Zirconia as a Biomaterial in Implant Dentistry

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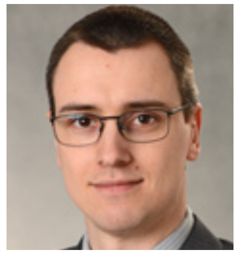

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ABSTRACT

Zirconia has been used in biomedical applications for a long time. Its biocompatibility is not in question. However for structural applications such as in dental implants, zirconia must show improved mechanical performance in addition to its biocompatibility and bone integration aspects. This paper addresses mainly the mechanical issues surrounding zirconia materials in four sections looking at zirconia as a structural biomaterial in terms of processing aspects, flaws and surface characteristics, and design as well as low temperature degradation.

Keywords: Zirconia, implant, aging

INTRODUCTION

Since the first publication referring to zirconia as the "ceramic analog of steel" in the 1970s (Garvie et al. 1975), zirconia-based materials have evolved significantly and are currently being applied in numerous clinical situations in the dental field with a relatively high success rate (Zhang & Lawn 2017). Zirconia was initially used as a biomaterial in the orthopedic field in the late 1980s when alumina femoral heads started to be replaced due to the their high brittleness (Chevalier 2006). The first ceramic dental implants used decades ago were also made of alumina, however, as with prosthetic femoral heads, alumina implants were rapidly substituted by stronger zirconia-based components (Andreiotelli et al. 2009). In the 2000s, zirconia-based materials were made widely available for dental applications, with yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) by far the most successful version used in dentistry (Reveron et al. 2017). Although other dopants like CaO, MgO, CeO_2 at varied concentrations have been proposed, the most prevalent dental zirconia is the one cation-doped with 3%mol of yttria (Chen et al. 2013).

As demonstrated in the groundbreaking publication by Garvie et al. in 1975, doping zirconia with yttria results in the retention of the tetragonal crystallographic form at room temperature (Garvie et al. 1975). Usually the tetragonal phase of zirconia only exists between 1170°C and 2370°C, and its existence via doping at room temperature makes monoclinic phase transformation possible upon stimuli-like stress concentration around a cracked tip (Piconi & Maccauro 1999). Since the monoclinic crystallographic form is approximately 4.5 vol% larger than the tetragonal form, this transformation results in the creation of beneficial compressive stresses that hinder crack propagation and ultimately avoid catastrophic failure of the component (Lughi & Sergo 2010).

The presence of this unique toughening mechanism makes Y-TZP a smart material with one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, temperature, moisture, pH, electric or magnetic fields (Ball 1998). According to Chevalier et al. (Chevalier et al. 2009), Y-TZP ceramics have the best combination of toughness and strength compared to other versions of the stabilized zirconia, such as partially stabilized zirconias (PSZ) currently used to produce translucent monolithic prosthetic crowns (Zhang 2014). PSZ contains larger amounts of yttria (5-8 mol%) to guarantee stabilization of the tetragonal phase and high content (>50 wt%) of the weaker zirconia cubic phase. The latter is more translucent but not able to deliver the transformation-toughening mechanism and therefore has much lower mechanical properties compared to Y-TZP (Zhang & Lawn 2017).

The typical microstructure of Y-TZP used in dental implants is composed of equiaxed grains of tetragonal phase sintered to 96-99.5% of their theoretical density (Kelly & Denry 2008). Grain sizes are kept in the range of 0.2 to 1 µm (Palmero et al. 2014), as larger grains result in instability of the tetragonal phase (Heuer et al. 1982).

Another important component present in dental Y-TZP is alumina, which began to be added to the starting powder in small concentrations (0.25 wt%) in order to increase the sinterability and consequently the final density of the component (Zhang & Lawn 2017). The addition of alumina later proved to effectively avoid low temperature degradation in Y-TZPs (Chevalier et al. 2009; Zhang et al. 2014).

In comparison to titanium implants, which display some immune reactions when evaluated in vivo, Y-TZP does not trigger local or systemic effects when used as an oral implant, and therefore has been indicated in patients with metal sensitivity (Kohal et al. 2004; Sevilla et al. 2010). Besides the high biocompatibility, Y-TZP is also known for giving much better esthetic results in comparison to titanium, especially regarding soft tissues surrounding the implant. In fact, the dark shade of titanium implants can compromise the esthetic result in patients with thin gingival biotype or after the implant base has been exposed due to gingival retraction (Heydecke et al. 1999). On the other hand, metallic implants have much higher fracture toughness, usually 6 to 10 times higher than their ceramic counterparts, and Y-TZP is a bioinert biomaterial (Cesar et al. 2017). Bioinert materials have poor interaction with surrounding living tissues and this feature may negatively affect the osseointegration process (Siddiqi et al. 2017). Therefore, the industry has proposed varied solutions to this problem usually by means of surface modifications of the zirconia implant in order to increase integration with bone (Wenz et al. 2008).

Although Y-TZP is currently the main biomaterial used in dental implants, clinical problems with Y-TZP hip prostheses in the early 2000s demonstrated that this material is prone to aging via a low temperature degradation phenomenon, which will be further explained in this review. In order to overcome this issue, alternative polycrystalline ceramic composites were developed to try to keep the same level of strength and fracture toughness, but with increased in vivo stability (Reveron et al. 2017). According to Osman and Swain, the main ceramic composite currently available for dental implants is alumina-toughened zirconia (ATZ) (Osman & Swain 2015).

