Monoclinic phase transformations of zirconia-based dental prostheses induced by clinically-practiced surface manipulations

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Abstract (100 to 200 words)

Full-ceramic zirconia partial-dentures have become very popular amongst dentists and patients alike, due to their excellent aesthetics and mechanical properties. We focused on phase transformations on the outermost surfaces of 3 mol-% yttria-stabilised zirconia (Y-TZP) bars of clinically relevant thicknesses and after surface manipulations encountered in everyday clinical practice: these are induced by technicians and practitioners while working with the dentures prior to and during delivery of the constructs to patients. While it is well known that the high resistance of Y-TZP against crack growth is due to toughening by a stress-induced phase transformation, the three-dimensional organisation and thickness of the transformed layer is yet not known. By means of laboratory- and synchrotron-based X-ray diffraction measurements together with a multimodal tomographic approach it was possible for the first time to visualise and quantify the phase transformation non-destructively. The obtained results

show that the thickness and the homogeneity of the layers strongly depend on the severity and mode of loading. Depending on the *in vivo* loading conditions, the phase transformations may have beneficial effects on the long-term survival of the dentures or not. All this has important implications for dental practitioners as to how they should treat these materials after sintering.

Keywords Given by BIOMATERIALS

ceramic structure; zirconia;
dental implant **or** dental restorative material
microstructure

surface treatment (**or**: modification)
XRD (X-ray diffraction)

non-given keywords we had put in:
dentistry: partial denture
phase transformation;
synchrotron radiation, microtomography

1. Introduction

Due to their excellent aesthetic properties, full-ceramic zirconia-based partial-dentures have become very popular amongst dentists and patients alike. They are frequently used in place of the well-established and long-lasting conventional porcelain-fused to metal dental crowns and bridges. The white translucent colour of the ceramics gives the artificial teeth a pleasing natural

appearance, while the material exhibits excellent inertness and biocompatibility coupled with favourable mechanical properties: the zirconia-cores provide the stiffness needed to support and prevent flexing of the external brittle tooth-shaped porcelain layers, while allowing the dentures to function for mastication under loads similar to normal teeth. Furthermore, high fracture toughness and resistance to crack propagation make the zirconia components of such dentures damage tolerant to an extent that is far greater than is possible by other ceramic materials [1, 2].

A standard preparation method in use by many dental laboratories is based on machining pre-pressed (non-sintered) blocks/blanks of zirconia that may be fitted and trimmed to match the specific teeth needing reconstruction. The shaped constructs are sintered at temperatures of 1350 °C to 1550 °C and are then covered by aesthetic dental porcelain that is used to provide the tooth shape, color-shade and function: the porcelain is incrementally placed and baked until the final tooth form is created [3-7]. The zirconia material most commonly used for core build-ups of dental crowns and bridges is a partially-stabilised zirconia ceramic. The pure polycrystalline material attains stability after adding various dopants, that freeze the tetragonal crystal structure of the zirconia polycrystals after heating and fusing. [2, 8, 9]. For dental purposes, the 3 mol-% yttria-stabilised zirconia (so-called Y-tetragonal zirconia polycrystals = Y-TZP) is used: in this material, nearly all of the crystals transform into the tetragonal phase during sintering and upon cooling, they are “frozen” in a metastable state, where the yittrium oxide prevents spontaneous transformation into the thermodynamically stable monoclinic phase. However, as will be outlined below, following mechanical stimulation, transformation may occur.

Ceramic materials are known for their high (compressive) strength which is usually accompanied by brittleness. In zirconia bioceramics however, the existence of a transformable phase gives rise to significant toughness and resistance to crack propagation when the tetragonal microstructure is not fully stabilised. Thus, Y-TZP ceramics are used because they remain in a metastable state that potentially transforms into the stable monoclinic phase if adequate activation energy is provided. This activation energy may originate from chemical, physical, or mechanical sources and all result in stresses that induce transformation from the tetragonal to the monoclinic phase (T-M-transformation). Toughening is obtained because the phase transformation is accompanied by a 3 to 5 % increase in volume which leads to the development of a local residual stress field. Specifically, near forming microcracks these stresses tend to close the crack and lead to shielding of the crack tips from the externally applied loads which effectively impedes further crack propagation [9-11]. Thus, Y-TZP structures attain a benign failure behaviour more typical to metals, and this is of course advantageous for the longevity and reliability of dentures made from these materials.

