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Influence of preparation method and alumina content on crystallization and morphology of porous yttria stabilized zirconia

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ABSTRACT

Influence of addition of alumina and preparation methods (sol-gel synthesis and mechanochemical preparation) on crystallization and morphology of yttria stabilised zirconia was examined. Presence of alumina was found to delay crystallization of zirconia, the effect being more pronounced at higher alumina content. The two oxides form easily distinguished separate phases. Milling lowers the crystallization temperatures of the sol-gel derived powders since nuclei are formed during the milling and smaller particle size allows easier removal of residual organic components. The milling results in crystallization of some monoclinic zirconia, both in sol-gel derived powders and in case of mechanochemical processing. There are no significant differences between the preparation methods in pore size and relative density of sintered tablets: powders obtained by mechanochemical processing and milled sol-gel derived powders both give tablets with homogeneous morphology. The advantage of sol-gel process is preparation of pure tetragonal zirconia phase without traces of monoclinic phase.

1. Introduction

Stabilized zirconia has diverse applications due to its excellent thermal, hydrothermal, chemical and mechanical stability [1], which makes it suitable for preparation of porous ceramic bodies [2]. It is used as a catalyst or as catalyst support, oxygen sensor, solid electrolyte, as membrane and as high-temperature thermal isolation [3,4]. For all these applications, controlled porosity of at least 20% is necessary [3,5–10]. Non-stabilised zirconia [5,6,10], partially-stabilised zirconia with 3 mol% of yttria [2,4,7] and fully stabilised zirconia with 8 mol% of yttria [4,7,8] were all investigated for these applications.

To prepare strong porous zirconia, it is necessary to control not only the porosity but also the grain size, where smaller grains give greater strength to the porous ceramic [2]. Addition of alumina has been shown to limit the grain growth of zirconia [9–11], and the segregation of alumina to the grain boundaries gives significant strengthening and toughening effect [12–15]. Alumina-strengthened zirconia is characterised by its improved mechanical properties at high temperatures, good thermal and corrosion stability, resistance to wear, low thermal conductivity and improved electrical properties [4,14,16]. In humid environment, transformation of zirconia from tetragonal into monoclinic phase on the grain surface (aging of zirconia) has been known to occur, degrading the mechanical properties of the ceramic. Addition of alumina decreases this influence and improves hydrothermal stability of the ceramic, since the presence of alumina prevents the continuation of phase transformation [16,17]. As both alumina and yttria can stabilise zirconia, we have selected to prepare zirconia stabilised with 5,7 mol% of yttria (10% by weight), as this should be enough to obtain stable non-transformable tetragonal zirconia while decreasing the possibility of reaction of yttria and alumina to form additional phases [18,19].

Sol-gel process and mechanochemical processing are both methods which allow optimization of morphology and synthesis of ceramics at relatively low temperatures, since they yield amorphous and homogeneous pre-ceramic powders. Advantage of sol-gel process is in preparation of very pure powders in mild conditions and requiring no special equipment [20,21]. The advantage of mechanochemical synthesis is that it does not require any additional chemicals [22], such as organic solvents necessary for sol-gel synthesis [21], which makes it potentially more environmentally friendly. On the other hand, it is almost impossible to avoid contamination of milled powder with the material from the jar [23]. Although both methods have been used to prepare

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alumina-strengthened zirconia [10,14,24–26], to our knowledge there was no work comparing the two methods. In this work, influence of preparation methods and addition of alumina on crystallization, morphology and porosity of yttria-stabilised zirconia was investigated.

2. Material and methods

2.1. Preparation and characterization of pre-ceramic powders

Target compositions and preparation methods for all samples are given in Table 1. To achieve yttria-stabilised zirconia (YSZ), yttria or its precursor was added in such quantity that the final mass ratio of Y_2O_3 to ZrO_2 would be 1:9 (ZrO_2-10% Y_2O_3). Designation of samples consist of preparation method (sg = sol-gel, mc = mechanochemical), composition (ZY = pure YSZ, AXX = YSZ with XX% of alumina) and additional modification (m = milling of sol-gel powders). All compositions are given as mass fractions unless otherwise stated.

Pre-ceramic powders by sol-gel method were synthesized from zirconium butoxide ($Zr(C_4H_9O)_4$, 80%, Sigma-Aldrich), yttrium acetate hydrate ($Y(CH_3COO)_3 \times x\ H_2O$, 99.9% metals basis, Sigma-Aldrich) and aluminium *sec*-butoxide ($Al(C_4H_9O)_3$, 97%, Sigma-Aldrich), stabilised with acetylacetone ($C_5H_8O_2$, Fluka) in 2-propanol solution. Quantity of acetylacetone was chosen from previous investigations on stability of sols [27,28], so that:

$$n(\text{acetylacetone}) = 0.6n(\text{Zn}) + n(\text{Al}).$$

Stabilised alkoxides were hydrolysed with 2 mol of water per mole of alkoxide, added as 4.64 mol/dm^3 nitric acid that served as catalyst. Transparent sol was left to gel at room temperature for 5 days, dried at 110 °C, ground and sieved to remove particles larger than 80 μm, calcined at 300 °C to remove residual organic content. In order to produce a more homogeneous pre-ceramic powder, part of the powder was milled for 2 h in air using a Fritsch planetary ball mill Pulverisette 6 with jar and balls of 94% zirconia, with rotation speed of 500 rpm and powder-to-ball weight ratio of 1:5.

