



The sintering-temperature-related microstructure and phase assemblage of alumina-doped and alumina–silica-co-doped 3-mol%-yttria-stabilized tetragonal zirconia

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The influence of higher sintering temperatures on the microstructure and equilibration of alumina-doped and alumina–silica-co-doped 3-mol%-yttria-stabilized tetragonal zirconia ceramics was investigated. The temperature-related (≥ 1550 °C) penetration of the silica phase from the grain junctions into the grain boundaries was accompanied by the emergence of a fraction of larger, heterogeneous grains. The overall partitioning process was slower in the co-doped material, increasing the resistance to ageing, while upon cooling the partitioned yttria-rich phase was found to be tetragonal (*t*-ZrO₂).

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The 3-mol%-yttria-doped tetragonal zirconia (*t*-ZrO₂; 3Y-TZP) ceramic is an attractive material for dental applications due to its excellent mechanical properties, biocompatibility and improved aesthetics [1]. However, it is sensitive to the moisture-induced tetragonal-to-monoclinic (*t*-*m*) transformation, commonly known as low-temperature degradation (LTD), i.e., ageing [2]. This LTD to a large extent depends on the chemical driving force, which is mainly governed by the amount of yttria in the solid solution, and the zirconia grain size, but is also sensitive to the presence of internal strains, residual surface stresses and the surface topography [2,3]. Recently, we have shown that the hydrothermal stability of 3Y-TZP when sintered for 4 h at 1450 °C can be substantially increased by alumina (0.25 wt.%) and silica (0.25 wt.%) co-doping, without affecting the material's mechanical properties [4]. This improvement was achieved without any substantial reduction in the grain size and was ascribed to the combined effect of reduced internal stresses, due to rounded grains with a glassy phase at multiple grain junctions, characteristic for the silica-doped material, and a predominantly transgranular fracture, reflecting the strong grain boundaries that are characteristic for alumina doping. However, in many instances the 3Y-TZP dental ceramics are sintered at

temperatures exceeding 1450 °C, with the intention being to increase the fracture toughness and the related damage tolerance [5], which result from a coarser microstructure. At the same time, larger tetragonal zirconia grains are known to have a greater sensitivity to ageing [2]. Knowing that 3Y-TZP ceramics are sintered in a bi-phasic, tetragonal + cubic (*t* + *c*) region [6], higher sintering temperatures are expected to result, not only in larger grains, but also in a higher degree of phase partitioning into the equilibrium assemblage of *t* + *c* phases, i.e., in a larger relative amount of un-transformable (yttria-rich) *c*-ZrO₂ co-existing in equilibrium with the more readily transformable (yttria-lean) *t*-ZrO₂, which, in turn, may additionally reduce the overall resistance to LTD of the as-sintered, coarser-grained material [7]. On the other hand, our previous, preliminary, diffusion-coupled experiments performed with undoped and alumina-doped 3Y-TZP granulated powders sintered at different temperatures in the presence of larger amounts of highly reactive SiO₂ revealed a much lower reactivity in the alumina-doped 3Y-TZP/SiO₂ system, implying that the alumina has an impact on the composition and the properties of the glassy phase as well as a substantial influence of the temperature on the reactivity in the two systems [4].

In the light of these findings, the goal of the present work was to investigate the effect of higher sintering temperatures on the microstructure evolution, the phase partitioning and the corresponding hydrothermal stability of the alumina–silica-co-doped 3Y-TZP in comparison with the

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alumina-doped 3Y-TZP, which was, until recently, the benchmark zirconia material used in the field of bioceramics.

The alumina-doped (0.25A-TZ) and alumina–silica-co-doped (0.25A-TZ/SiO₂) 3Y-TZP materials used in this study were both prepared from the same biomedical grade 3Y-TZP powder (TZ-3YSB-E, Tosoh, Japan), containing ~0.25 wt.% of alumina, by dry pressing into discs (20 mm in diameter and ~2 mm in thickness) and pre-sintering in air for 2 h at 1000 °C. The pre-sintered specimens were randomly divided into two groups. One group was left untreated and served as the benchmark alumina-doped control group. The other group of specimens was infiltrated with a silica sol, synthesized *in situ* using the sol–gel method via the hydrolysis of a sylan-based solution (Dynasylan[®] 6490, Evonik, Germany). The gravimetrically determined content of silica in the infiltrated discs was ~0.25 wt.%. Details of the experimental procedure for the preparation of the green samples are described elsewhere [4]. The sintering was performed in a chamber oven in the temperature range of 1500–1600 °C for 2 h in air with heating/cooling rates of 5 °C/min. The relative density of the sintered discs was determined with Archimedes' method, using distilled water as the immersion liquid. The relative densities were calculated by adopting a theoretical density of $\rho_T = 6.08 \text{ g/cm}^3$. The microstructures were characterized using FE-SEM (Jeol JSM-7600F, Japan), TEM and FIB (FEI Helios Nanolab 650) microscopy. The average grain sizes were determined using the planimetric method and ImageJ software. The accelerated ageing experiments were conducted in distilled water under isothermal conditions at 134 °C or 200 °C in a steel autoclave. The X-ray diffraction patterns were collected from the specimen surfaces before and after the accelerated ageing experiments using Cu-K α radiation (Endeavor D4, Bruker AXS). The relative amount of transformed monoclinic zirconia phase (*m*-ZrO₂) on all the surfaces was determined from the integral intensities of the monoclinic $(\bar{1}11)_m$ and $(111)_m$, and the tetragonal $(101)_t$ peaks according to the method of Garvie and Nicholson [8].

