Review

Low temperature degradation -aging- of zirconia: A critical review of the relevant aspects in dentistry

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ABSTRACT

This review presents a critical survey of all experimental data about the low temperature degradation of zirconia (often referred to as "aging") due to the tetragonal-to-monoclinic transformation, which have been collected at temperatures of interest for dental application (room temperature to about 100 °C). It is shown that the main factors affecting the aging phenomenon are (i) the stabilizer type and content, (ii) the residual stress and (iii) the grain size. It is also shown that extrapolating the low temperature degradation rate from accelerated aging tests can lead to unacceptable conclusions about the lifetime of the zirconia-based components. Finally, based on the experimental evidence, a set of engineering guidelines for the use of zirconia in restorative and prosthetic dentistry is proposed.

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1.   Introduction

Typing the words "zirconia OR ZrO_2" on any scientific search engine provides close to 25,000 publications from 1969 to 2008. Clearly also review papers centered on this material are numerous and, hence, it is necessary to justify the supposed need for a new one. We believe that the need stems from two concomitant aspects: (i) the world of dentistry has begun to deal with zirconium oxide only in the recent years and some aspects of the long-term behavior of this materials are not sufficiently known among dentists and researchers in the field [1–3], and (ii) more specifically, in spite of the above mentioned body of literature, there are actually few contributions reporting experimental data, and not extrapolations, on the long-term degradation (aging) of zirconia at temperatures low enough to be of interest for the dentists. For example, the comprehensive review of Lawson [4] on the degradation of zirconia due to the environment reports literally 3 data points below 100 °C. On the other hand, the case of the unusually large premature failures of ceramic heads in hip joint prostheses is widely known: between 2000 and 2002 a consistent number of ceramic balls made of yttria-stabilized zirconia, produced by Saint Gobain Desmarquest and marketed with the name Prozyr®, failed prematurely because of a change in the processing procedure which resulted in increased monoclinic content (the best clinical description of the episode can be found in [5] whereas a sound scientific interpretation of the problem has been proposed only very recently, in 2009 [6]).

Chevalier, a worldwide expert in the field of aging of zirconia, recently presented an informed opinion on this problem [7]; in the concluding remarks, he adds that "The use of zirconia for dental implants is quite young and in development phase. The issue of aging is still not discussed for these applications." Another review on the use of zirconia in dentistry concludes also very conservatively, warning that long-term studies are badly needed in the field [8]. A recent review focused on the bacteriological aspects of zirconia for dental applications concludes that "A need for references concerning resistance to failure in long-term clinical trials is of paramount importance for such systems." [3]. The cited work of Denry and Kelly [2] finishes stating that "It seems wise to keep in mind that some forms of zirconia are susceptible to aging and that processing conditions can play a critical role in the low temperature degradation of Zirconia". In yet another very recent review [6], in the few lines dedicated to zirconia in dental applications, the authors conclude that aging "is expected to be no less of an issue for their manufacturers" [6]. This should induce the dental community to be very cautious and in wont of a clear knowledge, based on experimental data, about the performances of zirconia at low temperatures and long terms.

Thus, the present contribution will focus on the experimental evidence gathered in the temperature range of interest for implanted dental materials, that is between 0 and 100 °C on the problem of long-term degradation, or aging, of zirconia.

The paper is organised as follows: firstly, a background on zirconia will be presented, then a paragraph will be dedicated to each of the three main factor affecting LTD: (i) stabilizer type and content, (ii) stress and (iii) grain size. Then the experimental methods used to study the LTD will be discussed followed by a section dedicated to a critical evaluation of the lifetime predictions of zirconia implants. Finally, based on a comprehensive evaluation of the experimental evidence, some engineering guidelines for the use of zirconia in restorative and prosthetic dentistry are proposed in the last section.

2.   Terminology and background

Zirconium oxide, ZrO_2, is chemically an oxide and technologically a ceramic material. It is basically insoluble in water. It can be dissolved in H_2SO_4 and in HF. In nature it is relatively abundant (about 0.02% of the earth crust) [9]. Large deposits are present in Brazil as baddeleyte (monoclinic zirconia) and in Australia and India as zircon ($ZrSiO_4$) sands. Pure zirconia presents the phenomenon of allotropy, that is same chemical composition but different atomic arrangement, among the following crystallographic structures [10]:

$$\text{Orthorombic} \leftrightarrow \text{monoclinic} \overset{1170\,^\circ C}{\longleftrightarrow} \text{tetragonal} \overset{2370\,^\circ C}{\longleftrightarrow} \text{cubic} \overset{2680\,^\circ C}{\longleftrightarrow} \text{liquid}$$

The cubic structure is of the fluorite type, with oxygen ions occupying a simple cubic lattice and the zirconium ions occupying the center of half of the anionic cubic cells [9]. Examined upon cooling, the transformation from cubic to tetragonal (c–t) and from tetragonal to monoclinic (t–m) is athermal and diffusionless (hence the term "martensitic" used to describe this transformation, in analogy to what happens in steel). Furthermore the t–m transformation occurs with a volume expansion (when unconstrained) of about 5 vol.% [9]. Till the late twenties, this enormous volume expansion prevented a large scale use of zirconia as refractory, because, upon cooling, it induced severe cracking of the bricks often leading to catastrophic failure. Then Passerini [11] and Ruff et al. [12,13], independently, discovered that the tetragonal, or even the cubic form could be retained metastably at room temperatures by alloying zirconia with other cubic oxides, thus preventing the catastrophic failure of pure zirconia. It becomes now clear why such oxides have been termed "stabilizers". To date there are reports of binary systems where zirconia is alloyed and stabilized with Cao, MgO, Y_2O_3, CeO_2, Er_2O_3, Eu_2O_3, Gd_2O_3, Sc_2O_3, La_2O_3 and Yb_2O_3. By and large, the most studied stabilizers for biomaterials applications are CaO [14], MgO [15], Y_2O_3 [16–19] and CeO_2 [20,21], but only ZrO_2–Y_2O_3 reached the actual status of having a dedicated ISO standard for surgical application [22].