ATZ is a composite ceramic material usually consisting of a mixture of 20 wt% alumina and 80 wt% of Y-TZP. This material is claimed to have increased fracture strength and reduced aging susceptibility compared to Y-TZP. According to Pieralli et al. (Pieralli et al. 2017), to date, no clinical studies including ATZ implants have been performed, and only studies on animals are available (Kohal et al. 2016; Schierano et al. 2015) that suggest an osseointegration capability comparable to Y-TZP.

Different compositions of ATZ have been developed, and the first alternative material was 12Ce-TZP/20wt%-Al_2O_3 intergranular composite (12 mol% CeO_2, zirconia grain size of 1.5 µm, and alumina grain size of 500 nm) (Reveron et al. 2017). Ceria was chosen as an alternative stabilizer in this case due to its ability to undergo a larger amount of stress-induced phase transformation, which in turn leads to higher fracture toughness when compared to Y-TZP (Tsukuma & Shimada 1985). This material later evolved to a refined version (10Ce-TZP-based composites) composed of 10 mol% CeO_2, zirconia grain size of 1 µm containing 30 vol% of nano-sized alumina particles (10 to 100 nm) and alumina particles around 500 nm containing a few nano-sized Ce-TZP particles (Nanozr, Panasonic Electric Works, Japan) (Li et al. 2014). Further improvements are still in an experimental stage with substitution of alumina for 16 vol% of nanometric $MgAl_2O_4$ (Apel et al. 2012) and the addition of elongated third phases, like $SrAl_{12}O_{19}$ and $LaAl_{11}O_{18}$ platelets, which may activate further toughening mechanisms like bridging or crack-deflection (Kern 2014; Reveron et al. 2017).

PROCESSING

Sintered ceramic products are sensitive to defects and stress concentrations. In order to obtain a high strength ceramic, the processing steps have to be well controlled for the production of a dense, defect-free material with the desired microstructure. The strength of zirconia products is mainly controlled by the shape, size and distribution of microscopic defects created during processing. Limiting these defects is the main challenge of manufacturers during each of the processing steps that are summarized in Fig. 1 (Rahaman 2007). Hence, the powder quality (production of granules), contaminations, consolidation techniques (powder compaction), machining and sintering all have the potential to create critical flaws that will be difficult to remove after sintering. Depending on the stress state present on the part in function, these flaws may critically influence the long-term clinical outcome.

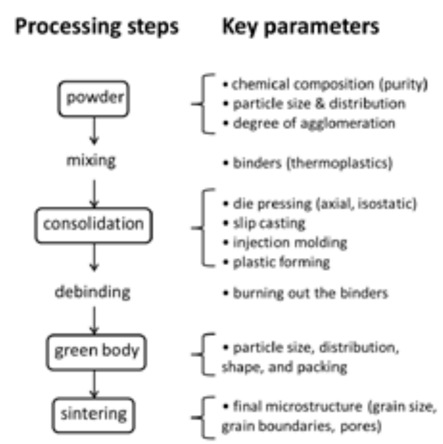

Fig. 1: Classic processing steps for zirconia products

The powder

Powder synthesis is a first critical step in which *agglomerates* are created (Fig. 2). An agglomerate is a cluster of primary polycrystalline particles, which are the smallest units in the powder with a clear, defined surface (Rahaman 2007). These primary particles within agglomerates are held together by surface forces. Agglomerates are porous and have interconnected pores between primary particles which may vary from 0.1 to 1 µm, whereas intergranular porosity will vary between 10 and 100 µm (Andrews et al. 2002). *Granules* are large agglomerates that have increased in size through the addition of granulating agents such as thermoplastics (paraffin wax) in polymer-based binders needed to improve the flow characteristics of the powder.

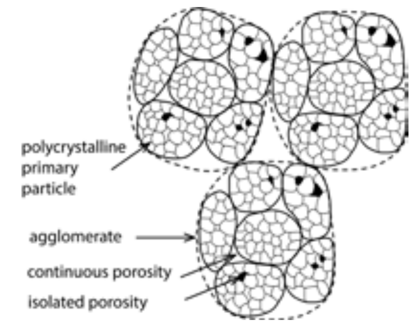

Fig. 2: Schematic powder representation showing agglomerates consisting of polycrystalline primary particle. Porosities may be intraparticle (isolated), interparticle (continuous) or interagglomerate. Schematic adapted from Rahaman M.N. (Rahaman 2007)

