Translucency and low-temperature degradation of silica-doped zirconia: A pilot study
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The purpose of this study was to examine the translucency and low-temperature degradation of silica-doped experimental Y-TZP (Yttria-stabilized tetragonal zirconia polycrystal) containing almost no alumina. The experimental Y-TZP samples were sintered at either 1,450 or 1,500°C. The samples of commercially available translucent Y-TZP and conventional Y-TZP were used as controls. The contrast ratio (CR) and translucency parameter (TP) were obtained to compare the translucencies. In addition, the specimens were also subjected to an accelerated aging test. The results showed that the experimental Y-TZP sintered at 1,500°C and translucent Y-TZP exhibited almost the same level of translucency. During the accelerated aging test, the translucent Y-TZP underwent a substantial increase in monoclinic content, an index of degradation after the aging test. However, neither the experimental Y-TZP nor the conventional Y-TZP exhibited any appreciable change. It was concluded that the silica-doped Y-TZP will develop translucency and resistance to degradation when sintered at 1,500°C.

Keywords: Zirconia, Silica, Translucency, Low-temperature degradation

INTRODUCTION
Zirconia is considered mechanically strong and tough dental ceramic material, but that it is not particularly translucent1-2. In recent years, concern about esthetics and biocompatibility has promoted the spread of the use of metal-free restorations, or all-ceramic crowns or fixed dental prostheses, where zirconia is used for the framework, and tooth colored porcelain is layered over that. However, crowns or fixed dental prostheses using zirconia frames often pose the problem that the porcelain layered on the frame fractures3-4.

More recently, translucent zirconia has been developed5-6, with a higher level of translucency than that of the conventional zirconia used for frames. The use of translucent zirconia could make it possible to fabricate very strong crowns or fixed dental prostheses using zirconia alone, with no need for a layer of porcelain. It has been reported that full contour zirconia crowns fabricated using such a translucent zirconia are more resistant to fracture than full contour glass ceramic crowns5-6 and produce less wear on the opposing dentition7-8.

Most of the zirconia materials currently used in dentistry are partially-stabilized zirconia containing yttria (Y-TZP). It is known that Y-TZP can degrade in a humid, low-temperature environment such as the oral cavity, when used there for long periods9. While conventional Y-TZP for frames contains a small amount of alumina to suppress degradation10, commercially available translucent Y-TZP used for full contour crowns has a reduced alumina content to improve translucency11. Therefore, translucent Y-TZP could be more subject to low-temperature degradation than conventional Y-TZP for frames12.

On the other hand, it has been reported that the addition of a small amount of silica to Y-TZP can suppress low-temperature degradation13-14. It has also been reported that silica-doped zirconia can suppress low-temperature degradation of the material15. Thus, it is expected that the addition of a small amount of silica might suppress low-temperature degradation in translucent Y-TZP that contains a reduced content of alumina.

In this study, the translucency of the experimental silica-doped Y-TZP containing almost no alumina was examined to compare it with that of commercially available Y-TZP for frames and commercially available translucent Y-TZP used for full contour crowns. In addition, an accelerated aging test was conducted to examine the low-temperature degradation of the experimental Y-TZP and the above commercially available Y-TZP samples.

