

available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.intl.elsevierhealth.com/journals/dema](http://www.intl.elsevierhealth.com/journals/dema)

# State of the art of zirconia for dental applications

Isabelle Denry<sup>a,\*</sup>, J. Robert Kelly<sup>b</sup>

<sup>a</sup> Department of Restorative and Prosthetic Dentistry, The Ohio State University, College of Dentistry, 305 West 12th Avenue, Columbus, OH 43210, USA

<sup>b</sup> Department of Reconstructive Sciences, University of Connecticut Health Center, Farmington, CT, USA

## ARTICLE INFO

### Article history:

Received 24 April 2007

Accepted 11 May 2007

### Keywords:

Dental ceramics

Zirconia

3Y-TZP

Machining

Clinical performance

## ABSTRACT

Zirconia has been recently introduced in prosthetic dentistry for the fabrication of crowns and fixed partial dentures, in combination with CAD/CAM techniques. This review encompasses the specific types of zirconia available in dentistry, together with their properties. The two main processing techniques, soft and hard machining, are assessed in the light of their possible clinical implications and consequences on the long-term performance of zirconia. An update on the status of clinical trials occurring worldwide is provided.

© 2007 Academy of Dental Materials. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Zirconia holds a unique place amongst oxide ceramics due to its excellent mechanical properties. This situation ensues from the considerable amount of research work that has been carried out since the discovery of the transformation toughening capabilities of zirconia in the mid-1970s [1].

At ambient pressure, unalloyed zirconia can assume three crystallographic forms depending on the temperature. At room temperature and upon heating up to 1170 °C, the symmetry is monoclinic ( $P2_1/c$ ). The structure is tetragonal ( $P4_2/nmc$ ) between 1170 and 2370 °C and cubic ( $Fm\bar{3}m$ ) above 2370 °C and up to the melting point [2,3]. The transformation from the tetragonal ( $t$ ) phase to the monoclinic ( $m$ ) phase upon cooling is accompanied by a substantial increase in volume (~4.5%), sufficient to lead to catastrophic failure. This transformation is reversible and begins at ~950 °C on cooling. Alloying pure zirconia with stabilizing oxides such as CaO, MgO, Y<sub>2</sub>O<sub>3</sub> or CeO<sub>2</sub> allows the retention of the tetragonal structure at room temperature and therefore the control of the stress-induced

$t \rightarrow m$  transformation, efficiently arresting crack propagation and leading to high toughness [1,4,5].

The recent introduction of zirconia-based ceramics as restorative dental materials has generated considerable interest in the dental community. The mechanical properties of zirconia are the highest ever reported for any dental ceramic. This may allow the realization of posterior fixed partial dentures and permit a substantial reduction in core thickness. These capabilities are highly attractive in prosthetic dentistry, where strength and esthetics are paramount. However, due to the metastability of tetragonal zirconia, stress-generating surface treatments such as grinding or sandblasting are liable to trigger the  $t \rightarrow m$  transformation with the associated volume increase leading to the formation of surface compressive stresses, thereby increasing the flexural strength but also altering the phase integrity of the material and increasing the susceptibility to aging [6]. The low temperature degradation (LTD) of zirconia is a well-documented phenomenon, exacerbated notably by the presence of water [7–12]. The consequences of this aging process are multiple and include

\* Corresponding author. Tel.: +1 614 292 0905; fax: +1 614 292 9422.

E-mail address: [denry.1@osu.edu](mailto:denry.1@osu.edu) (I. Denry).

0109-5641/\$ – see front matter © 2007 Academy of Dental Materials. Published by Elsevier Ltd. All rights reserved.

doi:10.1016/j.dental.2007.05.007

surface degradation with grain pullout and microcracking as well as strength degradation. Although LTD has been shown to be indirectly associated with a series of femoral head prostheses failures in 2001 and despite a well established definition of the conditions for which LTD is susceptible to occur, there seem to be no clear relationship between LTD and failure predictability when zirconia is used as a bioceramic [13]. Greater insight into LTD is proposed in a companion review.

The various types of zirconia commercially available in dentistry are summarized in the first part of this article. The adequacy of surface treatments and their possible consequences on the reliability of zirconia for dental restorations is also examined. An update on the status of clinical trials occurring worldwide is provided.

## 2. Different types of zirconia ceramics available for dental applications

Although many types of zirconia-containing ceramic systems are currently available [14,15], only three are used to date in dentistry. These are yttrium cation-doped tetragonal zirconia polycrystals (3Y-TZP), magnesium cation-doped partially stabilized zirconia (Mg-PSZ) and zirconia-toughened alumina (ZTA).

### 2.1. 3Y-TZP

Biomedical grade zirconia usually contains 3 mol% yttria ( $Y_2O_3$ ) as a stabilizer (3Y-TZP)[16]. While the stabilizing  $Y^{3+}$  cations and  $Zr^{4+}$  are randomly distributed over the cationic sites, electrical neutrality is achieved by the creation of oxygen vacancies [17,18]. 3Y-TZP has been used to manufacture femoral heads in total hip replacement prostheses since the late eighties but its use in orthopedic surgery has since been reduced by more than 90%, mostly due to a series of failures that occurred in 2001 [13]. 3Y-TZP is available in dentistry for the fabrication of dental crowns and fixed partial dentures. The restorations are processed either by soft machining of pre-sintered blanks followed by sintering at high temperature, or by hard machining of fully sintered blocks [19].

The mechanical properties of 3Y-TZP strongly depend on its grain size [14,20,21]. Above a critical grain size, 3Y-TZP is less stable and more susceptible to spontaneous  $t \rightarrow m$  transformation whereas smaller grain sizes ( $<1 \mu m$ ) are associated with a lower transformation rate [22]. Moreover, below a certain grain size ( $\sim 0.2 \mu m$ ), the transformation is not possible, leading to reduced fracture toughness [23]. Consequently, the sintering conditions have a strong impact on both stability and mechanical properties of the final product as they dictate the grain size [2]. Higher sintering temperatures and longer sintering times lead to larger grain sizes [21,24,25].

