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LOW TEMPERATURE DEGRADATION BEHAVIOUR OF 10Ce-TZP/Al_2O_3 BIOCERAMICS OBTAINED BY MICROWAVE SINTERING TECHNOLOGY

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Introduction

Zirconia is one of the most widely used ceramic materials as a biomaterial due to its outstanding mechanical properties and biocompatibility. This ceramic has three crystalline phases: monoclinic, tetragonal and cubic; but there is a spontaneous phase transformation during cooling - from the tetragonal to the monoclinic phase - which is accompanied by a volume expansion. This transformation produces significant residual stresses that induce micro-cracking and make the material useless for structural applications [1]. For this reason, the addition of a dopant is required to stabilize the tetragonal phase in zirconia at room temperature. Y_2O_3 is the most commonly used stabilizer, although in this study zirconia is doped with CeO_2, as it manages to improve some properties, such as fracture toughness and degradation [2].

Despite stabilizing zirconia with the addition of an oxide, phase transformation can occur spontaneously under humid conditions at temperatures of 20 ºC-300 ºC, leading to a drastic drop in its long-term mechanical properties. This phenomenon is generally known as low temperature degradation (LTD), hydrothermal degradation or aging [3].

Different factors can affect the aging behavior in zirconia materials, such as grain size and shape, porosity or stabilizer content, among others [4]. Some of these factors depend on the sintering process and its mechanisms. Commonly, ceramics are consolidated thanks to a heat treatment, where mass transfer mechanisms are activated. The most crucial parameters are temperature and dwell time, which set mechanical properties like hardness and its microstructure as grain size, for instance. The conventional sintering method is carried out in an industrial furnace, where the heat transfer mechanisms are conduction, convection and radiation. In this type of sintering, the heat flows from the surface to the bulk of the material. Conventional sintering requires high temperatures and long processing times and hence high energy consumption. Therefore, non-conventional sintering methods are currently being developed, such as microwave heating technology. Microwave sintering is based on the absorption of electromagnetic radiation, which causes the increase of the material temperature. The mechanism of this method differs from conventional sintering, as the

temperature gradient is on the contrary – from inside to outside. It is known as volumetric heating [5,6].
Most of the research carried out to date uses 2.45 GHz microwave applicators, however another frequency has been evaluated in this work, in particular 5.8 GHz, in order to evaluate the possible differences.
This research is focused on the study of the low temperature degradation of ceria doped zirconia/alumina composites and the effect of microwave sintering and the used frequency. In order to assess the phase change, hardness, surface roughness and monoclinic-phase transformation progression are evaluated as a function of degradation time.

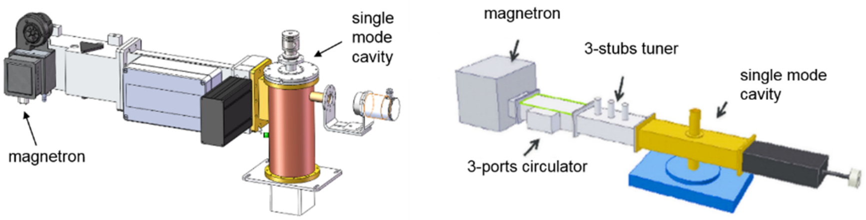
Materials and methods

A. *Sample preparation*

Ceria doped zirconia-alumina composites were employed in this work. The starting powders were 10Ce-TZP (ZrO_2 with 10 mol% CeO_2) provided by Daiichi Kigenso Kagaku Kogyo and Al_2O_3 (SPA 0.5) from Sasol. The composition 10Ce-TZP/Al_2O_3 was 65 vol.% of 10Ce-TZP and 35 vol.% of Al_2O_3, and it was selected on the basis of a previous study[7]..
The powders were pressed uniaxially at 200 MPa and sintered by microwave technology (MW) at two different frequencies (2.45 GHz and 5.8 GHz). The MW sintering conditions were 1300 ºC during 10 min of holding time. The specimens were also densified by conventional sintering (CS) in an electrical furnace at 1500 ºC and 120 min of dwell time.