In 1976, in what is arguably the seminal paper concerning zirconia, Hannink et al. [23], proposed that the t–m transformation with its ensuing volume expansion, could be used to enhance the fracture toughness of zirconia-based materials. The fracture toughness is defined as the capability of a mate-
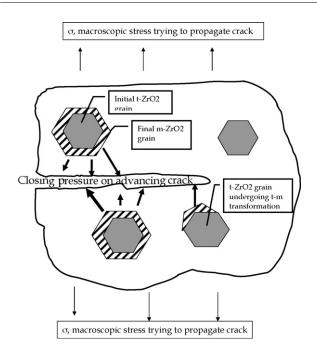
Fig. 1 – Schematic representing how the *t–m* transformation of ZrO$_2$ increases fracture toughness. When a part containing metastable *t*-ZrO$_2$ is subject to a remote macroscopic tensile stress, the stress intensification due to the presence of a crack tip is sufficient to transform some *t*-zirconia grains to the monoclinic form. Since this transformation entails a volumetric expansion which is constrained by the surrounding materials, the net result is a compressive stress acting on the surfaces of the crack, whose propagation is thus hindered.

rial to stand a load in presence of a pre-existing flaw. Using the Griffith approach [24] the fracture toughness, K_{Ic}, is defined as

$$K_{Ic} = Y\sigma_f\sqrt{c} \qquad (1)$$

where Y is a geometrical adimensional parameter, σ_f is the stress at failure (sometimes referred to as resistance, or fracture resistance) and c is the initial length of the defect at which failure started. The schematic presented in Fig. 1 helps to visualize how zirconia can improve the fracture toughness; the mechanism described in Fig. 1 is usually referred to as transformation toughening or, more completely, phase transformation toughening (PTT) [25–27]. Depending on the material surrounding the zirconia grains susceptible to the *t–m* transformation, different types of materials can be obtained; the most important ones are the following (the acronyms in brackets are the most widely used in the scientific literature):

(i) Partially stabilized zirconia (PSZ)—a matrix of cubic zirconia embedding transformable *t*-zirconia grains.
(ii) Zirconia toughened composites (ZTC)—a matrix with high elastic modulus embedding transformable *t*-zirconia grains. The most used matrix, with relevant biomedical application in prostheses, is alumina and the material is known as zirconia-toughened alumina (ZTA) [28].

(iii) Tetragonal zirconia polycrystals (TZP)—the whole material is constituted by transformable *t*-zirconia grains. Differently from the two previous cases, which are two-phases materials, TZP is single phase.

Table 2 of Ref. [1] reports the commercially available materials for dental use divided in the three aforementioned categories.

The basic, indispensable requirement for phase PTT to occur is that the *t*-ZrO$_2$ grains be in thermodynamic metastability at the conditions in which the crack is trying to propagate. It is exactly this thermodynamic metastability which lies at the base of the low temperature degradation, LTD, or aging, of zirconia: LTD (or aging) is defined as the spontaneous *t–m* transformation occurring over time at low temperatures, when the *t–m* transformation is not triggered by the local stress produced at the tip of an advancing crack. Apart from other drawbacks of the *t–m* transformation occurring under these conditions (enhanced wear rates [29,30] with release of small zirconia grains in the surrounding environment, roughening of the surface finish with both mechanical and aesthetic worsening [31]) it is clear that, once already transformed to the *m*-polymorph, zirconia cannot exhibit PTT, just like an used match cannot be lit again. Overall PPT and LTD are based upon the same phenomenon, the *t–m* transformation of zirconia, and, to date, we cannot exploit the remarkable possibility of the former without exposing ourselves to the risks of the latter.

The best way to understand the role of all factors involved in the *t–m* transformation is to consider it a chemical reaction governed by the pertinent free energy change:

$$t\text{-ZrO}_2 \Rightarrow m\text{-ZrO}_2 \quad \Delta G_{t-m} \qquad (2)$$

The free energy term, ΔG_{t-m}, takes into account all contributions relevant for the *t–m* transformation and can be split as follows:

$$\Delta G_{t-m} = \Delta G_{t-m}^{CHEM} + \Delta G_{t-m}^{STRAIN} + \Delta G_{t-m}^{SURF} \qquad (3)$$

ΔG_{t-m}^{CHEM} is the traditional term obtained from the chemical potentials: it takes into account the fact, imposed by nature, that at temperatures of interest for dental applications, the energy of the monoclinic form is smaller than that of tetragonal. If the two other terms are vanishingly small, at those temperatures zirconia will be monoclinic. This term can be made less negative, thus hindering the *t–m* transformation, by using the aforementioned stabilizers.

ΔG_{t-m}^{STRAIN} is the contribution to the total free energy change due to strain and this term is also known as the strain energy term. Stresses play a critical role in the *t–m* transformation, as demonstrated by an important study of Schmauder and Schubert [32]: they showed that the *t–m* transformation does not occur in stress-free grains of zirconia, even if these contain an amount of stabilizer far below the stability of the phase diagram.

ΔG_{t-m}^{SURF} takes into account the size of the particles involved in the *t–m* transformation and it is the contribution to the total free energy due to the presence of crystal surface of a given areal extension. It is important to note that, as ΔG_{t-m}^{CHEM} and

ΔG_{t-m}^{STRAIN} scale with the cube of the crystal size while ΔG_{t-m}^{SURF} with the square of it, this last term becomes important only when the size of the grains is small, tens of nanometers or so.

From all the above it is clear that

(i) stabilizer type and content modify the first term, applied and residual stresses the second and grain size, GS, the third term of Eq. (3); each of the following paragraphs will deal with one of the three terms.

(ii) the relative contribution of the different terms ultimately determines the possibility for the transformation to occur at an arbitrarily considered initial time.

(iii) If at the considered initial time the transformation is not occurring, aging takes place if and only if, over the elapsed time range, some kinetically driven phenomena occur, thus modifying one or more of the terms above.

