SEM observations of porcelain Y-TZP interface

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ABSTRACT

Objectives. The metastability of the tetragonal phase of yttria tetragonal zirconia polycrystalline (Y-TZP) ceramics is a cause for concern in dental crown and bridge applications. One specific problematic area is the nature of the interface between the veneering porcelain and the Y-TZP framework and whether the associated preparation procedures and reactions result in a reduction of the stability of the zirconia.

Methods. To investigate this aspect, high-resolution SEM observations were made of polished and etched (HF content gel) cross-sections of the interface area. Dry and moist veneering porcelain powders were built up on the zirconia base.

Results. In some instances the zirconia grains at the interface appear to show multiplicity of subgrain faceting whereas in other instances they do not. The latter indicate destabilisation of the tetragonal phase occurs and in addition that the porcelain veneering material wets and some dissolution of the Y-TZP occurs.

Significance. These results and their relevance to the long-term stability of the interface adhesion to the veneering porcelain as well as possible tetragonal to monoclinic crystal transformations at the interface are discussed.

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1. Introduction

Dental crown and bridge restorative materials are changing from porcelain fused to metal (PFM) to all-ceramic systems. Techniques, which have been developed over decades in the case of PFM systems, must now be redeveloped for all-ceramic systems. These changes include issues such as the need for veneering porcelains with better matching coefficients of thermal expansion because of the inability of ceramic copings to accommodate high tensile stresses by plastic deformation as with metallic copings. In addition the type of bonding and inter-diffusion that occurs at the interface is not well understood.

Recently with the advances in computer aided design and computer aided manufacturing (CAD/CAM) there has been marked interest in all-ceramic systems [1,2]. This has also been encouraged by the very high strength and toughness reported of some of these ceramics especially yttria partially stabilized tetragonal zirconia polycrystalline (Y-TZP) materials [3]. The same material has been widely used in orthopaedic surgery as a hip prosthesis ball because of its high mechanical properties as well as its fine grain size and excellent surface finish [4]. However there have been reports of moisture induced destabilisation of Y-TZP ceramics including a significant number of fractured implanted hip prosthesis that have been extremely harmful for this application [4]. Chevalier et al. [5] in a major review of Y-TZP for biomedical purposes recently summarized the influence of humidity at modest temperatures (lower than 250°C) on the metastability of Y-TZP. This group over the
course of many investigations found that impurity content, grain size, density and temperature all led to destabilisation of the tetragonal to the monoclinic phase. The problem with the hip implants were shown to be associated with the transformation instabilities of the tetragonal phase [6,7]. More recently in the case of all-ceramic crowns and bridges there have been clinical reports of excessive chipping of the veneering porcelain for zirconia based systems, although the origin of this failure is not well understood [8–11].

Pure ZrO2 exists as a monoclinic crystal structure at room temperature and transforms to tetragonal (1173 °C) and cubic (2370 °C) structures at increasing temperatures. The volume change associated with the cubic to tetragonal to monoclinic transformation induces very large stresses within the material, and will cause pure zirconia to crack on cooling down from high temperatures [12].

Zirconia for dental applications in its tetragonal crystalline state, which is achieved by the addition of 3-mole% yttrium oxide (Y-TZP), is metastable. An applied stress, magnified by the stress concentration at a crack tip, or associated with high stresses, caused by grading, can result in the tetragonal phase converting to monoclinic, with an associated approximate 4%-volume increase. This zone of transformation around the crack tip can result in closure forces about the tip enhancing the fracture toughness. This mechanism is known as transformation toughening [13].

Porcelain fused to metal crowns have been developed over more than 50 years with great attention being paid to the preparation of the interface prior to building up of the porcelain layer as well as the reactions that enhance adhesion of the porcelain to the underlying metallic substrate [14,15]. Metal oxides in alloys develop a chemical bond with the porcelain [16]. Mechanical bonding produced by sandblasting with aluminium oxide creates a keying effect, which provides a good retention of the porcelain. In addition the Coefficient of Thermal Expansion (CTE) mismatch between the veneering porcelain and Y-TZP must be small so as not to jeopardise the interface bonding by generation of high residual stresses [17].

