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Spherical engineering Ca-TZP ceramics made from baddeleyite: fabrication, structure and mechanical properties

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ABSTRACT

The spherification method was adapted to baddeleyite-based ceramics fabrication. Novel calcia stabilized tetragonal zirconia (Ca-TZP) ceramics with sufficiently high values of hardness (11.73 ± 0.12 GPa), fracture toughness (9.15 ± 0.24 MPa $m^{0.5}$) and Young's modulus (217 ± 14 GPa) was produced. Dependences of the material microstructure, its phase composition and mechanical properties on sintering temperature and the doping agent concentration were investigated. Fabricated spherical Ca-TZP ceramics made from baddeleyite may be considered as perspective engineering ceramics, for example, for milling processes as an alternative to grinding media made of chemically precipitated zirconia.

1. Introduction

Zirconia ceramics are widely used in different branches of industry due to their unique properties: excellent chemical, corrosion and temperature resistance, outstanding fracture toughness and flexural strength, high density and hardness, low friction coefficient and wear rate, low thermal conductivity, etc. [1–4]. The main sources of ZrO_2 are minerals zircon ($ZrSiO_4$) and baddeleyite containing ZrO_2 in the range 96.5–98.5 wt% and SiO_2 as a dominating impurity. Baddeleyite is much cheaper than ZrO_2 synthesized from zircon. There are two methods used to make ZrO_2 powders from zircon via zirconyl chloride ($ZrOCl_2$) being the intermediate product of zircon chemical treatment: thermal decomposition or precipitation of $ZrOCl_2$ [5]. The second method is preferable and frequently used because it enables control over the shape, size, specific surface area and agglomeration degree of synthesized ZrO_2 particles. Chemical ways of reducing particle size are not efficient, when applied to baddeleyite because of its chemical inertness. Besides baddeleyite is monoclinic ZrO_2 (m-ZrO_2) which is not acceptable for the majority of zirconia practical applications.

It is well known that required high temperature tetragonal (t-ZrO_2) and cubic (c-ZrO_2) phases can be stabilized at low temperatures by addition of different oxides (Y_2O_3, MgO, CaO, CeO_2 and others) to zirconia during the synthesis process to form solid solutions [2]. Therefore solving the problem of stabilizing agent incorporation into already existing zirconia particles is important for baddeleyite. High-energy milling is possible approach for baddeleyite processing providing size reduction and mechanoactivation of ZrO_2 particles. In [6] wet high-energy co-milling of CaO and baddeleyite was used to prepare ultrafine ZrO_2 powder, containing high amounts of t-ZrO_2 and c-ZrO_2. Calcia was chosen as an inexpensive alternative to yttria commonly used for producing zirconia ceramics with remarkable mechanical properties. The powder was uniaxially pressed and sintered to fabricate calcia-stabilized tetragonal zirconia (Ca-TZP) ceramics in pellet form with hardness ~ 11 GPa and fracture toughness ~ 13 MPa $m^{0.5}$, which are comparable with those of commercially used yttria-stabilized tetragonal zirconia (Y-TZP) ceramics fabricated from precipitated ZrO_2 [4].

The microstructure and, correspondingly, properties of ceramics critically depend on processing routes including methods of a powder preparation, green body forming and following sintering [1]. Thus, the development of forming methods alternative to uniaxial pressing, which expand the range of parts made from baddeleyite for engineering applications and simultaneously provide competitive mechanical properties of fabricated ceramics seems to be important.

Spherification is a simple and inexpensive approach applicable for producing spherical ceramic green bodies by dropping slurry containing ceramic particles and sodium alginate into $CaCl_2$ solution with further water-insoluble calcium alginate gel formation. Previously, spherification was successfully used for producing dense corundum ceramics [7].

The aim of this work was to examine the fabrication possibility of engineering baddeleyite origin ceramics with high mechanical properties considered, for example, as grinding media for milling processes via spherification technique.