MATERIALS AND METHODS
Zirconia samples
Y-TZP powder containing 3 mol% of yttria, 0.12 mol% of silica and 0.01 or less wt% of alumina was manufactured on a trial basis and used in this study. Samples of this experimental Y-TZP (ZrO2+HfO2: 94.6 wt%, Y2O3: 5.3 wt%, SiO2: 0.14 wt%, Al2O3<0.01 wt%) were sintered at either 1,450 or 1,500°C for 2 h each, shaped into discs with a diameter of 20 mm and different thicknesses: 0.5, 1.0, 1.5, and 2.0 mm, and then polished with a #800 diamond disc to yield experimental specimens (specimens Zr1450 and Zr1500).
In addition, commercially available Y-TZP blocks for frames (InCoris Zi F1 40/19, ZrO2+HfO2+Y2O3 ≥99.0 wt%, Y2O3: 5.4 wt%, Al2O3 ≤0.35 wt%, Sirona Dental Systems, Bensheim, Germany) and commercially available translucent Y-TZP blocks for full contour crowns and fixed dental prosthesess (InCoris TZI 40/19, ZrO2+HfO2+Y2O3 ≥99.0 wt%, Y2O3: 5.2 wt%, Al2O3 ≤0.35 wt%, Sirona Dental Systems) were sintered for 2 h at the temperature (1,500°C) specified by the manufacturer, shaped into strips measuring 15×19 mm, with thicknesses of 0.5, 1.0, 1.5 and 2.0 mm, and then polished with a #800 diamond disc to yield other experimental specimens (specimens ZI and TZI).

Since specimens Zr1450, Zr1500 and TZI are white, not pre-colored, and all ZI is pre-colored, the brightest shade, F1, was used. A total of 80 specimens were created: that is, five specimens with four different thicknesses were prepared from each of the four sample types.

**Translucency**

The translucency of the specimens was examined using their contrast ratios (CR) and translucency parameters (TP). Each specimen was placed against a white standard (L*:98.21, a*:−0.29, b*:4.41) and against a black standard (L*:7.39, a*:−0.13, b*:2.55), used as backgrounds, and their CIE LAB coordinates and reflectance values (Y) were measured using a spectrophotometer (CM-2600d, Konica Minolta, Tokyo, Japan). The measurements were taken three times and the average values were used.

After measurement, the CRs and TPs of each specimen were calculated using the following formula:\(^\text{16}\):

\[
CR = \frac{Y_B - Y_W}{Y_B}
\]

\[
TP = \frac{(L_B - L_W)^2 + (a_B - a_W)^2 + (b_B - b_W)^2}{2}
\]^\text{1/2}

Furthermore, using one of the five specimens made under each condition, the light which was transmitted through the specimen was measured using a spectrophotometer (CM-5, Konica Minolta) to determine the spectral transmission factors of the material in the 360 to 720 nm wavelength range of visible light. Finally, one specimen of each condition was fractured and the fractured surface was observed using SEM (FE-SEM, Hitachi High-Technologies, Tokyo, Japan). The measurements were taken three times and the average values were used.

For all specimen types, as the thickness increased, TP decreased. The greatest TP values and highest levels of translucency were observed for the TZI and Zr1500 specimens, regardless of thickness, with no significant difference in TP value between them. TZI and Zr1500 had significantly greater TP values than ZI and Zr1450, regardless of thickness (p<0.01), with the TP of Zr1450 significantly lower than those of the other 3 types (p<0.01) (Table 1).

The light transmission tended to decrease as the thickness of the specimen increased (Fig. 3). In addition, for each type of specimen there was a tendency for the light transmission to rise as the wavelength of visible light increased. Both TZI and Zr1500 had the propensity of having a larger light transmission than Zr1450 and ZI, regardless of the thickness of the specimen or the wavelength of visible light tested. All four sample types had a low light transmission for visible light in the shorter wavelength range. In particular, ZI allowed hardly any light at 400 nm or less to pass through it when it was no less than 1.0 mm in thickness.

SEM pictures of the fractured surface of specimen revealed many intragranular fractures in the ZI specimen. The other three sample types tended to have mostly intergranular fractures. Zr1500 had larger crystals than Zr1450 (Fig. 4). The mean particle size of crystals obtained by the intercept method was 0.45 μm for Zr1450, 0.64 μm for Zr1500, 0.47 μm for ZI and 0.60 μm for TZI, suggesting that Zr1500 and TZI tend to have larger particle sizes than Zr1450 and ZI (Fig. 4).

The monoclinic content of the specimens before the accelerated aging test was in the range from 1.6%
Fig. 1  Contrast ratio of Y-TZP specimens.