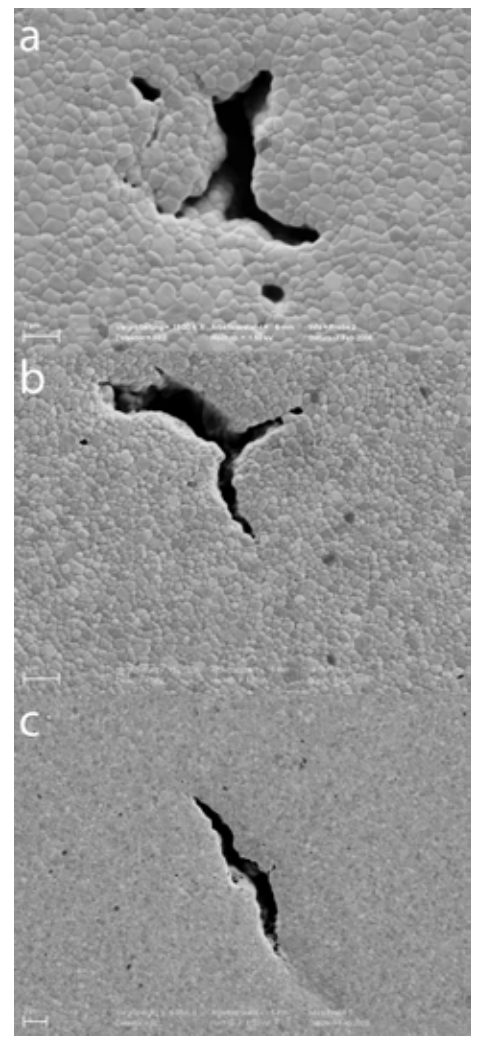

Fig. 3: Typical powder consolidation defects. Fig. 3a (15,000x) illustrates a non-critical defect size of approx. 5x6 µm and 3Y-TZP microstructure averaging 450 µm grain size. Figs. 3b (15,000x) and c (5,000x) show a different 3Y-TZP microstructure with an average grain size of 300 µm. The defect in Fig. 3b is similar to Fig. 3a, and is not critical, averaging 6x7 µm. Whereas the defect in Fig. 3c is elongated and approx. 15 µm in length, corresponding to a critical size starter crack for classic 3Y-TZP

The powder characteristics include granule morphology, size, density, type and wt% of binders, all of which influence compaction behavior and green body properties.
Most dental Y-TZPs are produced from high-purity powders usually obtained by co-precipitation techniques that guarantee homogenous distribution of the yttria content throughout the starting powder (Burger et al. 1997). Only companies that are highly knowledgeable about powder synthesis will provide the necessary powder quality for biomedical materials. Uniform submicrometer-particle-size powders are currently produced by companies like Tosoh in Japan (Chevalier et al. 2009; Palmero et al. 2014) or Metoxit (Switzerland) and have high sinterability, resulting in final components with a density near the theoretical values (Burger et al. 1997). Implant manufacturers usually choose their powder from the powder selections available and depending on the application, the consolidation method and sintering schedule used to obtain the desired microstructure. These powders will already have the specific mixture of binders and additives for improved flowability during the *consolidation* step.

Consolidation

Several methods can be used for pressing the powder into a form such as *die pressing, injection molding, slip casting* or *plastic forming*. Die pressing is usually performed using cold isostatic pressing (CIP) with pressures between 100 and 300 MPa. A 3Y-TZP green body (TZ3YSEB, Tosoh) CIPed at 300 MPa and presintered at 900°C for 2 hours will have a relative green compact density of 51% versus 47% if pressed at 100 MPa (Andrews et al. 2002). However, the granules should not be too dense as it has been shown that granules with 30% density will give the best biaxial flexure strength of the final sintered zirconia regardless if pressed at 100 or 300 MPa (Andrews et al. 2002). The strength of zirconia will be affected by the flaw population and distribution resulting during consolidation (such as die pressing or injection molding) as the granules may not be completely compacted. Defects (voids) may remain in between adjacent granules which could not be sufficiently deformed or joined during compaction. Fig. 3 shows such compaction defects visible in the microstructure of two different 3Y-TZPs after CIP and sintering. The zirconia in Fig. 3a had a sinter temperature of 1465°C (Zeno, Wieland), whereas the zirconia in Fig. 3b and c was sintered at 1350°C (Cercon, Dentsply). From known fracture mechanics relationships, the critical flaw size for a 3Y-TZP will be around 15 µm in depth for a zirconia that has a fracture toughness (K_{Ic}) of 5 MPa√m and a flexure strength of 1000 MPa. In Figs 3a and b, the flaws (voids) resulting from die pressing are not critical as they are approximately 6x7 µm in size. However, in Fig. 3c the flaw is elongated in shape and reaches a length of 15 µm. If such flaws are scarce and represent a very small volume, they may not be relevant. However, if such flaws are spread out over the surface, chances are that they will be located in an area were tensile stresses occur and concentrate, such as between two threads near the bone level. In this case the implant would be at risk for an early catastrophic fracture.

Sintering

During *sintering*, densification of the green body occurs by joining of the particles and reducing the number of pores until the desired microstructure is obtained. Depending on the sinter temperature and schedule, the microstructure will show different average grain sizes (Denry & Kelly 2014). Fig. 4 illustrates such grain size differences for two different 3Y-TZPs. Fig. 4a, Zeno (Wieland), sinter temperature 1465°C, grain size average of 380 µm; Fig. 4b, Lava colored (3M Espe), sinter temperature 1500°C, average grain size 640 µm (Scherrer et al. 2011).

Excessive localized grain growth of the cubic phase due to a local concentration of oxide stabilizers (Y_2O_3) from yttrium-depleted neighboring tetragonal grains

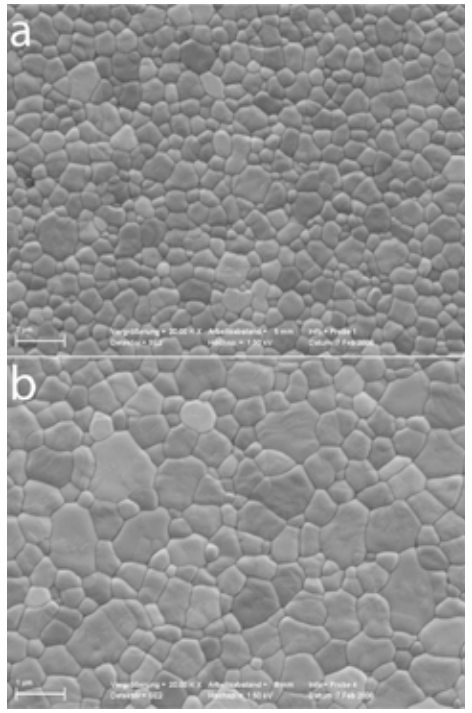

Fig. 4: Microstructure of two different 3Y-TZPs showing average grain sizes of 380 µm (a) and 640 µm (b) (Scherrer et al. 2011)

(Denry 2013) is detrimental to the mechanical properties. The more cubic zirconia phase that is present, the less tough the zirconia. This was already common knowledge back in 1982 with experimental observation in the ZrO_2 – Y_2O_3 system showing a decrease in toughness as the volume fraction of tetragonal phase decreases and the cubic phase increases. Around 7 mol% of the system is fully cubic and has a toughness not higher than 3 MPa√m (Lange 1982). Other research papers have shown excessive grain growth as being the origin of cracks in mechanically tested 3Y-TZP in vitro specimens (Scherrer et al. 2011; Scherrer et al. 2017).

