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Ytterbia–neodymia–costabilized TZP—Breaking the limits of strength–toughness correlations for zirconia?

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Abstract

TZP ceramics were manufactured by hot pressing of pyrogenic zirconia nanopowder which was costabilized by 1 mol% ytterbia and 2 mol% neodymia (1Yb–2Nd–TZP) via the nitrate route. The evolution of microstructure, phase composition and mechanical properties with variation of sintering temperature from 1200 °C to 1400 °C was investigated. 1Yb–2Nd–TZP consists of a bimodal microstructure of small very transformable tetragonal grains and large cubic grains. At intermediate sintering temperature the materials combine a bending strength of 1250 MPa with a fracture resistance >13 MPa $\sqrt{m}$. The high threshold stress intensity of 7 MPa $\sqrt{m}$ indicates high resistance to subcritical crack growth. An increase in fracture resistance before the crack tip induced by compressive residual stress shifts the strength–toughness correlations to higher values than previously considered possible.

Keywords: Hot-pressing; ZrO_2; Mechanical properties; Phase composition; Microstructure-final

1. Introduction

Zirconia and its composites are frequently used as structural ceramics for applications at ambient temperature due to their high strength, abrasion resistance and fracture toughness.[1] High toughness is caused by transformation toughening. The stress induced martensitic transformation of the metastable tetragonal phase is accompanied with volume expansion and shear. In order to preserve the tetragonal phase down to room temperature stabilizing oxides, in case of tetragonal zirconia polycrystals most frequently yttria or ceria, are added. A transformed zone on both sides of the crack wake shields the crack tip and thus increases the fracture toughness.[2] Swain has demonstrated that strength and toughness show a linear correlation as expected by Griffith's law only at toughness values lower than 8 MPa $\sqrt{m}$. At higher toughness values the materials become *R*-curve dominated.[3] This means that the zirconia is so transformable that low stress is sufficient to induce a transformation which then runs as a steady state process until the tetragonal phase is consumed. The materials then become very damage tolerant but their strength is limited. Typically 3Y–TZP, which is the most frequently used material for e.g. dental applications is flaw size dominated having a high strength (800–1500 MPa) but only moderate toughness (4.5–6 MPa $\sqrt{m}$).[4] Ce–TZP is a typical *R*-curve dominated material with high toughness (10–15 MPa $\sqrt{m}$) but very limited strength (300–500 MPa).[5] Especially for biomedical applications materials would be desired which combine high strength and toughness for the case of a catastrophic event like a traffic accident and high resistance to fatigue under long term cyclic loading conditions.

For the resistance against subcritical crack growth (fatigue) not the fracture toughness K_{IC} measured at fast loading condition is decisive but the fracture resistance at a crack growth velocity of zero.[6] This value K_0 characterizes the safe range of use. For standard TZP ($K_0 = 3.2$ MPa $\sqrt{m}$) and alumina ($K_0 = 2.5$ MPa $\sqrt{m}$) the resistance to subcritical crack growth is limited.[7] Recently some promising materials having high K_0 were reported: Ce–TZP/alumina ($K_0 = 5.5$ MPa $\sqrt{m}$),[8] Ce–TZP/spinel ($K_0 = 8$ MPa $\sqrt{m}$)[9] and 1Y–2Nd–TZP ($K_0 = 7$ MPa $\sqrt{m}$).[10] Moreover the materials should e.g. resist low temperature degradation, a slow phase transition of tetragonal to monoclinic[11] (which is not subject to the present study).

TZP materials costabilized with yttria and neodymia starting from stabilizer coated zirconia powder were first presented by Xu and Vleugels.[12,13] The materials have very high toughness

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but also some seemingly strange features. Increasing the neodymia content does not lead to higher stability but to a narrowing of the processing parameter range. Recently the mechanisms leading to high toughness were identified, the narrow tetragonal field in neodymia co-doped zirconia favours phase separation, which strongly affects the evolution of microstructure and the mechanical properties.[10]

Progress in the field of yttria–neodymia–costabilized TZP has given rise to the question whether costabilization with neodymia and other rare earth dopants can create materials with further improved properties. Ytterbium was used due to its lower ionic radius and different phase relations in the Yb_2O_3–ZrO_2 system. Recently Yb–TZP materials with very high strength and toughness were developed.[14,15]

