Zirconia-reinforced dental restorations
Chen, C.

Citation for published version (APA):
CHAPTER 2

The effect of sintering time and temperature on density, grain size, and biaxial flexural strength of zirconia
2.1 Abstract

Objectives: This study aimed to investigate the influence of sintering time and the final temperature on the density, grain size, and biaxial flexural strength of zirconia. 

Methods: 100 zirconia discs made from Cercon base were divided into three groups, L, H and the control. Group L: sintered at the final temperature of 1200°C, for 2, 4, 6, 8, 16, or 24 hr, respectively, with 10 specimens for each holding time. Specimens in Group H were first sintered at 1200°C for 2, 6, or 24 hr, respectively and then sintered again at a final temperature of 1350°C for 2 hr. Control specimens were sintered directly at 1350°C. The density, biaxial flexural strength (BFS), and grain size of all the specimens were measured, and analyzed by one-way ANOVA, and linear regression.

Results: The densities and BFS of Group H had no significant difference from those of the control (P > 0.05). In Group L, the densities and BFS increased with the holding time until 16 hr, while there was a decrease for 24 hr. Only the grain size of 2 hr holding in Group H was not significantly different from the control (P > 0.05), while all the other sintering procedures had significantly smaller grain sizes (P < 0.05). For every two factors in density, BFS, and grain size, there was a linear relation (P < 0.05).

Significance: The higher final sintering temperature is more important to reach a good BFS and density for zirconia, while the low temperature sintering can result in a smaller grain size.
2.2 Introduction

The yttria stabilized tetragonal zirconia polycrystals (Y-TZP) has been widely used in industry as a structural ceramic [1]. In recent decades, it has become an important advanced ceramic in dentistry, due to its esthetics, biocompatibility, high toughness, high thermal stability, and other superior properties. It has been used as endodontic posts, implant abutments, and framework cores for crowns and fixed partial dentures [2-4].

Zirconia is a polymorphic material and exists in three forms depending on the temperature: monoclinic (m), tetragonal (t), and cubic (c). Monoclinic phase is stable from room temperature up to 1170ºC, above this temperature, it transforms into tetragonal phase, and then into cubic phase over 2370ºC, which exists up to its melting point of 2680ºC. The tetragonal to monoclinic phase transformation is taking place in pure zirconia during the cooling stage, which is associated with a volume expansion of 3 – 5% [3, 5]. However, zirconia can also be stabilized in tetragonal phase at room temperature by adding some stabilizing oxides, such as Y$_2$O$_3$, CaO, MgO, and CeO [2-4], among which Y$_2$O$_3$ is the most widely used [6].

Y-TZP restorations in dentistry are always sintered at temperature ranging from 1300ºC to 1500ºC for more than 2 hr [7]. As at these final sintering temperatures, porosities in zirconia disappeared, grain sizes grow slowly, and the maximum relative density can also be achieved at this stage [7]. However, it was reported that when the final sintering temperature increased above 1500ºC, there was a decline in density and a sharp rise in grain size [7]. Although the monoclinic zirconia can already transform into tetragonal phase above 1170ºC, a final sintering temperature between 1170ºC and 1300ºC was seldom studied, especially related to its flexural strength.

It was reported that Y-TZP powders were densified largely at the temperature of 1200ºC [8], and the volume of green blank also shrank sharply around 1200ºC, with the disappearance of porosity at the same time [9]. It was reported that the density increased linearly as a function of holding time [9], and the pore size also reduced with the sintering time [10]. A relative density of 99% without a large grain growth of zirconia can be achieved by being sintered for 15 hr at a relatively low sintering temperature of 1305ºC [9-11]. Then we assumed that sinter Y-TZP at a relatively lower temperature for longer time could also get as good zirconia products as sintered in a standard way.
The aim of this study was to investigate the influence of holding time at 1200°C, and the final sintering temperature on the density, grain size, and biaxial flexural strength of zirconia.

