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# Effects of microwave sintering in aging resistance of zirconia-based ceramics

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ABSTRACT

Innovative techniques for materials processing that result in shorter times and lower energy consumption than conventional methods, such as microwave sintering, are currently under investigation in order to obtain fully-consolidated ceramic materials. Microwave sintering has important effects on the resulting properties of zirconia-based ceramics, which, in turn, affect its performance and durability, as in the case of their susceptibility to low temperature hydrothermal degradation (LTD), an ageing phenomenon that deteriorates their mechanical performance. The purpose of this work consists on assessing the effects of microwave sintering on the microstructure and mechanical performance of zirconia composites by comparing it to conventional sintering. Resistance to LTD of 3Y-TZP-only materials has also been evaluated. The results obtained in this work suggest that microwave sintering can reduce processing times and sintering temperatures when compared to conventional sintering while still obtaining dense zirconia-based ceramics and complying with the expected mechanical properties. At the same time, an increase in the resistance to LTD is also observed.



## 1. Introduction

Zirconia ($ZrO_2$) ceramics have become widely studied as a consequence of their outstanding mechanical properties, such as hardness, mechanical strength and fracture toughness, which allow them to cover a wide spectrum of applications as structural ceramics, including the field of biomaterials [1,2]. Zirconia materials are commonly stabilized with low ytrria ($Y_2O_3$) contents, ranging from 1.5–3.5 mol%, in what is known as yttria-stabilized tetragonal polycrystalline zirconia (Y-TZP) ceramics. The stabilization of the tetragonal (t) phase is responsible for such superb mechanical performance due to the transformation toughening mechanism that takes place. This mechanism consists of the spontaneous martensitic transformation of the metastable t-phase to the room-temperature stable monoclinic (m) configuration as a crack propagates through the material. The transformed particles surround and enclose the crack inhibiting its growth [3]. Therefore, it is very important that the material is completely stabilized in the t-phase. In order to further improve the characteristics of t-stabilized zirconia ceramics, zirconia-based composites have been developed. Particularly, the addition of zirconia as a second phase to an alumina ($Al_2O_3$) ceramic matrix combines the excellent hardness of $Al_2O_3$ with the high fracture toughness of $ZrO_2$ resulting in a material with enhanced mechanical behavior [4]. These materials are collectively known as Zirconia-Toughened-Alumina (ZTA) composites. Moreover, a composite configuration of a $ZrO_2$ matrix with $Al_2O_3$ acting as the dispersed phase is also possible, giving place to materials known as Alumina-Toughened-Zirconia or ATZ.

The advantageous t- to m-phase transformation of 3Y-TZP ceramics responsible for toughening can also become counterproductive when the material is exposed to humid environments at temperatures of 20–300 °C, due to a hydrothermal ageing phenomenon known as low-temperature hydrothermal degradation (LTD) [5,6]. The t-m transformation is accompanied by a change in volume that results in the introduction of defects in the material such as surface uplifts and microcracks [7]. As a consequence, surface roughening and microcracking arises and

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the mechanical and aesthetic properties are affected [8]. Therefore, it is extremely important to investigate the susceptibility of 3Y-TZP materials to LTD, especially when it comes to microstructure and mechanical properties. There are other factors that also affect the LTD behavior of zirconia materials including grain shape and size, stabilizer content and distribution, cubic phase content, porosity, and effect of residual stresses [9–11]. In general, these factors are directly influenced by the consolidation method employed to produce the resulting bodies from starting materials, which are usually powder-based. Solid-state sintering is a very common processing technique in ceramic engineering that requires high temperatures and, hence, a substantial amount of energy consumption in order to trigger the diffusion mechanisms that allow for densification of compacted powder bodies.

For that matter, non-conventional sintering methods are under investigation as they can modify sintering mechanisms that result in changes in the microstructure and phase composition of the consolidated materials, while, at the same time, reduce processing times and energy consumption. One such approach is microwave heating technology. Microwave heating consists of the absorption of electromagnetic radiation by materials due to their intrinsic dielectric properties [12,13]. Ceramic materials such as 3Y-TZP are able to absorb microwave radiation due to the presence of molecular dipoles [12]. These dipoles interact with the oscillating electric field induced by microwaves by rotating continuously in order to align with the field. Molecular resistance to these rotations generates heat, increasing the material's temperature, a process known as dielectric heating [14]. Several authors [15–18] have determined that highly dense materials without substantial grain coarsening may be obtained with microwave sintering since dwell times are considerably shortened and heating rates can be substantially increased. In some studies, lower sintering temperatures have been applied while obtaining materials with relative densities comparable to those of conventional sintering at higher temperatures [19,20]. As 3Y-TZP materials with a finer microstructure and a high degree of densification can be obtained, mechanical properties may be enhanced, improving the overall quality of the resulting material [16]. The modified microstructure that results from microwave sintering is very likely to affect the behavior of 3Y-TZP materials against hydrothermal degradation. Moreover, shortening dwell times and lowering sintering temperatures reduce the amount of energy consumption during the process.