Currently available 3Y-TZP for soft machining of dental restorations utilize final sintering temperatures varying between 1350 and 1550 °C depending on the manufacturer. This fairly wide range of sintering temperatures is therefore likely to have an influence on the grain size and later the phase stability of 3Y-TZP for dental applications. From the phase diagram established by Scott, 3Y-TZP contains some amount of cubic zirconia [24]. Chevalier et al. demonstrated

that the presence of cubic zirconia is not desirable in 3Y-TZP for biomedical applications and is caused by uneven distribution of the yttrium stabilizer ions. The cubic grains are enriched in yttrium while the surrounding tetragonal grains are depleted and therefore less stable [25]. As mentioned earlier, restorations produced by soft machining are sintered at a later stage (i.e. following the forming steps), this process prevents the stress-induced transformation from tetragonal to monoclinic and leads to a final surface virtually free of monoclinic phase unless grinding adjustments are needed or sandblasting is performed. Most manufacturers of 3Y-TZP blanks for dental applications do not recommend grinding or sandblasting to avoid both the  $t \rightarrow m$  transformation and the formation of surface flaws that could be detrimental to the long-term performance, despite the apparent increase in strength due to the transformation-induced compressive stresses. In contrast, restorations produced by hard machining of fully sintered 3Y-TZP blocks have been shown to contain a significant amount of monoclinic zirconia [26]. This is usually associated with surface microcracking, higher susceptibility to low temperature degradation and lower reliability [27]. Liu et al. studied the fatigue behavior of 3Y-TZP [28]. The preexisting processing flaws were identified as the fracture origin in all cases and microcracking was shown to be the dominant mechanism of fatigue damage. More recently, Zhang et al. studied the effect of sharp indentation damage on the long-term performance of 3Y-TZP. It was shown that both sandblasting and sharp indentations even at very low loads are detrimental to the long-term performance of 3Y-TZP when tested in cyclic loading [29–31]. These studies pointed out the importance of controlling the final surface state of 3Y-TZP for biomedical applications. In summary, even if high strength might appear as a beneficial property for dental applications, long-term performance and reliability should also be considered.

Several authors have reported that annealing at 900 °C for 1 h or relatively short heat treatments in the temperature range 900–1000 °C for 1 min induce the reverse transformation from monoclinic to tetragonal [32,33]. This phenomenon was accompanied by the relaxation of the compressive stresses at the surface and a decrease in strength. The firing of veneering porcelain during the fabrication of dental restorations is therefore likely to promote the reverse transformation with the consequences listed above. In addition, the reversibility of the transformation should not be confused as providing a mechanism for healing of the flaws previously introduced (Fig. 1).

The microstructure of 3Y-TZP ceramics for dental applications consists of small equiaxed grains (0.2–0.5  $\mu m$  in diameter, depending on the sintering temperature) [26]. A representative micrograph is shown in Fig. 2. The mechanical properties are well above those of all other available dental ceramics, with a flexural strength in the 800–1000 MPa range and a fracture toughness in the 6–8  $MPa m^{0.5}$  range. The Weibull modulus strongly depends on the type of surface finish and the processing conditions [34]. Fig. 3 shows a Vickers indentation in a commercially available 3Y-TZP for dental applications under a 98.1 N load. Only one short crack is emanating from one of the corners of the indentation. The absence of cracking from the other corners is indicative of the occurrence of the transformation toughening mechanism.

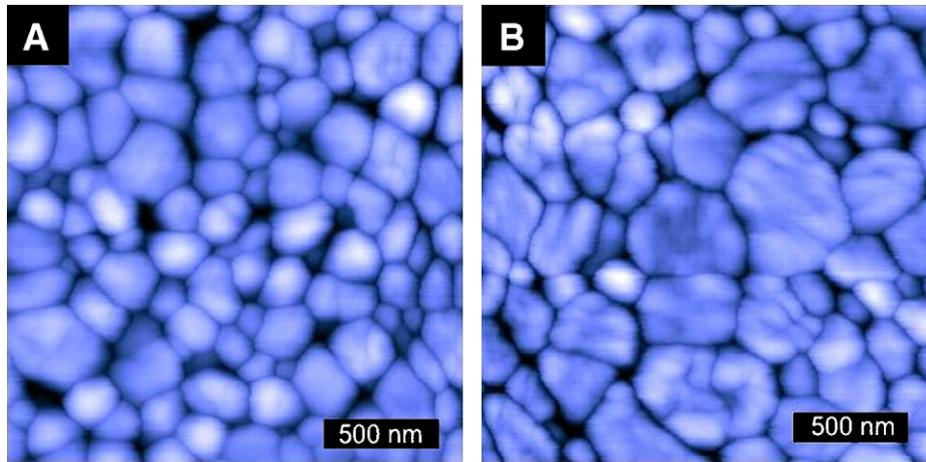


Fig. 1 – Atomic force micrographs (contact mode) of 3Y-TZP sintered at 1300 °C (A) and 1450 °C (B).

## 2.2. Glass-infiltrated zirconia-toughened alumina (ZTA)

Another approach to advantageously utilize the stress-induced transformation capability of zirconia is to combine it with an alumina matrix, leading to a zirconia-toughened alumina (ZTA) [35,36]. These materials have recently received interest as potential bioceramics [37,38]. One commercially available dental product, In-Ceram® Zirconia® (Vident™, Brea, CA), was developed by adding 33 vol.% of 12 mol% ceria-stabilized zirconia (12Ce-TZP) to In-Ceram® Alumina® [39]. In-Ceram® Zirconia® can be processed by either be slip-casting or soft machining. Initial sintering takes place at 1100 °C for 2 h, prior to this porous ceramic composite being glass-infiltrated. The glass phase represents approximately 23% of the final product. The microstructure of In-Ceram® Zirconia® is shown in Fig. 4, in which the zirconia grains appear brighter compared to the darker alumina grains. One of the advantages of the slip-cast technique is that there is very limited shrinkage. However, the amount of porosity is

greater than that of sintered 3Y-TZP and comprises between 8 and 11% [40]. This partially explains the generally lower mechanical properties of In-Ceram® Zirconia® when compared to 3Y-TZP dental ceramics [26]. It should be pointed out, however, that Ce-TZP ceramics usually exhibit better thermal stability and resistance to low temperature degradation than Y-TZP under similar thermo-cycling or aging conditions [41,42].

