Microstructure and mechanical properties of ZrO_2-TiB_2 composites

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Yttria-stabilised tetragonal zirconia polycrystals (Y-TZP) are well recognised for the excellent combination of bending strength and transformation toughness [1]. The modest hardness however restricts their use for tribological applications. Since the discovery of transformation toughening three decades ago [2], research efforts have been put forward to incorporate non-oxide hard phases such as borides, carbides, nitrides and carbonitrides into a zirconia matrix in order to increase the hardness of Y-TZP monoliths [3–5]. Titanium diboride (TiB_2), for example, has an excellent hardness, but poor fracture toughness and a moderate bending strength [6]. Therefore, TZP–TiB_2 composites are considered to be promising composite materials for tribological applications. In this communication, the microstructure and properties of hot pressed yttria-stabilised tetragonal zirconia polycrystalline (Y-TZP) ceramics with 30 vol% TiB_2 particles are reported. The ZrO_2 starting powders were of the yttria-coated monoclinic ZrO_2 type.

Commercial 2.8 mol% Y_2O_3-coated ZrO_2 powder (Tioxide grade YZ5N (Tio2.8)) and in-house processed yttria-coated zirconia starting powders (YZ grades) were used. The Tio2.8 powder is prepared by co-milling high purity yttria and plasma derived monoclinic zirconia powders [7]. The YZ grade powders were prepared by a chemical suspension coating technique [8, 9], in which a well-defined solution of Y_2O_3 (Aldrich Chemical Company) in HNO_3 (65 vol%) is mixed with monoclinic zirconia powder (Tosoh grade TZ-O) using Y-TZP milling balls (Tosoh grade TZ-3Y) in polyethylene containers for 48 hrs. After drying in a rotary evaporator, the powder was subsequently calcined in an alumina crucible in air at 800 °C for 1 hr to obtain yttria-coated zirconia powders with 2.5 and 2.75 mol% stabilizer, respectively, denoted as YZ2.5 and YZ2.75. H. C. Starck TiB_2 powder grade F, with an average particle size $<0.9\ \mu$m, and grade E, with an average particle size of 1.5–2 μm, were used.

50–100 g of powder with a ZrO_2/TiB_2 volume ratio of 70/30, was mixed for 24 hrs using alumina milling balls and subsequently dried. The dry powder mixture was hot pressed (FCT-Systeme, Rauenstein, Germany) at 1450 °C in vacuum ($\approx$0.1 Pa) for 1 hr at 28 MPa. The final thickness of the hot pressed sample was 5 mm. Additionally, powder mixtures were cold isostatically pressed at 300 MPa for 3 min and pressureless sintered for 1 hr at 1450 °C in vacuum ($\approx$0.1 Pa).

The density of the specimen was measured in ethanol, according to the Archimedes method (BP210S balance, Sartorius AG, Germany). The hardness and fracture toughness was measured using the Vickers indentation method with an indentation load of 10 kg. The indentation toughness was calculated according to the formula of Anstis et al. [10]. The reported values are the mean and standard deviation of at least five indentations. The elastic modulus (E) of the ceramic grades was measured by the resonance frequency method. The flexural strength at room temperature was measured in a 3-point bending test on ground specimens ($25.0 \times 5.4 \times 2.1$ mm) with a span length of 20 mm and a crosshead speed of 0.1 mm/min. The reported values are the mean of at least five measurements. Microstructural investigation of polished and fractured surfaces was performed using Scanning Electron Microscopy (SEM, XL-30-FEG, FEI, the Netherlands) and X-ray diffraction (XRD, Philips, the Netherlands). The martensitic transformation temperature, M_s, was measured by dilatometry experiments in air (TMA 800, Dupont).

A representative back-scattered electron micrograph of a hot pressed ZrO_2-TiB_2 (70/30) composite reveals a homogeneous TiB_2 phase distribution, as shown in Fig. 1a. The phases that can be distinguished are ZrO_2 (white), TiB_2 (grey) and Al_2O_3 (black). The presence of alumina is due to the use of alumina milling balls during powder mixing. All hot pressed ZrO_2 and ZrO_2-TiB_2 ceramics reached full density, since no porosity could be observed by means of scanning electron microscopy on polished cross-sectioned samples. The density of the composites is lower than that of the ZrO_2 ceramics due to the lower theoretical density of the TiB_2 phase (4.52 compared to 6.05 g/cm^3). The pressureless sintered ZrO_2-TiB_2 composite, however, has a residual closed porosity of 1.7%, as calculated from the density value reported in Table I.

