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TITLE OF PAPER: A Comparative Transmission Electron Microscopy, Electron Diffraction Spectroscopy and Spatially Resolved Micropillar Compression Study of the Yttria Partially Stabilised Zirconia – Porcelain Interface in Dental Prosthesis

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TITLE PAGE

A Comparative Transmission Electron Microscopy, Electron Diffraction Spectroscopy and Spatially Resolved Micropillar Compression Study of the Yttria Partially Stabilised Zirconia – Porcelain Interface in Dental Prosthesis

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Abstract

Recent studies into the origins of failure of yttria partially stabilised zirconia - porcelain veneered prosthesis have revealed the importance of micro-to-nano scale characterisation of this interface zone. Current understanding suggests that the heat treatment, residual stresses and varying microstructure at this location may contribute to near-interface porcelain chipping. In this study the chemical, microstructural and mechanical property variation across the interfacial zone has been characterised at two differing length scales and using three independent techniques; energy dispersive X-ray spectroscopy, transmission electron microscopy and micropillar compression.

Energy dispersive X-ray spectroscopy mapping of the near-interface region revealed, for the first time, that the diffusional lengths of twelve principal elements are limited to within 2 – 6 μm of the interface. This study also revealed that 0.2 – 2 μm diameter zirconia grains had become detached from the bulk and were embedded in the near-interface porcelain.

Transmission electron microscopy analysis demonstrated the presence of nanoscale spherical features, indicative of tensile creep induced voiding, within the first 0.4 – 1.5 μm from the interface. Within zirconia, variations in grain size and atomistic order were also observed within the 3 μm closest to the interface.

Micropillar compression was performed over a 100 μm range on either side of the interface at the spatial resolution of 5 μm . This revealed an increase in zirconia and porcelain loading modulus at close proximities ($< 5 \mu\text{m}$) to the interface and a decrease in zirconia modulus at distances between 6 – 41 μm from this location

The combination of the three experimental techniques has revealed intricate details of the microstructural, chemical and consequently mechanical heterogeneities in the YPSZ – porcelain interface, and demonstrated that the length scales typically associated with this behaviour are approximately $\pm 5 \mu\text{m}$.

Keywords

- Ytria partially stabilized zirconia – porcelain interface
- Scanning electron microscopy
- Transmission electron microscopy
- Energy dispersive X-ray spectroscopy
- Micropillar compression / Microcompression

1. Introduction

Yttria (Y_2O_3) Partially Stabilised Zirconia (ZrO_2) (YPSZ) is a ceramic material which has become widely used in the manufacture of dental prostheses due to its high compressive strength, appealing aesthetics, biocompatibility and toughness [1]. In dental prosthetics, zirconia frameworks are veneered with porcelain that is applied as a slurry and then “baked”. This process delivers excellent surface aesthetics, and reduces the surface hardness of the artificial tooth thereby reducing wear on the enamel of opposing natural teeth [2, 3].

Despite the benefits of using porcelain as an outer coating material, clinical trials have identified the primary failure mode associated with this veneering process – near interface chipping of the porcelain [4]. The origin of chipping is speculated to be associated with the residual stresses induced in both YPSZ and porcelain at the interface during manufacture [5-7].

A large number of studies have been performed on the YPSZ-porcelain interface region in order to quantify the bonding / adhesion strength [8-11], the fracture resistance [12, 13] and the overall statistics of structural integrity and reliability [14] of this region. The motivation for these studies has often been to optimise the prosthesis mechanical response as a function of processing conditions (sintering temperature, etc.), hence they have primarily focused on the macro scale behaviour of dental prosthesis as a whole.

In contrast to these macro scale investigations, recent publications have highlighted the importance of performing high resolution (micro-to-nano scale) chemical, structural and mechanical analysis in order to improve understanding of the origins of the failure occurring at the interface. Scanning Electron Microscopy (SEM) analysis of the interface zone has

YPSZ – Yttria Partially Stabilised Zirconia

SEM – Scanning Electron Microscopy

TEM - Transmission Electron Microscopy

EDS – Energy Dispersive X-ray Spectroscopy

SE – Secondary Electron

BSE – Back Scattered Electron

FIB – Focused Ion Beam

MBLEM – Multi-Beam Laboratory for Engineering Microscopy

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revealed the importance of crystal structure and orientation on such failures [15, 16], high resolution tomography studies have highlighted the presence of cracks in the interface zone [17, 18] and micro tensile bonding studies have demonstrated the importance of length scale considerations in this problem [19].