In-Ceram® Zirconia® for machining is thought to exhibit better mechanical properties due to more consistent processing compared to the slip-cast ceramic. Conversely, Guazzato et al. reported a significantly higher flexural strength for In-Ceram® Zirconia® processed by slip-casting ( $630 \pm 58$  MPa) compared to the machined material ( $476 \pm 50$  MPa) [43]. There was no significant difference in fracture toughness. The two materials exhibited a very similar microstructure with large alumina grains ( $6 \mu\text{m}$  long,  $2 \mu\text{m}$  wide) together

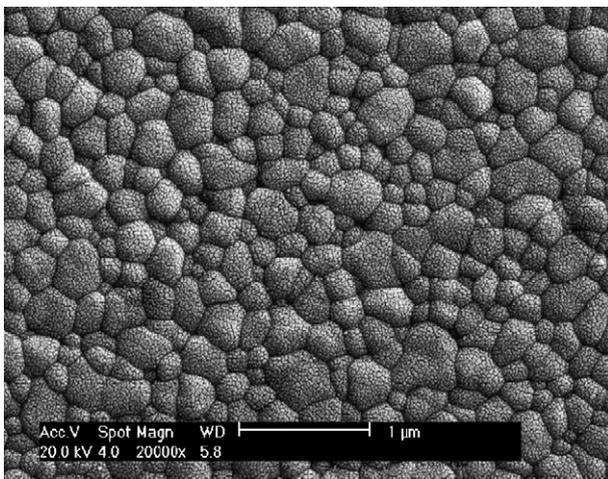


Fig. 2 – Scanning electron micrograph of 3Y-TZP for dental applications sintered according to manufacturer's recommendations (Cercon®, Dentsply Ceramco).

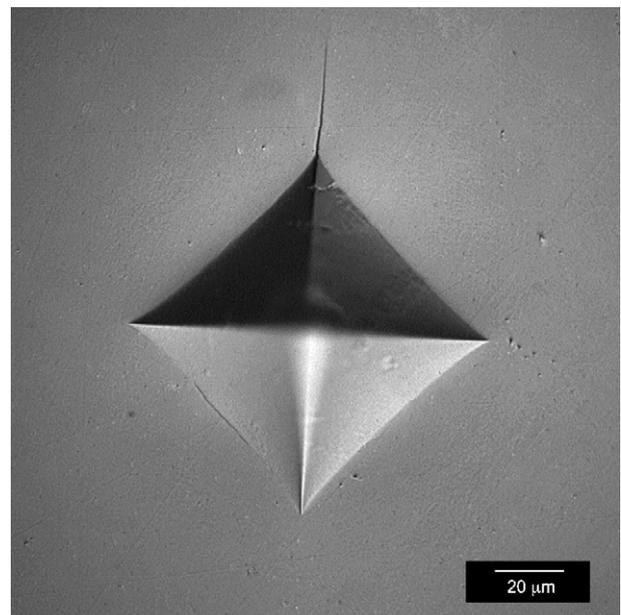
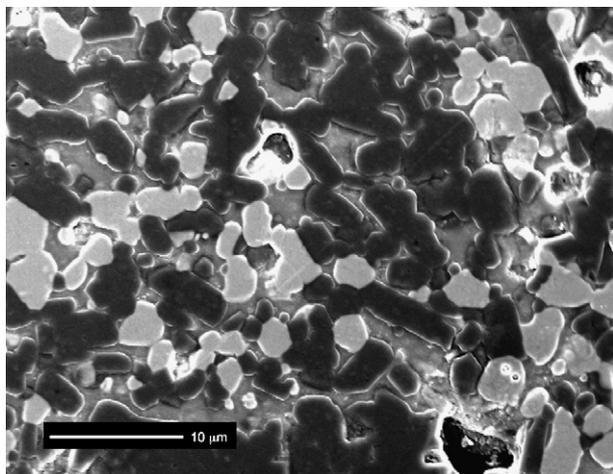


Fig. 3 – Optical micrograph of a Vickers indentation in a 3Y-TZP for dental applications (98.1 N load).



**Fig. 4 – Scanning electron micrograph of In-Ceram® Zirconia® (Vident™, Brea, CA). Zirconia grains appear in brighter contrast compared to darker alumina grains.**

with clusters of small zirconia grains (less than  $1\mu\text{m}$  in diameter). Some faceted zirconia grains ( $2\mu\text{m}$ ) were also observed. The crack patterns were consistently transgranular for  $\text{ZrO}_2$  and intragranular for  $\text{Al}_2\text{O}_3$ . In some of the newly developed ZTA for biomedical applications, excellent mechanical properties are obtained by promoting a fine and uniform dispersion of zirconia grains in an alumina matrix [38,44,45], such dispersion is readily obtained by sol-gel processing. An advancing crack triggers the  $t \rightarrow m$  transformation. The associated increase in volume creates microcracks in the alumina matrix surrounding the transformed particle. The toughness is therefore enhanced by microcracking [5,46].

### 2.3. Partially stabilized zirconia (Mg-PSZ)

Although a considerable amount of research has been dedicated to magnesia partially stabilized zirconia (Mg-PSZ) for possible biomedical applications, this material has not been successful due mainly to the presence of porosity, associated with a large grain size ( $30\text{--}60\mu\text{m}$ ) that can induce wear [14,16]. The microstructure consists of tetragonal precipitates within a cubic stabilized zirconia matrix. The amount of MgO in the composition of commercial materials usually ranges between 8 and 10 mol% [14]. In addition to a high sintering temperature (between  $1680$  and  $1800^\circ\text{C}$ ), the cooling cycle has to be strictly controlled, particularly in the aging stage with a preferred temperature of  $1100^\circ\text{C}$  [14]. Precipitation of the transformable  $t$ -phase occurs during this stage, which volume fraction is a critical factor in controlling the fracture toughness of the material [5,47,48]. Due to the difficulty of obtaining Mg-PSZ precursors free of  $\text{SiO}_2$ , magnesium silicates can form that lower the Mg content in the grains and promote the  $t \rightarrow m$  transformation [49]. This can result in lower mechanical properties and a less stable material. Denzir-M® (Dentronic AB) is an example of Mg-PSZ ceramic currently available for hard machining of dental restorations [50].

