Low temperature synthesis of zircon from silicone resins and oxide nano-sized particles

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Abstract

In this paper we present a new route for the realization of crack-free zircon monoliths, at very low temperature (1200 °C). Zircon ceramics are for the first time synthesized from a mixture of preceramic polymers, consisting of silicone resins, filled with active nano-sized fillers, being ZrO_2 nano-particles. The introduction of small quantities (up to 10 mol%) of TiO_2 as a sintering aid, and of zircon micro-powders, as seeds, has been also considered. The additives demonstrated to be extremely effective in increasing the zircon yield, with a synergistic effect when used together. Moreover, an appropriate mixture of different preceramic polymers as SiO_2 source was found to be critical for the obtainment of crack-free monoliths. This simple methodology demonstrated kinetic features comparable to those of sol–gel processes, but coupled with the possibility of an easy shaping of the desired ceramic before heat treatment.
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1. Introduction

Zircon (zirconium silicate, $ZrSiO_4$ or $ZrO_2 \cdot SiO_2$) is a ceramic material which is suitable for multiple applications, although most of them have been rather unexplored so far. The classical application is in the field of refractory materials, where zircon is appreciated mainly for its very low CTE, although the performance is generally lowered by the presence of impurities.[1] More recent high-technology applications are in the nuclear and electronic fields. In fact, zircon has been considered a promising nuclear waste host material,[2–4] owing to the possibility of introducing large amounts (up to 20 wt%) of radionuclide cations inside its crystal structure.[4] Electronic applications are in relation to the possibility to replace SiO_2 in silicon-based MOSFET, thanks to its relatively large dielectric constant, high band gap, high breakdown field, and good thermal stability in contact with silicon.[5–7]

According to several studies in the literature, zircon synthesis from SiO_2 and ZrO_2 raw materials is characterized by a very slow kinetic, and achieving high zircon yield through this reaction sintering is possible only at high temperatures (above 1500 °C). High synthesis temperatures, however, hinder the applicability: as an example, the hosting of nuclear waste may be compromised, due to the risk of volatilization of some radionuclides, lowering the immobilization efficiency.[4] The possibility of lowering the synthesis temperature of zircon has been explored in several studies, most of them based on the sol–gel route,[8–11] well known to be hardly applicable to the manufacturing of monoliths.

In the recent years, the use of Polymer Derived Ceramics (PDCs) in conjunction with nano-sized particulate fillers has proved to be a straightforward methodology for the realization of advanced ceramic monoliths, featuring a kinetic comparable, if not better, to the sol–gel method. In particular, silicates and sialons have been successfully obtained by the reaction between oxide particles, introduced in commercially available silicone resins, and the polymer-derived silicate matrix, at generally lower temperatures than those necessary in other common ceramic processing routes.[12–14] The coupling of the high reactivity of nano-sized particles with that of amorphous silica, provided by the ceramic conversion of silicones, leads to a high phase purity and to an interesting microstructure. In particular, it has been shown the possibility to produce nano-structured ceramics, i.e. fine grained monophasic ceramics or ceramic matrix nano-composites, such as zirconia-toughened mullite.[15]

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In this work we discuss for the first time the application of the method of nano-sized filled silicones to the manufacturing of zircon ceramics. The approach was found to enable the synthesis of crack-free and high purity zircon monoliths at low temperature (1200 °C), starting from a silicone and zirconia nano-sized particles, through a careful control of additional secondary fillers and seeds.

2. Experimental

A commercially available polysilsequioxane (Silres MK, Wacker-Chemie GmbH, Munchen, Germany) was dissolved in isopropanol under stirring. ZrO_2 nano-sized powders (VP Zirconium Oxide PH, 13 nm mean particle size, Evonik Industries AG, Essen, Germany) were subsequently dispersed into the solvent/polymer solution, without the addition of any chemical dispersant. A pure ZrO_2/MK system, where the ZrO_2/MK weight ratio was kept constant and equal to 1.682 was investigated first. The weight ratio value of 1.682 was calculated by considering both the stoichiometry of zircon (SiO_2 and ZrO_2 in equal molar concentration) and the ceramic yield of the polysiloxane, which is equal to 82 wt%. Although it should be considered that, in some cases, the introduction of secondary fillers could have some influence on the chemical composition of the final ceramic residue (particularly in the case of active fillers), during the present work calculations were made with the assumption that a pure SiO_2 ceramic residue from the polysiloxane(s) is obtained, thus neglecting possible polymer–fillers interactions during the pyrolysis step. This assumption seems to be reasonable, since heat treatments were carried out in oxidative atmosphere and only oxides were used as fillers. In other formulations, TiO_2 nano-powders (VP P90, 13 nm mean particle size, Evonik Industries AG) and/or zircon seeds (0.8 μm mean particle size, Industrie Bitossi SpA, Vinci, Italy) were also introduced. Considering the possibility that Ti^{4+} cations could enter into the zircon crystal lattice by substituting Zr^{4+} cations,[16] in all the dispersions containing TiO_2 the original ZrO_2/MK weight ratio was adjusted according to the relation $n_{SiO2} = n_{ZrO2} + n_{TiO2}$, with n_x = moles of species x. Samples were labeled "X-Y", where "X" and "Y" represent the molar TiO_2 and seeds concentrations in the final ceramic, respectively. All the dispersions were homogenized by magnetic stirring for 10 min, and then ultrasonicated for 20 min to reduce the size of the residual particles agglomerates, thus obtaining homogeneous and stable dispersions. After the evaporation of the solvent in oven at 90 °C, the material obtained was finely ground in a mortar with a pestle and sieved (75 μm aperture). Powders were uniaxially compacted at room temperature under a pressure of 40 MPa. Pellets were subsequently heat treated in air in the 1100–1500 °C range for 1 and 4 h (10 °C/min heating rate).