The treatment above is thermodynamic, time-independent in nature, and it allows to determine the boundaries of the thermodynamic stability of t- and m-phase. Before discussing the details of each term of Eq. (3), it is necessary to introduce the approach used to rationalize the t–m transformation in time-dependent, kinetic terms. Zirconia ceramics can exist in a metastable t-form even if the sum of conditions expressed by the three terms of Eq. (3) indicated that m-zirconia is the stable form; this is due to the fact that a triggering mechanism is needed for the t–m transformation to occur—just as water will need to be cooled well under $0\,^{\circ}C$ in order to freeze. Like many other phase transitions, the transformation of (meta)stabilized zirconia from t- to m-polymorph is

governed the by nucleation of the new phase followed by its growth. The starting point for a kinetic analysis can be conveniently assumed to be the Mehl–Avrami–Johnson, MAJ [33] equation, often used for time-dependent, isothermal phase transitions. The typical form is

$$f_m = 1 - \exp[-(bt^n)] \tag{4}$$

where f_m is the monoclinic volume fraction, t is the time, b is an activation energy term of the usual form ($b = b\,exp(-Q/RT)$) and n is an exponent related to the nucleation and growth conditions. Different kinetics of the t–m transformation will be a consequence of different process conditions, which affect the activation energy and the transformation driving force (i.e. the free energy difference between the metastable and stable state), as well as of different operating conditions, which define the trigger mechanisms involved and their efficiency. The shape of the MAJ equation is sigmoidal and, in the field of the t–m transformation and aging, it has had a considerable success since it allows an extrapolation of the times required for aging at low temperatures from data collected at high temperatures, which are much faster to acquire. As it will be shown later, this approach has some severe drawbacks, to the point of being almost useless in predicting lifetime of t-zirconia components.

3. LTD and stabilizers

Though, in principle, all stabilizers could be used to obtain both PSZ and TZP, practically alkaline earth oxides are used for commercially available PSZ and Y_2O_3 and CeO_2 for TZP. As all other stabilizers, they are characterized by a large solubility in zirconia and by the ability to form fluorite-type phases over large temperature and compositional ranges. By definition PSZ is a two-phase material, with the tetragonal phase precipitating in the cubic matrix [34]: the precipitation is a rather delicate processing step since it is influenced by several parameters: initial GS of the powder, stabilizer type and content, temperature and time for nucleation and growth of the tetragonal precipitates [35–37]. It is no surprise that one single product of this type has been available for the dental market (Denzir-M®, produced by Dentronic AB) which is a MgO-PSZ [38,39].

Y_2O_3 is the most widely used stabilizer in high-tech application of zirconia; because of charge balance reasons, the introduction of Y_2O_3 in the ZrO_2 lattice gives origin to oxygen vacancies which are one of the mechanisms proposed for the stabilization effect [40]. The portion of phase diagram reported in Fig. 2 indicates the most agreed-upon stability and metastability regions. Typically 3 mol% and 8 mol% of Y_2O_3 in ZrO_2 are used to stabilize down to room temperature the tetragonal (Y-TZP) and the cubic form, respectively. From an aesthetic point of view Y-TZP is white and can be rather easily colored by addition of traces of rare earth elements, for example adding soluble nitrites or nitrates of these elements to the Y-TZP powder; subsequent sintering gets rid of the nitrogen-containing anions leaving the cations in the lattice of Y-TZP, which ultimately confers coloration to the part. Since long it has been known that Y-TZP is prone to LTD in presence of water [41–44].
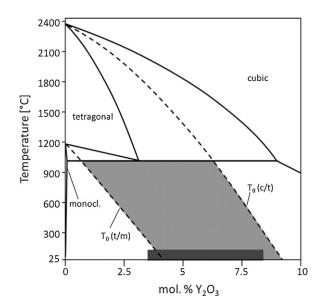

Fig. 2 – Y_2O_3–ZrO_2 phase diagram. The shaded area indicates the region of metastable tetragonal phase, separated from the monoclinic and the metastable pseudocubic region by the $T_0(t/m)$ and $T_0(c/t)$ dashed lines, respectively. According to the engineering guidelines presented in the last paragraph, it is suggested that Y-TZP for dental applications should have compositions and operating conditions included within the dark-shaded region.

There is clear evidence that few hours at 100 °C in water leads to more than 40% of monoclinic phase in 2Y-TZP (the number in front of Y indicates the percentage in mol of Y_2O_3 in ZrO_2) [45]. An yttria content of 5 mol%, thus with a large starting cubic content, diminishes the monoclinic value down to 15%. Sato and Shimada found that annealing provoked no t–m transformation at 62 °C, whereas an increase to 82 °C resulted in about 1 and 22 mol% of m-zirconia for annealing conducted in air and water, respectively (in this study the GS was 1.1 μm) [43]. In another study [46] aging of 3Y-TZP conducted at 70 °C resulted in more than 50% m-phase after 5000 h (less than 200 days), with an average GS less than 0.5 μm. At the same time, it is widely demonstrated that extensive transformation to the m-polymorph causes a deterioration of the mechanical properties, especially the bending strength. Interestingly enough, there is some evidence that, for aging performed above 300 °C, the mechanical properties are retained, whereas there is a minimum for temperatures around 200 °C, indicating that at this temperature the thermodynamic contribution in favor of the m-phase conjures up with the kinetic acceleration to yield the largest m-content [47].

To date, there is no accepted mechanism to explain the phenomenon, but only informed speculations. The soundest are, in our opinion, the following.

- Lange et al. [48] propose, based on some TEM observations, that water reacts with Y_2O_3 to form clusters rich in $Y(OH)_3$; this leads to a depletion of the stabilizer in the surrounding zirconia grains which are then free to transform to monoclinic.
- According to Yoshimura et al. [44], water vapor attacks the Zr–O bond, breaking it and leading to a stress accumulation due to movement of –OH; this in turn generates lattice defects acting as nucleating agents for the subsequent t–m transformation.
- Chevalier et al. [6] propose that O^{2-} originating from the dissociation of water, and not OH^-, is responsible for the filling of oxygen vacancies which is believed to be one of the causes of destabilization and, hence, of LTD and for the long diffusional path.

Irrespective of the mechanism, it is well established that the t–m transformation (i) starts from the surface of the sample and then proceeds inward; (ii) it causes a surface uplift [49,50] and microcracks [51] with ensuing aesthetic degradation [31], (iii) it open the possibility for water to penetrate below the surface, thus propagating the t–m transformation to the interior of the sample [45], and, finally, (iv) it leads to the development of major cracks [51]. It is in response to these problems affecting Y-TZP, that ceria, CeO_2 has attracted a lot of interest as stabilizer.