2.3 Material and method

100 zirconia discs were made from zirconia green blanks (Cercon base 38 colored, Shade: ivory; Degudent, Germany) with the diameter of 25.0 mm using a sawing machine (Isomet 1000; Buehler, USA). The discs were ground using SiC papers P400, P800, P1200 (Buehler, USA) in sequence to achieve a final thickness of 1.0 mm before sintering. Thereafter, the discs were divided into three groups. The first group (L) was sintered at a heat rate of 15°C/min to the final temperature of 1200°C in a dental furnace (STRATOS; Elephant Dental BV, The Netherlands). The specimens were further divided into 6 subgroups according to a holding time of 2, 4, 6, 8, 16, or 24 hr, with 10 specimens for each holding time. For the second group, Group H, the specimens were first sintered at 1200°C for 2, 6, or 24 hr, and then sintered again in a standard way at a final temperature of 1350°C for 2 hr by the standard program in Cercon Heat (Degudent, Germany). The specimens sintered directly according to the Cercon Heat program (rate 15°C/min, 2 hr at 1350°C) were used as control.

Density: All the specimens after sintering were ultrasonically cleaned in water bath by Bransonic 3510 (Branson Ultrasonics Corp, USA). The density of all the cleaned specimens were measured with a digital balance (Mettler AT 261, METTLER - Toledo AG, Switzerland), in the Archimedes method [12].

Biaxial flexural strength: After the density tests, all the specimens were subjected the Biaxial Flexural Strength (BFS) with the ball-on-ring method by a universal testing machine (Instron 6022, Instron Corp., MA, USA) [13]. The disc was supported by a ring with a diameter of 16 mm. It was centrally loaded, from the top until failure, with a stainless steel ball of 5 mm in diameter. The load at fracture was recorded and the BFS for each disc was calculated using Shetty’s equation [14] as below:

\[BSF = \frac{3F(1 + \nu) \cdot [1 + 2 \ln \left(\frac{D_s}{B}\right) + \left\{1 - \frac{B^2}{2 \cdot D_s^2}\right\} \cdot \left(\frac{D_s^2}{D^2}\right) \cdot \frac{1 - \nu}{1 + \nu}]}{4\pi T^2}\]

In this equation, the BFS is calculated using the force at fracture \((F)\); Poisson's ratio \((\nu)\) of 3.0; the diameter of the support circle \((D_s)\); the diameter of the disc \((D)\); the
thickness of the disc ($T$), and the diameter ($B$) of the circular area, with uniform stress on the bottom surface, which was about two thirds of the thickness of the disc [13].

*Grain size:* According to Montanaro L, *et al.* 1996, to enhance the determination of the grain structure the fractured specimens were thermal etched at 1150°C, 50°C lower than the sintering temperature, for 20 minutes, in the Stratos furnace [8, 12]. After that, they were ultrasonically cleaned in distilled water bath for 5 minutes and then gold sputtered (Sputter Coater S150B, Edwards Ltd, Crawley, West Sussex, UK). The surface topography was examined under a Scanning Electron Microscope (SEM) (XL 20; Philips, The Netherlands) at 20,000× magnification. The average grain size $G$ was obtained by the following relationship [12, 15]: $G = 1.56 \times G_x$, in which $G_x$ was the average linear intercept length, measured on the polished surface by a graphic software (XL Docu, FEI company, USA). For each specimen, at least 15 lines were taken, and their average was reported [12, 15].

*Statistics:* The results of density, BFS and grain size were analyzed by one-way ANOVA, and the Turkey test was used as post-hoc test. The relation between density, BFS and grain size were analyzed by linear regression. The statistical analysis was carried out with SPSS statistics 20 (IBM Corp., USA), at a significance level of $\alpha = 0.05$.

### 2.4 Results

The results for densities, BFS and grain sizes for each sintering procedure are summarized in Table 2.1. To observe the trend more clearly, the densities were graphically depicted in Figure 2.1. The densities of the specimens in Group H were not significant different from the control ($P > 0.05$). The density of specimens sintering at 1200°C for 2 hr in Group L was significantly lower than all the other subgroups ($P < 0.05$). Then the density increased with the increased holding time in Group L, until holding for 16 hr. The density of specimens sintered at 1200°C for 16 hr was also not significantly different from the control ($P > 0.05$). However, the density decreased when sintered for 24 hr at 1200°C, and it was significantly lower than that of the control ($P < 0.05$).