After sintering and during the porcelain production process of the partial dentures, technicians mechanically grind, etch and manipulate the outer surfaces of the zirconia cores. Furthermore upon fitting the completed crowns and bridges into the mouth, the dental surgeons often need to modify and adapt the sintered structures with the patient on the chair, and this is commonly done by mechanical and/or chemical manipulation (e.g. [5, 7]). The stresses induced by manipulating the dentures with treatments such as machining, sand-blasting or grinding, promote the T-M transformation much like service loads do. Surface

compressive stresses may arise with the potential outcome of increasing the quasi-static and fatigue strengths of the structures [12, 13]. However, the transformation may also have negative effects on the mechanical stability of the dentures: within a certain volume at and below the treated surface, the material loses all or part of its crack-stopping or crack-retarding capacity.

The T-M transformation of PSZ-type ceramics has been investigated by different groups since it was first described in 1975 [14]. Most work dealt with the phase transformation around an advancing crack (e.g. [15-19]): the thickness of the transformation layer and/or the amount of transformed volume around these cracks has been investigated by various methods, including transmission electron microscopy [15], X-ray diffraction (XRD) [16-18], and Raman microprobe spectroscopy [19]. Nevertheless, the exact nature of the transformed layer with respect to its three-dimensional organisation and extent and how these depend on widely-used surface manipulation techniques still remains unknown. For ceria- and yttria-stabilised TZP's, partial transformation of grains and increasing amounts of transformation have been shown under indentation or uni- or biaxial stress-controlled loading [9]. Yet, for clinically relevant materials and surface treatments, the questions still remain open whether all or only a part of the grains in the affected volume transform and whether the affected grains transform fully or only to a certain extent.

In the present work the phase transformation in a 3 mol-% Y-TZP was studied in tightly-controlled thin bar-specimens made by conventional dental processing techniques. The samples of thicknesses frequently encountered in the dental clinic down to 200 µm were prepared and manipulated using routine dental procedures and the resulting phase transformations were characterised. The

aim of the present work was to describe the influence of everyday routine clinical manipulation techniques such as grinding on the three-dimensional organisation of the transformed layer. The thickness of the transformed layer and local variations in transformation are described on the basis of laboratory and synchrotron-based XRD-measurements as well as a multimodal microtomographic approach combining phase-sensitive and powder-diffraction contrast [20-22]. Based on this, a model to interpret the data and the consequences is presented.

2. Materials and Methods

Y-TZP samples were fabricated in the form of bars, with thicknesses of 200 µm to 1200 µm so as to resemble clinically relevant structures (fig. 1). They were produced from a commercially available 3 mol-% Y_2O_3-stabilised ZrO_2 (DC-Shrink, Bien Air, Bienne, CH). Each sample was cut from bulk "green" (pre-sintered) blocks, using a water-cooled diamond saw (Isomet – Buehler GmbH, Duesseldorf, D) and subsequently ground on 1200 grit SiC paper with a micro-grinding system (400CS – Exakt, Norderstedt, D) to obtain reproducible cuboids. Following sintering at 1530 °C for 2 h in a VITA Zyrcomat oven (Vita Zahnfabrik, Bad Saeckingen, D) according to the procedures recommended by Bien Air [23] the final dimensions of the specimens were 20 x 4 mm^2 in lateral dimensions, with uniform thicknesses of either 0.2 mm, 0.4 mm, 0.8 mm or 1.2 mm. Following sintering, samples were subjected to surface manipulations that are commonly encountered in the dental setting: they were either polished with 3 µm diamond paste, cut with the same water-cooled diamond saw used before sintering, or fractured by 4-point bending until failure in a 10 kN testing device (Kammrath & Weiss, Dortmund, Germany). As a control for the production and surface manipulation processes the surface roughness of each specimen (R_a) was determined by white light interferometry (IFM 2.1.5 – Alicona Imaging GmbH, Grambach, A).