### 3. Soft machining of pre-sintered blanks

Since its development in 2001 [19], direct ceramic machining of pre-sintered 3Y-TZP has become increasingly popular in dentistry and is now offered by a growing number of manufacturers. Briefly, the die or a wax pattern is scanned, an enlarged restoration is designed by computer software (CAD) and a pre-sintered ceramic blank is milled by computer aided machining. The restoration is then sintered at high temperature. Several variations of this process exist depending on how the scanning is performed and how the large sintering shrinkage of 3Y-TZP ( $\sim 25\%$ ) is compensated for. For example, both contact scanners and non-contact scanners are available. Overall, non-contact scanners are characterized by a higher density of data points and a greater digitizing speed compared to contact scanners.

Typically the 3Y-TZP powder used in the fabrication of the blanks contains a binder that makes it suitable for pressing. The binder is later eliminated during the pre-sintering step. It also contains about 2 wt.%  $\text{HfO}_2$ , classically difficult to separate from  $\text{ZrO}_2$ . These powders have only minor variations in chemical composition. The powders consist of spray-dried agglomerates (about  $60\mu\text{m}$  in diameter, Fig. 5) of much smaller crystals that are about  $40\text{ nm}$  in diameter. The blanks are manufactured by cold isostatic pressing. The mean pore size of the compacted powder is very small in the order of  $20\text{--}30\text{ nm}$  with a very narrow pore size distribution [51].

The binder is eliminated during a pre-sintering heat treatment. This step has to be controlled carefully by manufacturers, particularly the heating rate and the pre-sintering temperature. If the heating rate is too fast, the elimination of the binder and associated burn out products can lead to cracking of the blanks. Slow heating rates are therefore preferred. The pre-sintering temperature of the blanks affects the hardness and machinability. These two characteristics act in opposite directions: an adequate hardness is needed for the handling of the blanks but if the hardness is too high, it might be detrimental to the machinability. The temperature of the



**Fig. 5 – Optical micrograph of spray-dried 3Y-TZP powder particulates.**

pre-sintering heat treatment also affects the roughness of the machined blank. Overall higher pre-sintering temperatures lead to rougher surfaces. The choice of a proper pre-sintering temperature is thus critical [51]. The density of each blank is carefully measured so that the appropriate compensating shrinkage is applied during final sintering. The final density of the pre-sintered blanks is about 40% of the theoretical density ( $6.08 \text{ g/cm}^3$ ). The density gradient within the blanks is lower than 0.3% of the theoretical density in all directions [19,51].

Machining is better accomplished in two steps. A first rough machining is done at a low feed rate while the final fine machining is performed at a higher feed rate [19,51].

Restorations can be colored after machining by immersion in solutions of various metal salts such as cerium, bismuth, iron or a combination thereof [52]. The color develops during the final sintering stage. The concentration of the solution strongly influences the final shade. Concentrations as low as 0.01 mol% are sufficient to produce a satisfactory coloration. The final sintering temperature influences the color obtained. Careful respect of the manufacturer's instructions is therefore important. Coloration with various dopants does not appear to affect the crystalline phases or mechanical properties of the final product. Alternatively, colored zirconia can be obtained by small additions of various metal oxides to the starting powder [53].

Sintering of the machined restorations has to be carefully controlled, typically by using specifically programmed furnaces. Shrinkage starts at  $1000^\circ\text{C}$  and reaches  $\sim 25\%$ . Sintering conditions are product-specific. Final sintering temperatures between  $1350$  and  $1550^\circ\text{C}$  with dwell times between 2 and 5 h lead to densities greater than 99% of the theoretical density. These variations in sintering conditions are likely to be due to the initial chemical composition of the 3Y-TZP powder. For example, small additions of alumina have been shown to act as a sintering aid, allowing the use of lower sintering temperatures and times. Prior to sintering, the frameworks are placed on zirconia sintering beads to avoid deformation. The minimum thickness for the copings is 0.5 mm, below which warpage could occur. The restorations are furnace-cooled to a temperature below  $200^\circ\text{C}$  to minimize residual stresses. As mentioned earlier, the sintering temperatures and times strongly influence the grain size [54]. Chevalier et al. also demonstrated that the amount of cubic phase in 3Y-TZP increases when the sintering temperature reaches  $1500^\circ\text{C}$  with a sintering time of 5 h. The presence of larger cubic grains is detrimental to the resistance of the ceramic to low temperature aging [25]. This points out the importance of carefully controlling the sintering step.

The restorations are finally veneered with porcelains of matching coefficient of thermal expansion. The nature of the interface between 3Y-TZP and the veneering porcelain has not been thoroughly studied. The veneering porcelain is baked at  $\sim 900^\circ\text{C}$ , with a hold time of 1 min. Although diffusion processes are time-dependent, chemical reactions could occur between the two ceramic materials. This point will be examined in greater detail later. Representative systems utilizing soft machining of 3Y-TZP for dental restorations are Cercon® (Dentsply International), Lava™ (3M™ ESPE™), Procera® zir-

conia (Nobel Biocare™), YZ cubes for Cerec InLab® (Vident™) and IPS e.max® ZirCAD (Ivoclar Vivadent).

#### 4. Hard machining of 3Y-TZP and Mg-PSZ

At least two systems, Denzir® (Cadesthetics AB) and DC-Zirkon® (DCS Dental AG) are available for hard machining of zirconia dental restorations. Y-TZP blocks are prepared by pre-sintering at temperatures below  $1500^\circ\text{C}$  to reach a density of at least 95% of the theoretical density. The blocks are then processed by hot isostatic pressing at temperatures between  $1400$  and  $1500^\circ\text{C}$  under high pressure in an inert gas atmosphere [33,55]. This latter treatment leads to a very high density in excess of 99% of the theoretical density.