Table 1  Statistically significant difference of CR and TP on the thickness of 1 mm

<table>
<thead>
<tr>
<th></th>
<th>Zr1450</th>
<th>Zr1500</th>
<th>ZI</th>
<th>TZI</th>
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<tr>
<td>Zr1450</td>
<td>—</td>
<td><strong>(CR),</strong>(TP)</td>
<td><strong>(CR),</strong>(TP)</td>
<td><strong>(CR),</strong>(TP)</td>
</tr>
<tr>
<td>Zr1500</td>
<td>—</td>
<td>—</td>
<td><strong>(CR),</strong>(TP)</td>
<td>NS</td>
</tr>
<tr>
<td>ZI</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td><strong>(CR),</strong>(TP)</td>
</tr>
<tr>
<td>TZI</td>
<td>—</td>
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</tbody>
</table>

(**: p<0.01)

Fig. 2  Translucent parameters of Y-TZP specimens.

Fig. 3  Light transmittance of Y-TZP specimens.
Fig. 4  SEM images of Y-TZP specimens. A: Zr1450, B: Zr1500, C: ZI, D: TZI

Table 2  Statistically significant difference of monoclinic content after 40 h aging

<table>
<thead>
<tr>
<th></th>
<th>Zr1450</th>
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<td>**</td>
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<tr>
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<td>**</td>
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<tr>
<td>TZI</td>
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</table>

(**: p<0.01)

Fig. 5  The monoclinic content of Y-TZP specimens subjected to accelerated aging test. (Zr1450) to 6.1% (ZI) (Fig. 5). The monoclinic content of the TZI specimens increased substantially to 43.2% at 20 h after the start of the accelerated aging test and 62.7% by 40 h. The monoclinic contents of the TZI at 20 and 40 h after the start of the accelerated aging test were significantly different from those of the other three sample types (p<0.01)(Table 2). The monoclinic contents of the other three sample types remained within the range of 11.9% (ZI) to 12.4% (Zr1450) at 40 h after the start of the accelerated aging test, almost unchanged from the start of the test. For all specimens, their Vickers hardness was within the range from 1164 HV to 1221 HV and their fracture toughness ranged from 10.02 to 11.35 (Table 3). There were no significant differences among the specimens in terms of Vickers hardness and fracture toughness.
Table 3  The mean values and standard deviation of Vickers hardness (HV), and fracture toughness values (KIC)

<table>
<thead>
<tr>
<th>Condition</th>
<th>Vickers hardness (HV)</th>
<th>Fracture toughness KIC, (MPa·m^{1/2})</th>
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<tr>
<td></td>
<td>X</td>
<td>SD</td>
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<tr>
<td>Zr1450</td>
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<td>1164</td>
</tr>
<tr>
<td></td>
<td>40 h aging</td>
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<tr>
<td>Zr1500</td>
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<td>1200</td>
</tr>
<tr>
<td>ZI</td>
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<tr>
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</tr>
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DISCUSSION