Samples were observed by scanning electron microscopy (SEM, FEI Quanta 600 FEG, FEI, Eindhoven, NL) prior to undergoing X-ray diffraction analysis in a laboratory-based XRD-diffractometer (Nonius PDS120, Bruker AXS, Karlsruhe, D) with an INEL CPS-120 curved position-sensitive detector (INEL Ltd., Swindon, UK). All laboratory XRD-measurements were performed in reflection

mode using a Cu $K_{\alpha 1}$ source (λ = 0.15406 nm) with recording times of 12 ~ 24 h and an angle of incidence of 5º. For the diffraction angles of the monoclinic and tetragonal phases (2Θ = 25° – 35°), a penetration depth of approximately 1 to 3 µm can be calculated from which 75 to 95 % of the diffracted signal stem [24]. The diffraction patterns were evaluated in order to obtain the relative proportions of the monoclinic (X_m) and cubic (X_c) phases, determined from the ratios, usually of the strongest, peak intensities of the respective phases. Therefore, to estimate the proportion between the monoclinic and the tetragonal+cubic phases, the $(1\ 1\ -1)_m$, $(1\ 1\ 1)_m$ and $(1\ 1\ 1)_{t+c}$ peaks were used. However, as the tetragonal and cubic (1 1 1) peaks cannot be separated, the sum of the $(0\ 0\ 4)_t$ and $(2\ 2\ 0)_t$ tetragonal peaks and the $(4\ 0\ 0)_c$ cubic peak were used to estimate the variations in the proportions of these two phases [14, 16, 17]:

$$X_m = \frac{1.311\left(I_m(11-1) + I_m(111)\right)}{I_m(11-1) + 1.311\left(I_m(111) + I_t(111)\right)} \qquad (1)$$

and

$$X_c = 1 - \frac{I_t(004) + I_t(400)}{I_t(004) + I_t(400) + I_c(400)} \qquad (2)$$

where $I_{m/t/c}$ represent the integrated intensities calculated by fitting the corresponding peaks with a Pseudo-Voigt distribution and determining the area under the curves.

Two of the bar samples were used to create small triangular shaped splinters of decreasing thickness for measurements by phase-sensitive full-field microtomography and scanning tomography with powder-diffraction based

contrast (XRD-μCT) [21, 25-27]. Experiments were carried out on the nano-probe station ID22NI of the European Synchrotron Radiation Facility [20, 28]. Figure 1 shows a schematic representation of the sample preparation and the XRD-measurements that were performed.

For all measurements, an X-ray beam focused by a multilayer KB-optics was employed. For the phase-sensitive full-field microtomography, ID22NI was operated in the pink beam mode at an X-ray photon energy of 17 keV. The sample was placed approximately 230 mm downstream of the position of the focal spot of the KB-optics (spot size 130 nm x 130 nm), 1500 projection images were recorded over 180° rotation, each sampled with an effective pixel size of approximately 0.4 μm (FReLoN 4m CCD camera with 25x magnification visible light optics and 24 μm-thin Tb-doped Lu_2SiO_5-scintillator [29]). Phase-retrieval on the acquired images was performed using a single-distance non-iterative algorithm via the ImageJ plugin ANKAphase [30]. This approach yields lower spatial resolution compared to, for example, holotomography, but is more robust towards sample instabilities as only one tomographic scan is required [25]. Tomographic data were reconstructed using the ESRF package PyHST [31] and visualised by VGStudioMax (Volume Graphics GmbH, Heidelberg, D). The tomographic volume images were used to select a region in one of the samples that was sufficiently thin so as to fit into the field of view for XRD-μCT with a nano-focused beam.

For collecting powder-diffraction patterns, ID22NI was switched to monochromatic operation by employing a double-crystal monochromator (Si(111) reflection) at an X-ray photon energy of 17 keV. Transmission diffraction images were acquired by scanning the specimen through the focal

spot of the KB-optics (spot size of approximately 200 nm x 200 nm) with the corresponding detector placed 150 mm away from the sample (FReLoN 4m with demagnifying taper optics, approximately 52 µm pixel size). For XRD-µCT, diffraction patterns were acquired by translating and then rotating the sample so as to obtain diffraction patterns on a single horizontal plane. As described in detail elsewhere [20, 22]the powder diffraction patterns were collected by recording 61 diffraction patterns on a line across the sample tip and then rotating the sample: measurements were then repeated over 180° in 151 angular steps [22] yielding a total of almost 10'000 diffraction images in transmission. Data was then processed with the free software package XRDUA [27] where XRD-µCT peak-intensity slices were reconstructed, depicting the spatial phase distributions of monoclinic and tetragonal phases. Additionally, a series of diffraction patterns was acquired by mapping a grid across the sample that had been ground on one side (see outline of scanned region in fig. 5). 5'800 diffraction patterns were obtained at vertical and horizontal increments of 5.0 µm and 1.0 µm across the surface, respectively (25 lines, each 234 steps). These diffraction patterns where used to quantify the amount of monoclinic fraction as outlined above for the laboratory-based measurements, providing a detailed sub-micrometer spatial distribution of the T-M transformed regions on the ground zirconia surface.

