Effect of sintering time on biaxial strength of zirconium dioxide

Jenni Hjerppe\textsuperscript{a,b,*}, Pekka K. Vallittu\textsuperscript{a}, Kaj Fröberg\textsuperscript{c}, Lippo V.J. Lassila\textsuperscript{a}

\textsuperscript{a} University of Turku, Department of Prosthetic Dentistry and Biomaterials Science, Turku, Finland
\textsuperscript{b} Järvenpää Health Care Center, Finland
\textsuperscript{c} Åbo Akademi, Process Chemistry Center, Turku, Finland

\textbf{A R T I C L E   I N F O}

Article history:
Received 2 August 2007
Accepted 29 May 2008

Keywords:
Dental material
Zirconia
Sintering time
Bi-axial flexural strength
Thermocycling

\textbf{A B S T R A C T}

Objectives. Aim of this study was to evaluate effect of sintering time on mechanical properties of yttrium partially stabilized zirconia (Y-TZP) (ICE Zirkon, ZirkonZahn, Italy).

Methods. Fifty-six zirconia discs were divided into two groups. Discs of the first group were sintered in sintering oven (ZirkonZahn) at 20–1500 \degree C temperature using rise time of 3 h and kept at 1500 \degree C for 2 h. Discs of the second group were sintered at 20–1500 \degree C using rise time of 1 h 40 min and kept at 1500 \degree C for 1 h. Half of the discs (\(n = 15\)) from both groups were thermocycled in distilled water for 20 000 cycles (5–55 \degree C). Biaxial flexural strength of the discs (diameter 19.0 mm, thickness 1.6 mm) were measured dry at room temperature. Surface microhardness (VHN) was also measured. X-Ray diffraction analysis was performed to evaluate the ratio of tetragonal to monoclinic phase in thermocycled discs. The data was calculated using Weibull and ANOVA analysis.

Results. No statistically significant difference (\(p > 0.05\)) was found between the groups in terms of sintering time or thermocycling. The biaxial flexural strength of the groups varied from 995 MPa to 1127 MPa. Surface microhardness varied from 1478 to 1532. The relative amount of the monoclinic phase was higher when zirconia was thermocycled and stored in water compared to control discs, which had no monoclinic phase at all.

Significance. Variation in the sintering time from 1.6 h to 3.0 h did not influence mechanical properties of Y-TZP zirconia.

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1. \textbf{Introduction}

Y-TZP zirconia is a durable and tough dental material, which has esthetical advantages over metals. Partially yttrium stabilized zirconia has been proved to be stronger than other dental ceramic materials [1–4]. In previous studies the mean flexural strength of zirconia has varied in the range of 608–1540 MPa depending on how the samples are treated [5–7]. For example, sandblasting increases significantly the static strength of zirconia [7].

Zirconium dioxide is a polymorphic material and occurs in three forms: monoclinic, tetragonal and cubic. Monoclinic phase is stable from room temperature to 1170 \degree C, tetragonal in 1170–2370 \degree C and cubic over 2370 \degree C. The phase transforma-
tion in pure zirconium dioxide from tetragonal to monoclinic phase is taking place, while cooling is associated with volume expansion of 3–5%. By addition some stabilizing oxides, like Y\textsubscript{2}O\textsubscript{3}, zirconia can be stabilized on tetragonal phase also on room temperature [8].

Tetragonal to monoclinic phase transformation in zirconia can be initiated by stress, temperature and surface treatments [7,9,10]. Low temperature aging via phase transformation of zirconia hip-joint heads at body conditions has been reported after 10 years of incubation [11]. After aging of yttrium stabilized zirconium dioxide in body fluid or water, some tetragonal to monoclinic phase transformation on the surface of zirconium dioxide has also reported [12-14]. Even though some phase transition occurs, reports are showing, that the effect on mechanical properties is been negligible [14,15]. On the other hand, there is also a study where after the low intensity corrosion in Milli-Q-water the surface elemental composition of zirconia remained unchanged [16] and a study where the presence of water did not detrimentally influenced on zirconia [17]. Aging specimens in 4% acetic acid did not affect significantly to the flexural strength of zirconia [18].

The aim of this study was to determine whether the sintering time of partially yttrium stabilized green stage zirconium dioxide or thermocycling of sintered one affect on some properties and the ratio of monoclinic phase of zirconia. The null hypothesis was that shorter sintering time does not weaken the zirconia.