B. *Microwave cavities*

Two microwaves equipments used are shown in Fig. 1. The first heating test was carried out in a cylindrical cavity operating in single-mode (TE_{111}) at 2.45 GHz frequency (Fig. 1a). In order to monitor the temperature, an optical pyrometer was used, which was previously calibrated in this temperature range. This cavity has been designed by ITACA[8].
The 5.8 GHz single-mode applicator (Fig. 1b) used for this work had a cavity with rectangular geometry (WR159). In this case, the temperature was measured simultaneously using a sapphire fiber (MIKRON M680 Infraducer, Mikron Infrared Inc., Santa Clara, CA, USA), that directly touched the free upper surface of the sample and was connected to a signal conditioner. These tests were performed in the *Microwave Application Group* at the *University of Modena and Reggio Emilia* in Italy[9].



(a) (b)

Fig. 1. Microwave systems operating at (a) 2.45 GHz and (b) 5.8 GHz.

C. *Degradation assessment*

Characterization of aged samples was assessed with a phase content analysis, roughness and assessment of mechanical properties. LTD test of 10Ce-TZP/Al_2O_3 was performed under conditions which promotes the hydrothermal degradation. Samples were aged in a steam autoclave at 120 ºC and 1.2 bar. These conditions are based on several studies which claim that 1 h corresponds to approximately 3 years in contact with human fluids. Degradation assessment was carried out as a function of time exposed in the autoclave.

A Raman spectrometer Horiba-MTB Xplora was employed in order to analyze the phase content. Measurement was made on the polished exposed surface for a Raman range 120 – 700 cm^{-1}.

Monoclinic phase in the degraded samples was estimated with the following equation, which was proposed by Lim [10,11]:

$$V_m = \frac{I_m^{181} + I_m^{190}}{0.33 \cdot (I_t^{147} + I_t^{265}) + I_m^{181} + I_m^{190}}$$

Where; V_m is the m-phase volume fraction, I_m^{181}, I_m^{190} represent the integrated area of the monoclinic peaks at 181 and 190 cm^{-1} and I_t^{147}, I_t^{265} are the integrated area of the tetragonal peaks at 147 and 265 cm^{-1}.

Surface topography and roughness were analyzed by atomic force microscopy (AFM) in tapping mode (Multimode, Veeco, Plainview, NY). Regarding mechanical properties, the hardness of the material has been measured by a nanoindenter (G-200; Agilent Technologies, Barcelona, Spain) with a Berkovich tip.

Results and discussion

Raman spectra for 10Ce-TZP/Al_2O_3 sintered by MW-2.45GHz, MW-5.8GHz and CS are shown in the Fig. 2. As can be seen, no peak of the monoclinic phase is observed after 80 hours of exposure to LTD conditions.