The similar trend of the BFS was observed. The BFS of the specimens in Group H were not significantly different from the control ($P > 0.05$). In Group L, the BFS also increased at a holding time of 16 hr. The BFS of specimens sintered at 1200°C for 16
hr was also not significantly different from the control \((P > 0.05)\). The BFS decreased again when sintered for 24 hr at 1200°C, however, which was not significantly lower than the control \((P > 0.05)\). The results are graphically depicted in Figure 2.2.

The trend of the grain size growth was shown in Figure 2.3, 2.5, and 2.6. In Group H, only the specimens first sintered at 1200°C for 2 hr had similar grain size to the control, whose difference was not significant \((P > 0.05)\). The specimens for the other two holding times at 1200°C showed significantly smaller grain sizes \((P < 0.05)\).

**Table 2.1** Densities, BFS, and grain sizes for each sintering procedure in different groups; (L) final sintering temperature of 1200°C; (H) final sintering at 1350°C for 2 hr, and the Control was directly sintered at 1350 °C for 2 hr.

<table>
<thead>
<tr>
<th>Holding time at 1200ºC (hr)</th>
<th>Density (g/mm³)</th>
<th>BFS (MPa)</th>
<th>Grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Group L</td>
<td>Group H</td>
<td>Group L</td>
</tr>
<tr>
<td>1200°C 2 hr</td>
<td>5.27 (0.11)</td>
<td>6.01 (0.01)</td>
<td>440 (149)</td>
</tr>
<tr>
<td>1200°C 4 hr</td>
<td>5.59 (0.09)</td>
<td>-</td>
<td>555 (169)</td>
</tr>
<tr>
<td>1200°C 6 hr</td>
<td>5.67 (0.05)</td>
<td>5.99 (0.01)</td>
<td>640 (186)</td>
</tr>
<tr>
<td>1200°C 8 hr</td>
<td>5.76 (0.11)</td>
<td>-</td>
<td>796 (264)</td>
</tr>
<tr>
<td>1200°C 16 hr</td>
<td>5.91 (0.17)</td>
<td>-</td>
<td>946 (189)</td>
</tr>
<tr>
<td>1200°C 24 hr</td>
<td>5.85 (0.04)</td>
<td>6.02 (0.03)</td>
<td>841 (166)</td>
</tr>
<tr>
<td>Control</td>
<td>6.04 (0.03)</td>
<td>6.04 (0.03)</td>
<td>1069 (167)</td>
</tr>
</tbody>
</table>

For each variable (density, BFS, or grain size): values with identical letters or numbers indicate no statistically significant differences \((P > 0.05)\).

**Figure 2.1** Densities for each group
In group L, there was also a trend that the grain size increased with holding time. Although the change seemed obvious during the holding time from 4 hr to 8 hr in the figure, there was no significant difference for the grain sizes from 6 hr holding to 24 hr (P > 0.05). All the grain sizes for the specimens in Group L were significantly smaller than that of the Group H or the control (P < 0.05).

The linear relationships between density, BFS and the grain sizes are shown in Figure 2.4. For every two factors, there was a linear relation (P<0.05), although the R² ranged from 0.47 to 0.58, which seemed not very strong.
Figure 2.4 Relations between density, BFS and grain size; (top) the relation between BFS and the density, (middle) the relation between BFS and the grain size, and (bottom) the relation between density and the grain size.
Figure 2.5  Typical SEM images, with the magnification of 20,000×. (Left) Group H, first holding at 1200 °C for 2 hr (top), 6 hr (middle), and 24 hr (bottom) respectively, and then sintered standardly at 1350 °C for 2 hr. (Right) Group L, holding at 1200 °C only, for 2 hr (top), 6 hr (middle), and 24 hr (bottom).
Figure 2.6  Typical SEM image with the magnification of 20,000× of the control, sintered directly in the standard way, holding at 1350 °C for 2 hr.