3. Results

SEM-imaging revealed a very fine-grained and homogeneous texture for the polished and subsequently sintered surfaces, as shown for example in fig. 2a.

Most grains have diameters spanning 0.3 to 1 μm. Within the tetragonal matrix, single larger cubic grains (see for example the delineated black lines in the figure) with diameters of 1 to 1.5 μm are seen. The average surface roughness (R_a), as measured by white-light interferometry was around 0.90 ± 0.05 μm for the specimens after polishing, but before sintering, 1.32 ± 0.08 μm for the sintered specimens and 0.78 ± 0.08 μm for the specimens polished after sintering. Cutting as well as fracturing in 4-point bending lead to much higher roughness values. These are above the measuring range of the interferometer of 4 μm. In the SEM-micrographs, the fractured surfaces appeared ragged and homogeneous at lower magnifications. Cracks seem to have progressed in different planes, resulting in steps on the fracture surface where the different crack planes met (arrow). Further, secondary cracks were observed (dashed arrow). At higher magnifications (figs. 2c and d), different morphologies can be distinguished: poorly structured areas of intergranular fracture of the tetragonal grains which appear glazed due to the glass phase at the grain boundaries usually observed in Y-TZP ceramics [F] (fig. 2c) are interspersed with smaller areas of irregular feathery topography (fig. 2d) which is typical for monoclinically transformed grains.

In figure 3, typical reflection XRD-patterns, acquired with the laboratory instrument, of the sintered, polished, and fractured surfaces of 400 μm-thick bar specimens are given. As to be expected, the typical peaks for the tetragonal (JCPDS file no. 42-1164), cubic (JCPDS file no. 49-1642) and monoclinic phase (JCPDS file no. 37-1484) are present. An average integrated intensity profile for the diffraction patterns acquired with the nm-sized beam in transmission at ID22NI is also shown. All intensities are given as relative values normalised with

respect to the tetragonal (1 1 1)-peaks. The Y-TZP phase proportions in the sintered and polished state (figs. 3a and b) based on equations 1 and 2 were approximately 90 % tetragonal, 8 % cubic, and 2 % monoclinic. While fracturing lead to a large increase in the relative proportion of the monoclinic phase, with values around 15 % (fig. 3c), the laboratory-based measurements on the cut surface gave values in the range of 2 % monoclinic phase, similar to the sintered and polished surfaces. The diffraction pattern shown in fig. 3d was determined in transmission mode from the synchrotron-XRD mapping experiment. The line plot in this figure is integrated from the average diffraction pattern obtained from all points on an area of 50 µm by 50 µm on the cut surface, where traces of monoclinic phase were detected. From about 600 transmission diffraction patterns collected, less than 7 % contained diffraction peaks relating to the monoclinic transformation. From the few points that did undergo transformation we found an average transformation percentage of 0.09 %. If the diffraction patterns are not averaged, but summed up, a slightly lower percentage of the monoclinic phase in the range of 0.05 % is determined. A map depicting the distribution of points showing zones of monoclinic transformation is shown - colour coded - in fig. 4. It is clear that the extent and distribution of the monoclinic transformation varies substantially in the plane of the cut surface. Overall, the monoclinic signal is extremely weak and the phase was not detectable in many surface points suggesting negligible or no monoclinic phase transformation in most regions across the surface.

The high-resolution tomography scans provided sub-micrometer details about the sample geometries and surface structure. Figure 5a shows the tomogram of the splinter specimen. The integrated sketch gives an idea of the location of the

mapped area and the orientation relationship of the X-rays and the differently modified surfaces of the specimen. A complicated fracture surface with ragged morphology is seen on the upper tip region where fracture was induced during the preparation of the splinter tip. Actually, two fracture surfaces were produced: one with a more ragged morphology and oriented at an angle of about 30° to the longitudinal axis of the specimen (fig. 5b), and one which appears less rough and is inclined at a more acute angle of approximately 50° to the longitudinal direction. In the following, the latter side is referred to as “chipped”. A rough surface with scratches caused by the diamond knife is seen on the sample side corresponding to the morphology of the cut surface as shown in the SEM-micrograph in fig. 5c. Slicing beneath this surface reveals that the scratches due to the diamond knife are more than 3 µm deep (fig. 5d). The value corresponds well with the estimates from the roughness measurements given above.