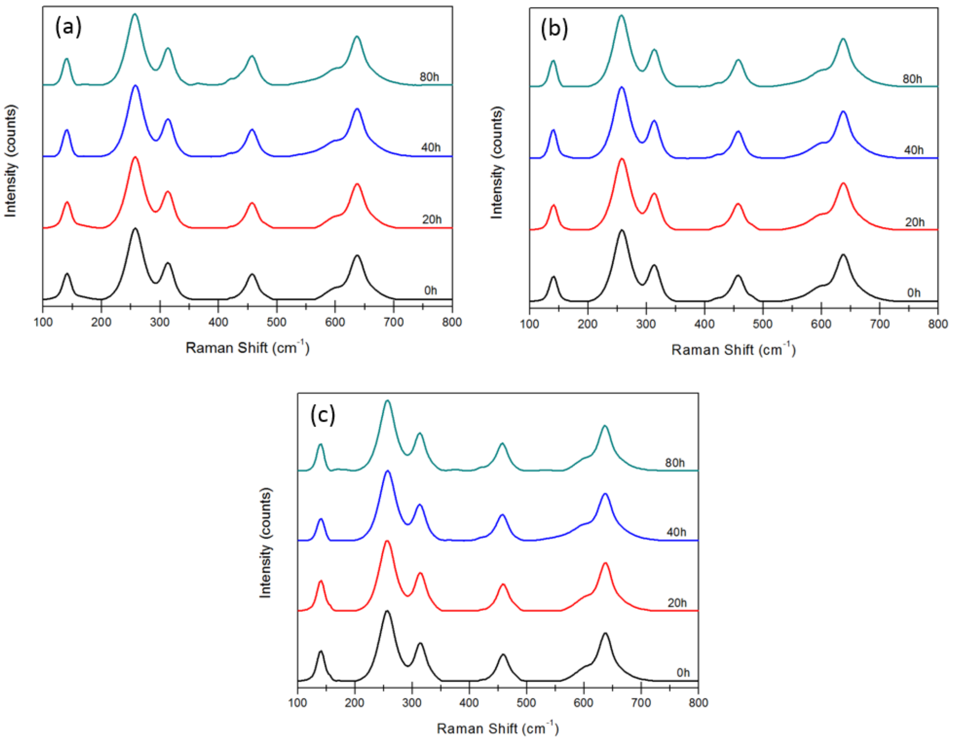


Fig. 2. Raman spectra obtained for 10Ce-TZP/Al_2O_3 sintered at different degradation times: (a) MW-2.45GHz, (b) MW-5.8GHz and (c) CS.

As there are no monoclinic peaks in the Raman spectra, it is not possible to quantify the percentage of monoclinic phase. Due to the measurement error in the Raman spectra, the percentage of monoclinic does not exceed 5%. In addition, the sintering method has not influenced on the degradation of 10Ce-TZP/Al_2O_3, as since in none of them appears monoclinic phase.

Fig. 3 shows the topographic AFM images for the conventional sintered sample. It can be verified that the roughness of the sample increases as the hours of LTD exposure rises. However, this increase is not significant, as the percentage of monoclinic is less than 5%.