Ceria is needed in larger amount than yttria, in order to maintain the same regions of stability on the phase diagram [52]. A typical Ce-TZP composition, capable of t–m transformation, contains 8 mol% of ceria. Above 12 mol% the system is non-transformable. Ce-TZP with 12 and 14 mol% showed negligible degradation even after 500 h at 150 °C in water vapor [53]; after 360 h in water at 80 °C Ce-TZP with 8 mol% ceria showed less than 10% monoclinic on the surface [54]. The difference with Y-TZP is striking (Fig. 3). Maybe even more
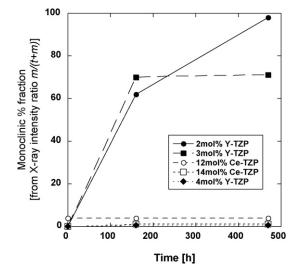

Fig. 3 – Results of hydrothermal aging tests at 150 °C for Y-TZP and Ce-TZP. Ce-TZP is much more resistant to LTD than Y-TZP, unless Y_2O_3 content reaches 4 mol%, which lies in the non-transformable Y-TZP region shown in Fig. 2. (Redrawn from Fig. 5 of Ref. [53] with permission from American Ceramic Society, Wiley-Blackwell).

important, the bending strength of these Ce-TZP samples is basically unaffected by the aging cycles in water vapor [53] and even studies more focused on the dental applications of Ce-TZP confirm this finding [55]. Another interesting feature of the ceria–zirconia system, is that it shows the most pronounced pseudo-plastic behavior among ceramic materials: to a certain extent, Ce-TZP can bend before fracturing [56]. Actually Ce-TZP can exhibit hysteresis loops on the stress-strain plane and even Shape Memory Effect, that is shape recovery after heating [57,58]. Chemically, Ce-TZP present the problem that Ce^{4+} can be relatively easily reduced to Ce^{3+}, which does not have the same stabilizing ability toward t-zirconia [59–61]. Even sintering in air can lead to a reduction, and there is evidence that the chemical reduction can be triggered also at room temperature by the stress locally generated by the t–m transformation [62]. From an aesthetic point of view, Ce-TZP poses more problems than Y-TZP to the dentists: CeO_2 is yellow and products based on commercially available Ce-TZP powders range from light yellow to almost brownish. A further complication is due to the fact that when Ce^{4+} is reduced to Ce^{3+}, due to the high concentration of oxygen vacancies Ce-TZP tends to became dark grey [61,62]. Since some foods have reducing capabilities (glucose and lactose, for example), the possibility cannot be excluded that, on the long range, Ce^{4+} could be reduced in the oral cavity with consequent darkening of the zirconia-based part. We have not been able to find a single commercially available product for the dental market made of Ce-TZP, but there are studies being conducted on mixtures between alumina, Al_2O_3, and Ce-TZP for applications in dentistry [54,63–65]. It is also worth mentioning that there is an important number of publications devoted to the study of zirconia stabilized with mixtures of CeO_2 and Y_2O_3, which show very good mechanical properties and also a good resistance to LTD [66,67].
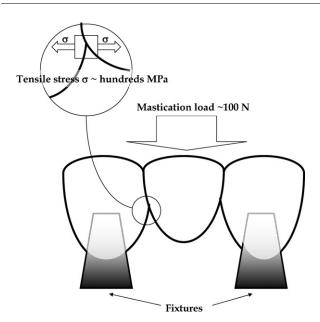
Fig. 4 – Schematic of a dental bridge subject to a mastication load. In the point indicated by the arrow, the tensile stress can easily reach values of the order of several hundreds MPa, often large enough to provoke locally the t–m transformation.

4.   LTD and stress

As mentioned in paragraph II, stress can affect the t–m transformation and the behavior of zirconia with respect to stress can be easily rationalized in terms of Le Chatelier principle: "when perturbed, a system in equilibrium tends to react in order to minimize the perturbation". When t-zirconia is put in tension, it minimizes this perturbation by expanding its dimensions and transforming to m-zirconia, because this expansion decreases the initially applied tensile stress (the same principle holds true for m-zirconia transforming to t-zirconia upon compression). Stresses can be applied or residual and zirconia-based materials are subject to both in dental applications. Applied stresses are immediate to visualize intuitively, but more difficult to compute precisely when it comes to dental prostheses, given the complicated geometries of the part and of the loading conditions; a situation like the one depicted in Fig. 4 can easily result in tensile stresses of the order of several hundreds of MPa. Given that stresses are defined as force/area, it is then possible to understand why manufacturers suggest lower bounds to cross-sectional areas in prostheses: areas smaller than suggested increase the local stress possibly pushing it close to the limit of failure of the material. This aspect is made more complicated by the concentration of stresses occurring at edges, discontinuities, crack tips, etc.

Residual stresses arise every time zirconia is fired at high temperature and then cooled down to room temperature for the practical use; fast cooling rates and/or coupling with other materials having a different coefficient of thermal expansion (CTE) lead to larger residual stresses. This is certainly the case of zirconia in dentistry, where a firing step is always involved

in the preparation of the dental part. The general formula to calculate residual stresses arising between two dissimilar materials is the following:

$$\sigma_1 = \frac{E_1}{1 - \nu_1}(\alpha_1 - \alpha_2)(T^{fir} - T^R) \tag{5}$$

where σ_1 is the stress, E_1 is the Young modulus, ν_1 is the Poisson ratio, α is the CTE, T^{fir} is the firing temperature and T^R is room temperature (in our case the body temperature); suffices 1 and 2 refer to the different materials. Eq. (5) predicts that, when implanted in the oral cavity zirconia coupled with alumina will be subject to an approximate tensile stress of 1 GPa: this value is sufficient to trigger the t–m transformation in several cases [61,68] (obviously depending on stabilizers, GS, etc.), and this t–m transformation can be a slow process [69], not necessarily a burst-like effect observed immediately upon reaching a certain tensile load [68]. Actually, the same approach to the determination of residual stresses is applicable if zirconia is coupled as a veneer/coating or as a laminate to another material, though in these latter cases the peculiar nature of stresses at and near the surface is not intuitive [70] and can lead to surface cracks [71].

We will now address the important issue connected with the consequence of the residual stresses generated by an initial t–m transformation on the prosecution of further t–m transformation, that is the "autocatalitic effect". This is explained with the help of Fig. 5. Basically, when some t-zirconia transforms to m-zirconia, we have a two-phase material with m-zirconia in compression and the remnant t-zirconia in tension, as predicted theoretically [72] and demonstrated experimentally [73]; as a rough estimate, for every 10 vol.% of t–m transformation, the tensile stress in the remnant t-zirconia increases by 250 MPa. Because of this tensile stress, t-zirconia will be more prone to further transformation to m-zirconia. This is the so-called autocatalitic effect which can be immediate at the moment of the crack propagation [68], but which can also be diffusion-controlled with much longer characteristic times [62,69]. In this latter case alumina/Ce-TZP samples were subject to bending and, at the beginning of the experiments, no m-zirconia could be detected on the samples. The bending induced an initial, burst-like, t–m transformation and, at some locations, the m-zirconia was 20% of the total zirconia amount. This initial transformation induced a tensile stress in the remnant t-zirconia of the order of 700 MPa. After 100 days at room temperature, because of this tensile stress, further t–m transformation was observed, with the monoclinic content increasing from 20 to 35% [69,73]. The exact nature of the change in the sample, which provoked the slow t–m increase was not known, but it was clearly a diffusional-type process [69].