The aim of this paper is to use scanning electron microscopy (SEM) and HF etching to evaluate the interface between veneering porcelain and Y-TZP prepared using different dental technology build-up procedures. It is hypothesized that the micro-structural changes of the Y-TZP grains observed at the interface are associated with moisture induced tetragonal to monoclinic zirconia.

### Materials and methods

In this study yttria partially stabilized tetragonal zirconia polycrystalline ceramic (Y-TZP, VITA In-Ceram® YZ, VITA Zahnfabrik, Germany) is used as a framework material. This material was prepared by sintering blocks, suitable for CAD/CAM machines Cerec® and InLab® (Sirona, Germany), at a temperature of 1530 °C for 2 h. For the observation of the interface bonding system, blocks with the dimensions of 10 mm × 10 mm × 1 mm were used. The observations reported have been repeated on at least 10 occasions and for this study representative illustrations are provided. As veneering porcelain, VITA VM® 9 (color shade 2M2), prepared in a variety of methods was built up on the zirconia surface in the manner listed in Table 1.

To observe only the initial bonding reaction between the two different materials no further firing process was conducted and no other porcelain layer was applied. The liquid application medium for the porcelain was systematically varied from complete absence in sample 2, the standard proprietary wetting liquid (VITA VM Modelling Liquid, VITA-Zahnfabrik, Germany) for samples 3-6, distilled water for sample 7 and ethyl alcohol for sample 8. The mixing with alcohol was for three reasons; one is that alcohol is a part of some modelling liquids used to assist porcelain build-up, secondly to also identify whether another humid atmosphere can react with zirconia and thirdly the alcohol evaporates very easily compared to modelling liquid and water. The furnace used during this study was a VITA Vacumat 4000T (VITA Zahnfabrik, Germany).

To enable an expanded view of the interface, taper sections at approximately 5° to the interface of all samples were cut

### Table 1 – Preparation methods of the Y-TZP frameworks.

<table>
<thead>
<tr>
<th>No.</th>
<th>Liquid medium</th>
<th>Porcelain</th>
<th>Firing process</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No</td>
<td>No</td>
<td>Wash-firing (950 °C)</td>
</tr>
<tr>
<td>2</td>
<td>No</td>
<td>VM9</td>
<td>Wash-firing (950 °C)</td>
</tr>
<tr>
<td>3</td>
<td>VITA VM-liquid</td>
<td>VM9</td>
<td>Wash-firing (950 °C)</td>
</tr>
<tr>
<td>4</td>
<td>VITA VM-liquid</td>
<td>VM9</td>
<td>Wash-firing (950 °C)</td>
</tr>
<tr>
<td>5</td>
<td>VITA VM-liquid</td>
<td>VM9</td>
<td>Wash-firing thicker layer (950 °C)</td>
</tr>
<tr>
<td>6</td>
<td>VITA VM-liquid</td>
<td>No</td>
<td>Wash-firing (950 °C)</td>
</tr>
<tr>
<td>7</td>
<td>Distilled water</td>
<td>VM9</td>
<td>Wash-firing (950 °C)</td>
</tr>
<tr>
<td>8</td>
<td>Alcohol</td>
<td>VM9</td>
<td>Wash-firing (950 °C)</td>
</tr>
</tbody>
</table>
Fig. 1 – Sample No. 1: pure Y-TZP refired at 950 °C after the recommended sintering process. Note the very fine irregular grain structure of the sputtered gold coating.

with a water-cooled diamond saw (600 μm Struers, Germany) and polished with diamond paste (3 μm VITA Zahnfabrik, Germany). In all instances the narrow porcelain-Y-TZP interface sections were etched using 5% hydrofluoric acid (VITA ETCH Gel) for 20 s in order to reveal the interface region in detail. The cross-sections of the samples were observed using SEM (LEO 438 VPi Carl Zeiss SMT and LEO 1530 Gemini, field emission microscope).

3. Results

Observations of the initial grain structure of the sintered Y-TZP prior to building up of the porcelain layer are shown in Fig. 1 after firing under conditions associated with the wash-dentin at 950 °C procedure. The resultant grain size as determined using the linear intercept technique after sintering of this material was 540 ± 240 nm. On such a sintered surface the veneering porcelain was fired for samples 2–8 as listed in Table 1. The pure Y-TZP (sample 1) does not show any influence of the 20 s exposure to the HF gel. Additionally in Fig. 1 the grain structure of the sputtered thin (approximately 5 μm thick) gold coating deposited prior to SEM observation may be detected. This appeared as approximately 50 nm grains with random grain structure. Such coating structure was present on every surface observed because of the very high resolution of the SEM system used.