The blocks can then be machined using a specially designed milling system. Due to the high hardness and low machinability of fully sintered Y-TZP, the milling system has to be particularly robust. A study by Blue et al. demonstrated that Y-TZP was significantly harder to machine than fully sintered alumina with lower material removal rates [56]. This was confirmed by Yin et al. who also reported that coarse diamond burs were more efficient for material removal with Y-TZP, while machining with fine burs led to a more ductile type of damage [57,58]. Huang studied the effect of grinding speed on the type of machining damage in Y-TZP and reported both brittle and ductile removal modes at high speed with less subsurface damage [27,59]. On the other hand, the fine grain size of Y-TZP leads to very smooth surfaces after machining [60]. As mentioned earlier, all surface treatments cause some degree of  $t \rightarrow m$  transformation at the surface of Y-TZP. Kosmac et al. showed that sandblasting was more efficient than grinding in inducing the transformation, thereby promoting a greater increase in strength [34]. Conversely, coarse grinding caused the formation of deep defects as well as a reverse transformation with elimination of the compressive stresses and a decrease in strength. These results were confirmed by Guazzato et al. [43] and Curtis et al. [61] on Y-TZP for dental applications.

The influence of residual stresses on the susceptibility of Y-TZP to low temperature degradation (LTD) has been thoroughly examined by Deville et al. [6]. It was concluded that the presence of residual stresses was more influential than the final roughness in promoting LTD. Smooth polishing led to preferential transformation after aging around the residual scratches. A thermal treatment at  $1200^\circ\text{C}$  for 2 h induced the relaxation of the stresses and a lower susceptibility to aging than the polished state. Grant et al. reported that hot isostatically pressed (HIPped) 3Y-TZP had a lower susceptibility to LTD than the unHIPped material [62]. The aging susceptibility of HIPped 3Y-TZP for dental applications is likely to follow a different scheme as the material is later machined. However, the difficulty of comparing the results of the numerous studies dedicated to surface treatments of Y-TZP should be pointed out, as there is no standardization of the treatments applied. In summary, questions remain about the surface state remaining after hard machining of Y-TZP, while soft machining seems to lead to a more consistent final state, provided that the machined restoration is left intact after sintering.

## 5. Clinical studies of ZrO<sub>2</sub> fixed prostheses

There are approximately fifteen major studies of zirconia prostheses underway at this time; characteristics of which are annotated in Table 1. It seems notable that these studies

mostly involve multi-unit and posterior prostheses. It is apparent that sponsoring manufacturers have some confidence in the structural potential of zirconia frameworks. This also signals some comfort regarding the performance of this core ceramic for the restoration of single anterior teeth; reflecting the clinical finding that many less strong/tough all-ceramic

**Table 1 – Characteristics of major clinical studies investigating zirconia-based prostheses**

Investigator	Patients	Prostheses	Initiated	Observ. time (mean)
I. Sailer C. Hämmerle Univ. Zürich Cercon (Dentsply)	45	57 multi-unit, posterior 3-Unit, 4-unit One 5-unit	1998	53 mos.
P. Pospiech Saarland Univ. Lava (3M ESPE)	36	18 single-unit, posterior 38 multi-unit, posterior	2000	42 mos.
S. Rinke Private Pract. Cercon (Dentsply)		89 single-unit, posterior	2000	
M. Kern S. Wolfart C-A Univ. Kiel e.MaxPress (Ivoclar)	68	36 3-unit, posterior 45 3-unit, posterior inlay retained	2000	62 mos. 47 mos. (10 Fx)
A. Huls Univ. Gottingen Cercon (Dentsply)		62 3-unit and 4-unit, posterior	2000	
P. Vultvon Steyern Malmö Univ. DC-Zircon	18	2 3-unit 12 4-unit (1 or 2 pontics) 6 5-unit (1 or 2 pontics)	2001	36 mos. [65]
A. Raigrodski U. Washington Lava (3M ESPE)	16	20 3-unit, posterior	2002	26 mos. [67]
M. Kern S. Wolfart C-A Univ. Kiel In-Ceram Zr (Vita)	58	65 3-unit, posterior	2002	31 mos.
M. Kern S. Wolfart C-A Univ. Kiel Cercon (Dentsply)	51	24 3-unit, posterior 37 3-unit, posterior Cantilever	2003	27 mos. 31 mos.
E. Durm W. Mörmann U. Zürich Vita YZ (CEREC)	42	42 3-unit, posterior	2003	
J. Sorensen Pacific Dent. Inst. Lava (3M ESPE)	48	38 3-unit, posterior 14 4-unit, posterior	2003	30 mos.
F. Beuer LMU München e.max ZirCad (Ivoclar Vivadent)	36	38 single-unit 22 3-unit, posterior 1 4-unit posterior	2004	12 mos.
R. Zajia, K. Chong, K. May, Univ. Mich. DC-Zircon	19	20 3-unit posterior FPD's on natural abutments	2004	12 mos.
F. Beuer L-M Univ. München Cercon (Dentsply)		21 3-unit, posterior	2005	12 mos.
C. Larsson Malmö Univ. DC-Zircon and In-Ceram Zr (Vita)	18	25 2-unit to 5-unit implant-supported	2005	12 mos. [66]

systems are found to have 90% or higher survival at 5–6 years [63]. It is also interesting that, other than for a few papers and IADR/AADR abstracts, there has been little reporting of early results [64–67]. This stands in contrast to other ceramic product launches for which 2-year and even 1-year study results were quickly published.

Bulk fracture appears to be quite uncommon in all studies to date, even with the majority of study prostheses being multi-unit replacing first molars or second premolars (personal communications with authors). The fractures that have occurred mostly involve connectors of multi-unit prostheses ( $\geq 4$ ) or second molar abutments. Results for single-unit molar prostheses may turn out to be at least as good as for alumina-based core systems; such supposition being tempered of course by the relatively limited observation times (Table 1). It is also obviously too early to judge whether microstructural or processing differences among zirconia systems will be reflected in clinical performance. That said, it is rather remarkable to have such an emphasis on clinical examination of a new technology in dentistry (at least 692 prostheses under study within 9 years).