The mechanical property data summarised in Table I reveal an excellent combination of hardness (12–14 GPa) and toughness (7–10 MPa $\cdot$ m$^{1/2}$) for the ZrO_2-TiB_2 (70/30) composites. The addition of TiB_2 clearly

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TABLE I Mechanical properties of Y-TZP based 30 vol% TiB_2 composites, sintered at 1450 °C for 1 hr

Material designation[a]	HV_{10} (GPa)	E (GPa)	ρ (g/cm^3)	K_{Ic} (10 kg) (MPa · m$^{1/2}$)	$\Delta K_{Ic}/K_m$ (%)	Flexural strength (MPa)
			Hot pressing in Vacuum			
Tio2.8	12.1 ± 0.2	204	6.07	8.7 ± 0.3	/	945 ± 54
Tio2.8E	12.9 ± 0.1	268	5.52	9.9 ± 0.6	13.8	952 ± 105
YZ2.75	12.8 ± 0.4	215	6.00	4.1 ± 0.4	/	/
YZ2.75F	13.6 ± 0.3	288	5.45	7.8 ± 0.5	90.2	1324 ± 83
YZ2.5	11.2 ± 0.2	212	6.04	4.4 ± 0.2	/	/
YZ2.5F	13.2 ± 0.3	270	5.45	8.1 ± 0.8	84.1	/
			Pressureless sintering in Vacuum			
YZ2.5F	12.1 ± 0.2	/	5.36	7.6 ± 0.4	/	/

[a] The material designation indicates the combination of zirconia matrix code (e.g. YZ2.5, Tio3 etc.) and TiB_2 powder ('F' in the material code refers to H. C. Starck grade F). ΔK_{Ic} represents the difference between the composite fracture toughness and the matrix fracture toughness.

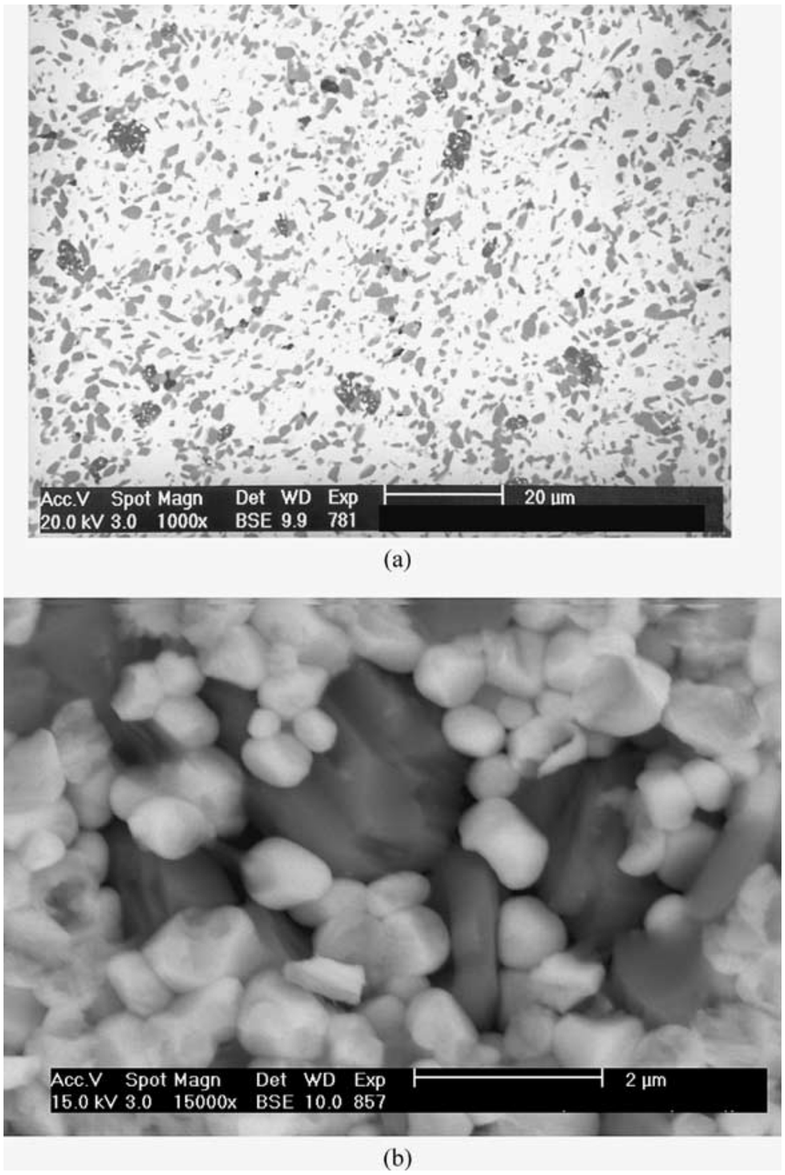

Figure 1 Scanning electron micrographs of polished (a) and fracture (b) surfaces of ZrO_2-TiB_2 (70/30) composite grade YZ2.75F, hot pressed for 1 hr at 1450 °C. The constituent phases are ZrO_2 (white), TiB_2 (grey) and Al_2O_3 (black).

improves the hardness, E-modulus as well as the toughness of the composites when compared to the corresponding pure ZrO_2 matrix materials.

