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Magnetic field oriented tetragonal zirconia with anisotropic toughness

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Abstract

(0 0 1)-oriented 3 mol% yttria stabilized tetragonal zirconia (3Y-TZP) has been developed by reactive synthesis of undoped pure monoclinic zirconia and co-precipitated 8 mol% yttria-stabilized zirconia (8Y-ZrO_2). The dispersed pure monoclinic ZrO_2 powder, having magnetic anisotropy, was first aligned in a strong magnetic field and co-sintered in a randomly distributed cubic 8Y-ZrO_2 fine matrix powder. The reactive sintering resulted in a 3Y-TZP ceramic with a (0 0 1) orientation. The (0 0 1)-oriented 3Y-TZP showed a substantial toughness anisotropy, i.e. the toughness along the [0 0 1] direction is 54% higher than that of its perpendicular direction. Moreover, the toughness along the [0 0 1] direction is 49% higher than that of a non-textured isotropic reactively synthesized 3Y-TZP and 110% higher than that of an isotropic co-precipitated powder based 3Y-TZP. The substantially enhanced toughness was interpreted in terms of the tetragonal to monoclinic martensitic phase transformability.

Keywords: Suspensions; Magnetic alignment; Sintering; Toughness and toughening; ZrO_2

1. Introduction

Zirconia ceramics are one of the most important engineering ceramics and are widely used in various applications such as thermal barrier coatings for high temperature protection, solid electrolytes for oxygen sensors, high-temperature fuel cells, and recently dental material.[1,2] Zirconia ceramics have become increasingly popular due to their unusual combination of strength, fracture toughness, ionic conductivity, and low thermal conductivity.[3] The most attractive feature of zirconia is its high fracture toughness (2–10 MPa m$^{1/2}$).[4] This is dominantly attributed to the stress induced transformation of the tetragonal to monoclinic phase in the stress field of the propagating cracks, i.e. a phenomenon well known as 'transformation toughening'.[1,3–6] Transformation toughening is considered to be the dominant toughening mechanism of partially stabilized ZrO_2 and extensive efforts have been devoted to understand the transformability of tetragonal zirconia. However, most studies have focused on polycrystalline ZrO_2 ceramics without any orientation, and there are hardly reports on the textured ZrO_2 ceramics.

Textured ceramics have attracted much interest due to their improved properties. Various techniques, like hot forging, deformation and templated grain growth are commonly used to produce textured ceramics.[7–9] With the development of superconducting magnets, the alignment of feeble non-cubic magnetic particles, such as Al_2O_3, ZnO, TiO_2, SiC and Si_3N_4, becomes possible in strong magnetic fields.[10,11] Taking α-alumina as an example, hexagonal single crystal alumina particles in a low viscosity suspension can be aligned in a strong magnetic field (∼10 T) when the magnetic crystal anisotropy energy ΔE is larger than the energy of thermal motion:[10,12]

$$\Delta E > k_B T \tag{1}$$

with k_B the Boltzmann constant and T the absolute temperature. The crystal anisotropy energy ΔE in a magnetic field is expressed by:

$$\Delta E = -\frac{\Delta\chi V B^2}{2\mu_0} \tag{2}$$

where $\Delta\chi = \chi_{a,b} - \chi_c$ is the anisotropy of the magnetic susceptibility, with $\chi_{a,b}$ the magnetic susceptibility along the crystallographic *a*- or *b*-axes and χ_c the magnetic susceptibility along the crystallographic *c*-axis of alumina, μ_0 is the perme-

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ability of vacuum, B is the applied magnetic field and V is the particle volume.

In this study, the possibility of texturing zirconia using a strong magnetic field was assessed and subsequently the mechanical properties of the obtained textured zirconia were evaluated. The objective of this study was to achieve textured 3 mol% yttria-stabilized tetragonal zirconia (3Y-TZP), which can be used in many applications.[4,13] Since it was reported that 3 mol% co-precipitated ZrO_2 powder was negligibly oriented in a magnetic field of 12 T,[13,14] we aimed at the alignment of pure undoped monoclinic zirconia (m-ZrO_2) in a starting powder suspension of pure m-ZrO_2 and co-precipitated 8 mol% yttria-stabilized zirconia (8Y-ZrO_2) in a strong magnetic field to obtain a textured 3Y-TZP after sintering to full density.

