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Resistance of $InO_{1.5}$-stabilized tetragonal zirconia polycrystals to low-temperature degradation

Diógenes Honorato Piva [a,*], Roger Honorato Piva [a], Marina Campos Rocha [b], Oscar Rubem Klegues Montedo [c], Márcio Raymundo Morelli [a]

[a] Laboratory of Ceramic Synthesis and Formulation, Federal University of São Carlos, São Carlos, SP, Brazil
[b] Department of Genetics and Evolution, Center of Biological Sciences and Health, Federal University of São Carlos, São Carlos, SP, Brazil
[c] Laboratório de Cerâmica Técnica – CerTec, Universidade do Extremo Sul Catarinense, Criciúma, SC, Brazil

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ABSTRACT

9 mol% $InO_{1.5}$-stabilized zirconia (ISZ) was synthesized using a coprecipitation method. Sintered samples were hydrothermally degraded for periods of up to 40 h in an autoclave at 134 °C and 2 bar. The tetragonal to monoclinic phase transformation (t–m) was observed by X-ray diffraction (XRD) and atomic force microscopy (AFM). An increase in surface roughness, associated with the martensitic t–m transformation was observed by AFM. According to XRD patterns, 30 vol% of the tetragonal phase initially present in the ISZ sample transformed into the monoclinic phase after the hydrothermal degradation. The impact of the transformation was evaluated in terms of structural integrity. Vickers hardness was not affected, however the flexure strength decreased by about 43% after autoclave treatment for 10 h. A key finding from this study is that, despite a rapid decrease of flexure strength during initial autoclaving step, ISZ presents a lower trend to t–m transformation than the currently used 3 mol% yttria-stabilized zirconia material. The high concentration of oxygen vacancies and low tetragonality of 9 mol% ISZ seem to be responsible for its superior resistance to hydrothermal degradation.

1. Introduction

M_yO_x-stabilized tetragonal zirconia, where M_yO_x is an oxide of an aliovalent cation, has been widely considered for use in dental and orthopedic applications [1,2]. Tetragonal zirconia (t-ZrO_2) is used as a biomaterial mainly because of its esthetics, biocompatibility, and excellent mechanical properties. The high strength and toughness observed in t-ZrO_2 are attributed to a stress-induced transformation from a tetragonal to a monoclinic (t–m) phase that occurs near crack tips and is accompanied by a volumetric expansion that hinders crack propagation [3]. However, this transformation is also a major drawback since it can be induced at the surface of samples when they are exposed to humid or aqueous environments at low temperatures (20–300 °C) which leads to formation of microcracking and loss of strength. This phenomenon is commonly referred to as low-temperature degradation (LTD) or aging [4,5].

Several hypotheses have been proposed to explain how the presence of water results in this t–m transformation. According to one report, the adsorption of water molecules on the surface and the subsequent annihilation of oxygen vacancies is likely responsible for LTD [6]. Many researchers have argued that tetragonal zirconia is stabilized as a direct result of the presence of oxygen vacancies, which are introduced by alloying aliovalent stabilizers [7]. To date, tetragonal zirconia stabilized with cations such as Mg^{2+}, Ca^{2+}, Y^{3+}, Ce^{4+}, Sc^{3+}, Er^{3+}, Gd^{3+}, La^{3+}, Yb^{3+}, Eu^{3+} [5], and other rare-earth metal oxides have been reported. Finding new stabilizers for zirconia largely remains a matter of experimentation. Among the aforementioned stabilizers, yttria is the most popular, and, consequently, many LTD studies have focused on commercially available 3 mol% yttria-stabilized zirconia [4].

Although not widely known as a zirconia stabilizer in the biomaterial field, indium (III) oxide (In_2O_3) has been reported to stabilize zirconia in a manner similar to that of yttria. In_2O_3-stabilized tetragonal zirconia (InSZ) has attracted significant attention as a candidate for thermal barrier coating (TBC) applications because of its high temperature corrosion resistance [8,9]. The potential for In_2O_3 stabilizer to be applied as a TBC was found to be limited by its poor high-temperature stability; however, researchers concluded that the stability of In_2O_3 may not be a problem at lower temperatures. Since substantial effort has been invested in seeking alternative stabilizers for the tetragonal phase with LTD resistance and little is known about the behavior of InSZ

* Corresponding author.
E-mail address: diogenespiva@gmail.com (D.H. Piva).