Problems with the porcelain veneer seem to trouble all studies. In three published reports of four separate systems, 8, 15, 25 and 50% of prostheses developed crazing or cracking with minor loss of material after only 1–2 years of observation [64–67]. Investigators involved with studies not yet published admit to porcelain problems as well (personal communications with authors). However, this picture is somewhat confused by non-research clinical experience; for example one university-based investigator reports only sporadic problems seen in over 500 units per year (F. Beuer, personal communication). This may signal that the difficulties are material-specific, as was the conclusion in one published study of two systems exhibiting, respectively, 8 and 50% incidence of porcelain cracking [66]. It may also indicate that non-materials factors such as thickness ratios or framework design play a role in porcelain cracking. For comparison, porcelain problems on metal–ceramic prosthesis over a 10 years observation period was reported to be on the order of 4% for a gold–palladium alloy, no higher than 6% for most alternative alloys, and only as high as 15% for one nickel-based alloy without beryllium [68]. Consistent findings have been reported for another gold-based alloy, with 98% completely intact porcelain at 5 years [69]. Lower survival percentages are reported for porcelain on titanium (84–87% survival at 5 years); [69,70] a metal known to have an issue involving development of a weak “alpha case” layer during porcelain firing. Thus, porcelain–zirconia compatibility appears problematic in light of past experience with metal–ceramic systems.

Ceramic–ceramic compatibility is not easily characterized. All manufacturers appear to be using standard slow-heating dilatometry measures of expansion coefficients ( $\alpha$ ) and thermal shock testing during product development. Most manufacturers provide veneering porcelains having a slight mismatch ( $\Delta\alpha$ ) between their porcelain and zirconia, with the porcelain having approximately  $1\alpha$  unit ( $\Delta L/L \times 10^{-6} K^{-1}$ ) lower than the zirconia, which generally have an  $\alpha$  in the range of  $(10.5\text{--}11.0) \times 10^{-6} K^{-1}$ . This approach is used for most metal–ceramic systems and non-zirconia all-ceramic systems. Therefore, if a compatibility issue is occurring with Y-TZP it

is likely not due to a simple thermal expansion coefficient mismatch between the bulk materials.

Crazing and chipping during function signal the presence or development of tensile stresses, likely associated with the zirconia–porcelain interface. Since the origin of such stresses does not appear to be related to bulk thermal expansion/contraction mismatches, perhaps surface property changes are involved. Silicate glasses are known to be aggressive solvents towards refractory materials at high temperatures [71]. Aluminum oxide has been shown to be soluble in dental porcelains under firing conditions [72]. More recently both cerium and zirconium were shown to diffuse into a glass used to infiltrate a partially sintered Ce-TZP powder [73].

Depletion of stabilizing dopants (e.g., Y and Ce) might conceivably lead to local changes in unit cell tetragonality [74] resulting in destabilization of the t-phase or development of local thermal expansion anisotropy [75]. If significant c-phase is present near grain-boundaries or triple-points [54], destabilization might result in  $c \rightarrow m$  transformation with quite high local associated strains. Liquid silicate penetration of grain boundaries may be another consequence to consider, perhaps analogous to water penetration of Y-TZP at moderately elevated temperatures [76].

All manufacturers of porcelains for dental Y-TZP ceramics now provide “liner” materials, presumably to increase porcelain bonding as well as to provide some chroma and fluorescence. Although “bonding” does not appear to be at issue, perhaps these liners help assure wetting or have chemistries adjusted to reduce possible interactions with the Y-TZP. It does not appear that prostheses have needed to be replaced in any studies due to porcelain crazing or minor chipping.

## REFERENCES

- [1] Garvie RC, Hannink RH, Pascoe RT. Ceramic steel? *Nature* 1975;258:703–4.
- [2] Subbarao EC. Zirconia—an overview. In: Heuer AH, Hobbs LW, editors. Science and technology of zirconia. Columbus, OH: The American Ceramic Society; 1981. p. 1–24.
- [3] Kisi E, Howard C. Crystal structures of zirconia phases and their interrelation. *Key Eng Mater* 1998;153/154:1–35.
- [4] Garvie RC, Nicholson PS. Phase analysis in zirconia systems. *J Am Ceram Soc* 1972;55:303–5.
- [5] Heuer AH, Lange FF, Swain MV, Evans AG. Transformation toughening: an overview. *J Am Ceram Soc* 1986;69:i–iv.
- [6] Deville S, Chevalier J, Gremillard L. Influence of surface finish and residual stresses on the ageing sensitivity of biomedical grade zirconia. *Biomaterials* 2006;27:2186–92.
- [7] Sato T, Ohtaki S, Shimada M. Transformation of yttria partially stabilized zirconia by low-temperature annealing in air. *J Mater Sci* 1985;20:1466–70.
- [8] Sato T, Shimada M. Crystalline phase-change in yttria-partially-stabilized zirconia by low-temperature annealing. *J Am Ceram Soc* 1984;67:C212–3.
- [9] Sato T, Shimada M. Transformation of yttria-doped tetragonal  $ZrO_2$  polycrystals by annealing in water. *J Am Ceram Soc* 1985;68:356–9.
- [10] Lange FF, Dunlop GL, Davis BI. Degradation during aging of transformation-toughened  $ZrO_2\text{--}Y_2O_3$  materials at 250 °C. *J Am Ceram Soc* 1986;69:237–40.
- [11] Chevalier J, Calès B, Drouin JM. Low-temperature aging of Y-TZP ceramics. *J Am Ceram Soc* 1999;82:2150–4.