2.5 Discussion

In our study, the densities of Group H had no significant difference from that of the control. However, in Group L, the density increased with the holding time at 1200°C until 16 hr, while there was a decrease for 24 hr. This implied that simply elongating the sintering time at a lower temperature was probably not enough to reach a relatively high density. The final sintering temperature played an important role in the final densification. It was reported that densification of zirconia was generally considered by two stages, the initial stage when \( D_0 < D < 0.9 \), and the final stage \( (0.9 < D < 1) \), in which \( D_0 \) represented the initial packing relative density and \( D \) was the relative density [15, 16]. The densification for the initial stage can be achieved by prolonged sintering time at a relative low temperature [8, 9, 15]. Even a relative density of 99% could be achieve at the temperature below 1300°C [11], usually exhibiting a large shrinkage from 1200°C to 1300°C [8-10]. However, it seemed the last step at final stage, increasing the relative density above 99%, only occurred at a relative high temperature which is usually above 1300°C [7, 10]. It was reported that at these temperatures all porosity disappeared [17]. However, a decline in density was also observed when the sintering temperature was above 1450°C [7].

The BFS resulted in a similar trend to the densities in this study. The BFS for Group H and the control around 1100 MPa, was similar to the results from previous studies [3, 18]. It is known that the high flexural strength of Y-TZP is related to its t - m phase transformation toughening mechanism [19], which can be induced by localized high stress, caused by grinding, sandblasting, cyclic loading and high
The effect of sintering time and temperature on zirconia

temperature thermal aging [2, 20]. The toughness grows with the increasing transformation zone size when sintered at higher temperature [18, 21]. However, when the micro cracks grow to some extent, the toughness does not increase any more [22], or the ceramic will even be weakened due to the excessive m phase [23-25].

As shown in our study, it was also reported that the flexural strength increased with the sintering temperature above 1300°C [6]. Li et al. found that in the range of 1300 to 1450°C, higher sintering temperature leads to more (t/c)-ZrO$_2$ phase fraction [7]. This may be an explanation to the higher BFS in Group H and the control in our study. They also found that the (t/c)-ZrO$_2$ phase fraction decreased when sintering temperature increased from 1450°C to 1500°C [7]. It was also reported that there was a significant decrease in tetragonal and increase in monoclinic phase for zirconia sintered above 1750°C [18]. Furthermore, it was reported that the flexural strength declined with sintering temperature increased above 1600°C [6].

Although there was a positive relation between grain size and BFS or grain size and density, the grain growth had a slightly different trend from the other two factors. We found that if the Y-TZP was sintered at 1200°C for more than 2 hours and then sintered again in the standard way at 1350°C for 2 hr, it would have a smaller grain size and relatively the same density and BFS as the control. It was reported that the superior properties of Y-TZP could to be enhanced when the grain size is retained at nano-meter range [1], while larger grains transform at lower applied stress than smaller grain sized ones [26]. The grain size grew slowly from 1300°C to 1450°C, while sharp rise in grain size occurred above 1450°C [4, 7], and others reported that the grain size grew rapidly when sintering temperature was higher than 1300°C [12]. As in our study, grain sizes grew with the growth of longer holding time [3, 8]. We may summarize that with the increase of sintering time and temperature to a certain extent, the grain size of zirconia will increase and lead to a higher BFS and density. However, if the sintering procedure performed over the extent, the grain size will come to extremely large and result in a decrease of BFS and density.

Since the grain size of zirconia can influence other properties such as the translucency [6], we can sinter zirconia in multiple ways to fulfil different requirements. This also open a way to perform surface pre-treatments like grinding, sandblasting or chemical treatments.
2.6 Conclusion

The higher final sintering temperature is more important to reach a good BFS and density for zirconia, a final sintering temperature around 1350°C is recommended. The low temperature sintering can result in a smaller grain size, for this purpose, sintering zirconia first at a relatively low temperature can be considered.

2.7 Reference


[21] Ohnishi H, Naka H, Sekino T, Ikuhara Y, Niihara K. Mechanical properties of 2.0-3.5 mol% Y(2)O(3)-stabilized zirconia polycrystals fabricated by the solid