Additional density can be obtained by Hot Isostatic Pressing (HIP), in which an isostatic pressure (100-200 MPa) is applied through a gaseous (argon) or liquid (nitrogen) medium at an elevated temperature. HIP is important to further densify the bulk of the product, mainly by closing up some porosity by viscoplastic deformation of the grains, but will not be able to repair surface flaws or larger volume defects (Scherrer et al. 2013).

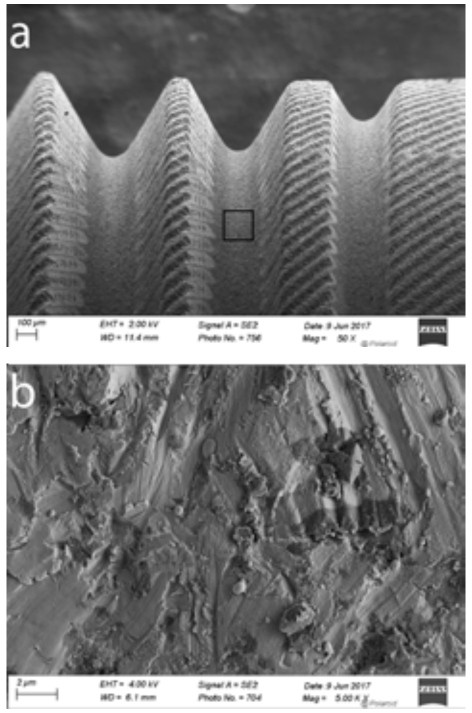

Fig. 5: Zirkolith Z5m implant (Z-Systems) showing a variety of surface textures. The area of interest is marked with a black rectangle (a). At 5,000x magnification, (b) the surface shows grinding and sandblasting marks

Characterization of implant surfaces
Depending on the processing, the final surface will have different characteristics and textures depending on the location on an implant such as the collar, the threads or the portion in between two threads in terms of micro- and macro-roughness. The implant surface is critical on all levels. Firstly, the surface integrity will dictate the mechanical behavior of the zirconia much more than the bulk of the implant as tensile stresses will concentrate on the surface at locations under tension or bending where minute surface defects, scratches, microcracks from sandblasting or grinding damage are present. Secondly, the surface characteristic will play a major role in the osseointegration for which some roughness is needed but not exclusively. As osseointegration is covered later in this issue, we will focus on the mechanical part of the implant surface. It would go beyond the scope of this paper to summarize all the newest surfaces from every zirconia manufacturer of dental implants. This paper therefore focuses on a few examples of current surface textures documented in the center region between two threads

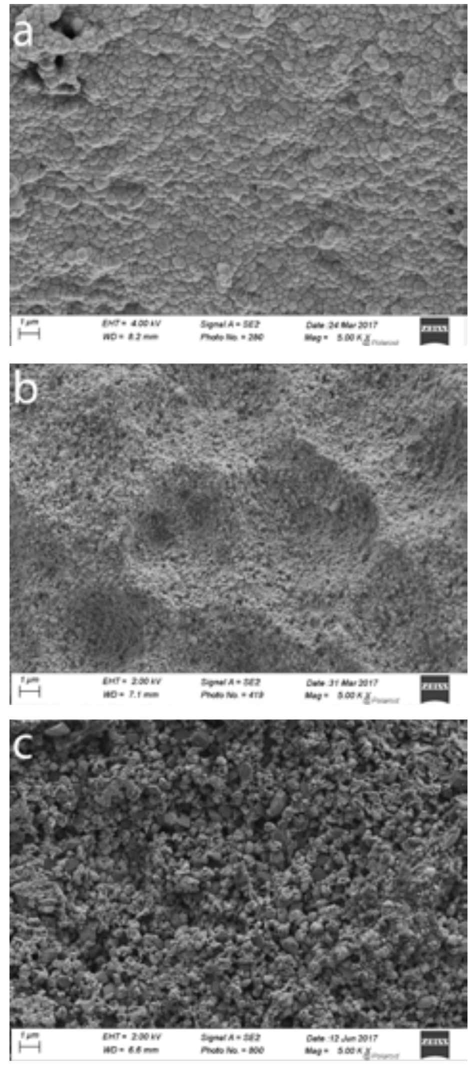

Fig. 6: (a) Axis Monobloc (Axis Biodental) processed by injection molding and further HIPed. Zirconia grains are densely sintered; (b) Straumann PURE Ceramic (3Y-TZP) (Straumann) after sandblasting followed by acid etching; (c) Zeramex P6 (ATZ) (Dentalpoint AG, CH) after sandblasting and acid-etching. The alumina particles of the ATZ are the larger and darker grains, which were not affected by the etching process, partially eroding the zirconia grains. All images are taken at 5,000x magnification and without any goldsputtering