The purpose of this study is to investigate the sinterability via microwave heating technology of 3Y-TZP-based ceramics, including ZTA composites with three different concentrations (5, 10 and 15 vol% $ZrO_2$) and an ATZ (5 vol% $Al_2O_3$) composite, and the resulting mechanical properties and microstructure. Additionally, the effect of microwave sintering on LTD susceptibility of 3Y-TZP materials is also evaluated. Conventional sintering is used for reference purposes. Assessment of LTD degradation is performed by analyzing induced phase transformation, surface roughening and crack propagation.

## 2. Materials and methods

The experimental procedure is divided in three parts. In the first part, the mechanical properties and microstructure of ZTA composites at different concentrations of $ZrO_2$ sintered via microwaves are investigated and compared to those obtained by conventional sintering. In this case, a commercial 3Y-TZP powder from Tosoh containing 3 mol% yttria has been employed after deagglomeration in a carefully-prepared colloidal suspension. The preparation procedure of this powder can be found in Reference [21]. The concentrations of the composites are 5 vol% 3Y-TZP/95 vol % $Al_2O_3$ (5ZTA), 10 vol% 3Y-TZP/90 vol% $Al_2O_3$ (10ZTA), and 15 vol% 3Y-TZP/85 vol% $Al_2O_3$ (15ZTA). Additionally, a 95 vol% 3Y-TZP/5 vol % $Al_2O_3$ (5ATZ) has also been processed. The starting materials are powder-based mixtures. The second part consists of a LTD study of 3Y-TZP materials in order to investigate the effect of microwave sintering on the resistance to LTD by comparing it to conventional sintering. The third part consists on a study regarding crack propagation in degraded and non-degraded 3Y-TZP material to show the importance of resistance to LTD.

For the ZTA composites, microwave sintering conditions were as follows: 1300 and 1400 °C, 10 min, 100 °C/min for final dwell temperatures, dwell time and heating rate, respectively. Conventional sintering was carried out at 1400 °C, 2 h and 10 °C/min. All specimens were sintered in air. These selected parameters are based on previous studies in our research group, where sintering conditions were optimized for 3Y-TZP-based materials [16,20,22]. For the full 3Y-TZP material, microwave sintering was carried out at 1200 and 1300 °C, keeping the other sintering parameters as in part one, and conventional sintering was performed under the same conditions as in part one. A lower temperature has been selected because zirconia requires lower sintering temperatures with respect to alumina-containing materials.

Conventional sintering (CS) was performed in an electrical furnace (Thermolyne type 46100, USA). Microwave (MW) heating technology has been employed as a non-conventional sintering technique. In this case, samples were introduced in a mono-mode (2.45 GHz) rectangular cavity that is automatically adjusted to optimize microwave absorption and control the heating rate. The configuration of the microwave system is shown in Fig. 1. A variable power output from 0 W to 1200 W is possible. In this case, the power has been set to 700 W.

Sample characterization in the first part consisted of carrying out Vickers hardness, $H$, and fracture toughness, $K_{IC}$, measurements via microindentation methods with a Shimadzu HMV-20 Vickers indenter. A total of five samples for each condition were measured. Relative density has been determined following ASTM-C-373 and using the corresponding theoretical density values. Analysis of the microstructure was performed with Field Emission Scanning Electron Microscopy (FE-SEM, S4800 Hitachi, Japan). Average grain size has been measured for 100 grains using the linear-intercept method with the Image-Pro Plus image analysis program.

Characterization of the second part consisted of the evaluation of mechanical properties, phase content change and penetration of transformed layer as a function of LTD exposure time. Specimens are mirror polished and autoclaved in steam at 125 °C and 1.6 bar. Characterization of aged samples is performed after every 20 h of exposure to LTD conditions until 200 h treatment is reached. Mechanical properties, such as $H$ and elastic modulus, $E$, were determined with the nanoindentation technique (G-200, Agilent Technologies, USA) using the Continuous Stiffness Measurement (CSM) technique. X-ray diffraction (XRD) has been performed with an XRD 3003-TT (Seifert, Ahrensburg, Germany) using Cu Kα radiation at 40 kV and 40 mA in pre-sintered and sintered specimens, as well as after 200 h of LTD exposure. Rietveld refinement of X-ray diffractograms monoclinic, tetragonal and cubic (c) phases. Phase content analysis was also assessed with a micro-Raman spectrometer (LabRam HR UV, HORIBA Jobin Yvon, France) coupled with a thermoelectrically-cooled multichannel CCD detector after every 20 h of LTD exposure. Raman spectra has been recorded for a Raman shift range from 120 to 700 $cm^{-1}$. An average of two successive measurements, each with an integration time of 2 min, has been performed to obtain a well-defined spectrum. A laser wavelength of 532 nm (green laser) through a 50 x objective with a lateral resolution of approximately 2 μm has been employed. For quantification of m-phase volumetric content,

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