2. Materials and methods

Fifty-six partially yttrium stabilized zirconia (Y\textsubscript{2}O\textsubscript{3} 3 mol%) green stage discs (ICE Zirkon, ZirkonZahn GmbH, Italy) supplied by the manufacturer were divided into two groups. Discs of the first group were sintered in sintering oven (ZirkonZahn) at 20–1500°C temperature using rise time of 3 h and kept at 1500°C for 2 h (manufacturers’ recommendation). Discs of the second group were sintered at 20–1500°C using rise time of 1 h 40 min and kept at 1500°C for 1 h (Table 1).

Half of the discs (n = 14) from both groups were thermocycled (tc) in distilled water for 20 000 cycles in 5–55°C. Each cycle lasted 60 s: 20 s in 5°C bath, 10 s to transfer samples to another bath, 20 s in 55°C bath and 10 s to transfer samples back to 5°C bath. Thickness (1.6 mm) and diameter (19.0 mm) of all sintered discs were measured with digital micrometer (Mitutoyo Ltd., Andover, England) before the fracture test. According to recommendations of ISO Standard 6872 [19] biaxial bending test was used for determining biaxial fracture strength values. Discs were tested dry at room temperature with universal testing machine (Model LRX, Lloyd Instruments Ltd.) where they rested on three symmetrically based balls and the load was applied to the center of the top surface by the piston (diameter 1.60 mm) until fracture occurred. Cross-head speed of the piston was 1.0 mm/min. Results were recorded with the PC-software (Nexygen, Lloyd Instruments Ltd., Fareham, England). Hardness of the discs was determined by indentation technique [20]. Surface microhardness (Vickers hardness number, VHN) of the discs was measured by using load of 9.81 N. All the tested discs were used and to some of them two indentations were made resulting totally 20 indentations per group.

The data was calculated using one-way analysis of variance (ANOVA) followed by Tukey’s HSD test (p < 0.05). Variability of the flexural strength values was determined by Weibull-analysis [21]. Higher value of Weibull modulus (m) indicated the homogeneity of the group.

One disc from each group was cleaned ultrasonically and thermal etching was performed at sintering oven at 20–1500°C temperature using rise time of 3 h and kept at 1500°C for 30 min. The grain size determination of zirconia for each group was made on scanning electron microscope (SEM) (Princeton Gamma-tech X-ray microanalysis) with magnification of 6000× using semiautomatic image analysis for calculation.

One disc from both thermocycled groups was stored (non-tested) in distilled water for 7 months. Additionally two discs (tested) from thermocycled groups were stored dry at room temperature for 7 months. The relative amount of the monoclinic phase after thermocycling, short/long sintering time and dry/wet storage was determined by X-ray diffraction (XRD) analysis (Philips PW 1830 Generator) using 40 kV and 30 mA Cu Kα radiation. The ratio of the monoclinic phase in thermocycled and water stored groups was also measured after 13 months. Two control discs of the green stage zirconia block were cut with saw (Leitz 1600) and sintered in ZirkonZahn sintering oven at 20–1500°C temperature using rise time of 3 h and kept at 1500°C for 2 h. One disc was left as such and the other was polished with diamond paste. XRD-analysis of the control discs was performed after sintering.

The relative amount of monoclinic zirconia was determined according to the polymorph method recommended by Garvie and Nicholson [22] from the integral intensities of two monoclinic peaks M(III) and M(III)\textsubscript{1} and one tetragonal peak T(III). The equation for monoclinic phase is:

\[
\chi_m = \frac{\left[I_m(\text{III}) + I_m(\text{III})\right]}{\left[I_m(\text{III}) + I_m(\text{III}) + I(\text{III})\right]}
\]

3. Results

Summary of biaxial flexural strength is seen in Fig. 1. One-way ANOVA analysis revealed no statistically signifi-
Table 1 – Classification of the zirconium dioxide discs to the groups according to sintering time

<table>
<thead>
<tr>
<th></th>
<th>N</th>
<th>Time for temperature rising from 20 °C to 1500 °C</th>
<th>Time for keeping temperature at 1500 °C before cooling down (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal sintering (recommended by manufacturer)</td>
<td>14 (two study groups)</td>
<td>3 h</td>
<td>2</td>
</tr>
<tr>
<td>Short sintering</td>
<td>14 (two study groups)</td>
<td>1 h 40 min</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 2 – Weibull characteristic biaxial strength, modulus, surface Vickers microhardness and mean grain size of normally and short sintered and thermocycled (tc) zirconia groups