because this is the area where stresses concentrate and fractures may occur (El-Anwar & El-Zawahry 2011). The SEM images are taken without any goldsputtering of the surface. Fig. 5 represents a 3Y-TZP-A Bio-HIP implant (Zirkolith Z5m, Z-Systems). The black rectangle area has been magnified at 5,000x in Fig. 5b showing a sandblasted surface with large alumina particles (> 100 µm size) combined with grinding marks from machining. In a similar configuration area between two threads, Figure 6a is an injection-molded 3Y-TZP-HIP with a densely sintered tetragonal grain structure (5,000x). Fig. 6b represents a 3Y-TZP implant surface (5,000x) that has been sandblasted with large alumina particles (105-140 µm) and acid-etched (H_3PO_2) (PURE ceramic, Straumann). The zirconia particles have been in part etched away, providing a micro-rough and alveolar-like structured pattern. Fig. 6c shows a Zeramex P6 implant (Dental Point AG), which is an alumina-toughened zirconia (ATZ) with a composition of 76 wt% ZrO_2, 20% Al_2O_3 and 4% Y_2O_3. As with the Straumann PURE Implant, the surface has been sandblasted and acid-etched. The larger and darker particles are alumina grains that were not eroded by the acid treatment.

CERAMIC ENGINEERING DESIGN

In contrast to titanium or titanium alloys, zirconia and its modifications present a highly brittle material response to mechanical loading. While titanium might plastically compensate certain overloads, zirconia would result in spontaneous fracture, despite its enhanced fracture toughness (Cesar et al. 2017). Overloading with regard to implant failure might arise either from manufacturing defects, improper placement or from biomechanical overloading during mastication (Gahlert et al. 2012; Osman et al. 2013).

Specific limitations in ceramic implant reliability can be assigned either to a macroscopic, design-controlled level or to a microscopic, surface-controlled level. The macroscopic engineering design of brittle zirconia implants could not be simply adopted from a ductile titanium implant, and new concepts needed to replace existing designs, with a special focus on the overall shape and thread design.

Implants are generally exposed to high loads either during placement or oral function. Bending and torque moments are often superimposed, leading to a complex load transfer through an implant. Design optimization thus often employs the aid of numerical simulation (finite element method, FEM) in order to analyze the stress state (maximum principle stress theory) based on a specific loading scenario and specific material conditions (Ashby 2017).

A proper ceramic engineering design seeks to prevent local stress concentrations arising from geometrical insufficiencies, sharp angles or surface defects. The art of ceramic engineering design therein is to convert deleterious tensile stresses into a more favorable bending or compressive stress state (Clark et al. 2006). High tensile stresses commonly concentrate along the implant axis during functional loading and at the thread surface while torquing the implant. Therefore the main regions to be focused on are the implant geometry and the thread design. The implant-abutment interface in two-piece implants (not the focus of this contribution) with the accompanying internal threads are even more complex to design.

Design of the implant
Fig. 7 shows different zirconia implant designs. Failure analysis of broken implants have identified the transition between the neck and the microtexturized thread (commonly the first one or two helices) as the weak link leading to fracture (Gahlert et al. 2012; Osman et al. 2013).

The critical factor is definitely the cross-sectional area in the root of a thread. One clinical study reports 10% fractures in the neck/thread interface region after 3 years of service (Gahlert et al. 2012). The authors observed a 92% fracture rate on diameter-reduced implants (3.25 mm) mainly in the anterior and premolar region, accounting for a clear bending overload. For proper biomechanical integrity of a ceramic implant, the length, diameter and tapering of the implant body are of major importance (Osman et al. 2013). Finite element studies on implant geometries reveal the importance of a sufficient cross-sectional area (El-Anwar & El-Zawahry 2011; Himmlova et al. 2004). These numerical studies in principal conclude that the longer the design of an implant, the less important its cross-section. It is clear that smaller and shorter implants increase the stress to the bone level (Rieger et al. 1990). The implant aspect ratio might be interesting for the bone-implant stability since the interfacial surface area of implants with different aspect ratios remain comparably constant, but this has only little effect on the bending moment at the neck/thread interface. The cross-section – especially in the root of the thread – is of major importance and should not fall below 4 mm in diameter (Gahlert et al. 2012). A tapered intraosseous implant geometry is therefore favorable over cylindrical shapes (Rieger et al. 1990). In order to prevent structural fracture and to retain implant stability, the implant diameter at the gingival level needs to be sufficiently wide. Tapering should be kept to a minimum in order to preserve the strength arising from a sufficiently wide cross-section (Osman et al. 2013).

Over time, ongoing bone resorption decreases the osseous support around an implant, leading to increasing bending moments in the gingival region of the exposed thread (Osman et al. 2013).

While one-piece ceramic implants are becoming increasingly accepted in clinical application, two-piece implants are still controversial. This is mainly due to their complex interface between the intraosseous implant and the prosthetic

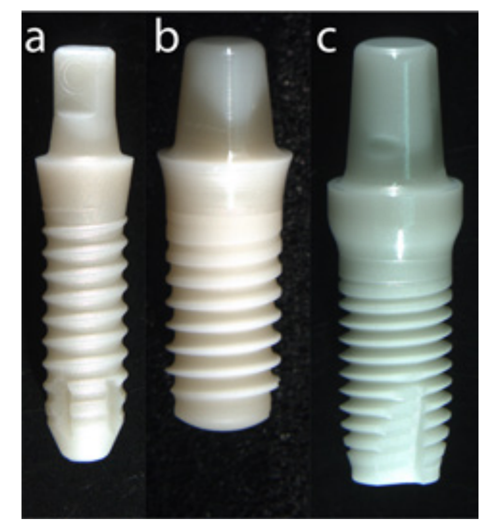

Fig. 7: Three different one-piece implants: a) Axis Monobloc (Axis Biodental, CH), b) PURE Ceramic (Straumann, CH) and c) Zirkolith Z5m (Z-Systems, CH)