The XRD-µCT data and corresponding tomographic reconstructions revealed the spatial distribution of intensities of peaks in the transmission nano-diffraction patterns. Due to the nano-focused beam and the polycrystalline nature of the sample, high intensity spots dominate all diffraction patterns, with extreme intensity fluctuations seen along lines on rings corresponding to the known diffraction pattern of the tetragonal and monoclinic phases in Y-TZP [JCPDS files nos. 42-1164, 37-1484]. The identification of the tetragonal and monoclinic phases in the XRD-µCT data was performed based on the averaged diffraction pattern of almost 10’000 diffraction images acquired while subsequently translating and rotating the specimen, where crystal orientations and diffraction spots fuse to become continuous rings. Upon reconstruction, the distribution of

identified phases is seen on a slice across the tip of the specimen as shown in fig 6. The XRD-μCT images in figs. 6a and b depict the appearance of the monoclinic (blue) and the tetragonal (yellow) phase within a 200 nm-thick plane/slice corresponding to the path traversed by the nano X-ray beam upon translation and rotation of the splinter tip. Figure 6c shows the two phases overlaid, clearly revealing the existence of a monoclinic phase only on the outer margins of the slice. Our diffraction patterns of the polycrystalline Y-TZP obtained using a nano-focused beam preclude precise quantification of the amount of monoclinic phase based on the diffraction intensity. However due to the beam size, we are able to locate the thickness of the layer where monoclinic transformation occurred to within +/- 200 nm. As can be seen, the tetragonal signal appears throughout the entire slice, as expected. The thickness of the transformed layer is about 1 μm for the cut and the chipped sides, while on the fractured side, a thicker and very inhomogeneous layer of 2 to 5 μm transformed zone can be seen. Note in particular the rugged and convoluted margins of the inner interface between the pure tetragonal and the mixed tetragonal-monoclinic zone on the fractured side.

4. Discussion

Transformation layer

The results of this study shed light on several elusive aspects of surface transformations occurring in a standard Y-TZP product, representing what is commercially available and in wide clinical dental use. We are concerned mainly with the phase transformations occurring on the outermost surfaces of

the biomaterials that form the backbone of partial dentures: parts of the structure that are used to seat crowns and bridges on teeth or implants where the zirconia is not covered with aesthetic tooth-form porcelain. Transformations of these surfaces are induced by technicians and practitioners while working with the dentures prior to and during delivery of the constructs to patients. Zirconia dentures are meant to be bonded to the teeth, and this is normally achieved by roughening the denture surfaces so as to create mechanical interlocking when applying luting cements. Understanding the microstructure and transformations within the surface outermost layers (several micrometers thick) is of paramount importance for long-term and maintenance-free service times in the oral cavity. Necessary surface manipulations such as cutting, grinding or polishing by air-borne particle abrasion (e.g. [5, 7]) obviously change the surface morphology and help improve the denture fit. However these treatments - and especially accidental chippings - also affect the microstructure and in particular they may compromise strength and/or toughness. It is perhaps because of this, that cracking is seen on zirconia surfaces that are aggressively prepared (e.g. [5]).

Our results show that gentle water-cooled diamond-knife sawing (“cut” surface) resulted in a very low degree of tetragonal to monoclinic transformation, even though scratches several micrometers deep (> 3 μm) were created. Fracture and cracking however resulted in transformed zones that were up to several micrometers thick with locally varying thicknesses across the surface. Presumably the toughness and crack resistance of these zones is significantly reduced, and consequently such surfaces would be prone to delamination or even whole-denture fracture under cyclic mechanical loading in the mouth.

The monoclinic proportions determined from the various reflection and transmission XRD-measurements in our experiments are in good agreement with values reported previously, based on XRD or Raman spectroscopy [18, 19]. However, the synchrotron measurements allowed for the first time to reveal the full extent of the surface transformations induced by slow water-cooled cutting. Clearly slow water-cooled milling should be preferred when manipulating these dentures while working with the patient.