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2. Materials and methods

We used nanostructured calcia-stabilized ZrO_2 powders prepared by wet high-energy co-milling of CaO and baddeleyite concentrate with zirconia content of at least 99,3% (Kovdorsky GOK, Russia) using the planetary mill Pulverisette 7 Premium Line (Fritsch, Germany). Calcia concentration was in the range 0–4 wt%. Milling and drying conditions were the same as those in Santos et al. [7]. The powders consisted of submicron soft agglomerates composed of nanoparticles with sizes of about 20 nm. Slurries for spherification were prepared in the following way. 1 g of calcia-stabilized ZrO_2 powder was mixed with 0.5 ml of distilled water and 0.5 ml of 3.5 wt% sodium alginate solution to prepare 50 wt% zirconia suspensions. Dolapix CE 64 was added as a dispersant (0.5 wt% of solid content). The slurry was homogenized by the ultrasonic processor Vibra-Cell VC 750 (Sonics & Materials, Inc., USA) for 12 min at 20 kHz. To avoid slurry heating the following regime was chosen: 50 s of pause time after sonication for 10 s. The power of sonication was about 1 W. Then the slurry was degassed at 0.2 bar for 1 min in vacuum oven OV-11 (Jeio Tech Co., Ltd, S. Korea) at room temperature. A solidification solution composed of calcium chloride and distilled water was thoroughly mixed for 1 h. The concentration of calcium chloride was 2 wt%. The slurry was dropped into $CaCl_2$ solution with a syringe by hand. 21 G blunt tip needle was used. The space between the nozzle and the surface of the reacting solution needed to obtain spherical beads was about 1.5 cm. For beads with average diameter of 2 mm gelling time was experimentally determined to be about 5 min. Green beads were washed with distilled water and dried for 24 h at room temperature. They were sintered in air atmosphere at 1250, 1300, 1350 and 1400 °C for 4 h in a muffle furnace. Heating and cooling rates were 5 °C/min. The samples were cooled naturally from 300 °C to room temperature.

Sintered ceramics microstructure was analyzed by the scanning electron microscope (SEM) Merlin (Carl Zeiss, Germany). XRD patterns were recorded in the 20–80° 2θ range by the diffractometer D2 Phaser (Bruker AXS, Germany) using CuKα1 monochromatic radiation. The diffraction patterns were assigned using the PDF-2 Diffraction Database File compiled by the International Center for Diffraction. Phase content was determined from the XRD patterns by the Rietveld method in the TOPAS software (Bruker AXS, Germany).

Hardness of the samples was measured by Vickers indentation with load of 30 N on Duramin A300 (Struers, Denmark). Fracture toughness was calculated from length of radial cracks starting from the corners of the indents by the formula (1) [8]:

$$Kc = 0.016\left(\frac{E}{H}\right)^{0.5}\frac{P}{c^{1.5}} \tag{1}$$

where H is Vickers hardness, E is Young's modulus, P is indentation load and C is the crack length (the distance between the center of the indent and crack tip).

Loads of 200–300 N on the Vickers indentation fracture toughness tests were used. Young's modulus was measured on G200 nanoindentometer (MTS Nano Instruments, USA). Cracks lengths were calculated using optical microscope Axio Observer.A1m (Carl Zeiss, Germany). Before mechanical properties tests all the samples were polished with diamond-containing slurries. All the measurements were carried out at room temperature.

3. Results and discussion

Typical appearance of fabricated spherical baddeleyite origin ceramics is illustrated in Fig. 1. Monodisperse beads about 1 mm in diameter with a smooth surface can be clearly seen.