The taper sections cut at approximately 5° to monitor the interface of a veneered sample at a higher resolution showed the zirconia slightly covered by the veneering porcelain after HF etching and a typical example is shown in Fig. 2. The structure of the grains of the framework material in some instances, following the different sample preparation procedures as listed in Table 1, was obviously affected during the veneering process. Also in all of the SEM figures the fine irregular grain structure of the sputtered gold coating as in Fig. 1 is detected.

Twenty seconds exposure to the HF gel at the polished taper section specimen revealed the grain structure of the Y-TZP grains below the porcelain layer as shown in Fig. 2. On the left hand side of the image the remnant veneering porcelain, still in contact with the YZ material, is evident.

A typical high-resolution observation of the HF etched tapered interface is shown in Fig. 3. The veneering porcelain has been completely removed by the HF gel and the underlying grains of the Y-TZP may be seen. The surface shown in Fig. 3 was that for the porcelain powder without any liquid application medium, specimen number 2. The zirconia grains in this image are very similar to those shown for the Y-TZP material wash fired without any veneering porcelain (Fig. 1).

The etched interface and associated Y-TZP grains for sample number 3 (wash dentin fired at 900 °C with VM-Liquid) are shown in Fig. 4. The grain structure of the zirconia was unaltered but there were a few larger more linear crystallographic features on the surface of the Y-TZP grains than observed for 950 °C fired surfaces in the absence of veneering material.

Fig. 2 – SEM observation of the HF etched polished taper section of the interface region. The grains of the Y-TZP below the surface of the veneering porcelain are visible in the region adjacent to the interface.

Fig. 3 – Sample No. 2: image of etched surface showing the Y-TZP interface following removal of the veneering porcelain after the firing of veneering powder particles without a liquid onto the Y-TZP at 950 °C.
Observations of the Y-TZP grains with the same veneering porcelain layer thickness and modelling liquid but fired at 950 °C (specimen 4) are shown in Fig. 5. The surface reveals crystallographic faceting of the YZ grains more extensively than specimen 3. These faceting features are present on nearly all grains. These features are shaper and clearly linear unlike the fine grain structure of the sputtered gold coating as revealed in Fig. 1 with sample number 1.

Fig. 6 reveals a more pronounced faceting of the zirconia grains below the thicker layer of wash-dentin (specimen 5) compared to sample number 4, also fired at 950 °C. In this image the sharp faceting of the grains along with the fine grain structure of the gold coating is readily observable.

Also specimen 6, VM-liquid without any veneering porcelain powder, indicated that even in this case some faceting of the Y-TZP grains was observed. At some grain boundaries the grain structure has started to change. By using the wash-dentin firing cycle with the powder mixed with the same amount of distilled water (specimen 7), as with the modelling liquid there were again the same features observed. Sample 8, prepared with alcohol instead of modelling liquid or distilled water, also showed the same noticeable features on the surface of the zirconia grains as with all other used liquids in this study. All the above observations were found to be very repeatable in that all surfaces prepared in the same manner showed near identical features to those presented above.

4. Discussion

The SEM observations presented above clearly indicate a number of features that develop on the Y-TZP grains at the zirconia–porcelain interface. The use of only the porcelain powder without any liquid resulted in no obvious faceting of the zirconia grains, indicating that the powder itself cannot be the reason for this development of the Y-TZP grains. In contrast, the changes observed using a liquid medium with the same porcelain powder clearly show a visible effect. This noticeable change does not appear to depend on the type of moisture medium used although the intensity of the faceting does. Distilled water, alcohol and the corresponding modelling liquid together with porcelain powder had a similar effect on the zirconia grains although the intensity appeared to increase with aqueous based solutions. The percentage of powder and liquid used during all tests was the standard recommended mixtures for dental technicians to build porcelain-veneered restorations, for fusing to metal and to zirconia.