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when exposed to humid environments, we report herein on the hydrothermal degradation of 9 mol% $InO_{1.5}$-stabilized tetragonal zirconia (ISZ). X-ray diffraction (XRD), atomic force microscopy (AFM), Vickers hardness and flexure strength testing were used to characterize the t–m transformation.

2. Experimental

$InO_{1.5}$-stabilized zirconia (9 mol%) was synthesized using a coprecipitation method. This indium (III) oxide concentration was selected because it provides a higher tetragonal phase content at 1300 °C (the sintering temperature used in this work) according to the phase diagram proposed by Sheu et al. [10]. $ZrOCl_2 \cdot 8H_2O$ (99.9%, Alfa Aesar) and $InCl_3$ (99.99%, Alfa Aesar) were used as precursores. Water was removed from the coprecipitated amorphous hydrous gel by azeotropic distillation [11]. The dried precipitate was then calcined at 600 °C for 1 h to obtain a crystallized ISZ powder.

Cylindrical pallets, 10 mm in diameter and 2 mm in length, were uniaxially die pressed using a pressure of 200 MPa. The green bodies were sintered at 1300 °C for 3 h in air using heating and cooling rates of 5 °C min^{-1} (sintering density reaching 6.15 g cm^{-3}). Prior to hydrothermal degradation, samples were polished with diamond pastes of decreasing size (9, 6, and 3 μm) and then with a silica colloidal suspension to achieve the final smooth surface. In addition, specimens were thermally etched at 1200 °C for 15 min to expose their microstructures. Samples were hydrothermally degraded for 0, 5, 10, 20, and 40 h in an autoclave (Type 102, Fabbe Primar, Brazil), in the presence of water steam, at 134 °C and 2 bar (i.e., under the conditions prescribed by ISO standard 13356). Autoclaving for longer time was achieved by cycling of 5 h.

The crystal structures of the samples were identified by XRD (Siemens D5005) using a Cu $K\alpha$ radiation (30 mA, 40 kV), scan range of 5–80° (2θ), step size of 0.02°, and scan time of 2 s per step. Phase analyses of ISZ powders were also performed using Raman spectroscopy (Renishaw, inVia), at 25 °C. Excitation was achieved using a 532 nm laser and spectra were recorded from 1–1000 cm^{-1}. The microstructure of the sintered sample was observed by scanning electron microscopy (SEM; FEI Inspect S 50). The surface topographies of selected specimens were analyzed by AFM (Multimode Nanoscope IVa, Bruker). Surface roughness (R_a) was assessed using the NanoScope Analysis software package. Monoclinic phase content (V_m) were calculated using the Garvie and Nicholson's equation [12], as modified by Toraya et al. [13]. Surface hardness measurements were performed using a Vickers indentation tester (Shimadzu Micro Hardness Tester HMV G20 Series), using an applied force for of 9.807 N and a dwell time of 15 s. The presented values indicate the mean value and standard deviation of 10 indentations. Flexure strength of the specimens hydrothermally degraded for 0, 5 and 10 h were performed in a universal testing machine (EMIC DL10000, Brazil) at a loading rate of 0.1 mm min^{-1} according to ISO 6872/2008. For flexural strength test, bar-shaped specimens (7 mm × 2 mm × 1.5 mm) were obtained in the same experimental conditions as aforementioned to the cylindrical pallet preparation. The flexural strength was calculated as mean of 10 specimens.

3. Results

Preliminary qualitative observations of the XRD pattern of the ISZ powder calcined at 600 °C (Fig. 1a) indicated the sample to be predominately either tetragonal or cubic phase. Moreover, no In_2O_3 peaks were observed in the XRD pattern, suggesting that indium (III) oxide was fully alloyed into the ISZ structure.

