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Development of a novel zirconia dental post resistant to hydrothermal degradation

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Abstract. Tetragonal Zirconia Polycrystals stabilized with 3% mol. content of yttria (3Y-TZP) has excellent properties in terms of strength and fracture toughness. These properties are mostly imputable to the transformation toughening mechanism, by which the doped metastable tetragonal phase of zirconia transforms to monoclinic under applied stress ahead of a crack. This phenomenon is accompanied by a volume expansion of 5%, and increases the resistance to crack growth, thus leading to higher toughness and strength. An important drawback of this material is represented by the Low Temperature Degradation (LTD or aging), which consists in the progressive tetragonal-to-monoclinic phase transformation by the influence of water. This work focuses on the improvement of 3Y-TZP aging behavior in order to develop a novel dental post, by means of the addition of ceria from the surface. This was achieved through the impregnation of the pre-sintered samples with a solution containing Cerium, followed by sintering. Various pre-sintering temperatures were studied in terms of microstructure, mechanical properties and aging resistance. The novel zirconia dental posts developed in this work are much more resistant to LTD as compared to the base material with no loss in mechanical properties.

1. Introduction
Zirconia-based ceramics have been used in different engineering applications because of their excellent strength, fracture toughness, hardness and chemical stability. In the 90’s, biomedical grade 3 mol% yttria-tetragonal polycrystalline zirconia (3Y-TZP) became an alternative to alumina as structural bio-inert ceramic in orthopaedics because of its substantially higher fracture toughness. The use of 3Y-TZP in orthopaedics paved the way to new implant designs that were not possible with alumina, which is more brittle. Examples of medical applications are smaller 3Y-TZP femoral heads, 3Y-TZP knees and, more recently, a large range of dental devices (crowns, bridges, abutments and dental implants) [1]-[3].

Pure zirconia exhibits three allotropes: monoclinic (m) phase from room temperature up to 1170 °C, tetragonal (t) phase from 1170 °C up to 2370 °C and cubic (c) phase for temperatures above 2370 °C. The t – m phase transformation is martensitic and is accompanied by a volume expansion of approximately 5%. In 3Y-TZP, yttria is employed to retain the t phase, in a metastable condition, down to room temperature, avoiding the t - m transformation and related expansion during cooling. In addition, stress can locally activate the transformation of the metastable phase; when this occurs ahead of a growing crack, the expansion produces a net compressive residual stress which contributes to
hinder crack extension. The mechanism is called transformation toughening and results in a material with higher toughness [4].

The strong drawback of this material is represented by its poor resistance to Low Temperature Degradation (LTD or aging): the metastable \( t \) phase tends to convert spontaneously and progressively into the monoclinic one when the material is exposed to moderate temperatures and humid environment [5]. The transformation starts from the exterior and is accompanied by micro-cracking [6], leading to an increase in roughening and loss of surface mechanical properties [7], [8].

Although the kinetics of transformation is maximal at temperatures around 250 \(^\circ\)C, there is now evidence that LTD is also possible even at human body temperature. This fact contributed to a high rate of failures for some batches of 3Y-TZP femoral heads in 2001, with the consequence that zirconia is not used anymore in these prosthesis [9].

Several authors have developed different methods for increasing the resistance to aging, as long as LTD sensitivity is affected by many variables such as grain size, stabilizer type and content, composition and homogeneity, residual stresses, temperature and environment, porosity and phase separation [7]. The use of stabilizers like Cerium oxide seems to be a promising way to reduce LTD [10]. The slower kinetics of degradation related with the use of Ce stabilizer appears to be due to the lower content of vacancies (Ce\(^{4+}\) does not generate vacancies in ZrO\(_2\) lattice), which allows a reduced mobility of water species responsible for the LTD, if compared with the yttria stabilized material. Nevertheless, the addition of such stabilizers tends to compromise mechanical properties of 3Y-TZP, especially in terms of strength, as a result of grain growth [11], [12]. A way to improve aging resistance and maintain the bulk mechanical properties of the base material is represented by the diffusion of Cerium oxide from the surface after sintering [13].

In the common processing route for 3Y-TZP dental implants, sintering is split into two stages: pre-sintering and full sintering, the second at higher temperature. At the pre-sintered state, blanks are soft enough to allow machining via CAD-CAM technology in order to shape the final geometry. After machining, parts are sintered and post-processed.

In the present work, Cerium oxide is added through infiltration of a solution containing Cerium into the pre-sintered porous ceramic piece, previous to final sintering. In a preliminary study, the process was optimized investigating different ceria contents in terms of mechanical properties, chemical composition and aging resistance after sintering and accelerated aging. A set of dental implant prototypes was prepared according to the process previously developed and their flexural strength was measured before and after aging to verify that mechanical properties are not affected either by ceria introduction or by LTD. The final aim is to improve LTD resistance without affecting mechanical properties.

2. Materials and methods
The base material was 3Y-TZP powder provided by Tosoh Corp. In a preliminary study, samples were produced in form of discs, in order to facilitate their manipulation and test. Here, cylindrical prototypes approx. 16 mm long with 2.9 mm in diameter, i.e. with geometry similar to commercial dental implants, were manufactured.