Variations in microstructure of beads sintered at various temperatures are shown in Fig. 2. Ceramic sintered at 1250 °C is characterized by irregular porous structure (Fig. 2a). Pores of any form are randomly located. Their size attains several micrometers. Fine zirconia grains with the average size of 120 ± 25 nm are observed too. Increase in sintering temperature up to 1300 °C reduces porosity (Fig. 2b). Only solitary pores are visualized, while ZrO_2 grains grow and their average size attains 144 ± 31 nm. Further rise in sintering temperature leads to complete disappearing of porosity and formation of dense ceramics with microscopically uniform structure (Fig. 2c). Zirconia grain growth proceeds. The average grain size becomes 182 ± 35 nm.

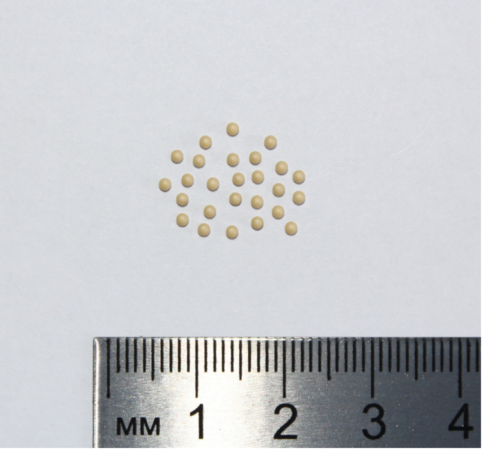

Fig. 1. The photo of baddeleyite origin beads sintered at a temperature of 1350 °C.

Finally, at 1400 °C the value of an average ZrO_2 grain size increases up to 231 ± 42 nm due to more intensive grain growth (Fig. 2d). The observed increase in zirconia grain size with rise in sintering temperature is a typical phenomena connected with mass transfer intensification with temperature increasing. Cracks propagation along the grain boundaries occurs when sintering temperature is 1400 °C (Fig. 2d). Cracking is most likely associated with tetragonal to monoclinic (t→m) transformation of ZrO_2 accompanied by a large shear strain (∼ 14–15%) and a large volume increase (∼ 3–5%) which create significant internal stresses upon cooling [9]. As mentioned before, the transformation can be prevented by alloying ZrO_2 with stabilizing oxides that provides the stability of t-ZrO_2 and c-ZrO_2 at room temperature. For t-ZrO_2 stabilization lesser concentrations of doping agent are required than for c-ZrO_2. With ZrO_2 grain growth the stabilizer concentration may not be sufficient to stabilize large zirconia grains in tetragonal phase at room temperature. Additionally the stabilizer content in ZrO_2 grains may decrease with their growth due to the stabilizer segregation at grain boundaries [10]. When the stabilizer concentration in ZrO_2 grains drops below the critical value t→m transformation of ZrO_2 grains accompanied by cracking occurs upon cooling. In our case it was observed when sintering temperature was 1400 °C (Fig. 2d). CaO may chemically react with ZrO_2 forming calcium zirconate that leads to decrease in CaO content too, but according to CaO-ZrO_2 phase diagram much higher temperatures and larger CaO concentrations are required than the ones used [11]. Also no calcium zirconate characteristic peaks were observed in the obtained XRD patterns (Fig. 3).

XRD patterns recorded for baddeleyite origin beads sintered for 4 h at various temperatures are presented in Fig. 3.

When sintering temperature is 1250 °C, ceramics contain only t-ZrO_2. Main t-ZrO_2 characteristic peaks at 2θ = 30.2°, 34.6°, 35.2°, 50.2°, 50.7°, 59.3°, 60.2° and 62.8° are observed. Increase in sintering temperature up to 1350 °C has no effect on peaks position and no new reflections appear. At 1400 °C m-ZrO_2 becomes dominant and t-ZrO_2 content sharply decreases. Two intensive peaks at 2θ = 28.2° and 31.5° and a large number of lower intensity peaks of m-ZrO_2 in the 2θ range of 20–80° occur. Peaks broadening at 1400 °C is caused by significant mechanical stresses resulting in ceramics cracking (Fig. 2d). The ceramics phase composition analysis data are given in Table 1.

Table 1 shows that t-ZrO_2 remains the prevailing phase with the