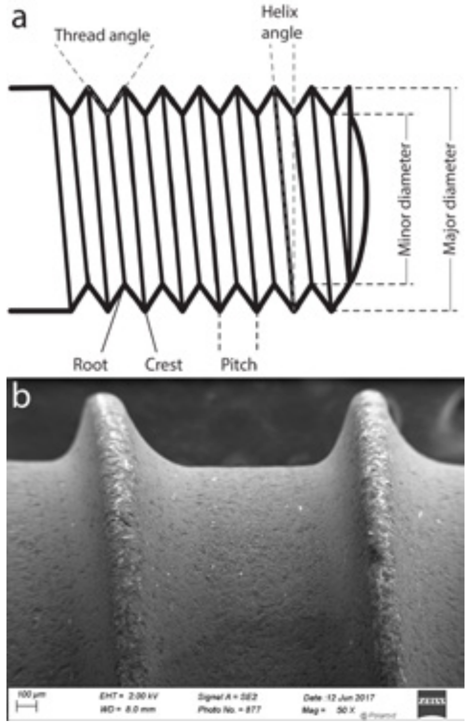

Fig. 8: Principle thread description (a) and optimized thread crest-root design for a zirconia implant (Zeramex P6, Dentalpoint AG, CH)

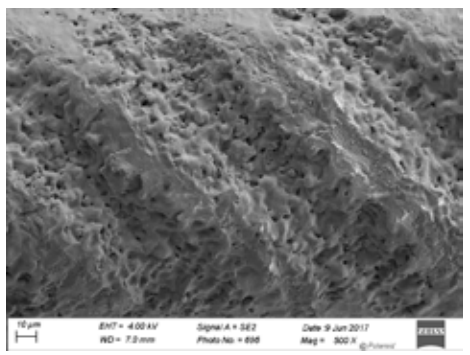

Fig. 9: Detailed magnification of Fig. 5a showing the textured surface at a crest (Zirkolith Z5m implant). Laser treatment has modified the zirconia. Note the presence of regularly spaced grooves (magnification 500x)

abutment. This is the engineering design issue to be solved that today still limits the clinical acceptance of zirconia implants.

Design of a ceramic thread

Threads on implants can be found on the external intraosseous surface of an implant as well as internally in a two-piece implant in order to connect with the abutment. While the stability of the internal thread is mainly defined by the cross-section of the remaining implant support, the external thread is exposed to torque moments during placement and bending moments during function. A thread is generally characterized as shown in Fig. 8a. The design will vary quite a bit between zirconia implants (Fig. 7). Areas such as the crest, the thread angles, and especially the minor root diameter will all play a role in the final mechanical behavior (Himmlova et al. 2004). Fig. 8b shows an ATZ implant (Zeramex P6) with a much wider root portion in between two crests when compared to the Z-System implant in Fig. 5a.

High contact loads and high stress concentrations in the thread roots might lead to problems, particularly if the bone-implant joint is over-tightened. Thus extreme care should be taken when designing ceramic threads and best practice (correct torque) must be employed.

Sharp angles are contraindicated in ceramic engineering as well as any sites for stress concentration (Clark et al. 2006). For a ceramic thread, this focuses particularly on the root design, the thread angles and the sharpness of the crest. While numerical simulation identified an optimal stress distribution in titanium implants using a v-shaped thread design (Geng et al. 2004), an ideal ceramic thread requires rounded root and crest regions, a reduced thread depth and moderate helix angles (Osman et al. 2013). An example is shown in Fig. 8b. On the other hand, it has been demonstrated that the stress distribution in cortical bone seemed not to be influenced by the thread design (Geng et al. 2004).

Microtexturization of the implant surface

The microscopic design of the intraosseous implant surface is of key importance regarding osseointegration and long-term stability (Rupp et al. 2017). The determining parameters not only for titanium but also for zirconia implants are the surface roughness and the three-dimensional topography (Al Qahtani et al. 2017). As with titanium alloys, zirconia surfaces are treated via machining, sandblasting, etching or coating processes (Bormann et al. 2012). Severe sandblasting, typically applied using rough alumina powders (250 µm) at high pressure (5 bars) results in a mean roughness of below 1µm (Gahlert et al. 2007). Some more macroscopic texturization is applied on the external thread during machining in order to increase the level of osseointegration or by modification with laser treatment, as can be seen in Fig. 9 (Z-Systems). Surface grooves in the range of up to 20 µm can be recognized at the crest of a thread.

Considering microscopic texturization as potential surface defects and bearing in mind the stress concentration arising from surface defects, zirconia is still able to retain high strength due to its comparably high fracture toughness between 4 and 6 $MPam^{0.5}$ (3Y-TZP: $K_{Ic} = 4.6\ MPam^{0.5}$) (Belli et al. 2015; Scherrer et al. 2017). However, grinding on zirconia with 75 µm diamond disks may create some critical damage (Canneto et al. 2016). Based on principles of fracture mechanics, the authors calculated a drop of 41% in strength for maximum chip sizes of 28 µm in depth. Further superimposed, repetitive loading over time and during oral function might induce material degradation leading to slow crack growth at the zirconia surface (Scherrer et al. 2011).