There exists also an influence of the amount of moisture present in the veneering porcelain, as it did appear to have an influence on the extent of grain faceting. The Y-TZP grains beneath a thicker coating of porcelain (sample number 5, Fig. 6) had a greater degree of faceting. It is also observed that the complete grain structure on the surface is more severely faceted and not just with some of the grains as for the thinner wash coating. The implications of these observations are that more moisture and higher final heating temperature acceler-
ates the observed faceting of the Y-TZP grains at the interface to the veneering porcelain.

Another clear outcome is that of increasing firing temperature. Comparing the results in Figs. 3 and 4 for firing of exactly the same porcelain application liquid coating at 900 °C versus 950 °C, shows the more severe faceting at the higher temperature fired porcelain. From the observations in Fig. 1 it is clear that the 950 °C firing temperature itself does not affect the surface crystal structure of the zirconia grains. In addition the firing of dry veneering powder did not lead to the Y-TZP grains at the interface developing a faceted nature. These observations point to the clear role of moisture leading to the faceting behavior of the interface Y-TZP grains. This behavior is in agreement with the well-documented phenomenon of degradation of Y-TZP in the presence of moisture [18].

The present results of the faceting of the Y-TZP grains are very similar to the initial stages of moisture induced tetragonal to monoclinic phase transformation observed for these materials using atomic force and optical microscopy by Chevalier et al. [5]. The AFM observations presented in Chevalier’s recent review paper are almost identical with the high-resolution SEM images seen in many of the figures above. At the onset of such surface features the volume fraction of transformation is very small and only within the very surface layer of the individual grains exposed to moisture. In addition Chevalier et al. [5] were unable to detect the presence of monoclinic phase using X-ray diffraction as the layer thickness and amount of tetragonal transformed to the monoclinic phase was very limited. Indeed during this first part of the study it was also virtually impossible to detect the presence of monoclinic zirconia using X-ray diffraction of such surfaces as those shown above. This behaviour was also seen by Chevalier et al [5] as the depth penetrated by X-rays for zirconia is typically 10 mms whereas the initial surface layer transformed is only the outer sub micron region which does not contribute significantly to the overall diffracted pattern of the X-ray beam. It is also not very precise for monoclinic contents lower than 5%, making it unsuitable for monitoring the initiation of the transformation. It is however possible to improve the quality of the measurement at short aging times by using XRD at grazing incidence angles [1–5 °] [20]; as the effective penetration depth of X-rays is even lower [5]. There are relatively few published reports on the application of grazing angle XRD to the characterization of LITD, although it appears to be a very promising technique [19].

What is the cause for such a reaction occurring on the surface of the Y-TZP grains? According to Schubert et al. [20] the diffusion of water radicals into the Y-TZP crystal grains leads to a lattice contraction, which results in the formation of tensile stresses in the surface grains that can destabilize the tetragonal phase and the martensitic transformation to the monoclinic phase will than proceed. This process is also influenced by the size of the tetragonal grains and their composition. The higher the initial firing temperature of the Y-TZP the coarser the resultant grains with cubic grains growing faster than tetragonal grains. In addition the smaller tetragonal grains surrounding the larger cubic grains will have a lower yttria stabilising content as may be deduced from the yttria–zirconia phase diagram [18].

Another feature that contributes to the destabilisation of the tetragonal grains is the porosity of the Y-TZP with fully dense structures showing less propensity for transformation than slightly porous materials with equivalent grain sizes. In their studies Chevalier et al. claim that the moisture induced tetragonal to monoclinic transformation is a classic Avrami–Johnson nucleation and growth reaction [5]. It starts mostly at grain corners, where residual tensile stresses are largest and that one given grain does not transform all at once but progressively due to water attack. That is, the transformation of the surface of Y-TZP takes place by an apparent nucleation and growth mechanism, i.e. once a grain is transformed, the extension of the transformation occurs not only at random sites on the surface but also at the neighboring grains because of additional localized stress concentrations [5].