The current study aims to investigate the local micron-scale changes in chemical, microstructural and mechanical properties across the YPSZ-porcelain interface of a completed dental prosthesis using Transmission Electron Microscopy (TEM), Energy Dispersive X-ray Spectroscopy (EDS) and microcompression testing. These studies have focused on two differing length scales: $\pm 5 \mu\text{m}$ from the interface (TEM and EDS analysis) and $\pm 100 \mu\text{m}$ from the interface (micropillar compression and EDS analysis).

One TEM study focusing on the impact of different YPSZ surface treatments on the YPSZ – porcelain interface in disc samples has previously been performed by Grigore et. al [20]. This study revealed distinct differences in the near-interface YPSZ microstructure of these specially prepared samples and therefore that YPSZ surface preparation is highly influential in the YPSZ-porcelain bonding characteristics. In contrast to this study, in the present TEM analysis our focus is instead placed on mapping both the YPSZ and porcelain near-interface regions. Importantly, the study was carried out over much larger distances than previously considered, and on a sample representative of clinically relevant copings.

EDS analysis at the YPSZ – porcelain interface has also previously been performed in disc samples to determine the impact of different thermal processing routes on zirconium and silicon concentrations within the first few microns of the interface [21]. In the present analysis, we consider the distribution of all elements detected by EDS, and also compare the results obtained at the two differing length scales ($\pm 5 \mu\text{m}$ and $\pm 100 \mu\text{m}$) examined in this study.

In terms of microscale mechanical characterization, nanoindentation has previously been performed to determine the bulk mechanical properties of both porcelain [22] and YPSZ [23,

24]. A number of previous micro-compression studies on various forms of zirconia have also been reported [25, 26], which revealed clearly the length scale dependence of the behaviour of this material. As no such analysis has been performed on dental porcelain or the YPSZ – porcelain interface, using this technique brings new insights into the yield strength and modulus behaviour at microscale resolution, which is known to be critical in this region.

2. Experimental

2.1. Sample Preparation

The focus of this study was an incisal YPSZ – porcelain dental prosthesis which was manufactured by dental technicians for the ‘Specialists Dental Group’, Singapore. This tooth was selected from a series of prosthesis manufactured for patients, and was therefore as representative as possible of the samples in which porcelain chipping had previously been observed [4].

In the manufacture of the prosthesis, a YPSZ coping was machined from a Wieland Dental Zenotec Zr Bridge green body using a computer-aided manufacturing process. Following the implementation of the YPSZ recommended sintering regime by the manufacturer, IPS e.max[®] porcelain (by Ivoclar Vivadent) was veneered onto the surface [27]. This process involved initially applying viscous liquid porcelain to the YPSZ, before further sintering. Multiple (mm scale) layers of porcelain of differing composition were applied to produce the desired combination of bonding strength and toughness in addition to realistic aesthetic appearance.

To facilitate access to the YPSZ – porcelain interface, a 2 mm thick cross section of the prosthesis was cut using a Buehler Isomet Diamond Saw after mounting in a polymer resin. A very slow cutting speed (25 rpm on a 127 mm diameter blade) was used to reduce the impact of cutting on the sample microstructure and residual stresses. The samples were then metallographically polished using progressive grinding up to 4000 grade grit followed by diamond polishing down to 0.1 µm diamond paste, in order to reduce further the impact of the

residual stresses induced by cutting. A careful ultrasonic cleaning process was then applied to remove any remaining surface residue or debris. The polished prosthesis slice was mounted on a SEM stub using silver paint in order to reduce the effects of charging during SEM imaging and Focused Ion Beam (FIB) machining. The Secondary Electron (SE) SEM image of the sectioned and polished sample is shown in Figure 1. The interface region selected for further examination was chosen to be the location at which the interface was most straight in order to reduce the effects of interface curvature on the analysis.

Lamellae for TEM observation were fabricated using the software module ‘AutoSlicer’ [28] and the Tescan Lyra-3 XM FIB SEM at the Multi-Beam Laboratory for Engineering Microscopy (MBLEM), Oxford, UK. A $20 \times 5 \mu\text{m}^2$ area lamella containing the YPSZ-porcelain interface with an average thickness in the range of 100 – 150 nm, was milled out for TEM analysis. A very low magnitude polishing current (100 pA) was used to control carefully the sample thickness while minimising the impact of gallium ion implantation.