<table>
<thead>
<tr>
<th>Parameters</th>
<th>1500 °C 3 h dry</th>
<th>1500 °C 3 h tc</th>
<th>1500 °C 1 h 40 min dry</th>
<th>1500 °C 1 h 40 min tc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Characteristic strength (MPa)</td>
<td>1138.7</td>
<td>1210.0</td>
<td>1134.9</td>
<td>1104.2</td>
</tr>
<tr>
<td>Weibull modulus</td>
<td>7.95</td>
<td>14.33</td>
<td>14.32</td>
<td>11.07</td>
</tr>
<tr>
<td>𝜌</td>
<td>0.98</td>
<td>0.97</td>
<td>0.97</td>
<td>0.97</td>
</tr>
<tr>
<td>Surface microhardness VHN (SD)</td>
<td>1519.2 (85.1)</td>
<td>1478.2 (76.6)</td>
<td>1532.1 (81.0)</td>
<td>1502.6 (76.3)</td>
</tr>
<tr>
<td>Mean grain size 𝜇m (S.D.)</td>
<td>1.05 (0.39)</td>
<td>0.98 (0.32)</td>
<td>0.77 (0.22)</td>
<td>0.83 (0.24)</td>
</tr>
</tbody>
</table>

Significant differences between the groups (p > 0.05). Summary of Weibull-characteristic biaxial strength, modulus and surface microhardness is seen in Table 2. In spite of the n = 14/group, Weibull-analysis revealed higher 𝜌-values showing homogeneity of the groups according to characteristic biaxial strength (Fig. 2). The Weibull-modulus was lower (7.95) on the first group (sintered at 20–1500 °C temperature using rise time of 3 h and kept at 1500 °C for 2 h) comparing to other groups (11.07–14.33). Thermocycling did not influence on mechanical properties of zirconia (p > 0.05, ANOVA).

Thermal etching revealed a minor difference on the grain size of the groups (Fig. 3). The mean grain size varied from 0.77 to 1.05 between the groups. Specimens with shorter sintering time had slightly smaller grain size but the difference was not statistically significant (p > 0.05, Table 2).

The relative amounts of monoclinic zirconia are seen in Table 3. On the surface of sintered control discs there was not found any monoclinic zirconia. When the control disc was stored on distilled water for 6 months the relative amount of monoclinic phase was slightly increased (0.7%). Control discs were sintered according to manufacturer’s instructions, at 20–1500 °C temperature using rise time of 3 h and kept at 1500 °C for 2 h. Shorter sintering was not performed to the control discs. Biaxial flexural strength testing increased also slightly the amount of monoclinic zirconia on the surface of the disc (2.2%). The highest amount of monoclinic phase was on the thermocycled discs and the relative amount was rising from 4.0% to 6.0% after storage in distilled water for 13 months compared to the discs stored in distilled water for 7 months. Discs with short sintering times seemed to have less monoclinic phase than the discs sintered for a longer period of time (Fig. 4).

4. Discussion

This study was undertaken to demonstrate the possible change in strength of sintered green stage zirconia discs by varying the sintering conditions. This is of interest because questions have arisen whether the properties of some green stage milled zirconia can reach higher strength by changing the sintering temperature. Also, potential risk of phase shift from tetragonal to monoclinic against sintering process is of interest. Clinically, shorter sintering time would be also beneficial for faster manufacturing process for zirconia based prosthetics devices.

No change in static strength of zirconia was found in four study groups of this study. It needs to be noticed that the study was performed by static loading test and that the dynamic (fatigue) test would imitate closer clinical masticatory forces. However, there is a correlation between static and fatigue properties. This would have been analogous to studies of where the different damage mode or degradation of strength has been seen when comparing cyclic loading to monotonic loading tests [23,24]. Itiinoche et al. [25] found slight difference on the flexural strength of zirconia between static and cyclic loading tests but it was not statistically significant.
In our study, there was no difference between the groups on surface Vickers microhardness. Theoretically, monoclinic phase transition at surface would cause compressive stress to outer layer of zirconia, which could increase surface microhardness. However, in this microhardness of the surface does not depend on sintering phase or possible phase changes from tetragonal to monoclinic phase on the surface of the specimens.