- [12] Guo X. On the degradation of zirconia ceramics during low-temperature annealing in water or water vapor. *J Phys Chem Solids* 1999;60:539–46.
- [13] Chevalier J. What future for zirconia as a biomaterial? *Biomaterials* 2006;27:535–43.
- [14] Green D, Hannink R, Swain M. Transformation toughening of ceramics. Boca Raton, FL: CRC Press; 1988.
- [15] Hannink RHJ, Kelly PM, Muddle BC. Transformation toughening in zirconia-containing ceramics. *J Am Ceram Soc* 2000;83:461–87.
- [16] Piconi C, Maccauro G. Zirconia as a ceramic biomaterial. *Biomaterials* 1999;20:1–25.
- [17] Eichler A. Tetragonal Y-doped zirconia: structure and ion conductivity. *Phys Rev B* 2001;64:174103–8.
- [18] Fabris S, Paxton AT, Finnis MW. A stabilization mechanism of zirconia based on oxygen vacancies only. *Acta Mater* 2002;50:5171–8.
- [19] Filser F, Kocher P, Gauckler LJ. Net-shaping of ceramic components by direct ceramic machining. *Assembly Autom* 2003;23:382–90.
- [20] Burger W, Richter HG, Piconi C, Vatteroni R, Cittadini A, Boccalari M. New Y-TZP powders for medical grade zirconia. *J Mater Sci Mater Med* 1997;8:113–8.
- [21] Ruiz L, Readey MJ. Effect of heat-treatment on grain size, phase assemblage, and mechanical properties of 3 mol% Y-TZP. *J Am Ceram Soc* 1996;79:2331–40.
- [22] Heuer AH, Claussen N, Kriven WM, Ruhle M. Stability of tetragonal ZrO<sub>2</sub> particles in ceramic matrices. *J Am Ceram Soc* 1982;65:642–50.
- [23] Cottom BA, Mayo MJ. Fracture toughness of nanocrystalline ZrO<sub>2</sub>–3 mol% Y<sub>2</sub>O<sub>3</sub> determined by Vickers indentation. *Scripta Mater* 1996;34:809–14.
- [24] Scott HG. Phase relationships in the zirconia–yttria system. *J Mater Sci* 1975;10:1527–35.
- [25] Chevalier J, Deville S, Münch E, Jullian R, Lair F. Critical effect of cubic phase on aging in 3 mol% yttria-stabilized zirconia ceramics for hip replacement prosthesis. *Biomaterials* 2004;25:5539–45.
- [26] Guazzato M, Albakry M, Ringer SP, Swain MV. Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics. *Dent Mater* 2004;20:449–56.
- [27] Huang H. Machining characteristics and surface integrity of yttria stabilized tetragonal zirconia in high speed deep grinding. *Mater Sci Eng A: Struct* 2003;345:155–63.
- [28] Liu SY, Chen IW. Fatigue of yttria-stabilized zirconia. I. Fatigue damage, fracture origins, and lifetime prediction. *J Am Ceram Soc* 1991;74:1197–205.
- [29] Zhang Y, Lawn B. Fatigue sensitivity of Y-TZP to microscale sharp-contact flaws. *J Biomed Mater Res: Appl Biomater* 2005;72B:388–92.
- [30] Zhang Y, Pajares A, Lawn BR. Fatigue and damage tolerance of Y-TZP ceramics in layered biomechanical systems. *J Biomed Mater Res B: Appl Biomater* 2004;71B:166–71.
- [31] Zhang Y, Lawn BR, Rekow ED, Thompson VP. Effect of sandblasting on the long-term performance of dental ceramics. *J Biomed Mater Res B: Appl Biomater* 2004;71B:381–6.
- [32] Kosmac T, Oblak C, Jevnikar P, Funduk N, Marion L. Strength and reliability of surface treated Y-TZP dental ceramics. *J Biomed Mater Res* 2000;53:304–13.
- [33] Sundh A, Molin M, Sjögren G. Fracture resistance of yttrium oxide partially-stabilized zirconia all-ceramic bridges after veneering and mechanical fatigue testing. *Dent Mater* 2005;21:476–82.
- [34] Kosmac T, Oblak C, Jevnikar P, Funduk N, Marion L. The effect of surface grinding and sandblasting on flexural strength and reliability of Y-TZP zirconia ceramic. *Dent Mater* 1999;15:426–33.
- [35] Lange FF. Transformation toughening. Part 4. Fabrication, fracture-toughness and strength of Al<sub>2</sub>O<sub>3</sub>–ZrO<sub>2</sub> composites. *J Mater Sci* 1982;17:247–54.
- [36] Lange FF. Transformation toughening. Part 5. Effect of temperature and alloy on fracture-toughness. *J Mater Sci* 1982;17:255–62.
- [37] Deville S, Chevalier J, Fantozzi G, Bartolome JF, Requena J, Moya JS, et al. Development of advanced zirconia-toughened alumina nanocomposites for orthopaedic applications. *Euro Ceram* 2004;VIII(1–3):2013–6.
- [38] Deville S, Chevalier J, Fantozzi G, Bartolome J, Requena J, Moya J, et al. Low-temperature ageing of zirconia-toughened alumina ceramics and its implication in biomedical implants. *J Eur Ceram Soc* 2003;23:2975–82.
- [39] Guazzato M, Albakry M, Quach L, Swain MV. Influence of grinding, sandblasting, polishing and heat treatment on the flexural strength of a glass-infiltrated alumina-reinforced dental ceramic. *Biomaterials* 2004;25:2153–60.
- [40] Guazzato M, Albakry M, Swain MV, Ringer SP. Microstructure of alumina- and alumina/zirconia-glass infiltrated dental ceramics. *Bioceramics* 2003;15:879–82.
- [41] Tsukuma K. Mechanical properties and thermal stability of CeO<sub>2</sub> containing tetragonal zirconia polycrystals. *Am Ceram Soc Bull* 1986;65:1386–9.
- [42] Tsukuma K, Shimada M. Strength, fracture toughness and Vickers hardness of CeO<sub>2</sub>-stabilized tetragonal ZrO<sub>2</sub> polycrystals (Ce-TZP). *J Mater Sci* 1985;20:1178–84.
- [43] Guazzato M, Albakry M, Quach L, Swain MV. Influence of surface and heat treatments on the flexural strength of a glass-infiltrated alumina/zirconia-reinforced dental ceramic. *Dent Mater* 2005;21:454–63.
- [44] Fantozzi G, Chevalier J, Guilhot B. Processing microstructure and thermomechanical behavior of ceramics. *Adv Eng Mater* 2001;3:563–9.
- [45] Tanaka K, Tamura J, Kawanabe K, Nawa M, Oka M, Uchida M, et al. Ce-TZP/Al<sub>2</sub>O<sub>3</sub> nanocomposite as a bearing material in total joint replacement. *J Biomed Mater Res* 2002;63:262–70.
- [46] Porter DL, Heuer AH. Mechanisms of toughening partially stabilized zirconia (PSZ). *J Am Ceram Soc* 1977;60:183–4.
- [47] Heuer AH. Transformation toughening in ZrO<sub>2</sub>-containing ceramics. *J Am Ceram Soc* 1987;70:689–98.
- [48] Hannink RHJ, Howard CJ, Kisi EH, Swain MV. Relationship between fracture toughness and phase assemblage in Mg-PSZ. *J Am Ceram Soc* 1994;77:571–9.
- [49] Leach CA. Sintering of magnesium partially-stabilized zirconia—behavior of an impurity silicate phase. *Mater Sci Technol* 1987;3:321–4.
- [50] Sundh A, Sjogren G. Fracture resistance of all-ceramic zirconia bridges with differing phase stabilizers and quality of sintering. *Dent Mater* 2006;22:778–84.
- [51] Filser FT. Direct ceramic machining of dental restorations. Ph.D. thesis. Zurich: Swiss Federal Institute of Technology Zurich; 2001.
- [52] Suttor D, Hauptmann H, Schnagl R, Frank S, inventors; 3M Espe AG, assignee. Coloring ceramics by way of ionic or complex-containing solutions. US Patent 6,709,694; March 23, 2004.
- [53] Cales B. Colored zirconia ceramics for dental applications. In: LeGeros RZ, Legeros JP, editors. *Bioceramics*. New York: World Scientific Publishing Co. Pte. Ltd.; 1998.
- [54] Matsui K, Horikoshi H, Ohmichi N, Ohgai M, Yoshida H, Ikuara Y. Cubic-formation and grain-growth mechanisms in tetragonal zirconia polycrystal. *J Am Ceram Soc* 2003;86:1401–8.
- [55] Piconi C, Maccauro G, Pilloni L, Burger W, Muratori F, Richter HG. On the fracture of a zirconia ball head. *J Mater Sci Mater Med* 2006;17:289–300.

