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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.

Contents

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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-