Our map of diffraction patterns determined from more than 3000 points sized 200 nm by 200 nm on a rectangular grid on the diamond-sawed ("cut") face of our sample revealed a fine and surprisingly low density of monoclinic transformed regions. The few points that did exhibit some presence of a monoclinic phase presented an extremely low proportion as compared to previous reports. This may be explained by understanding the origin of the signal in our experiment: whereas the monoclinic signal only stems from the thin transformation layer on the cut sample surface, the whole 160 µm-thick bulk volume of the specimen contributes to the tetragonal signal in the diffraction patterns. This leads to a relatively weak monoclinic and a relatively strong tetragonal signal, resulting in low ratios for the monoclinic phase. In contrast, in reflection mode, the signal stems from a layer 1 to 1.5 µm thick which is approximately the thickness of the transformation layer as we know from the XRD-µCT results. Consequently, higher proportions of the monoclinic phase are calculated, because the tetragonal signal is relatively weaker. Figure 7 clarifies this concept. Hereby, monoclinic transformation is indicated by partially grey grains.

The results of the mapping XRD-experiments further allow us to estimate the transformation layer geometry, based on several different model assumptions on possible ways that transformation might take place (fig. 8). From earlier work describing an increasing monoclinic proportion with increasing load [F] it may be assumed that, depending on the severity of loading, grains may transform fully (100 %; “grey” grains) or to a certain percentage (x %; partially grey grains) within the surface layer. With increasing depth, the outer loading conditions change as does the internal stress state. When the transformed volume is at a free surface or near a pore, the restraints are much lower than if it is fully surrounded by other grains. Based on this, a realistic set-up might be a high degree of transformation near the free surface, gradually decreasing with increasing distance into the bulk. However, two extreme conditions may arise: 100 % transformation in 100 % of the grains versus partial transformation in some percentage of the grains. With an estimated path length of 160 µm through the bulk (essentially 100 % tetragonal), a measured monoclinic phase fraction in the range of 0.5 %, and neglecting attenuation, a layer thickness of 0.8 µm may be estimated for the first case. If we assume only 10 % transformation and this – based on the results of the mapping experiment – in only 7 % of the grains, the layer would be about 700 µm thick. Clearly, considering the results of the XRD-µCT measurements, the latter case overestimates the layer thickness by far.

As shown above, the mapping showed many points with apparently no transformation, while the XRD-µCT measurements showed a more continuous layer of transformation, even though single “holes” in the monoclinic layer are visible. This apparent contradiction may be explained as follows: in the case of

the XRD-μCT measurements, the X-rays travel through a volume with a thickness of about 10 μm to 25 μm, while in the mapping experiment, the radiographed volume was approximately 160 μm thick. Because of the different ratios of the transformed layer thickness to the bulk thickness with no transformation, clearly, for the tomographic XRD-μCT slice, the monoclinic signal appears relatively much stronger as compared to the mapped volume. Additionally, in the case of XRD-μCT, nearly the full volume was scanned: the distance of the measuring points is about 400 nm, and therefore much lower than in the mapping experiment (1 μm). This is in the range of the grain size, so that only a part of the actually transformed volume contributes to the signal. It is most likely, therefore, that the transformed fraction varies locally, with the rare occasion of zero transformation.

Clinical relevance

In the present work, the phase transformation in zirconia structures of clinically relevant sizes and surface treatments was investigated by combining different methods to probe the surface and the bulk. By means of hard synchrotron radiation and a multimodal tomographic approach it was possible for the first time to actually visualize and quantify the depth of the transformation layer non-destructively, following different surface treatments. Transformation toughening is the most important mechanism responsible for the benign failure behaviour of zirconia ceramics of the Y-TZP group of materials. To retain as much as possible of the original tooth, crowns and bridge structures are often very thin, and moreover they are often manipulated mechanically and/or chemically after sintering: either by the dental technician to prepare the surface of the artificial tooth for blending with a porcelain layer thereby increasing the interfacial

strength, or by the dentist to adapt and prepare the inner surface of the construct before connecting it to the remnants of the natural tooth. Mechanical manipulations such as cutting, grinding, polishing, or sand-blasting incur the possibility of a stress-induced local phase transformation near the surface, introducing beneficial compressive stresses but also reducing the toughening capacities of the material. Whether the negative or positive effects prevail, strongly depends on the local loading situation. For example, the inner surface of the artificial tooth, or the lower surface of a bridge connector, may be assumed to experience cyclic tensile loads under usual chewing conditions. Under these circumstances, a compressive residual stress state will be beneficial as the service loads felt by the structure are decreased. Moreover, as fracture mechanics show (Marshall et al. 1990), there is a decreased crack tip shielding for stress intensities lower than a critical value, which is usually the case for cyclic loading. When overloads occur however, the situation reverses, and the lack of transformation toughening in the surface allows cracks to grow more rapidly into the bulk.