In some alumina–zirconia laminate composites [74] we have found that tensile stresses as low as 400 MPa could lead to aging of 3Y-TZP after 5 years at room temperature and ambient humidity. Actually the data are even more surprising: layers of pure zirconia in macroscopic tension did not show aging after 4 years at room temperature and ambient humidity, whereas layers of intimately mixed alumina/zirconia under macroscopic tension aged considerably, up to 25 vol.%, and the same layers under macroscopic compression still showed aging, up
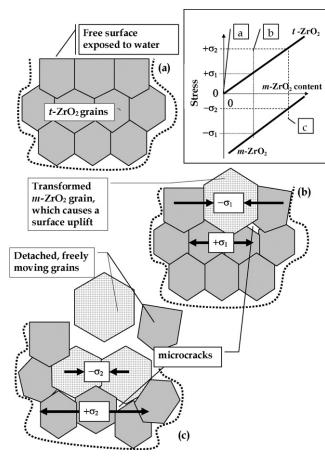
Fig. 5 – Schematic representation of how a partial transformation of zirconia grains to the *m*-polymorph increases the tensile stress in the remnant *t*-zirconia grains. (a) The whole microstructure of the sample, extending also around the thick broken line, is composed by t-ZrO$_2$ with the top surface exposed to water (liquid or vapor). (b) One grain transform to monoclinic; on the top surface, it is free to expand, provoking an uplift of the surface itself. On the left, right and below, the newly formed *m*-grain is constrained by the surrounding untransformed material. Since this grain is limited in its expansion, it implies that it is in a large compression, $-\sigma_1$, whereas its push against the surrounding materials gives origin to a small tensile stress, $+\sigma_1$. (c) When more grains transform to monoclinic, they are less constrained and the compressive stress diminishes to $-\sigma_2$, whereas they put in larger tensile stress, $+\sigma_2$, the remaining t-ZrO$_2$. The length of the thick black arrows in (b) and (c) is qualitatively proportional to the magnitude of the stress (arrows pointing outwards indicate tensile stress and vice versa). Microcracks originating from the *t–m* transformation facilitate the inward diffusion of water. The inset above right reports qualitatively the effect of the *m*-content on the residual stress in the remnant *m*- and t-ZrO$_2$. Roughly, an increase of 10% of m-ZrO$_2$ increases the tensile stress in t-ZrO$_2$ by 250 MPa [73].
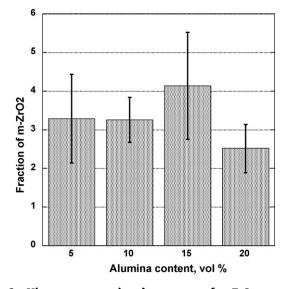

Fig. 6 – Histogram reporting the amount of *m*-ZrO$_2$ present in alumina/zirconia samples aged for 8 years at room temperature and ambient humidity. The bars in the figure refer to scatter among samples subject to different cooling rates and with different grain size but same alumina content, and, hence, they do not represent experimental errors. The GS of ZrO$_2$ in these samples is about 300 nm and the stabilizer content is 2.5 mol% Y$_2$O$_3$. These data were collected in 2008; at the beginning of the experiments, in 2000, no trace of *m*-ZrO$_2$ could be detected on any of the sample [75].

to 5 vol.%. (For a correct definition of macro- and micro-scopic stresses see ref [70,74].)

Even more surprisingly, in a series of experiments conducted on alumina–zirconia samples (10:90 in volume) after 7 years at room temperature and ambient humidity, we have found evidence of spontaneous *t–m*: some preliminary data are reported in Fig. 6 and they will be the subject of a dedicated paper. The samples belonged to a batch prepared in 2001 to study the effect of GS and cooling rate on the stress accumulated at room temperature [75]. In 2001 no *m*-zirconia could be detected and the *t*-zirconia (2.5Y-TZP) was subject to tensile stresses in the range 50–200 MPa, with a GS of 300 nm. As can be seen from Fig. 6, in 2008 the average *m*-content among all samples was more than 3 vol.%, with peaks of 6 vol.%. To our knowledge these are the only available data on LTD obtained after such long times and at room temperature. It is interesting to note that, according to the phase composition/stability phase diagram developed for Y-TZP with accelerated aging tests [76], 2.5Y-TZP with a GS of 300 nm should be well within the *t*-stability region: our data demonstrate that submicrometric GS and an yttria content of 2.5 mol% are not sufficient to prevent LTD over some years in presence of a relatively low tensile stress.

5. LTD and grain size

Numerous researchers have reported that reducing the average GS in zirconia-based ceramics has a beneficial effect on

Ref.	Reported critical grain size (μm)	Notes
Table 1 – Critical grain sizes for LTD-resistant 3Y-TZP ceramics. Rows 1 through 4 report experimental data where retention of the tetragonal phase is also dependent on kinetic factors; Row 5 shows a theoretical prediction of the grain size that guarantees thermodynamically stable tetragonal zirconia.		
[42]	0.3	Aging 1000 h at 300 °C in air
[92]	0.36	Aging 8 h at 100 to 260 °C in water
[93]	0.37	Aging 100 h at 100 to 500 °C in water
[106]	0.52	Aging 100 h at 100 to 500 °C in air
This work	∼0.05	Prediction based on the thermodynamic approach proposed in Refs. [80,82]

the stability of the tetragonal phase [42,48,77–79], and therefore on LTD. Some confusion seems to arise in the literature on this subject, much of it generated by the ambiguous definition of the critical GS. Some researchers, who have focused on a purely thermodynamic approach to the problem, identify it as the maximum GS for which the tetragonal phase is thermodynamically stable, i.e. it will never transform. On the other hand, there is a number of contributions where the critical GS is simply associated to the maximum size for which the tetragonal phase is observed under given conditions–thereby implying (i) *metastability* of such phase rather than thermodynamic *stability*, and (ii) the need to account for kinetic considerations. This ambiguity leads to reports of the critical GS that spread over a broad range.