Arrays of micropillars were FIB-milled across the YPSZ-porcelain interface using a two-step milling process: coarse milling using 2.5 nA milling current followed by fine milling at 0.75 nA. The average pillar diameter and height were $\sim 1.9 \mu\text{m}$ and $\sim 5 \mu\text{m}$ respectively, and an aspect ratio of ~ 2.5 (Figure 2) was selected to reduce the impact of pillar buckling during compression, as successfully validated in previous studies [29, 30]. The pillars were separated from each other by $\sim 10 \mu\text{m}$ and two arrays of 10 pillars each, offset by $\sim 7 \mu\text{m}$, were milled in order to attain the overall spatial resolution of $\sim 5 \mu\text{m}$ in terms of the distance from the interface, as shown in Figure 3. The relative variation in mechanical properties parallel to the interface is believed to be such that an offset of this size should not significantly influence the properties calculated. This is further demonstrated by the consistent trends observed between these two profiles as shown in Section 3.2.

2.2. Chemical, Structural and Mechanical Measurements

The JEM-2100F Transmission Electron Microscope located at the Research Complex at Harwell, Rutherford Appleton Laboratory, UK was used to image the resulting lamella using bright field TEM imaging. Imaging was performed by capturing multiple micrographs of size 2056×2056 pixels ($863.5 \times 863.5 \text{ nm}^2$) which were stitched together to obtain a larger overview of the area of interest as shown in Figures 4 and 5.

EDS was performed across the YPSZ-porcelain interface using an Oxford Instruments® X-max silicon drift detector mounted on the chamber of FIB-SEM (Tescan Lyra-3 XM) at MBLEM, Oxford, UK. Calibration of the EDS software AZtecEnergy, was performed using Au, Si and Cu EDS calibration standards immediately prior to the EDS mapping. The optimisation of the beam intensity and dwell time were performed in order to minimise the detector ‘dead time’ and to reduce noise at the 30 kV accelerating voltage selected, with the final values being selected as 12 a. u. and 850 ms per pixel, respectively. Mapping at two different magnifications (with image sizes of 2048×2048 pixels) was performed across this region, the first corresponded to a $200 \times 200 \text{ }\mu\text{m}^2$ viewfield (nominal pixel size 97 nm) and the second to a $10 \times 10 \text{ }\mu\text{m}^2$ viewfield (with a nominal pixel size of 2.5 nm) in order to examine elemental distributions at these two length scales.

Micro-compression of the pillars was performed using a $5 \text{ }\mu\text{m}$ diameter diamond flat punch in an Alemnis SEM Indenter [31] which was mounted inside a Zeiss SEM DSM96 (EMPA, Thun). This in-situ (in-SEM) testing approach enabled precise alignment of the flat punch to the pillar centre and also provided live imaging of pillar deformation during the compression tests.

In this study, micropillar diameter and height were calculated from SE SEM images of each pillar taken from directions normal to the surface and with stage tilt angle of 55° (with a corresponding tilt correction of 35°) as shown in Figure 2. A scaling factor equal to $\cos 55^\circ / \cos 35^\circ \sim 0.700$ was required to correct the vertical diameter of the ellipse fitted

in this tilted image (Figure 2 – marked as “Ea”) into a value representative of the diameter. Typically, the uncertainty in height and diameter measurements, calculated from multiple measurements, was less than 2%.

Based on the pillar height, the displacement rate was adjusted so as to attain loading and unloading strain rates of 0.005 s^{-1} for each pillar. The pillars were unloaded from the point at which the first significant load drop was observed, most likely due to crack initiation and brittle failure. The raw load-displacement data obtained from microcompression experiments was then converted to stress-strain data by taking pillar height and cross-sectional area (diameter) into consideration. In addition, compliance correction and elastic sink-in correction was applied while converting load-displacement data into stress-strain curves. The compliance of the system was measured by performing deep (100 mN) indents on fused silica with a Berkovich tip

3. Results and Discussion

3.1. Composition and Microstructure

Figure 4 shows a bright field TEM image of the interface between porcelain and YPSZ. The interfacial region exhibits a markedly different microstructure in comparison to the bulk. A band of spherical structures can be clearly observed in porcelain at a distance between $0.4 \mu\text{m}$ and $1.5 \mu\text{m}$ from the interface. These spheres have cross sizes in the range of $\sim 5 - 150 \text{ nm}$ and are present at the location at which tensile residual stress has previously been shown to be induced during manufacture [32]. The combination of relatively low stresses and the sintering temperatures (up to $750 \text{ }^{\circ}\text{C}$) applied to this interface region can induce creep in a broad range of porcelain materials [33-35] including dental porcelain compositions [36]. Tensile creep of porcelain has previously been shown to induce voiding in other silica-based ceramics [37] and could offer a likely origin of the spherical type particles observed in this region.