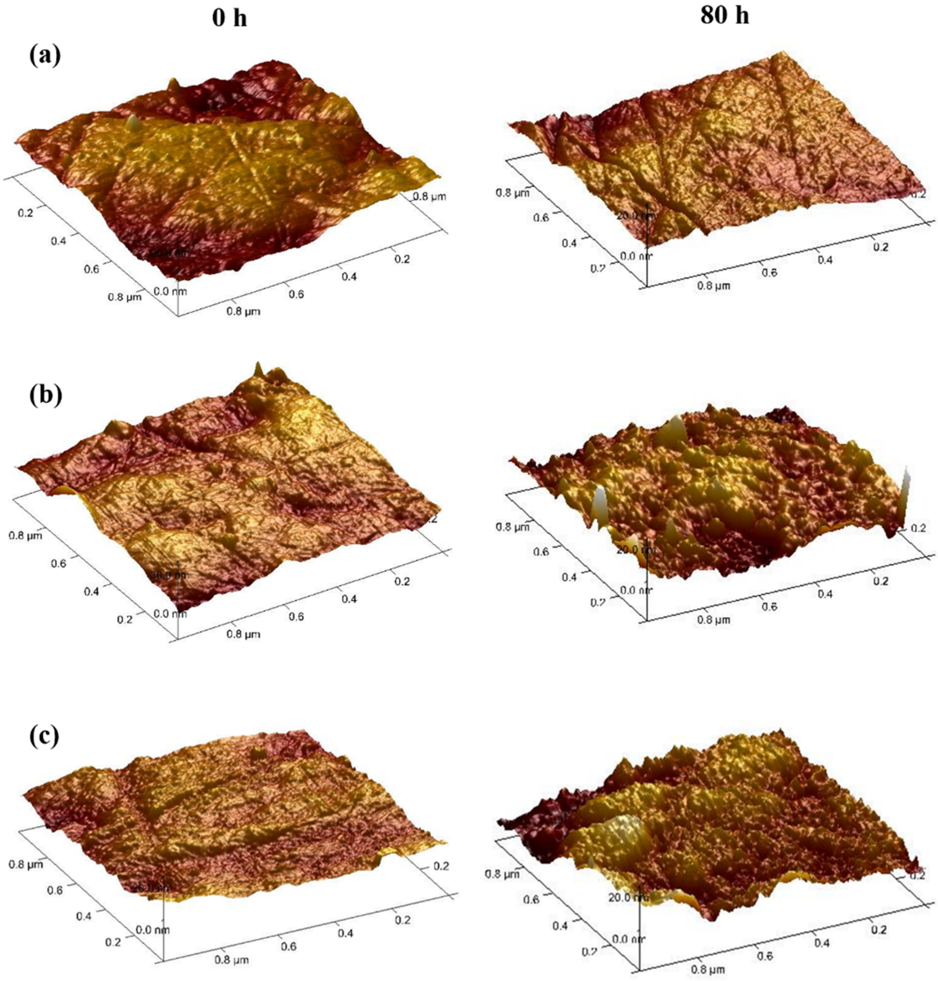


Fig. 3. Topographical AFM images at 0 h (left) and 80 h (right) of LTD exposure of 10Ce-TZP/Al_2O_3 sintered (a) MW-2.45GHz (b) MW- 5.8GHz and (c) CS.

Regarding hardness values (see Fig. 4), there are not high differences between samples at 0 h and 80 h of LTD exposure (not more of 1GPa). It proves that there is practically no aging in 10Ce-TZP/Al_2O_3 composites.

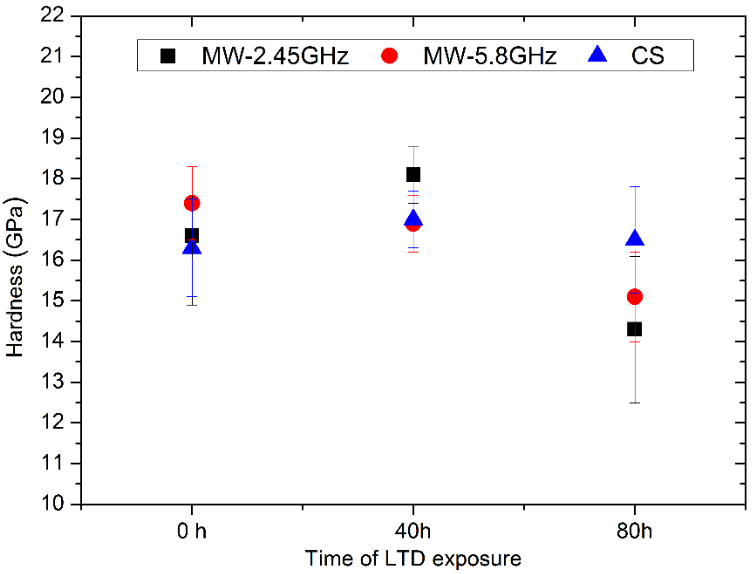


Fig. 4. Hardness values for 10Ce-TZP/Al_2O_3 sintered by MW and CS as a function of LTD exposure time

In the literature, a composite with similar proportions of zirconia and alumina but using Y_2O_3 as dopant, is already degraded after 80 h exposure[12]. Therefore, the use of the CeO_2 stabilizer has been shown to prevent low hydrothermal degradation. Therefore, 10Ce-TZP/Al_2O_3 can be used for applications where resistance to aging is required.

Moreover, the effect of the sintering method on the aging could not be verified in this work, because until 80 h exposed to LTD does not appear monoclinic. However, it is possible that at higher times, differences between CS and MW can be observed[3].

Lastly, 80 h of exposure to LTD is over enough, since it corresponds to more than 200 years in the human body, thus achieving the purpose of the prosthesis.

Conclusion

Low temperature degradation of 10Ce-TZP/Al_2O_3 has been investigated in the present study, as well as, the effect of two different sintering method (MW and CS) and frequency (2.45 GHz and 5.8 GHz) on the aging of this material. After the analysis of the Raman spectra, the following can be claimed:

- The use of CeO_2 as a dopant prevents the ageing of 10Ce-TZP/Al_2O_3.
- No differences in LTD between MW and CS nor between the two frequencies used for MW (2.45 and 5.8 GHz) up to 80 h of exposure have been evidenced.

To sum up, microwave sintering technology allows to obtain highly densified 10Ce-TZP/Al_2O_3 composites with a resistance to degradation similar to those obtained by conventional. Therefore, microwave technique is an exceptional alternative for sintering this material, as it requires lower sintering temperatures (1300 ºC) and dwelling time (10 min) than conventional sintering (1500 ºC and 120 min, respectively), leading to a reduction in energy costs and processing times and, consequently, the microwave technique has a lower environmental impact.

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