In the following, in order to frame the role of GS on the phase stability of zirconia and, in turn, on LTD, we will review the thermodynamic approach – which sets the intrinsic limits of this complex phenomenon – and then briefly mention the main factors that influence the thermodynamic equilibria and the kinetics by which transformation occur. We will then provide some of the key data (Table 1) selected among the most significant when keeping in mind LTD, thus laying the basis for a discussion and for drawing some engineering guidelines in the following section.

Though here we shall discuss the specific role of GS as a separate matter, as mentioned, chemical stabilizers, stress, and GS are actually interlinked and affect one another in a complex way. For example, an increase in the content of stabilizer induces a reduction of the grain size [80], while a larger grain size leads to higher local stress [81].

As for a purely thermodynamic approach, one important implication of Eq. (3) is that, for small crystal sizes, the overall free energy is heavily influenced by the term associated to the crystal surface. By developing the ΔG_{t-m}^{CHEM} and the ΔG_{t-m}^{SURF} terms, one can see (details can be found for example in Refs. [77,78]) that for a given temperature, even below the transformation temperature of an infinitely large solid (∼1170 °C, as seen above), ΔG_{t-m} can be negative if the radius is less than a critical value. The approach outlined here also leads to the prediction that the critical size depends on the temperature T as $1/r_c = A - BT$ where A and B are constants depending on the surface energy and the transformation enthalpy [82]. Practically, the lower the temperature, the smaller is the critical size.

The key implication for the purpose of the present review is that there exists a critical radius r_c such that for $r < r_c$ a zirconia crystal can be thermodynamically stable in the t-form even at low temperature. In other words, a reduction of the grain size below a certain critical value has the potential of

fully inhibiting LTD. This simple thermodynamic approach successfully predicts the critical size at various temperatures for powders of both pure and stabilized zirconia. Although the vast majority of the available data refer to measurements conducted above 100 °C, a number of reports suggest that at room temperature for pure zirconia powders the critical size is in the range of 5–10 nm [77,83,84]; similar values can be calculated following a general framework proposed by Mayo and co-workers and well tested for temperatures above 300 °C [85]. This approach also enables the calculation of the critical size for Y-TZP powders, which is about 90 nm for 1.5Y-TZP.

While powder data provide a useful framework for reasoning on design guidelines (for example about the choice of the starting GS), they alone are of little practical interest; it is more important to focus on the relationship between GS and LTD in zirconia-based densified components, a problem with important consequences but much more complex to tackle. The complexity arises from the fact that crystals in a solid (*grains*) are constrained by each other and are not free to expand or contract as they are in a powder. This leads to stress generation due to changes of volume/shape associated with thermal expansion or phase transformations; moreover, in a solid body, stresses can be concentrated by local defects. The role of stress in LTD has already been described; here we will only remark that, generally, an applied hydrostatic pressure has the effect of increasing the critical size, while non-hydrostatic stresses introduce a broadening of the transition between the m- and t-phase—i.e. the coexistence of the two phases over a range of temperatures [78]. All in all, the t-form can be stable in zirconia solids even if the grains are much larger than the critical GS identified above for powders. By including the effect of strain energy on the formation of microcracks and twins [81,86], or the effect of the stabilizers [82,85], accurate predictions of the critical GS in densified solids as a function of the temperature in Y-TZP ceramics have been obtained at temperatures above 300 °C. At room temperature, a critical GS of 31 nm has been calculated by Garvie for pure zirconia ceramics [78], while Mayo and co-workers derive the critical GS at various temperatures and for various contents of stabilizer: for example, from their work it is possible to extrapolate a value of about 150 nm for zirconia stabilized with 1.5 mol% Y_2O_3 (once again, in dense ceramics). Table 1 presents experimental data (thus affected by kinetic issues) about the critical GS of 3Y-TZP dense ceramics, together with the theoretical prediction of the thermodynamic critical GS.

As mentioned above, much of the confusion that seems to emerge from the literature about the critical GS arises from the fact that it is customary to indicate by this term the maximum size for which a t-form can be observed, regardless for

its stable or metastable nature. This distinction, however, is of primary importance when the role of the GS on LTD is considered: while a thermodynamically *stable* tetragonal zirconia will never transform, a *metastable* phase is prone to transformation upon even slight variations of the system conditions and these variations are likely to occur if given enough time [74,87–90].

From an engineering point of view, in the design process of a zirconia ceramic product it is of little importance if the tetragonal phase is *stable* and will never degrade, or if it is *metastable* and will degrade in a time that is longer than the lifetime of the product. In the latter case, however, it is critical to know the transformation kinetics of the material.

One key factor affecting the kinetics in a number of ways is once again GS. First, local stress arises from the thermal mismatch between grains, due to the slight anisotropy of the CTE along the different crystallographic axes in zirconia, and this stress is higher for larger grains [81]. GS also affects the kinetics of transformation in metastable t-zirconia due to the influence it has on the nucleation process. It has been mentioned that the metastable t-form transforms to monoclinic via thermally activated nucleation and growth processes. The kinetics, therefore, depends on the number of nuclei that can form. In a number of ways, including one described in the following, grain boundaries can be considered as preferential nucleation sites, and this leads to the expectation that the transformation becomes kinetically favored when a large number of grain boundaries is available—i.e. when the GS is small. In summary, although reducing the GS of metastable t-zirconia ceramics has a beneficial effect as it reduces the thermodynamic driving force for transformation, from a kinetic point of view a small GS might favor a faster transformation through efficient nucleation of the m-phase at the grain boundaries. This effect was in fact experimentally observed in experiments conducted on 2 and 3Y-TZP more than 98% dense ceramics: after exposure in water at 80 and 120 °C, samples with grain size of less than 0.6 μm showed more m-content than those with grain size ranging between 0.6 and 0.8 μm [91]. This evidence is somewhat in contradiction with other experimental observations indicating that a grain size of ∼0.35 μm or smaller hinders degradation [92,93]. The guidelines presented in the last paragraph are based on the fact that even a small amount of porosity contributes to enhancing the nucleation effect observed in Ref. [91]: consequently, the increase of transformation rate associated with the reduction of grain size might be avoided in ceramics close to the theoretical density [92,93].