TEM imaging of simple voiding type behaviour typically results in brighter regions in the captured images [38]. On the other hand, the random arrangement of atoms in amorphous material is known to result in darker regions in TEM images [39]. The combination of these two effects, a void surrounded by amorphous region, has previously been shown to result in darker spherical type regions in ZnO/Zn [40] and Mg [41] nanocrystals. The appearance of these void type regions is very similar to the darker spherical type regions observed in this study and therefore, based on the residual stress and thermal history of the interface region, along with the known nano-voiding behaviour of this material [37], we suggest that similar amorphous shell type voiding may be present at the YPSZ-porcelain interface region.

On the YPSZ side, a band of small grains (ranging in size from $\sim 5 - 70$ nm) was observed in the first 200 nm of YPSZ closest to the interface (as shown in the insert in Figure 4). This band was found to be present along the entire length of the $\sim 5\mu\text{m}$ region interface section which was imaged using TEM. The grains in this region appear to be loosely bound in comparison to the bulk material and are much smaller than the nominal recommended grain size of YPSZ copings (220 – 900 nm) [42]. This suggests that the parameters affecting grain growth behaviour in this region are different to those of the bulk material, or may be associated with coping surface preparation prior to porcelain application (which is used to improve veneer adhesion).

Another composite TEM image of the first 6 μm of the near-interface YPSZ is shown in Figure 5. Following the 200 nm grain refined zone, a $\sim 1 - 2 \mu\text{m}$ high contrast region can be observed in YPSZ showing no clear facets or grain boundaries. One explanation may be the presence of amorphous zirconia which has previously been observed at the interface between two dissimilar materials [43]. However, the relatively large length scales over which this zone extends ($\sim 1 - 2 \mu\text{m}$) makes it unlikely that this is in fact the case.

An alternative and more likely explanation is that this $\sim 1 - 2 \mu\text{m}$ high contrast region YPSZ region contains a large number of twinning domains and stacking faults. Multiple

layers of twinned material can provide appearance of multi-directional facets and similar high contrast seen in Figure 5 has previously been observed at the interfaces of zirconia-based thermal barrier coatings [44, 45]. These microstructural changes are speculated to be the result of the residual stresses and the complex thermal histories present at such interfaces, and suggest that similar behavioural responses are induced at the YPSZ – porcelain interface. Further experimental analysis is needed to determine the exact origin of this high contrast region and to determine whether amorphous content or the presence of twins is the primary contributing factor. Following this high contrast zone, grains of size 550 – 770 nm are observed which are consistent with previous observations reported in literature [42].

Examination of the composite TEM images in Figures 4 and 5 clearly demonstrates that the local microstructure in both the porcelain and YPSZ layers 1 – 2 μm from the interface is different from the nominal bulk structures of amorphous porcelain and polycrystalline YPSZ. Recent studies have highlighted the effect of both thermal treatment and localised stresses on the grain size characteristics of YPSZ in veneered dental crowns [46]. These observations, in combination with the TEM results presented here, suggest that this grain size variation is localised to a micron-scale region at the interface. The result of this varying grain size across the interface region has previously been shown to impact fracture behaviour of interfaces between materials of differing mechanical behaviour [47] and therefore may partially explain the failures observed at this interface.

In the first lower magnification EDS map, twenty elements were identified as present in the examined region, and eight elements were found to be present in only trace amounts (< 0.1%): C, Mg, Fe, Ni, Rb, Sb, Ce and W. The EDS maps of the 4 elements showing greatest variation, Al, Si, K and Zr, are shown in Figure 6. SE and Back Scattered Electron (BSE) SEM images of the same region have been included to in order to facilitate comparison between the EDS results and the local microstructure. The BSE and SE images clearly show variations in contrast across the surface and careful examination of these regions demonstrates

that these particles are embedded in the surface. Further, comparison between the location of this electron contrast and the EDS analysis demonstrates that these regions are distinct in terms of concentration of Al, Si or K, compared to the surrounding area.

Initial examination of Figure 6 clearly demonstrate that element distribution within the YPSZ is more consistent than in porcelain. Correlations between the porcelain elemental maps reveal quartz (high Si, low Al and K content) and fluorapatite (high Ca, F and P, reduced Si) regions of size $\sim 5 - 80 \mu\text{m}$ as expected in dental porcelains of this type [48]. In contrast to the elemental variation within porcelain, the EDS maps of YPSZ show a high level of consistency across the entire imaged region.

