. Lughy, et al., *Acta Biomater.*, 48(15) (2017) 423-432.
- [20] F. Zhang, J. Chevalier, Ch. Olagnon, B. Van Meerbeek, and J. Vleugels, *J Euro. Ceram. Soc.*, 37(4) (2017) 1865-1871.
- [21] V. P. Faradin, V. Guarconi de Paula, E. A. Bonaforte, and P. G. Coelho, *Dent. Mater.*, 32(12) (2016) 1542-1554.
- [22] F. Zhang, M. Inokoschi, M. Batuk, J. Hadermann, I. Naert, and B. Van Meerbeek, *J. Vleugels, Dent. Mater.*, 32(12) (2016) e327-e337.
- [23] G. T. Rocca, P. Sedlakova, C. M. Saratti, R. Sedlacek, L. Gregor, N. Rizcalla, I. Feilizer, A. J. Krejci, *Dent. Mater.*, 32(12) (2016) e338-e350.
- [24] J. Fischer, B. Stawarczyk, I. Sailer, and H. F. Hammerle, *J Prost. Dent.*, 103(5) (2010) 267-274.
- [25] E. Y. Choi, J. Lee., S. J. Lee, S. Jeon, S. H. Cho, S. Chuloh, et al., *J Nuc. Mater.*, 475 (2016) 57-61.
- [26] EN ISO 13356:2013, *Implants for surgery. Ceramic materials based on yttria-stabilized tetragonal zirconia (Y-TZP)*.
- [27] M. Cattani-Lorente, S. Durural, M. Amez-Droz, H. W. A. Wiskott, and S. S. Scherrer, *Dent. Mater.*, 32(3) (2016) 394-402.