2. Experiment

Unstabilized m-ZrO_2 (SF-extra grade, Z-Tech LLC, USA) and co-precipitated 8Y-ZrO_2 (TZ-8Y grade, Tosoh Co., Japan) were used as the starting powder. For comparison, a commercial co-precipitated 3Y-TZP powder (TZ-3Y grade, Tosoh Co., Japan, Fig. 1(a) and (c)) was also used. A mixture of SF-extra/TZ-8Y (mixed 3Y-TZP grade) with a molar ratio of 5:3 was mixed and deagglomerated by bead milling (Dispermat SL, VMA Getzmann GmbH, Germany) in ethanol at 6000 rpm for 4 h using zirconia beads with an average size of 1 mm (TZ-3Y, Tosoh Co, Japan). The morphology and particle size distribution of the mixed powder after bead milling is shown in Fig. 1(b) and (d). The particle size of SF-extra and 8Y-ZrO_2 powders were also measured separately and the average particle sizes were calculated according to the statistics. It was determined that the monoclinic SF-extra powder has an average particle size of 205 nm, while the TZ-8Y powder has an average particle size of 75 nm after deagglomeration by bead milling.

To prepare a stable suspension, the milled powder (powder load 250 g/L) was dispersed with 1 wt% (relative to the powder load) phosphate ester (JP-506H grade, Johoku Chem. Co. Ltd, Japan) as charging agent and binder. Pre-test experiments showed that the addition of 1.1 wt% (relative to the powder load) poly(vinyl butyral-*co*-vinyl alcohol-*co*-vinyl acetate) (PVB, Sigma-Aldrich Corp., USA) as binder and 0.03 wt% (relative to the powder load) polyethyleneimine (PEI, Sigma-Aldrich Corp., USA) as surface charging agent and stabilizer was effective to form a thick and crack-free deposit.[15] The mixed zirconia powder was deposited from the freshly prepared suspension by electrophoretic deposition (EPD). A horizontal strong magnetic field of 9.4 T (Bruker, Germany) was applied to the suspension during EPD at room temperature with parallel magnetic and electric field directions. In other words, the deposition electrode was placed vertically and was perpendicular to the magnetic field. For comparison, the mixed 3Y-TZP grade as well as the commercial co-precipitated TZ-3Y grade was prepared by EPD outside the magnet. Moreover, in order to check the alignment of the m-ZrO_2 powder, an SF-extra powder suspension was investigated with and without magnetic field.

The green compacts were dried outside of the magnet and sintered in air at 1500 °C for 3 h (Nabertherm, Germany). The sintered zirconia ceramics were analyzed by scanning electron microscopy (SEM, XL30-FEG, FEI, The Netherlands) and X-ray diffraction (XRD, Seifert 3003T/T, Germany) to evaluate the microstructure and texture formation. Grain size distributions were obtained from the linear intercepts of 130 grains measured on the well dispersed powder or on the thermally etched surfaces. The grain size data are presented as measured since no mathematical corrections were performed.

The Lotgering factor, based on XRD spectral analysis, was used to quantify the degree of orientation. The Lotgering factor, f, is defined as:[16]

$$f = \frac{P - P_0}{1 - P_0} \tag{3}$$

with $P = I_{100}/\Sigma I_{hkl}$ and $P = I_{001}/\Sigma I_{hkl}$ for monoclinic and tetragonal ZrO_2, respectively. P_0 is calculated from a randomly oriented sample according to the same formula. I_{hkl} is the peak intensity of all the $h\,k\,l$ reflections in the 20–80° 2θ range. The f factor of an isotropic material is 0, while f equals 1 for a single crystal. The Lotgering factor, f, is considered to be an estimate of the degree of orientation in the textured material.

The Vickers hardness (HV_5) of the sintered ceramics was measured (Model FV-700, Future-Tech Corp., Japan) on polished surfaces with an indentation load of 5 kg. Vickers hardness indent to measure fracture toughness (K_{Ic}) has been widely used and analyzed due to the relative ease of the technique.[17] A useful analysis method in the determination of K_{Ic} from Vickers indent in tetragonal zirconia (t-ZrO_2) polycrystalline ceramics was proposed by Anstis et al.[18] The K_{Ic} was calculated from the diagonal length of the radial cracks originating in the corners of the Vickers indentations, according to the formula:[18]

$$K_{Ic} = 0.0154\sqrt{\frac{E}{H_V}}\left(\frac{P}{c^{1.5}}\right)(\text{MPa m}^{1/2}) \tag{4}$$

with E, the Young's modulus (GPa), H_V, the Vickers hardness (GPa), P the indentation load (N) and c, half of the total crack length (m). For the ceramic deposited in the magnetic field, the indent was oriented so that one of its diagonals was parallel to the magnetic field direction. For anisotropic materials, the diagonal length of the radial cracks in a specific direction was measured to derive the K_{Ic} for cracks propagating in that direction. The E value used in the calculation according to Eq. (4) is 210 GPa. The reported hardness and toughness values are the average and standard deviation for five indentations.

The ZrO_2 phase transformation at the crack tip of the Vickers indentations was analyzed with an InVia micro Raman spectrometer (Renishaw, Wotton-under-Edge, UK), equipped with an argon laser (514.5 nm, Spectra Physica, The Netherlands) with a maximum laser power of 50 mW. The spectra were obtained with a 50× magnification objective.