The powder was compacted by cold isostatic pressing (CIP) at 200 MPa with a dwell time of 10 minutes. The rod compacted bodies were then pre-sintered in air during one hour in a tubular furnace (Hobersal ST-18). The heating and cooling rate was 3 \(^\circ\)C/min. Half of the pre-sintered rods were submerged in a solution containing Cerium for 2 hours to ensure its infiltration in the open porosity. The prototypes were then sintered at 1450 \(^\circ\)C during 2 hours with a heating/cooling rate of 3 \(^\circ\)C/min and tested “as fired”.

2.1. Aging sensitivity
The degradation process was simulated in autoclave under water vapour at 131 \(^\circ\)C, 2 bar, during 30 h, for the doped and undoped prototypes. According to the degradation kinetics studied by other authors
[14], this treatment corresponds roughly to more than an average human lifetime at the body temperature (37 ºC) and atmospheric pressure. Thus, the process may be used as a good indicator of resistance to LTD for the lifespan of an implant. To quantify aging resistance, monoclinic phase content was measured after artificial aging through X-ray diffraction (XRD) analysis on mirror-polished samples. The equipment was a Bruker AXS D8 Advance diffractometer using Cu-Kα radiation and θ/2θ configuration. The monoclinic phase was calculated employing the equation proposed by Toraya et al. [15].

2.2. Mechanical characterization
Density and apparent porosity were measured using the Archimedes’ method in distilled water, after pre-sintering and full sintering. Mechanical tests were carried on before and after artificial aging. Hardness and fracture toughness were determined by the Vickers indentation method, applied on the polished surface of the samples. For fracture toughness, the formula of Niihara et al. was employed [15]. Three-point bend test was performed on prototypes to evaluate their flexural strength, before and after aging treatment, for doped and undoped conditions (base material). Crosshead speed was set at 0.001 mm/s as indicated by the standard ASTM C 1161-02c [17].

Figure 1. Prototypes after sintering.

2.3. Microstructural and elemental characterization
The microstructure was evaluated from SEM micrographs of mirror-polished and thermally etched samples. The average grain size was calculated using commercial image processing software. The chemical composition of the material was determined using a CAMECA SX50 Electron Probe and the results were converted to a molar basis (CeO₂ mol%).

3. Results and discussion
The measured density at the pre-sintered state was of 3.17 ± 0.05 gr/cm³, 51.7 % of the theoretical one. An apparent porosity of 47.2 ± 0.2 % was calculated. After sintering, the density was 6.08 ± 0.02 gr/cm³, reaching almost the theoretical value.

Electron Probe Micro Analysis (EPMA) measured CeO₂ surface contents of approx. 4 mol%. Thus, significant amounts of ceria were introduced into the material. Moreover, repeating the measurement along the cross section of the specimens, it was shown that less ceria reached the bulk, leading to a value of approx. 2.5 mol% at 1 mm depth from the surface.

The grain size calculated from analysis of SEM micrographs was similar for the doped and undoped specimens, with values of the average circular diameter around 0.35 µm, as showed in Figures 2 and 3. The hardness resulting from Vickers testing (load = 1 and 30 Kg) was of 12.8 ± 0.5 GPa for specimens either with and without ceria, before and after aging treatment. Indentation fracture toughness tests gave values of approx. 4.5 MPa-√m for all the conditions. Therefore, it can be stated that ceria addition did not modify substantially the microstructure of the material and its mechanical properties measured on the surface.
Figures 2, 3. SEM micrographs of the base material (left) and the ceria doped one (right). Scale = 2 µm.

As shown in Figure 4, the diffraction patterns of the base and doped materials were quite different after aging. For the base material, the $m$ phase peaks were noticeable, resulting in a calculated 60% approx. of transformed phase. On the other side, for the doped material, $m$ peaks were barely perceptible, corresponding to only approx. 5% of $m$ phase. The treatment was then effective in improving the aging resistance.

Figure 4. XRD patterns of aged specimens. (A) Material doped with ceria, (B) 3Y-TZP base material. The representative peaks for monoclinic ($m$) and tetragonal ($t$) phases are highlighted as they appear on the spectra.

The results of the three-point bend test are presented in Figure 5. The average strength was ranging between 530 and 600 MPa for all the four conditions of the material tested. Therefore, there was no evidence that the treatment proposed for ceria addition could affect the mechanical strength of the prototypes. These values do not represent the true mechanical strength of the material as long as the surface of the prototypes had not been prepared, in terms of defects elimination, before testing. Nevertheless, they provide a way to compare the strength of prototypes processed under different conditions and the effect of ceria on actual devices.
Figure 5. Three-point bend test results. Legend: white color, only 3Y-TZP; light-yellow colour, Ce doped-3Y-TZP; blank, tested “as sintered”; crosshatched, tested after aging. Red bars represent the standard deviations.

4. Conclusions
Ceria was effectively introduced into the material using the impregnation method. The amount of ceria was higher in the superficial regions than into the bulk, reaching a maximum of 4 mol%. The microstructure of the material was not appreciably modified by the infiltration. Mechanical properties were not significantly affected by ceria infiltration, both before and after artificial aging, satisfying the requirements for biomedical 3Y-TZP. The introduction of ceria into the ceramic was effective in reducing LTD after artificial aging. The results of three-point bend test on the implant prototypes revealed that the treatment proposed does not affect the strength of such devices.

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References