For some samples, part of Silres MK was substituted by another polysiloxane (Silres H62C, Wacker-Chemie GmbH, Munchen, Germany), which is characterized by a different SiO_2 yield (approx. 58 wt%) and does not releases gaseous products during the curing step. For these samples, a partial pre-curing treatment (250 °C, 30 min) was necessary before the grinding step.
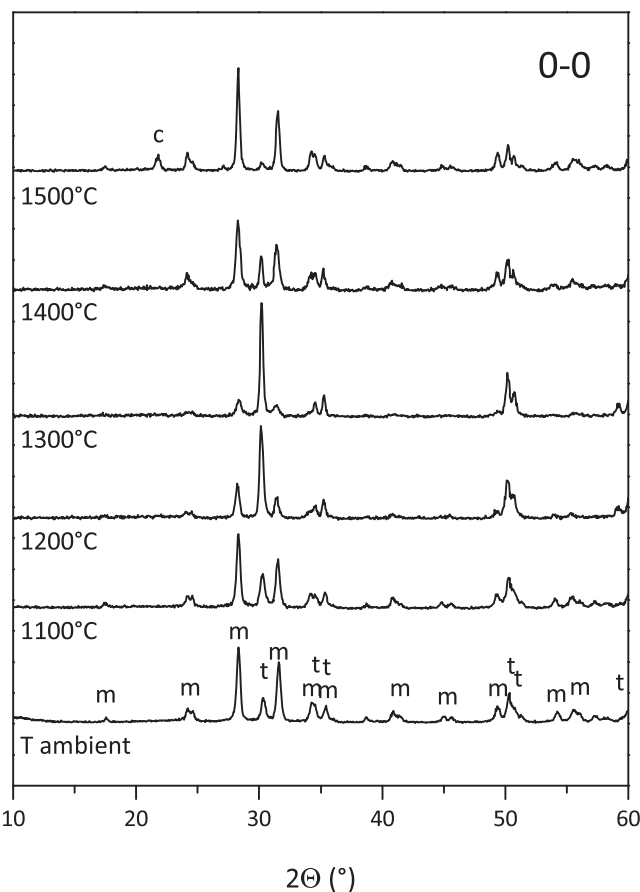

Fig. 1. XRD patterns as a function of the treatment temperature of 0-0 sample. m = m-ZrO_2, t = t-ZrO_2, c = cristobalite.

The identification of crystalline phases was performed by means of X-ray diffraction analysis (XRD; Bruker AXS D8 Advance, Bruker, Germany). All XRD pattern were collected in 10–60 °C 2-theta range (0.05 °C stepsize). Rietveld refinement was applied on all the patterns by the MAUD software package,[17] thus obtaining the volumetric fractions and an estimate of the mean crystallite size of the phases present in the final ceramics. After Rietveld refinement, a zircon yield parameter was calculated as vol%$_{zircon}$/(vol%$_{zircon}$ + vol%$_{m-ZrO2}$ + vol%$_{t-ZrO2}$). Differential thermal and thermo-gravimetric analysis (DTA/TG) were done up to 1500 °C in air (DTA/TGA, STA409, Netzsch GmbH, Selb, Germany). Microstructural investigations were carried out by Scanning Electron Microscopy (SEM; FEI Quanta 200 FEG, FEI Company, The Netherlands).

3. Results and discussion

In Fig. 1, XRD data for a pure MK/ZrO_2 system are reported as a function of the temperature (1 h soak time). As it can be observed, zircon is virtually absent even at 1500 °C, as a confirmation of the already reported extremely slow nucleation kinetic, and unreacted ZrO_2 and SiO_2 continue to be the predominant phases. Below 1500 °C, ZrO_2 is the only crystalline phase, and the SiO_2 component deriving from the pyrolysis of