For mechanochemical processing, very pure oxide powders were used: zirconia (ZrO_2, puratonic; 99.978% (metals basis), Alfa Aesar), yttria (Y_2O_3, 99.999%, Sigma-Aldrich) and alumina (Al_2O_3, −100 mesh, 99.9%, Aldrich). Necessary quantities to achieve target compositions were weighed on analytical balance and milled in the above-mentioned mill and jar, with rotation speed of 500 rpm and powder-to-ball weight ratio of 1:10 for 3 h. After every hour, amorphisation of the powders was checked by X-ray powder diffraction (XRD).

Particle size distribution of pre-ceramic powders and powders calcined at 1400 °C was determined by means of dynamic light scattering (DLS) using a photon correlator spectrophotometer equipped with a 532 nm "green" laser (Zetasizer Nano ZS, Malvern Instruments, UK). 1 mg of powder was suspended in 1 mL of ethanol (sgZY, sgZYm, sgA20, sgA20m pre-ceramic powders) or water (mcA20 pre-ceramic powder and all calcined powders), and suspensions were sonified for 15 min prior to analysis. Intensity of scattered light was detected at the angle of 173°. Each sample was measured 3 times and the results were expressed as the average value. The hydrodynamic diameter (d_h) was obtained as value at peak maximum of size volume distribution functions. The data processing was done by Zetasizer software 6.32 (Malvern instruments). All measurements were conducted at 25.0 ± 0.1 °C, with pH_{init} = 7.4.

Surface area of pre-ceramic powders was determined by BET method from nitrogen adsorption-desorption isotherms at liquid N_2 temperature on a Micromeritics ASAP 2000.

Thermal behaviour of all pre-ceramic powders was investigated by combined differential scanning calorimetry and thermogravi-

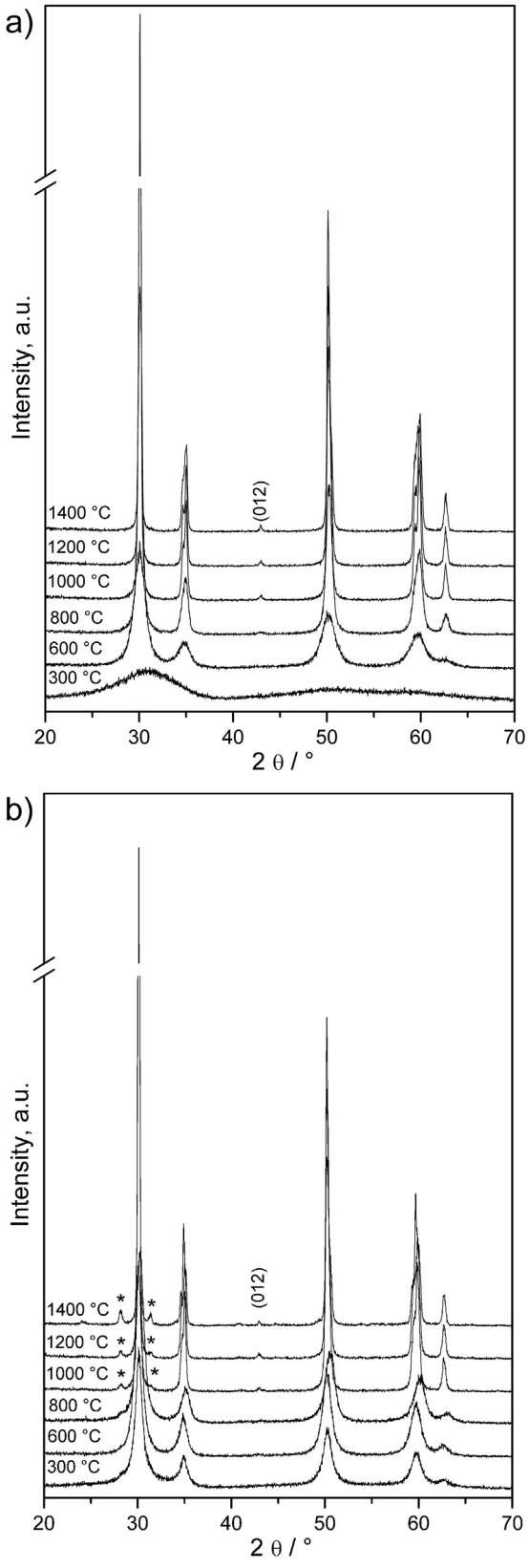

Fig. 1. Diffractograms of samples (a) sgZY and (b) sgZYm calcined at listed temperatures. Monoclinic zirconia marked by *, all other maxima correspond to tetragonal zirconia, marked is the (012) maximum which is characteristic for tetragonal zirconia.

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