The hardness of the YZ powder based composites is higher than that of the Tio2.8E composite due to the coarser TiB_2 powder grade E which was used in the latter. The hardness of the pressureless sintered YZ2.5F ceramic is lower than that of the hot pressed composite, due to the presence of residual closed porosity.

A high strength of 1.3 GPa was measured for the YZ2.75F composite. The mean strength of the Tio2.8E composite is comparable to that of the ZrO_2 matrix ceramic, but significantly lower than that of the YZ

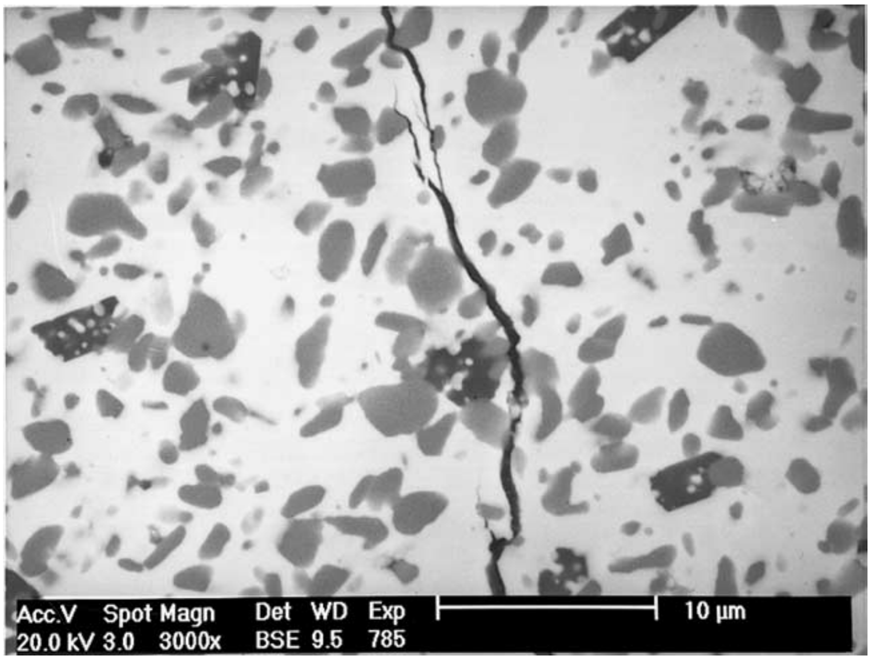

Figure 2 Indentation crack propagation revealing active crack deflection by the TiB_2 (grey) phase.

grade composites. This is due to the presence of coarser cubic ZrO_2 grains in the Tio2.8 based composites, as reported elsewhere [11]. Moreover, a finer TiB_2 powder grade was used for the YZ composite, contributing to an increased strength.

The toughness of the pure Tio2.8 ceramic is double that of the YZ grade ZrO_2. A detailed microstructural characterisation of the YZ monoliths is given elsewhere [9]. Besides the overall yttria content, the yttria distribution was identified as a critical parameter in transformation toughening of Y-TZP ceramics [12]. The higher amount of lower yttria-containing tetragonal zirconia grains in the Tio2.8 monolith compared to the YZ ceramic grades have to be considered as highly transformable in the crack tip stress field, explaining the higher toughness of the Tio2.8 monolith. The significant variation in toughness (4.5–9 $\text{MPa} \cdot \text{m}^{1/2}$) obtained with the TZP monoliths over a relatively small variation in the yttria content (2.5–2.8 mol%) originates from the inherent difference in the powder processing route.

This large difference in matrix toughness, however, is not reflected in the composite toughness. A significant increase (85–90%) in toughness compared to that of the corresponding matrices ($\Delta K_{IC}/K_m$) was recorded for the YZ based materials, whereas the toughness of the Tio2.8E composite was only 14% higher than that of the corresponding matrix material. The slightly higher toughness of the YZ2.5 monolith when compared to the YZ2.75 material is directly related to the lower stabiliser content, which is also reflected in a slightly higher toughness of the YZ2.5F composite. The influence of a small change in the yttria content (2.5–2.8 mol%) on the toughness of the YZ powder based ZrO_2-TiB_2 (70/30) composites is limited.