Figure 7 shows the variation in average elemental composition across the interface calculated from the low resolution EDS maps in which a large change in elemental composition at the interface region can clearly be observed. The elemental diffusion zone obtained from this low resolution imaging appears to be of the order of $\pm \sim 5 \mu\text{m}$. However, since the surface roughness is $\pm 2 \mu\text{m}$, the resulting convolution of interface roughness and diffusion makes it difficult to comment on the exact depth to which this behaviour extends.

To overcome this, a second EDS map at a higher magnification was obtained (Figure 8) from a region embedded within the low resolution EDS region previously analysed, as shown in the BSE image in Figure 6. Eighteen elements were recorded in this analysis, in which trace amounts ($< 0.2\%$) of six elements were identified: Mg, Fe, Ni, Sb, Ce and W. Figure 8 shows a montage image of the Al, Si, Zr and K, the elements which most clearly show variation in this region, along with the SE and BSE SEM images of the region investigated.

Several grains of differing electron contrast (sized in the range $\sim 0.2 - 2 \mu\text{m}$) can clearly be seen embedded in the near-interface porcelain. Examination of the corresponding regions in the EDS maps reveals that these locations have lower levels of Si and K than the neighbouring porcelain, but contain high amounts of Al or Zr. Although the Al rich grain is typical of the grain like structure of porcelain, the Zr rich grain suggests that YPSZ particles

have detached from the YSPZ surface and became embedded in the porcelain during manufacture. The loose bonding of near interface YPSZ grains highlighted in the TEM study may be a demonstration of a similar effect to that observed here, however the grain sizes observed in EDS are approximately a factor of 1,000 times larger than those observed in TEM. Despite this size difference, previous studies also have highlighted similar 1 – 5 μm diameter Zr rich grains embedded in the near interface porcelain of similar dental coping systems [49].

In order to remove the influence of the embedded YPSZ grains, the 1D elemental distribution plots (in weight %, Figure 9) were obtained from a reduced region of the higher magnification EDS map as shown in the BSE image in Figure 8. The average roughness of the interface was determined from the higher magnification SEM imaging and was found to have a maximum amplitude of 330 nm . Although this variation is much smaller than the $\pm\sim 5\ \mu\text{m}$ observed over the 200 μm region, this will act to blur the effective diffusional distances by a length scale approximately equal to this distance. Careful consideration of the size of the interaction volume is also necessary in order to determine the nominal area from which X-rays will be emitted at each location. Monte Carlo simulations of these processes have previously been used to study the size of this behaviour [50] and empirical relationships for the average distance between the entrance point and its final resting place (R_{av}) have been determined. Based on the manufacturer's published elemental compositions [51, 52], these distances have been determined as 1.5 μm and 1.2 μm for porcelain and YPSZ respectively. The teardrop shape interaction volume associated with EDS ensures that most emission is emitted from a region parallel with the incident beam and a distance of approximately R_{av} into the material. Further simulations, beyond the scope of the current paper, would be necessary to precisely quantify the cross sectional area of the interaction volume. A critical examination of the EDS mapping performed, particularly of the Al rich grain, reveals that the cross-sectional resolution of technique is far greater than R_{av} , however here we propose to

use this value as an upper bound. This will result in apparent elemental diffusion over a maximum distance approximately equal to R_{av} and therefore this will act as a limit to the effective diffusional limits which can be determined by EDS.

The average diffusional zones of $\pm \sim 3 \mu\text{m}$ observed in this figure are smaller than the $\pm \sim 5 \mu\text{m}$ calculated from low magnification analysis and clearly demonstrate that diffusion has occurred between YPSZ and porcelain at length scales similar to the variations observed in the TEM results. Si and Zr appear to show the largest diffusional distances (6 – 7 μm) and the greatest changes in composition across the interface is present in Si (~ 400 fold reduction). Characteristic slope changes can be seen at the 0.5 μm position in Al and Na, suggesting that this location may be indicative of an elemental barrier after which diffusion was greatly reduced. This point can therefore be considered as the nominal elemental interface position. Previous studies have found diffusion zones of approximately similar sizes (8 – 10 μm) in fractured tensile specimens of the YPSZ – porcelain interface [53] suggesting that diffusion is typically limited to these very small length scales in this system.

At the nominal 0.5 μm position, a peak in the elemental weight % of O can also be seen. Previous studies have highlighted this oxygen-rich interface band at the YPSZ – porcelain interface [54], although the exact origin of this behaviour is unknown. Potential explanations for the increased oxygen content include variations in stoichiometry in the near-interface oxides, or this may alternatively be indicative of oxygen trapped in the voids during the manufacturing process. The positioning of this zone in relation to the “knees” observed in the elemental weight % distributions of the Al and Na oxides does however suggest that these two responses are directly related.