2. Materials and methods

The starting powders for this study were unstabilized zirconia VP-Ph (Evonik, Germany, $S_{BET} = 60\,m^2/g$) and α-alumina APA0.5 (Ceralox, USA, $S_{BET} = 8\,m^2/g$). The zirconia was coated via the nitrate route[16] with 1 mol% Yb_2O_3 and 2 mol% Nd_2O_3 neodymia (Chempur, Germany, 99.9% purity) basically following a coating procedure adapted to ultrafine zirconia.[15] The resulting calcined powder was blended with 0.5 vol% of alumina and milled for 4 h in 2-propanol using Y–TZP balls ($d = 1$ mm). (Alumina was added with respect to lower decomposition tendency of YNd–TZP and improved sinterability as published by Xu[12]). The milling media were separated, the powder was dried and screened. Samples were consolidated by hot-pressing (KCE, Germany) at 1200–1400 °C for 1 h under 60 MPa axial pressure. The resulting plates with a dimension of 42 mm × 22 mm × 2 mm were lapped with 15 μm and polished 15–1 μm diamond suspension and cut into bending bars. Sides and edges of the bars were carefully ground and polished to eliminate machining defects. The final dimensions of the bars were 3.8 (±0.1) mm × 1.7 (±0.1) mm × 22 mm. The microstructure of polished and thermally etched surfaces (1200 °C/10 min/air) with a conductive PdPt coating was investigated by SEM (Zeiss, Germany) in SE mode at 3 kV acceleration voltage. EDX measurements (Oxford, UK) were made on the same SEM. The phase composition was measured on polished surfaces and fracture faces by integrating the areas of monoclinic and tetragonal XRD reflexes in the 27–33° 2θ-range applying the calibration curve of Toraya[17] (Bruker D8, Germany, CuKα, graphite monochromator). The very smooth and flat fracture faces studied were derived from ISB-tests on HV10 pre-indented specimen. Mechanical properties measurement included measurement of Vickers hardness HV10 (five indents) and HV0.1 (12 indents), determination of the indentation modulus E_{IND} and the measurement of 4pt bending strength in a setup with 10 mm inner and 20 mm outer span at a crosshead speed of 2.5 mm/min (10 samples). Fracture resistance was determined by two methods. Fracture resistance by indentation strength in bending K_{ISB} was measured according to Chantikul[18] by determination of the residual strength (in the same 4pt setup) of four bars pre-indented with a HV10 indent in the middle of the tensile side. In order to determine the threshold stress intensity stable indentation crack growth in flexure was measured in the same 4-pt setup at a crosshead speed of 5 mm/min. The procedure was proposed by Braun[19] and refined by Dransmann[20] and Benzaid.[8] Samples were pre-indented with four HV10 indents each with the diagonals parallel and perpendicular to the sides at 2 mm distance in the middle of the tensile side of a bending bar. The samples were then stored for 2 weeks to allow the cracks to grow subcritically to a stable extension. Samples were initially loaded with 30% of their residual strength (determined in ISB test). The load was subsequently increased in 50–100 MPa increments until fracture. The length of the cracks perpendicular to the sides was measured after each loading step. A plot of the applied stress intensity $K_{appl} = \psi \cdot \sigma \cdot \sqrt{c}$ versus the residual indentation stress intensity $K_{res} = P \cdot c^{-1.5}$ allows the determination of the subcritical stress intensity K_0. If $K_{res} > K_{appl}$ no crack growth occurs. The onset of crack growth visible by the kink in the curve is the value $K_{appl,0}$. The fracture toughness K_{IC} is obtained at the intercept of the straight linear part (with the slope χ starting from the kink) and the ordinate. The threshold K_0 is given by $K_0 = K_{IC} - K_{appl,0}$.[8] The parameters for the calculation are the indentation load $P = 98.1$ N, the crack geometry parameter $\psi = 1.27$, the measured crack length c in μm, and the stress σ in MPa. For materials with R-curve behaviour some restrictions have to be respected. Lube and Fett[21] have shown that the extrapolation to the ordinate intercept can lead to unrealistically high values for the fracture resistance. Moreover fracture resistance rises with crack length thus by definition a fixed value K_{IC} does not exist. It was thus assumed that K_{ISB} is the upper boundary of the fracture resistance. The transformation toughness increment was calculated from the formula of McMeeking and Evans[22] (Eq. (1)).

$$\Delta K_c^T = -\frac{X \cdot E \cdot V_f \cdot \varepsilon^T \cdot \sqrt{h}}{(1-\nu)} \tag{1}$$

E is the elastic modulus, V_f the transformed fraction of zirconia, ε^T the transformation strain (0.05) h the transformation zone height and ν the Poissons's ratio (0.3). The factor X depends on the characteristics of the transformation and may vary from 0.22 (pure dilatation) to 0.48 (dilatation plus shear). For Y–TZP the factor $X = 0.27$.[3]

The height of the transformation zone h was calculated according to Kosmac[23] from the phase composition of the fracture face (X_{meas}) and the polished surface (X_{bulk}) according to Eq. (2).

$$h = \frac{\sin(15°)}{2\mu} \cdot \ln\left(\frac{X_{bulk} - X_{trans}}{X_{meas} - X_{trans}}\right) \tag{2}$$

The X-ray absorption coefficient μ was set at 0.0642 as for Y–TZP. It was further assumed that the zirconia can transform to 100% ($X_{trans} = 1$).

3. Results

3.1. Microstructure

Fig. 1 shows the microstructure of TZP materials sintered at different temperatures. The TZP has a bimodal microstructure