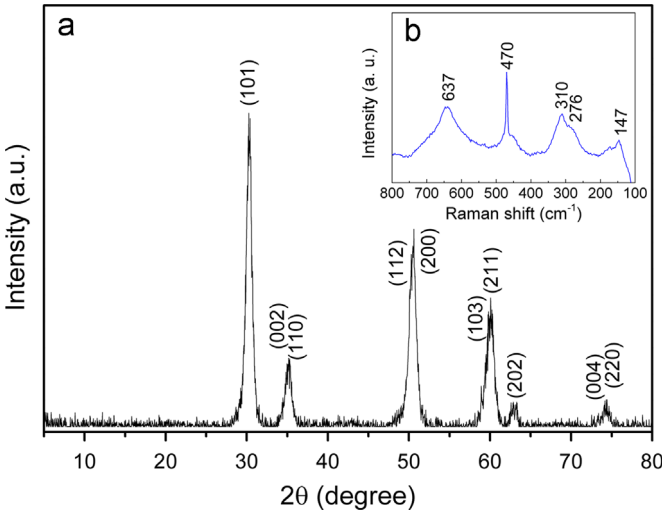

Fig. 1. (a) XRD pattern and (b) Raman spectrum of the calcined ISZ powder.

Normally, splitting of the (110) and (002) peaks at 2θ (~35°) is used to identify the presence of tetragonal symmetry. However, this splitting was not observed unambiguously because of peak-broadening effects, as shown in the XRD pattern presented in Fig. 1a. This made it difficult to confirm the presence of the tetragonal phase in the ISZ powder by XRD. Thus, Raman spectroscopy study was carried out to further confirm the predominance of the tetragonal phase in the calcined ISZ powder (Fig. 1b). The cubic phase is, theoretically, reflected by a single broad band at ~465 cm^{-1} [14]. However, the Raman spectrum of the ISZ powder showed five major bands, at 147, 276, 310, 470, and 637 cm^{-1}, which represent 5 of the 6 Raman-active modes predicted for the tetragonal phase by group theory [14,15]. This observation confirms, therefore, the predominance of the tetragonal phase after calcination of the 9 mol% $InO_{1.5}$-stabilized zirconia powder.

SEM image of a polished and thermally etched surface prior to aging is shown in Fig. 2. The SEM image shows a virtually fully dense microstructure with an average grain size of 320 nm. Note that only few intergranular pores were observed. Representative AFM topography images obtained from samples aged in an autoclave at 134 °C for 0, 5, and 40 h are shown in Fig. 3. AFM analyses revealed that the surfaces of the ISZ specimens clearly became

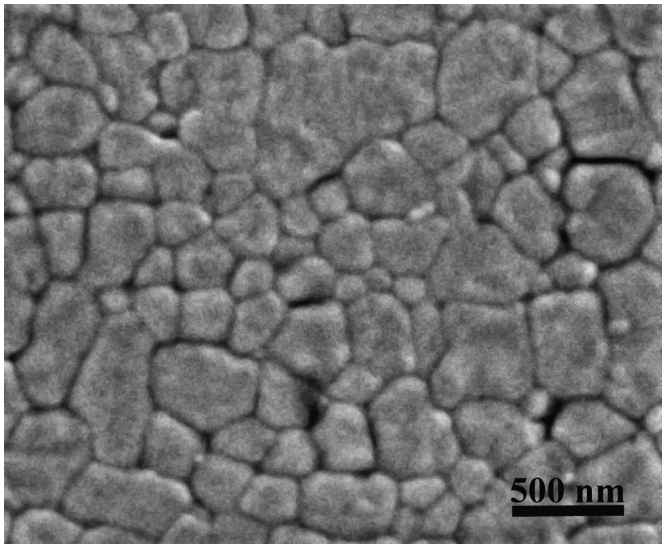

Fig. 2. SEM image of the polished and thermally etched surface of an ISZ sample prior to hydrothermal degradation.