All the sintered samples were nearly fully dense (about 99% TD), irrespective of the composition (doping) and the sintering temperature. However, the SEM/EDS examination of the polished and thermally etched surfaces of the sintered 0.25A-TZ and 0.25A-TZ/SiO₂ discs revealed substantial differences in the microstructure between the alumina-doped and the alumina–silica-co-doped materials when sintered at different temperatures. Sintering at 1500 °C resulted in uniform microstructures (Fig. 1a and b) with similar grain sizes (Table 1). Previous TEM studies have shown that the microstructures are different in that the grains in the alumina-doped material are faceted, whereas those in the co-doped material are rounded with a silica phase positioned at the multiple-grain junctions [4]. Furthermore, clearly discernible, distinct alumina inclusions are present in the alumina-doped material (the dark grains in Fig. 1a and c). After sintering at temperatures ≥ 1550 °C, another striking difference in the microstructures for the two materials became observable: while the grains in the alumina-doped material preserved their size uniformity (Fig. 1c), the grain size distribution of the 0.25A-TZ/SiO₂ material became bi-modal, with a minor fraction of evidently larger grains surrounded by (about four times) smaller grains of the major fraction (Fig. 1d). The corresponding average grain sizes for all the materials are listed in Table 1, indicating that co-doping had practically no effect on the grain size of the materials sintered at 1500 °C, and also that after sintering above this temperature, the overall average

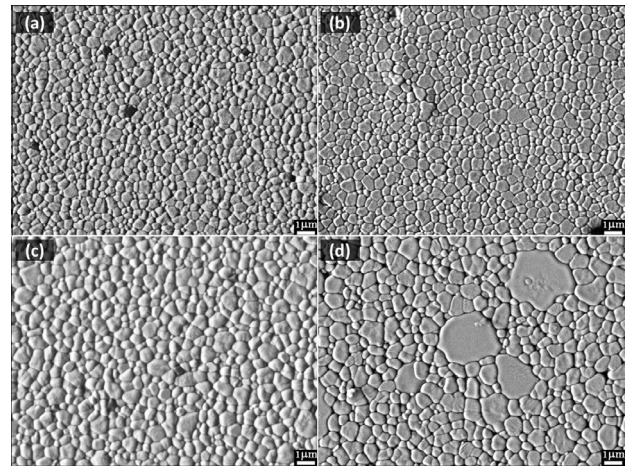


Figure 1. SEM micrographs of polished and thermally etched surfaces of the (a) 0.25A-TZ and (b) 0.25A-TZ/SiO₂ sintered at 1500 °C for 2 h; (c) 0.25A-TZ and (d) 0.25A-TZ/SiO₂ sintered at 1550 °C for 2 h.

Table 1. Average grain sizes in microns for the 0.25A-TZ and 0.25A-TZ/SiO₂ materials sintered in the temperature range of 1500–1600 °C for 2 h.

	0.25A-TZ	0.25A-TZ/SiO ₂
1500/2	0.43	0.44
1550/2	0.52	0.6 (2.5)*
1600/2	0.83	0.78 (3.17)*

* Average grain size representing the fraction of larger grains in the 0.25A-TZ/SiO₂ materials.

grain size in the alumina-doped ceramic was comparable to the average size of the finer grains in co-doped ceramics. Additional EDS analyses performed on the 0.25A-TZ/SiO₂ material sintered at 1600 °C revealed that the larger grains contained a higher yttria content (5–6 mol.%), while a considerably lower yttria content (2.2–2.7 mol.%) was found in the smaller grains. Similar microstructures, with obviously larger grains in the 3Y-TZP, have already been observed [5,8,11,12]. Due to a larger amount of yttria being found in the larger grains, the latter were labelled as cubic, but no explanation was given for the mechanism of their formation. High sintering temperatures (>1550 °C) or longer dwell times (5–8 h) were usually needed for them to evolve, but there was no indication of the possible role of the powder purity and/or the dopant level during the formation of the large cubic grains. Here we demonstrate that in 3Y-TZP ceramics the bi-modal microstructure is likely to be formed, provided that small amounts of alumina and silica are simultaneously present and the material is sintered at temperatures ≥ 1550 °C. The driving force for the sudden appearance of the bi-modal microstructure above a certain temperature may well be connected to the penetration of silica along the grain boundaries, but this speculation remains to be proven.

The phase composition of the sintered at 1600 °C ceramics was checked with X-ray diffraction (Fig. 2a and b). No monoclinic (*m*) ZrO₂ peaks could be found in the patterns obtained from the surfaces of the sintered specimens, implying that they were mainly composed of the *t*-ZrO₂ phase, displaying three characteristic peaks located at 2θ equals 30.2°, 34.7° and 35.2°, corresponding to the $t(101)$, $t(002)$ and $t(110)$ planes, respectively (Fig. 2a). Considering Scott's phase diagram [6] this phase is expected to co-exist with the

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