Y-TZP is a polycrystalline material; reduction in translucency occurs due to light scattered at the interfaces between the crystal grains. The level of translucency of Y-TZP can be increased by reducing alumina content in its raw material, to suppress the precipitation of alumina particles, the main factor causing light-scattering in this material. Commercially available translucent zirconia usually contains less alumina to make it more translucent [20]. In this study, therefore, Y-TZP was created on a trial basis that contained a small amount of silica (0.12 mol%) to suppress low-temperature degradation but that had almost no alumina included. The authors previously reported that Y-TZP containing 0.2 mol% of silica had the same flexural strength as conventional Y-TZP and was less likely to degrade in a low temperature environment [20]. Prior to this study, a preliminary experiment was performed using Y-TZP containing 0.2 mol% of silica, but this did not appreciably increase its translucency. This suggested that silica, like alumina, will tend to reduce the level of translucency of Y-TZP if too much is added. Taking the results of the preliminary experiment into account, in this study Y-TZP containing 0.12 mol% of silica was used. In addition, the sintering temperature was changed within a range of 1,400 to 1,600°C in the preliminary experiment, wherein the translucency of the Y-TZP sample was reduced at both 1,400 and 1,600°C. In this study, two experimental temperatures were chosen for sintering: 1,450 and 1,500°C. As controls, InCoris Zi (Y-TZP for frames) and Tzi (translucent Y-TZP) were used because their block form of delivery makes it relatively easy to fabricate strip specimens. Since all Zi is pre-colored, S 0.5 (the closest to white) was selected. It has been reported that the application of a coloring agent to Y-TZP does not cause any change in the level of translucency, even though the shade changes [21]. It was assumed that the Zi used in this study was only slightly tinted, but did not exert any appreciable effect on its level of translucency.

The contrast ratio (CR) and translucency parameter (TP) were used to examine the translucency of the Y-TZP. CR and TP are often used to determine the translucency of dental ceramics and the two parameters are said to be strongly correlated [22,23]. In this study, the levels of translucency indicated by CR and by TP were indeed closely related. Among the four sample types, Zr1500 and TZI both had the lowest CR values and the highest TP values. Thus, both of these parameters indicated that Zr1500 and TZI had higher levels of translucency than the other two sample types. This result suggests that Zr1500 has almost the same level of translucency as commercially available translucent Y-TZP. As the thickness of the specimens increased, CR also increased but TP decreased, resulting in a lower level of translucency; this is the same tendency as has been reported in the past [24,25]. In addition, another report [26] states that TZI was found to have a lower CR value but a higher level of translucency than Zi, corroborating the results of our study. Elsewhere [27], it was reported that TZI, in the thickness range of 0.6 to 1.5 mm, was found to have lower CR values and higher levels of translucency than other commercial translucent Y-TZP products (ZENO Translucent, LAVA Plus High Translucency).

It is also reported that translucent Y-TZP develops lower CR values and higher levels of translucency when the sintering temperature is raised from 1,350 to 1,500°C [27] or 1,460 to 1,530°C [28]. In this study, the Zr1500 also had a lower CR value than ZI, indicating that, as the above reports state [27,28], the level of translucency increases as the sintering temperature is raised. It is thought that in oxide ceramics, pores present between the crystals increase light-scattering and therefore reduce the level of translucency [29]. It is assumed that raising the sintering temperature eliminates these pores and increases the density of the Y-TZP, thus reducing light-scattering and resulting in increased translucency [28].

Since the determination of translucency using CR and TP is a relative evaluation, we therefore examined the light transmission of the specimens at various light wavelengths. As expected, the light transmission of the thinner specimens was large, regardless of the
wavelength. In a study using other types of Y-TZP samples, it was also reported that, as was found in this study, light transmission tended to increase as the wavelength of visible light increased\(^{39}\). The results of this study confirmed that when actual transmitted light is measured, both Zr1500 and TZI have higher levels of translucency than the other two types.

Since SEM observation will not reveal internal structure if polished specimen surfaces are examined, all the specimens were broken to reveal interior fractures. SEM pictures showed that the Zr1500 had larger crystals than the Zr1450, probably because the crystals grew larger due to grain growth under the higher sintering temperature condition\(^{31}\). The quality of the ZI fractures was quite different from that of the TZI. That is, the ZI specimens exhibited many images of intragranular fractures while the TZI had images that appeared to be intergranular fractures. In general, intragranular fractures are often observed in strong materials\(^{22}\). ZI is the Y-TZP used for frames and is stronger than translucent Y-TZP\(^{33}\). We think that this is consistent with these many intragranular failures.