Weibull-analysis was performed to see whether the study groups were homogenous. Neither shorter sintering time nor thermocycling influenced on material reliability because the Weibull-modulus was lower only for the group that was sintered normally. *p*-values were above 0.95, meaning that the data fits to the Weibull-distribution.

In this study, there was no statistically significant difference on the biaxial flexural strength between thermocycled and non-thermocycled zirconia discs. However, thermocycling increased the amount of monoclinic phase on the surface of the discs. Sato and Shimada [12] found that when annealing zirconia discs in the water (65–120 °C) tetragonal to mono-

**Table 3 – Relative amounts of monoclinic zirconium dioxide (\(X_M\) %) determined by X-ray diffraction analysis**

<table>
<thead>
<tr>
<th>Treatment type</th>
<th>Normal sintering (1500 °C 3 h): the amount of monoclinic phase (%)</th>
<th>Short sintering (1500 °C 1 h 40 min): the amount of monoclinic phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control disc, normal sintering</td>
<td>0.0</td>
<td>–</td>
</tr>
<tr>
<td>Control disc, normal sintering, polished</td>
<td>0.0</td>
<td>–</td>
</tr>
<tr>
<td>Control disc, normal sintering, water storage for 6 months</td>
<td>0.7</td>
<td>–</td>
</tr>
<tr>
<td>Control disc, normal sintering, polished, water storage for 6 months</td>
<td>0.0</td>
<td>–</td>
</tr>
<tr>
<td>Biaxial flexural strength tested, stored at dry conditions</td>
<td>2.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Thermocycling, storage in distilled water for 7 months</td>
<td>4.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Thermocycling, storage in distilled water for 13 months</td>
<td>6.0</td>
<td>4.3</td>
</tr>
<tr>
<td>Thermocycling, storage in dry conditions for 13 months (tested)</td>
<td>2.6</td>
<td>2.4</td>
</tr>
</tbody>
</table>

Short sintering was not performed to control discs.
Fig. 4 – Relative amounts of monoclinic zirconium dioxide determined by X-ray diffraction analysis: (a) normal control (XM 0%); (b) normal sintering time, thermocycled and stored in water for 7 months (XM 4.0%); (c) short sintering time, thermocycled and stored in water for 7 months (XM 2.2%).

clinic phase change occurs mainly on the surface and only little inside of the sintered ceramic. In the mouth, temperature can reach up to 65°C, but that is hardly relevant concern with respect to clinical survival of ceramic restorations [26].

XRD-analysis was performed to see the possible phase change on the surface of the discs. Monoclinic peaks were seen on the surface of the disc that had been stored in water. Smaller monoclinic peaks were seen on the disc that was thermocycled but stored in dry conditions. In this study monoclinic peaks were missing on unexposed specimens, conforming results of previous studies [12,18,27]. In our study discs with shorter sintering time had lower ratio of the monoclinic phase than discs that were sintered according to manufacturer’s instructions, even if the short sintered discs were thermocycled or stored in water.

Kosmač et al. [27] found that after aging in 4% acetic acid solution the relative amount of monoclinic zirconia exceeded 14.7–30% depending on how fine-grained the material was. The more fine-grained material was, less monoclinic zirconia was found. Also Sato and Shimada [12] found that the rate of tetragonal to monoclinic transformation slightly increased with increasing grain-size in the sintered zirconia. Swain [28] has shown that the grain-size of zirconia is increasing after longer sintering time. This was also seen in our study as the grain-size was smaller in the groups with shorter sintering time.

Shorter sintering time does not affect on the static biaxial flexural strength of zirconia but it has meaning to the surface composition of the samples. As some amount of monoclinic phase exist on the surface of zirconia after water exposure, it should be also noted that zirconia on dental application is covered with porcelain and thus clinical situation is not equal as in this study. Further studies are required to determine whether the shorter sintering time
affects on the durability of Y-TZP zirconia on the clinical use.

5. Conclusions

Variation in sintering time from 1.6 h to 3.0 h did not influence on mechanical properties of Y-TZP zirconia.

Acknowledgements

This study was supported by Finnish Dental Society Apollonia.

Gratitude to Enrico Steger (ZirkonZahn) for donating the material and C.D.T Jasmina Bijelic and B.Sc. Mikko Jokinen for helping with this study.

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