LOW TEMPERATURE DEGRADATION (LTD)

In the case of Y-TZP, being a smart material comes with a drawback. The very property of metastability that is responsible for the transformation toughening mechanism that provides resistance against crack initiation and growth, also enables spontaneous phase *(t → m)* transformation in the absence of any triggering mechanical stress. This can take place at temperatures as low as body temperature (Keuper et al. 2014), thus the term *low temperature degradation* (LTD). For this, the mere presence of moisture suffices (therefore, the alternative terminology *hydrothermal aging*), which plays a role in a process that is still not entirely understood. The most accepted theory points the finger at the oxygen anions dissociated from the otherwise seemingly harmless water molecule; they are believed to occupy free spaces (vacancies) in the crystal's basic structure (lattice), causing it to change shape (Chevalier et al. 2009). After that, distances and angles between atomic bonds are no longer those found in the tetragonal form. This is invariably accompanied by a slight increment in volume that apparently increases the susceptibility of the surrounding structure to undergo the same fate, in what is known as a nucleation-and-growth process (Chevalier et al. 1999). Starting at the surface, continuous contact with water feeds the transformation mechanism further to progress into the interior of the material (Fig. 10). This is not a process of water sorption, but rather a diffusion-controlled chemical reaction. The repercussions of this phenomenon are felt first at the nanometric scale without much danger to the material's integrity, but slowly evolve into macroscopic alterations like surface roughening, micro-cracking, grain pull-out and ultimately surface pitting. Such apparently innocuous degradation effects suddenly gained attention after an abnormally large number of medical grade zirconia (3Y-TZP) femoral heads fractured in service in the early 2000s much sooner than anticipated for this material class. Analyses of those broken hip joint prostheses revealed advanced signs of LTD, which in association with the concomitant mechanical wear process, accounted for the cause of the mechanical deterioration leading to premature fractures (Chevalier & Gremillard 2009). Since then, most of the research effort involving zirconia-based materials has been directed towards understanding LTD. The inertia of this endeavor has caught up with the dental research materials science community due to the increasingly popular use of 3Y-TZP in prosthodontics and implantology.

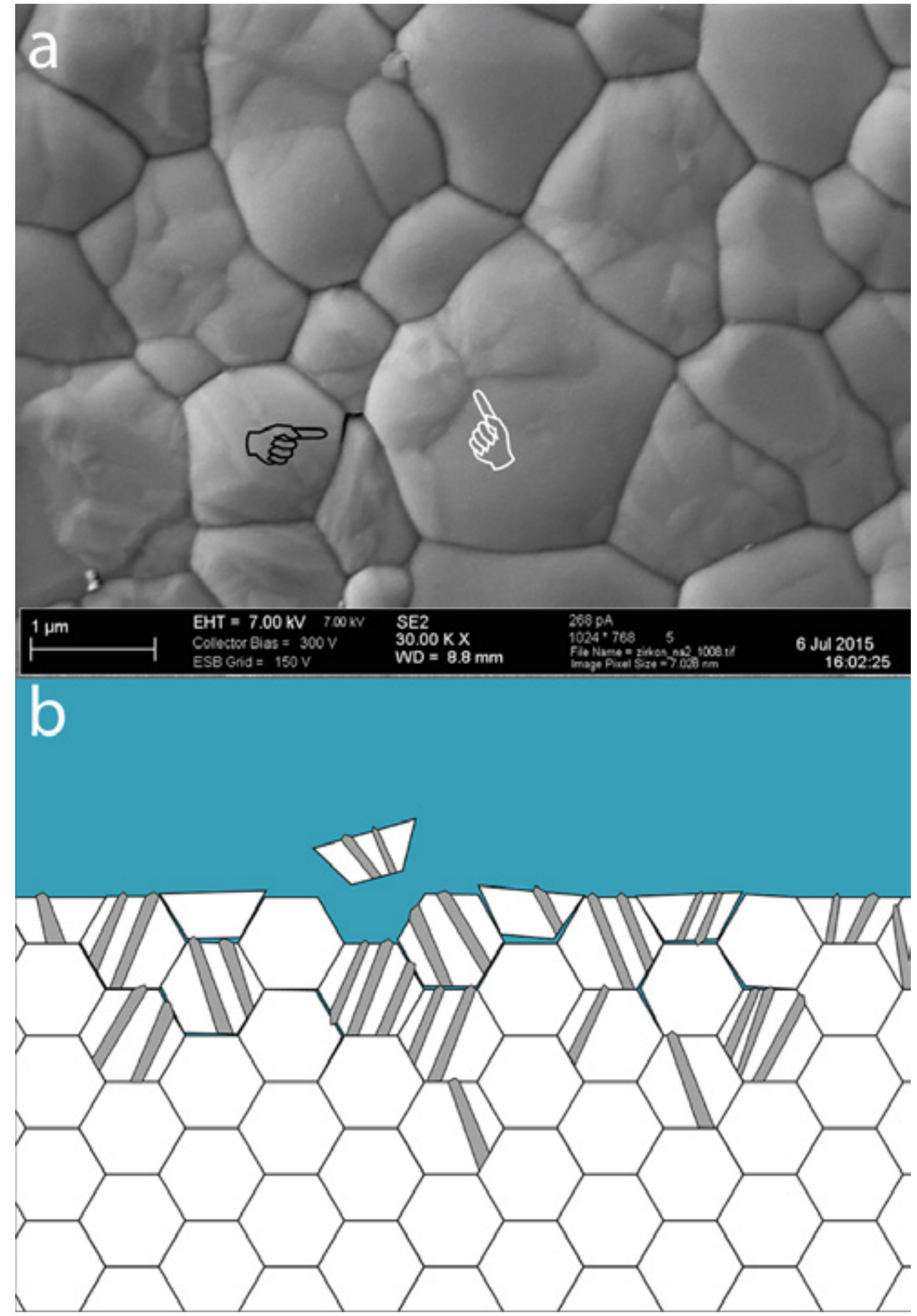

Fig. 10: (a) SEM image of a dental zirconia showing initial signs of LTD on the surface with partially transformed grains (white pointer) and cracking at grain boundaries (black pointer). (b) Schematic of LTD evolving into the zirconia bulk, showing cracking at grain boundaries between partially transformed grains (stripes) and untransformed grains (no stripes) creating a path for water diffusion