The reported results show an inhomogeneous transformation layer strongly dependent on the severity and mode of loading and give important hints for the treatment of Y-TZP-based partial dentures in everyday clinical practice. Dentists and dental technicians should take great care in how they treat the sintered structures. Necessary machining has to take into consideration that certain areas in the denture may benefit from surface phase transformations, while others have to be treated in a gentle way to keep the phase transformation in the surface to a minimum to retain the toughening mechanism. Thereby, premature failure of bonded layers in these structures after short service times

or due to (moderate) overloads can be avoided. Further work is necessary to achieve a better understanding of just how different treatments change the mechanical behaviour of zirconia structures under *in vivo* loading conditions.

5. Conclusions

In the present work, we were concerned with the phase transformation following clinically relevant surface treatments of yttria-stabilised zirconia bioceramic bars of thicknesses generally encountered in dental practice:

- Surface manipulations gently performed like water-cooled diamond sawing lead to a clearly defined, very thin transformed surface layer while fracturing and cracking result in much thicker and inhomogeneous transformation zones.
- As transformation strongly depends on the severity and mode of loading, the thickness of the layer and the amount of transformed phase may be influenced by the choice of surface treatment.
- Depending on the location within a denture, the corresponding everyday loading mode, and unforeseen single extreme loading events, phase transformations in the surface may be beneficial or not.
- Therefore, the results imply that dental technicians and practitioners should take great care when mechanically manipulating Y-TZP dentures after sintering.

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Missing references:

F: Green, D.J., R.H.J. Hannink, M.V. Swain: Transformation toughening of ceramics, CRC Press Ind., Boca Raton, Florida, 1989

I think reference 9 should be this book (Green et al.) and not Claussen et al.; please check this! If Claussen et al. applies to where it is cited, fine, but then Green et al. have to be cited at that part as well. And anyway, we need Green et al. to be included as it is cited in the text under “F”

Further, this reference has to be added – also see text.

Marshall et al. 1990: D.B. Marshall, M.C. Shaw, R.H. Dauskard, R.O. Ritchie, M.J. Readey, A.H. Heuer: Crack tip deformation zones in toughened zirconia. Journal of the American Ceramic Society Volume 73, Issue 9, September 1990, 2659–2666,

Figure captions:

Figure 1: Survey of specimen treatments and measurements; note that the specimens are not shown to scale: the bar specimens have lateral dimensions of 20 mm x 4 mm and thicknesses of 0.2 mm, 0.4 mm or 0.8 mm. The dimensions of the splinter are in the 10 µm to 100 µm range.

Figure 2: SEM-micrographs of sintered (a) and fractured (b) surfaces of the bar specimens. The black lines in (a) delineate cubic grains. The micrographs (c) and (d) show magnified views of the tetragonal and monoclinic areas of the fracture surface, respectively.

Figure 3: Typical reflection XRD-patterns, acquired with the laboratory instrument, of the sintered (a), polished (b), and fractured (c) surfaces of 400 µm-thick bar specimens, and averaged transmission XRD-pattern, acquired with the synchrotron set-up (d).

Figure 4: Distribution of the monoclinic phase fraction for the area of the splinter specimen scanned in the synchrotron mapping experiment. The different scales in images (a) and (b) highlight the very low transformation rate with only locally higher transformation.

Figure 5: Tomogram (a) of splinter specimen depicting the surface manipulations and the volume scanned in the mapping experiment. The SEM-micrographs (b) and (c) show the microstructure of the fracture surface of the splinter tip and of the cut surface. The section shown in (d) is a reconstructed slice of the cut surface to highlight the depth of the cutting lines.

Figure 6: Spatial distribution of the monoclinic (a) and tetragonal (b) phases in a slice of the splinter tip achieved by tomographic reconstructions of the XRD-µCT data. The two images are overlayed in (c).

Figure 7: Schematic drawing of the origin of the XRD-signals of the monoclinic and tetragonal phases in transmission (a) and reflection (b) experiments. The white hexagons depict tetragonal grains, grey colouring of grains indicates partial monoclinic transformation.

Figure 8: Schematic representation of transformed layer thickness for different transformation models: all or some grains may either transform fully or partially. The white and grey hexagons depict fully tetragonal and monoclinic grains; partial grey colouring of grains indicates partial monoclinic transformation.