- [56] Blue DS, Griggs JA, Woody RD, Miller BH. Effects of bur abrasive particle size and abutment composition on preparation of ceramic implant abutments. *J Prosthet Dent* 2003;90:247–54.
- [57] Yin L, Huang H. Ceramic response to high speed grinding. *Mach Sci Technol* 2004;8:21–37.
- [58] Yin L, Jahanmir S, Ives LK. Abrasive machining of porcelain and zirconia with a dental handpiece. *Wear* 2003;255:975–89.
- [59] Huang H, Liu YC. Experimental investigations of machining characteristics and removal mechanisms of advanced ceramics in high speed deep grinding. *Int J Mach Tool Manuf* 2003;43:811–23.
- [60] Kou W, Molin M, Sjogren G. Surface roughness of five different dental ceramic core materials after grinding and polishing. *J Oral Rehab* 2006;33:117–24.
- [61] Curtis AR, Wright AJ, Fleming GJP. The influence of surface modification techniques on the performance of a Y-TZP dental ceramic. *J Dent* 2006;34:195–206.
- [62] Grant KL, Rawlings RD, Sweeney R. Effect of HIPping, stress and surface finish on the environmental degradation of Y-TZP ceramics. *J Mater Sci: Mater Med* 2001;12:557–64.
- [63] Kelly JR. Dental ceramics: current thinking and trends. *Dent Clin North Am* 2004;48:513–30.
- [64] von Steyern PV. All-ceramic fixed partial dentures. Studies on aluminum oxide- and zirconium dioxide-based ceramic systems. *Swed Dent J Suppl* 2005;173:1–69.
- [65] von Steyern PV, Carlson P, Nilner K. All-ceramic fixed partial dentures designed according to the DC-Zircon<sup>®</sup> technique. A 2-year clinical study. *J Oral Rehab* 2005;32:180–7.
- [66] Larsson C, von Steyern PV, Sunzel B, Nilner K. All-ceramic two- and five-unit implant-supported reconstructions. A randomized, prospective clinical trial. *Swed Dent J* 2006;30:45–53.
- [67] Raigrodski AJ, Chiche GJ, Potiket N, Hochstedler JL, Mohamed SE, Billiot S, et al. The efficacy of posterior three-unit zirconium-oxide-based ceramic fixed partial dental prostheses: a prospective clinical pilot study. *J Prosthet Dent* 2006;96:237–44.
- [68] Anderson RJ, Janes GR, Sabella LR, Morris HF. Comparison of the performance on prosthodontic criteria of several alternative alloys used for fixed crown and partial denture restorations: Department of Veterans Affairs Cooperative Studies project 147. *J Prosthet Dent* 1993;69:1–8.
- [69] Walter M, Reppel PD, Boning K, Freesmeyer WB. Six year follow-up of titanium and high-gold porcelain-fused-to-metal fixed partial dentures. *J Oral Rehab* 1999;26:91–6.
- [70] Lovgren R, Andersson B, Carlsson GE, Odman P. Prospective clinical 5-year study of ceramic-veneered titanium restorations with the Procera system. *J Prosthet Dent* 2000;84:514–21.
- [71] Sandhage KH, Yurek GJ. Direct and indirect dissolution of sapphire in calcia–magnesia–alumina–silica melts: dissolution kinetics. *J Am Ceram Soc* 1990;73:3633–42.
- [72] Kelly JR. Clinical fracture behavior and colloidal processing of glass-matrix dental ceramics. DMedSc Thesis. Cambridge, MA: Harvard University; 1989.
- [73] Durschang B, Raether F. Development of a glass-infiltrated ceramic for dental applications. Fraunhofer ISC Annual Report; 2002. <http://www.isc.fraunhofer.de/german/improfil/presse/publikationen/media/e60-61.pdf>.
- [74] Kim D-J. Effect of Ta<sub>2</sub>O<sub>5</sub>, Nb<sub>2</sub>O<sub>5</sub>, and HfO<sub>2</sub> alloying on the transformability of Y<sub>2</sub>O<sub>3</sub>-stabilized tetragonal ZrO<sub>2</sub>. *J Am Ceram Soc* 1990;73:115–20.
- [75] Schubert H. Anisotropic thermal expansion coefficients of Y<sub>2</sub>O<sub>3</sub>-stabilized tetragonal zirconia. *J Am Ceram Soc* 1986;69:270–1.
- [76] Kobayashi K, Kuwajima H, Masaki T. Phase change and mechanical properties of ZrO<sub>2</sub>–Y<sub>2</sub>O<sub>3</sub> solid electrolyte after aging. *Solid State Ionics* 1981;3(4):489–95.