6. Experimental methods

In this section we briefly present the experimental methods which can provide evidence for the occurrence of the aging phenomenon. A more extensive review can be found in Ref. [18], with the exception of the stress measurements, which are not treated at all in that work.

Low temperature aging of zirconia is usually conducted in autoclave or steam chambers, where the pressure of water vapor, the temperature and the elapsed time are the controlled experimental variables. In some cases the ceramic samples are simply immersed in water. The observed experimental variable is the m-zirconia content.

By definition, the difference between the t- and m-polymorphs is crystallographic and, hence, the sovereign technique to investigate crystallographic differences is X-ray diffraction. The most famous contribution on the use of XRD to distinguish between m- and t-zirconia is due to Garvie and Nicholson [94]. In this contribution it was shown how the monoclinic content X_m, relative to the zirconia phase (and not to the overall material), could be determine by the following formula:

$$X_m = \frac{I_m^{(\bar{1}11)} + I_m^{(111)}}{I_m^{(\bar{1}11)} + I_m^{(111)} + I_t^{(101)}} \qquad (6)$$

where I represents the intensity of the XRD peaks and the numbers in brackets are the miller indices of the pertinent crystallographic planes. Practically, a XRD scan between 25 and 30° of 2theta covers the range necessary to observe all peaks used in the formula above. Though well established and widely known, XRD is somewhat limited in the lateral resolution on most of the commonly available instruments; the typical spot is of the order of some millimeters and the sample should be flat. Another technique which can yield a much higher lateral resolution is based on the Raman effect, that is the inelastic scattering of light due to the interaction with vibrating matter [95]. This forms the basis of Raman spectroscopy and, when implemented with an optical microscope in a back-scattered configuration, the same objective lens used to observe the sample is then used to deliver a laser light on the region of interest of the sample [96]. The light rejected by the sample is dispersed/analyzed in the frequency domain, providing vibrational information (similar in nature to those provided by Infra Red spectroscopy) on the sample under analysis. Zirconia has a very strong Raman signal both in the t- and m-variants and the two vibrational spectra are very much different. Using Raman spectroscopy, the amount of m-zirconia with respect to the total amount of zirconia can be determined according to [97]:

$$X_m = \frac{I_m^{(181)} + I_m^{(192)}}{I_m^{(181)} + I_m^{(192)} + 0.97(I_t^{(148)} + I_t^{(264)})} \qquad (7)$$

where now the apices indicate the position of the pertinent Raman bands expressed in wavenumbers (cm^{-1}). For the specific issue of t–m transformation, Raman spectroscopy is a far more convenient method than XRD, as recognized also by Chevalier et al., in their review on LTD [98]: beside the better lateral resolution (which can be as good as some μm), on typical spectroscopes a good Raman spectrum of t- and m-zirconia can be acquired in few seconds, as opposed to the tens of minutes necessary for XRD. A further specific advantage of spectroscopic methods is that they allow to determine mechanical stresses experimentally, since most Raman and luminescence bands change their position with stress [99]: practically, it is possible to determine stresses from the shift of the spectroscopic bands, measured with respect to a reference stress-free state. This method is known as piezo-spectroscopy [99,100] and it has provided a unique insight

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Table 2 – Key low-temperature aging parameters of some 3Y-TZP available in the literature. Predicted lifetime and degradation at 37 °C (last two columns) have been calculated based on AMJ kinetics where the exponent n in Eq. (5) is taken to be 1—a particularly benign case. The reported spread on the values is calculated based on the uncertainty of the linear regression applied to the experimental data extracted from the original references. The predicted lifetime at 37 °C is the time it takes for the monoclinic phase to reach 25% of the volume, i.e. the amount indicated by the ISO standards as the acceptable monoclinic content after accelerated tests. The column labeled "Predicted degradation – 10 years at 37 °C" represents the volume fraction of monoclinic expected to be found after 10 years at 37 °C. The values marked with an asterisk are experimental data at room temperature or predictions interpolated from data that include at least one room temperature data point.

Ref.	Density (% theoretical)	Grain size (m)	Average residual stress (MPa)	Temperature range[a] of data collection (°C)	Environment	Calculated activation energy (kJ/mol)	Predicted lifetime at 37 °C (years)	Predicted degradation – 10 years at 37 °C (% monocl.)
[46]	99.9	0.5	N/A	70–130	Water	106	6–12	21–36
[104]	98.9	0.4	N/A	83–120	Water	93.8	1–2	73–90
[104]	99.3	0.6	N/A	83–120	Water	78.7	<1	96–99
[104]	99.9	1.1	N/A	83–120	Water	76.2	<1	>99
[105]	99.8	0.5	N/A	130–220	Air	81	15–48	6–18
[88]	N/A (porous coatings)	>1	0	25–300	Air	56	<1 (*)	>99
[74]	N/A (alumina–zirconia composites)	0.3	400	25	Air	N/A	6 (*)	N/A

[a] Range of temperatures where experiments have been performed, and over which the activation energy has been calculated as linear regression of the experimental transformation rates.

about the interplay between t–m transformation, aging and stress [69,73,74,101]. For the materials of interest here (Y-TZP, Ce-TZP and alumina) piezo-spectroscopy is the only viable method to determine stresses experimentally and it has the advantage that the same spectroscopic data provide information also on the phase composition of the material under investigation.

Thermal methods (differential thermal analysis, DTA; differential scanning calorimetry, DSC; thermal dilatometry, TD) can also provide evidence of the t–m transformation, but they are limited to the transformation occurring during the experiment and, hence, they are practically useless for aging studies.

Methods sensitive to the surface topography (optical interference, OI; scanning electron microscopy, SEM and atomic force microscopy, AFM) can provide indirect evidence of the t–m transformation in the form of uplift from flat surfaces. If the same sample is observed after time they can also provide indirect evidence of aging, but they cannot be used for bulk quantitative assessment.

7. Limits of lifetime predictions at low temperature derived from accelerated aging tests

Degradation rates at room or body temperature of Y-TZP ceramics are currently not available, and accelerated tests at intermediate temperature (100–300 °C) are the only basis for extrapolating an estimate of the transformation rate and, hence, of the product lifetime. This approach relies on the assumption that the transformation rate follows the same Arrhenius-like trend down to room/body temperature. Unfortunately, such extrapolation could lead to a significant error in estimating room/body temperature lifetimes.