XRD analysis of the polished samples of TZP monoliths and composites revealed the predominant presence of the tetragonal ZrO_2 phase, indicating that the stress induced t-ZrO_2 to m-ZrO_2 transformation is the primary toughening mechanism in the investigated Y-TZP based composites. SEM observations of the crack pattern of the radial cracks generated at the corners of Vickers indentations revealed crack deflection toughening by the TiB_2 particles in all composites, as illustrated in Fig. 2. Following the crack deflection model of Faber and Evans [13], assuming an aspect ratio of 2 for the TiB_2 particles, a toughness increase of about 15% is predicted for the composites containing 30 vol% TiB_2. The measured relative toughness enhancement of the Tio2.8 based composite of 13.8%, with respect to the matrix ($\Delta K_{IC}/K_m$ data in Table I), is in good agreement with the predicted toughness increment of 15% by crack deflection. It should be clear however that the toughness increase of the YZ2.5F and YZ2.75F composites is significantly higher, indicating the presence of a transformation toughening enhancing mechanism in the YZ-based composites.

A representative fracture surface of a hot pressed YZ grade composite is shown in Fig. 1b. The topography of the fracture surface indicates that the predominant mode of fracture is intergranular in nature. The ZrO_2 grain size is around 0.5–0.6 μm. The grain size measured on the YZ grade monolith is around 0.4–0.5 μm [8]. Similar observations were made on all YZ composites. Taking into account a volume expansion of 4–5% during transformation upon fracturing, it should be clear that only limited grain growth of the t-ZrO_2 phase occurred in the TiB_2-containing composites. This limited grain growth cannot explain the dramatically increased toughness of the YZ powder based composites.

Therefore, the influence of the actual presence of residual thermal stresses on the transformation toughening of the composites has to be considered. Due to the lower coefficient of thermal expansion of TiB_2 ($\alpha_{300-800\,K} = 5 \times 10^{-6}\ K^{-1}$ and $\alpha_{950-2000\,K} = 9 \times 10^{-6}\ K^{-1}$) [14] compared to Y-TZP $\big(\alpha_{300-2000K} =$

$10 \times 10^{-6}\ \text{K}^{-1}$) [15], tensile residual stresses are developed in the ZrO_2 matrix during cooling from the hot pressing temperature. The presence of these tensile residual stresses will trigger the transformation at a much lower level of applied external tensile stress, since tensile stresses activate the t-ZrO_2 transformation in the crack tip stress field [2]. Following the model proposed by Taya *et al.* [16], using an elastic modulus of 210 and 500 GPa for ZrO_2 and TiB_2 respectively, the tensile residual stress in the zirconia matrix is calculated to be 263 MPa. The influence of the presence of this residual tensile stress on the increased t-ZrO_2 transformability is reflected in the measured M_s temperature. Dilatometry measurements revealed an M_s temperature of 290–300 °C for the YZ grade composites, whereas that of the corresponding monoliths is below room temperature, indicate an increased tetragonal ZrO_2 phase transformability in the investigated composites.

Considering the relatively comparable fracture toughness of the composites and the large difference for the ZrO_2 monoliths, one has to infer that the influence of residual stresses is much more pronounced for the in-house processed lower transformable YZ ceramic based composites.

In summary, the present work demonstrated that an excellent combination of indentation toughness (around 8 $\text{MPa} \cdot \text{m}^{1/2}$), hardness (13–14 GPa) and flexural strength (>1 GPa) can be achieved in hot pressed (1 h, 1450 °C) yttria-coated ZrO_2 powder based composites with 30 vol% TiB_2 particles. Although crack deflection was identified as an active toughening mechanism, stress-induced ZrO_2 phase transformation is the major toughening mechanism in the composites. The thermal residual tensile stress in the ZrO_2 matrix due to the TiB_2 phase addition was found to be an important factor, strongly influencing the transformability of the ZrO_2 phase and therefore also the toughness of the composites. The extent of the increased ZrO_2 phase transformability due to the residual thermal stresses however is influenced by the yttria-coating procedure of the starting powder.

Acknowledgment

This work was supported by the Brite-Euram programme of the Commission of the European Communities under project contract no. BRPR-CT96-0304.

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Received 17 June 2003
and accepted 18 May 2004