In contrast to the O weight % peak at the interface, a plateau in concentration can be observed in Y at its transition, which again may be indicative of a limiting diffusional distance characteristic of the interface region. Changes in YPSZ doping composition are known to impact a whole range of properties, from mechanical behaviour [55] to grain size

[56] and fracture toughness [57]. The interplay between these effects requires further detailed study and simulation in order to understand fully the impact this effect has on the system.

A final check on the reliability of our EDS results, analysis was performed to compare the average compositions of the YPSZ and porcelain regions with those provided by their respective manufacturers. The areas over which the averaging was performed were selected as 20 – 100 μm from the interface for the low magnification imaging and 2 – 5 μm for the higher magnification imaging (in the region highlighted in the BSE image in Figure. 8) as a compromise between averaging over a suitable number of points and minimising the impact of gradients in the near-interface region.

In the case of YPSZ, the oxide weight percent tolerances published for Zenotec Zr Bridge [51] were used to calculate the weight % bounds for the five main elements present within this material; Al, Hf, O, Y and Zr. These manufacturer's tolerances, along with the results of both low and high magnification elemental composition averaging are shown in Figure 10. It can be seen that the averages are representative of the composition found in Zenotec Zr Bridge for all elements except for the high magnification Al and O.

A similar elemental weight % composition calculation was performed for the porcelain using the oxide content tolerances provided Ivoclar Vivadent [58]. The bounds calculated for the nine principal elements (Al, Ca, F, K, Na, O, P, Si and Zn) were then plotted with the results of the high and low magnification averaging, as shown in Figure 11.

Both materials generally showed good correlation, with 21 out of 28 elemental weight % values being found to be within tolerance. The issue of representative averaging in terms of porcelain regional variation as well as the impact of the interface diffusion mean that some variation is expected. Added to this effect, the known decreased sensitivity of EDS to lighter molar mass elements [59] may explain why outliers are only present in elements with molar masses less than or equal to that of Al.

3.2. Micromechanical Measurements

Microcompression offers the possibility of uniaxial compression testing at small length scales [60] with high spatial resolution. It has been successfully used to study deformation behaviour of wide range of materials including metals [61], ceramics [62], polymers [63], glasses [64] and biological materials [65-67]. Typical microcompression stress-strain responses for porcelain and YPSZ micropillars are shown in Figure 12. Both of these materials exhibit a drop in stress beyond elastic limit due to crack nucleation and propagation. The average loading modulus, calculated from the elastic linear stress-strain regime, of YPSZ (~ 214 GPa) was higher than that of porcelain (~ 72 GPa). Although the accuracy of the extracted loading modulus from microcompression data depends on a more rigorous data analysis with additional corrections applied for elastic sink-in and geometric factors like pillar taper and root radius, [68] not considered here, these results are in reasonable agreement with those provided by the manufacturer for YPSZ (210 GPa) [51] and values reported in the literature for e.max[®] Ceram (60 GPa [69] and 64 GPa [70]). Post compression imaging of the deformed pillars showed evidence of brittle fracture and therefore the unloading modulus was not analysed.

A plot of loading modulus and 2% yield strength of the pillars as a function of distance from the YPSZ-porcelain interface for both Line 1 and 2 is shown in Figure 13. In the context of this study, the 2% yield strength has been defined as the intersection point between the stress-strain curve and a line subtended from 2% strain with a slope equal to the calculated loading modulus. Although this approach was consistently applied to the data set, the impact of random brittle failure was observed to influence this measure, particularly in the YPSZ region. The modulus and yield strength 95% confidence intervals were calculated based on the standard deviations of micropillar height and diameter measurements, along with the fit quality associated with each measure.

Typically the confidence intervals for the YPSZ loading modulus are larger than for the porcelain measurements. This can be explained on the basis of high elastic anisotropy [55] and reduced numbers of grains (~ 47 grains, on average) interrogated in a YPSZ micropillar volume. A number of outliers were observed in the data set, most notably in the 2 % yield strength in porcelain at a distance of 49 μm from the interface and the loading modulus in YPSZ at a distance of 51 μm from the interface. The singular nature of these variations in an otherwise relatively consistent data set suggests that these are unrepresentative.

A critical examination of the trends in YPSZ loading modulus reveals that this value is approximately constant (within experimental scatter) at a value of 216 GPa for distances greater than 40 μm . Two distinct trends in the loading modulus are observed up until the interface: a decreasing trend from 40 μm to 10 μm (to a value of 193 GPa) followed by an increase in modulus within the 10 μm band closest to the interface (up to a maximum of 242 GPa). The limited diffusion zones (< 5 μm) highlighted by EDS analysis may explain the increase in modulus within the first 10 μm . However, this does not explain the modulus variation at distances greater than 10 μm . Despite this, the proximity to the YPSZ – porcelain interface suggests that this is a direct result of the interaction between these two materials; most likely as a direct result of grain size effects, thermal processing behaviour or the impact of residual stress [5].