Firstly, the uncertainty associated with the determination of the activation energy is generally high. In Table 2 we report the estimates for the amount of m-phase formed after 10 years (a reasonable lifetime for dental applications), as well as the time it takes for 25% of monoclinic to develop (i.e. the maximum acceptable amount, based on current international ISO standards [22]). The effect of the activation energy uncertainty is clearly dramatic, so that no sound lifetime predictions can be made on the reliability of these ceramics at low temperature.

Secondly, the only available data for LTD at room temperature indicate faster transformation rates than those derived by extrapolating data obtained at medium-low temperature. For example, Lughi and Clarke [88–90] showed that in zirconia thermal barrier coatings (3Y-TZP and 4.5Y-TZP) obtained by electron-beam deposition, significant amounts of monoclinic (up to 100%, depending on the processing) appear after only few months in laboratory air at room temperature. Also, Sergo [74] showed that up to 25% monoclinic can form at room temperature after only 6 years in 3Y-TZP zirconia/alumina laminates. It should be noted, however, that coatings and laminates are not expected to behave exactly like Y-TZP ceramics: the microstructure of the coatings is columnar and presents some inter-columnar open porosity; also, in zirconia–alumina composites, zirconia is under significant residual stress. This residual stress, in particular, is expected to be a factor in accel-

erating the transformation rate at room/body temperature, since lower temperatures imply higher residual stress: considering the example of alumina–zirconia composites, from Eq. (5) one can estimate that in the zirconia phase the tensile residual stress is 40–50 MPa higher at room temperature than at temperatures commonly used for the accelerated tests (e.g. 134 °C as in the ISO Standards [22]). This difference might become significant in accelerating LTD. Analogous considerations hold even in pure Y-TZP, where a thermal stress arises from the anisotropy of the thermal expansion coefficient in zirconia. Although in this latter case much lower residual stress is expected at room temperature with respect to intermediate temperature (<10 MPa), such temperature difference is expected to enhance local stress concentration as well, with negative effects on LTD.

Lastly, one critical point in the current design approach of TZP is specific to the International ISO Standards for Y-TZP-based implants for surgery. The standard imposes that a maximum of 25 wt.% of monoclinic is present after an accelerated aging test conducted for 5 h at 134 °C and 2 bar [22]. However, this requirement does not provide any information about the actual lifetime at near-room temperature. The main reason, apart from the spread in predicted lifetimes associated to the abovementioned uncertainty in the determination of the activation energy, arises from the fact that the activation energy for the t–m transformation in a given material cannot be derived from such a "single datapoint" procedure (indeed, at least two accelerated tests at different temperatures would be the minimum requirement for a rough estimate). Therefore, lifetime prediction at room or body temperature according to the ISO standards relies on the assumption that the activation energy is approximately the same for all stabilized zirconia ceramics—a risky assumption, considering the wide spread of values reported in the literature (Table 2).

8. Conclusions and engineering guidelines for the use of zirconia as dental materials

After presenting the most relevant experimental data, we proceed now to formulate some possible guidelines for a practical use of zirconia as dental materials. First of all the issue must be addressed whether the aging of t-zirconia to the m-polymorph should be avoided or can be lived with, also in light of the fact that there is some evidence that a limited and superfi-

cial t–m transformation can causes an increase of the strength of the material [102]. The reason is that the t–m transformation induces a local overall compressive stress on the surface, which tends to close a potential advancing crack (clearly the superficial compression must be accompanied by an equilibrating sub-surface tension, otherwise the part would not be in mechanical equilibrium). The data presented, however, are limited to strength values collected right after sintering and the possible effect of aging has not been examined. In principle, a surface engineering approach could be imaginable, whereby a tight control of the superficial transformation in the samples is adopted, but this is totally impracticable in a standard dentistry laboratory.

Some studies indicate that alumina/zirconia mixtures are less prone to LTD than pure zirconia [103,104], but the data presented here induce us to suggest that at or near room temperature and everything else been equal (GS of t-zirconia and stabilizer type and content), ZTA is probably more sensitive to ageing than pure t-zirconia because of the microscopic tensile stress to which t-zirconia is subject when mixed to alumina [74].

In order to establish viable engineering guidelines, we firstly need to assess the design constraints as they can be gathered from the experimental evidence presented in the previous sections and substantially summarised in Table 2:

- LTD occurs in pure zirconia samples stabilized with as much as 2.5 mol% Y_2O_3;
- LTD occurs in alumina/zirconia samples where zirconia is stabilized with 2.5 mol% Y_2O_3 and 8.5 mol% CeO_2;
- tensile stresses of the order of some hundreds MPa are sufficient to promote long-term LTD;
- intimately mixed alumina/zirconia (where zirconia is in microscopic tension) samples are more prone to LTD than layers of pure zirconia subject to macroscopic tensile stresses;
- zirconia samples with GS of the order of 300 nm can exhibit LTD over some years;
- All experimental evidence points to the fact that the t–m transformation occurs initially on the samples surface, and thence penetrate underneath;
- water vapor possibly causes and certainly accelerates LTD.

The guidelines that we are about to propose are based on the previous conclusions and on the following hypoth-

Property	Unit	Requirement
Density	% of Theoretical density	>99%
Stabilizer content: Y_2O_3	mol%	$3.5 < x < 8$
Grain size	μm	GS < 0.3
Residual stress	MPa	$\sigma < 300$ (tensile)
Monoclinic content	Fraction wrt to total zirconia	
Initial		Negligible
After aging test (134 °C, 2 bar H_2O, 1 h)		Negligible
Strength in 4 point bending	MPa	
Initial		600
After aging test		600

Table 3 – Engineering guidelines for use of zirconia-based materials in restorative and prosthetic dentistry.

esis: the key properties of zirconia (high chemical stability, biocompatibility, low Young's modulus, large natural availability, consolidated industrial know-how) justify its use even in absence of phase transformation toughening, because to implement PPT on zirconia-based dental components implies, to date, exposing them to LTD on a time scale not acceptable in restorative and prosthetic dentistry. Simply stated, *t*-zirconia should be prepared and implanted in a way to make it non-transformable. This will reduce the strength by some amount, but will also make the material completely unaffected by LTD [47].

Based on all the above, the engineering guidelines for the use of zirconia as dental materials are presented following the scheme of ISO standards [22] in Table 3.

Acknowledgement

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