Y-TZP doped with 3 mol% of yttria, which is used extensively in dentistry, is subject to degradation due to phase transformation in a humid environment under low ambient temperatures. It is thought that Y-TZP undergoes a phase transformation on the surface from a tetragonal to a monoclinic phase, accompanied by an increase in volume of about 4% after it has been maintained for a certain period of time in a humid environment, such as in the oral cavity\(^{34,35}\). Unlike Y-TZP for frames, translucent Y-TZP is used mainly in the posterior region, as a full contour zirconia crown. For this reason, translucent Y-TZP is exposed directly to the environment in the oral cavity. It is not only constantly in contact with saliva, but also always subjected to strong occlusal forces. In addition, since the amount of alumina\(^{36,38}\), a material that is effective in suppressing degradation, is reduced in order to improve its translucency, it seems to be more susceptible to low-temperature degradation. In this study, an accelerated aging test was performed in water at 134°C at 2 bar, as specified in ISO 13356, the standard for medical Y-TZP\(^{37}\). The TZI, a commercially available translucent Y-TZP product, had 43% monoclinic contents after 20 h of the accelerated aging test and 62% after 40 h, indicating that its degradation progressed extremely more quickly than that of the other sample types. This was probably because its alumina content was reduced in the interest of translucency, while the intended effect of adding alumina is to help suppress the progress of degradation.

A study in which dental Y-TZP was subjected to a degradation test at the same temperature (134°C) as was used in this study found that the monoclinic content of polished Y-TZP specimens was around 10% at most, by 20 h after the start of the accelerated aging test\(^{38}\). That is, the extent of low-temperature degradation in the TZI in the present study seems to be very high. The ISO standard for medical Y-TZP implants requires the transformation from tetragonal to monoclinic phase at the end of a five-h accelerated aging test in an autoclave at 134°C and 2 bar to be 25% or less\(^{37}\). Although dental Y-TZP is slightly different from medical Y-TZP in composition, TZI meets the requirements of this ISO standard. However, it was reported that the application of repeated loads promotes the low-temperature degradation of Y-TZP\(^{39}\). That is the reason why the translucent Y-TZP used in the posterior region must be highly resistant to degradation.

On the other hand, the experimental silica-doped Y-TZP had the same level of monoclinic content as did ZI, or Y-TZP for frames, and no substantial low-temperature degradation after the end of an accelerated aging test. In our previous study, we reported that Y-TZP doped with 0.2 mol% of silica was resistant to low-temperature degradation and that there are no difference in fracture of copings fabricated by using this material before and after an accelerated aging test\(^{15}\). The results of the accelerated aging test in the present study revealed that the degradation of Y-TZP could be suppressed by adding a small amount (0.12 mol%) of silica, without adding alumina.

In this study, TZI, which had a large monoclinic content, an index of degradation, did not develop a large difference in Vickers hardness and fracture toughness in the period from before to after the accelerated aging test. It will be necessary to evaluate the deterioration of such commercially available translucent Y-TZP products, by fabricating them into samples of crowns.

The reason why silica is effective in lending Y-TZP resistance to degradation is reported to be as follows: the addition of silica alters the microstructure of the material, giving the zirconia particles a slightly spherical shape, so that the internal stresses in the material are reduced, improving its resistance to cracks\(^{16}\). In addition, it appears that degradation of Y-TZP is triggered by \(\text{H}_2\text{O}\) penetrating into the grain boundaries of \(\text{ZrO}_2\)\(^{40}\), and that it progresses by hydrolysis. Therefore, the presence of silica in the grain boundaries of the zirconia might also help reduce the diffusion of water into those boundaries, making it difficult for hydrolysis to begin, thus contributing to suppression of the occurrence of low-temperature degradation.

**CONCLUSIONS**

The experimental silica-doped (0.12 mol%) Y-TZP specimens (containing almost no alumina) sintered at 1,500°C were as translucent as commercially available translucent Y-TZP. In addition, an accelerated aging test revealed that this experimental Y-TZP was more resistant to low-temperature degradation than commercially available translucent Y-TZP.

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