A similar examination of porcelain loading modulus shows an approximately constant value of 70 GPa between 100 μm and 10 μm from the interface, and an increase in modulus up to 87 GPa within the 10 μm closest to the interface. This increase in modulus may be explained by the elemental inter-diffusion detected by EDS studies, and the associated impact on the mechanical properties [71].

The average value of the YPSZ 2 % yield strength in this study was found to be 4.5 GPa. To the best of the author's knowledge, the yield strength of YPSZ has not been reported in literature. However, the maximum compressive strength of this material (Zenotec Zr bridge)

has been reported to be 2.0 GPa by the manufacturer [72]. This difference between bulk and microscale behaviour suggests that length scale effects are present in YPSZ, as previously outlined in the literature [73]. The relatively low ductility of this ceramic ensures that this parameter is highly influenced by the statistical likelihood of brittle failure in the micropillar. For this reason, the yield strength values show relatively large levels of scatter and no clear trends in spatially resolved behaviour could be identified.

In contrast, the ductile behaviour associated with porcelain was found to result in more consistent 2 % yield strength values, with an average magnitude of 3.44 GPa. To the best of the authors' knowledge, this study is the first to perform micropillar testing on porcelain of any type. This being said, previous micropillar studies have been performed on amorphous silica, the primary constituent of porcelain, which showed a uniaxial compressive yield strength of 5.22 GPa [74].

In terms of macro-scale yield strength comparisons, no compressive testing data was available for IPS e.max[®] Ceram. However, macroscopic compression studies performed on similar powder-based dental porcelains have reported compressive strengths of 340 MPa [75]. Despite the lack of any evidence for microstructural features of this size (for example, grain size, etc.) this indicates different responses for the bulk and microcompression behaviour, which is most likely to be associated with the statistical likelihood of failure at these different length scales.

An increased yield strength value of 3.91 GPa was observed in the porcelain at a distance of 4 μm from the interface. This location is within the region of elemental diffusion previously observed in EDS and is likely to be associated with the mechanical response modification due to compositional change, as highlighted elsewhere [71].

4. Conclusions

In this study, three complimentary micro-scale experimental techniques were applied across the YPSZ – porcelain near-interface region of a cross section of a dental prosthesis.

High magnification imaging of this region was performed using bright field TEM. Elemental distribution analysis was quantified using EDS. Micropillar compression was used to quantify the micromechanical behaviour variation across the interface.

At distances greater than 40 μm from the interface YPSZ was found to be highly uniform and consistent with published values both in terms of elemental composition and mechanical behaviour. The grain sintered structure of porcelain ensures that slightly larger spatial variations were observed in the mechanical behaviour and elemental composition of this material, however this nominally uniform region was present at distances greater than 10 μm from the interface. This suggests that at distances greater than a few 10's of microns the 'bulk' parameters can be reliably used to describe YPSZ and porcelain in this system.

In the near interface YPSZ, the TEM analysis demonstrated clear variations in grain morphology within the first 3 μm of the interface. This length scale closely matches the limits on elemental diffusion of Si, K, Zn and Al and suggests that these two effects are likely to be directly related. This position also corresponds to a peak in loading modulus (242 GPa at 5 μm from the interface), which demonstrates that these compositional and microstructural changes have influenced the mechanical behaviour in this location.

At distances beyond this point minimal variations in composition or microstructure could be identified, however variations in loading modulus were observed up to 40 μm from the interface. This suggests that other factors such as residual stress or varying thermal history are likely to be influencing the mechanical behaviour of YPSZ over these larger length scales.

TEM imaging of the near interface porcelain demonstrates creep induced nano-scale voiding within the first few microns of the interface. In this region, EDS analysis has revealed elemental diffusion of Zn and Y along with the presence of YPSZ particles which have detached from the YPSZ surface and become embedded in the porcelain. The impact of these three effects on the mechanical behaviour of porcelain has been seen in the variations of loading modulus and yield strength in the two porcelain micropillars closest to the interface,

Overall, this study demonstrates that the microstructural, mechanical and elemental variations across the YPSZ – porcelain interface are primarily localised to within 5 μm closest to the interface. The complex interplay between diffusion, thermal treatment, grain growth kinetics, residual stress, creep behaviour and grain cohesion in this region presents a challenging prospect to optimise and characterise fully. However, in order to improve the understanding of the failure modes characteristic for this interface, and thereby ultimately to reduce the prosthesis failure rates, further investigation is required. This must initially take the form of improving the understanding of the YPSZ and porcelain near-interface characteristics, in order to facilitate the development of reliable simulations of this interfacial zone.