The implications of this study are that there are two distinct parts of the process that results in the observed faceting of the Y-TZP grains at the interface with the porcelain. During initial preparation water is incorporated in the veneering build-up procedure. Upon preheating the moist veneering powder on the Y-TZP the temperature rapidly exceeds 100 °C and the moisture is converted to steam that with time escapes from the heated veneering powder and supporting Y-TZP framework. At the temperatures between 100 °C and 250 °C the rate of tetragonal to monoclinic transformation in a damp environment is most rapid [5] and this is the regime that the Y-TZP will be experiencing during the evaporation of the moisture within the veneering powder. Once the monoclinic phase is formed at the surface it will persist in some parts to temperatures in excess of 1000 °C [1]. The absence of creep in Y-TZP materials till much higher temperatures means that there will remain persistent residual stresses at the boundaries between monoclinic and tetragonal portions of the same grain. At elevated temperatures the veneering porcelain will become almost fluidic and some degree of dissolution of the zirconia grains will occur in the feldspathic glass. This reaction is anticipated to be enhanced by the presence of localized regions where high stresses persist, such as grain boundaries and at the tetragonal to monoclinic boundary interfaces within individual grains of the original Y-TZP [21].

Etching with HF gel (20 s) most rapidly dissolves the glass phase and areas where the glass has preferentially dissolved the Y-TZP grains such as the grain boundaries and tetragonal to monoclinic interfaces as mentioned above. Thus for the higher fired veneered materials (950 °C versus 900 °C) with the same veneering moisture content, as the pre-heating process was identical, then the moisture exposure of the Y-TZP interface grains would have been identical. That is, a similar extent of tetragonal to monoclinic transformation would have occurred. However upon further heating to the final maximal temperature one would expect greater dissolution of the zirconia grains by the porcelain at the higher firing temperature. This would enable more dissolution of the stressed tetragonal to monoclinic interfaces and grain boundaries, which upon subsequent HF etching would result in deeper faceting of the Y-TZP grains as seen in Fig. 5 for specimen 5 heated to 950 °C versus Fig. 4 (specimen 4) heated to only 900 °C.

In the present study the chemical dissolution by the veneering porcelain of the Y-TZP would be much higher at 950 °C than at 900 °C. The powder itself has not affected the Y-TZP as shown with sample number 2 (Fig. 3). Only with the presence of liquid in the veneering porcelain to initiate the tetragonal to
monoclinic transformation will this stress enhanced glass dissolution accelerate at this high temperature (950 °C) and will also attack the grain boundaries.

The extent to which the presence of moisture induced tetragonal to monoclinic transformation influences debonding of the veneering porcelain in clinical situations is unknown. Limited interfacial fracture toughness tests using the Charalambides test [1] of freshly bonded specimens indicate that crack extension occurred through the porcelain rather than at the porcelain/Y-TZP interface. Other shear bond strength tests of porcelain–Y-TZP interfaces observed fracture also within the porcelain [12] in contrast to porcelain fused to metal where cracking occurs directly at the interface layer on top of the framework surface [17]. There have been reports of a higher incidence of failure of zirconia based compared with porcelain fused to metal crowns [8,9], however the basis of this increased incidence of failure in the zirconia based materials is not understood. Further observations on the role of the surface preparation of the zirconia and prior to veneer to ascertain whether sandblasting or grading of the Y-TZP surface further influences the transformation effects at the interface are required. However, due to the metastability of tetragonal zirconia, stress-generating surface treatments such as grading or sandblasting are liable to trigger the \( \text{t} \rightarrow \text{m} \) transformation with the associated volume increase leading to the formation of surface compressive stresses, thereby increasing the flexural strength but decreasing the resistance to aging [20]. More detailed cross-sectional transmission electron microscopy and possibly AFM observations are required to completely prove the proposed hypothesis and substantiate the plausible interpretation provided above.

5. Conclusion

Veneering porcelain appears to wet and bond well to zirconia frameworks. However upon HF etching the interface it is observed that moisture present in the veneering powder during the preparation of these porcelain to Y-TZP structures, which were identical with all-ceramic crown firing procedures, generates grain faceting at the surface of the zirconia grains beneath the veneering porcelain. The extent of this surface faceting is dependent upon the moisture content of the porcelain powder and the firing temperature. The nature of the surface faceting of the zirconia grains is almost identical with the observations of the moisture induced tetragonal to a monoclinic structure observed by Chevalier et al. [5] using AFM.

It is argued that the observed increased faceting seen after high veneering porcelain firing temperatures are a consequence of the glass induced dissolution at sites of higher residual stresses at the tetragonal/monoclinic interfaces. The long-term consequence of the presence of such transformed grains at the porcelain-Y-TZP interface needs to be further investigated.

Acknowledgement

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REFERENCES