But is LTD of any relevance to the mechanical stability of dental zirconia prostheses/implants over time? This response is not unjustified, it merely embodies the general lack of consensus in the scientific literature. We have to put our intuition to one side and look at the evidence. In that one episode of mass fracture of orthopedic 3Y-TZP hip implants, the underlying cause in a chain of events was attributed to newly introduced – deficient – fabrication steps leading to high porosity batches (Chevalier et al. 2007). Further machining the sintered piece induced surface residual stresses, which is believed to have given a too high momentum to a process (LTD) that normally takes a long time to become significant in the body. There are some mixed messages, as some in-vitro mechanical testing in simple specimen geometries have shown the negative effect of LTD on bending strength (Marro et al. 2014; Siarampi et al. 2014), while many others found the opposite (Kim et al. 2009; Virkar et al. 1987), also when using actual implants in load-to-fracture tests (Sanon et al. 2013). The mechanisms behind the effect of LTD on a material's strength are related to the zone of compressive (strengthening) stresses generated by the transformation itself, the resulting tensile (weakening) stress zone generated underneath the transformed zone (Caravaca et al. 2017), and how this change in stress state affects the natural defect population of the material. In addition, new surface/subsurface defects are generated, which at some point begin to dominate fracture initiation behavior (Marro et al. 2014). It all seems to depend on how far LTD is allowed to evolve (Siarampi et al. 2014); either way, it seems clear that testing methodologies for surgical Y-TZP implants (e.g., ISO 13356) are inadequate and need to adapt their requirements to accommodate more clinically relevant aspects (Sanon et al. 2015).

Here is what is known so far: more than a handful of factors affect the susceptibility and evolution rate of LTD in zirconia-based ceramics. In regard to Y-TZP, these are mainly grain size (controlled mainly by sintering temperature) (Cotic et al. 2016; Hallmann et al. 2012a; Li & Watanabe 1998), amount of alloying oxides (Y_2O_3, CeO_2, Al_2O_3) (Hallmann et al. 2012b; Palmero et al. 2015; Tsubakino et al. 1993; Zhang et al. 2014) and initial amount of cubic phase in the as-sintered material (Chevalier et al. 2009). Of special concern to dental implants are factors relating to surface modification. Post-sintering sandblasting and roughening the surface, for example, as opposed to polishing it, induce compressive stresses beneficial to the strength of the piece and its resistance to LTD (Cattani-Lorente et al. 2014; Deville et al. 2006). Annealing seems to reverse those effects and further increase the LTD rate (Cattani-Lorente et al. 2014). The production of ever more complex – patentable – surface topographies has become a gold rush for companies, often disregarding the potential effects on the material's mechanical integrity. It has been observed, for instance, that creating a surface texture by crater formation may induce large surface defects that reduce the implant's load to failure (Sanon et al. 2015). In a similar approach, a porous surface produced by sintering a coat of zirconia powder + pore former resulted in a surface scaffold of tridimensional interconnecting channels with pre-transformed grains around the pores, which showed increased susceptibility to LTD (Sanon et al. 2015). That particular surface coating was abandoned in 2011 by the manufacturer. The same coated implant however, when subjected to accelerated aging, showed increased resistance against mechanical cyclic fatigue (Sanon et al. 2013). A morphological analysis of differently surface-treated zirconia implants also found that the effects of LTD simulating up to 60 years *in vivo* were limited to the outer 5-µm-layer (Monzavi et al. 2017). Despite that, authorities in the field seem reluctant to endorse LTD as a phenomenon that is benign to the long-term stability of zirconia dental implants, and recommend avoiding it altogether (Lughi & Sergo 2010; Sanon et al. 2013). This is based on the general scarcity of experiments that probe the fracture behavior of LTD-degraded zirconia mechanistically, not just deterministically. How LTD would evolve in the body over time and which influencing variables are involved, are all unknowns. Added to that, the highest level of evidence – one resulting from well-controlled clinical trials – does not seem to exist to have a say.

Yet, despite the insufficient amount of evidence showing that LTD may or may not be prejudicial to the long-term mechanical stability of dental implants, dentists are adhering to the zirconia trend. The elephant never left the room.

CONCLUSION

Zirconia implants will always have two equally important challenges 1) The biomechanics and fracture behavior of the zirconia or zirconia composite dictated by the material's processing, design, surface stress, surface texture within a clinical environment; 2) the biology for best osseointegration dictated by surface texture and surface functionalization.

From the biomechanics side only the analysis of clinically failed implants will be able to provide the necessary scientific information on the nature of flaws responsible for failure, the fracture pattern and the possible LTD on the surface of the implant (LTD) along with all the other critical parameters such as implant diameter, design and bending moment.

Unfortunately there is little to no fractographic failure analysis currently performed on zirconia implants mainly due to the difficulty of obtaining clinically fractured parts. However, in order to improve design, surface treatment, processing and composition, such fractographic analyses are desperately needed, even if the statistics for failures are small. This group of authors has shown expertise and capability in fractographic failure analysis as well as research on low temperature degradation and would welcome the opportunity to help clinicians who experience zirconia implant fractures to understand the reasons for failure.

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