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List of Figure Captions

Figure 1. SE SEM image of prosthesis cross section mounted on an SEM stub using silver paint. The outer porcelain veneer, intermediate YPSZ coping and the inner remnants of the polymer mounting (showing large voiding regions) can be observed in this image. The location of experimental analysis is highlighted in this image.

Figure 2. SE SEM images of a completed porcelain micropillar at a distance of 33 μm from interface showing measurements recorded. a) Sample tilted at 55° with a tilt correction of 35° applied. b) Sample normal to the detector.

Figure 3. SE SEM image of milled micropillars showing location relative to the YPSZ – porcelain interface and offset between Line 1 and Line 2. The impact of charging can be seen by the appearance of shadowing on the porcelain micropillars.

Figure 4. Composite TEM image of the YPSZ – porcelain interface. Nanoscale spherical features can be observed in a band of the near interface porcelain (between 0.4 μm and 1.5 μm from the YPSZ – porcelain interface). A band of small YPSZ grains (ranging in size from $\sim 5 - 70$ nm) can also be observed in the first 200 nm from the interface, as shown in the insert.

Figure 5. Composite TEM image of the YPSZ – porcelain interface and neighbouring YPSZ grains. Within the first 200 nm from the interface a band of small YPSZ grains can be observed. This is followed by a $\sim 1 - 2$ μm high contrast zone showing no clear facets or grain boundaries. Grains of cross sectional area in the range $0.3 - 0.6$ μm^2 (representative of bulk characteristics) are observed at distances greater than 2 μm .

Figure 6. Montage of Si, Zr, Al and K elemental distributions within a 200×200 μm^2 region of the YPSZ – porcelain interface. High resolution SE and BSE SEM images of the same location is included in order to highlight the nominal roughness of the interface and to enable direct comparison with the EDS results. The location of the high resolution EDS map is also shown on the BSE image.

Figure 7. Logarithmic plot of average elemental weight % within the first 100 μm from the YPSZ – porcelain interface. Variations in elemental composition in the porcelain region show greater variation due to the presence of grains in this region. The impact of interface roughness is demonstrated by the gradual elemental transitions (of the scale $\pm\sim 5 \mu\text{m}$) in the near interface region. We note that the logarithmic scale used in this figure and reduced precision of EDS at low concentrations leads to unrepresentative large variations elemental composition at low wt %.

Figure 8. Montage of Si, Zr, Al and K elemental distributions within a $10 \times 10 \mu\text{m}^2$ region of the YPSZ – porcelain interface. High resolution SE and BSE SEM image of the same location is included in order to highlight the nominal roughness of the interface and to enable direct comparison with the EDS results. The reduced area over which elemental diffusional analysis was performed is highlighted in the BSE image.

Figure 9. Logarithmic plot of average elemental weight % within the first 5 μm from the YPSZ – porcelain interface. Noticeable variation in elemental composition is observed at this length scale with the exact interface location proving difficult to locate (a nominal position based on the SEM imaging is used in this figure). We note that the logarithmic scale used in this figure and reduced precision of EDS at low concentrations leads to unrepresentative large variations elemental composition at low wt %.

Figure 10. Average elemental weight % of the 5 main elements in YPSZ near-interface region; Al, Hf, O, Y and Zr. Differences in elemental composition are likely to be as a result of improved averaging in the low magnification measure. 95% confidence intervals from EDS peak fitting intervals have also been included.

Figure 11. Average elemental weight % of the 9 main elements in porcelain near-interface region; Al, Ca, F, K, Na, O, P, Si and Zn. Differences in elemental composition are highly dependent upon the specific grain averaging performed in the area examined. 95% confidence intervals from EDS peak fitting intervals have also been included.

Figure 12. Nominal stress-strain plot showing the typical response of a porcelain and a YPSZ micropillar. The linear region associated with the loading modulus is observed, as well as the typical load drops associated with failure of the micropillars.

Figure 13. Loading modulus (solid markers, left) and 2% yield strength (bordered markers, right) for the YPSZ and porcelain micropillars as a function of distance from the interface.

The results obtained from the two lines are distinguished by the circular and rectangular markers. 95 % confidence intervals are shown by the error bars on this plot.