

## **Toughness Optimisation of ZrO<sub>2</sub>-TiB<sub>2</sub> composites**

B. Basu, J. Vleugels and O. Van Der Biest

Department of Metallurgy and Materials Engineering, Katholieke Universiteit Leuven,  
Kasteelpark Arenberg 44, B-3001, Belgium.

**Keywords:** Y-TZP; TiB<sub>2</sub>; Transformation Toughening; Residual Stress; Ytria Distribution.

**Abstract.** Ytria-stabilised tetragonal zirconia (Y-TZP) composites with 30 vol. % TiB<sub>2</sub> are fabricated by hot pressing in vacuum for 1 hour at 1450°C. Commercial co-precipitated zirconia starting powder as well as a range of experimental powder mixture grades of monoclinic and co-precipitated 3Y-TZP powders were used to study the influence of the zirconia matrix composition on the fracture toughness of the composites. The observed variation in mechanical properties of the composites is explained in terms of the microstructure, the residual stresses due to the presence of TiB<sub>2</sub> and the stabiliser content. Whereas the overall yttria content is very crucial, the residual stress is found to be an additional important parameter influencing the t-ZrO<sub>2</sub> transformability that needs to be taken into account when optimising the toughness of the composites. Beside transformation toughening, crack deflection was identified as an active toughening mechanism in the composites. A simple approach to tailor the toughness of ZrO<sub>2</sub>-TiB<sub>2</sub> composites is proposed.

### **Introduction**

Ytria-stabilised tetragonal zirconia polycrystalline (Y-TZP) monoliths have an excellent transformation toughness [1]. The modest hardness of Y-TZP materials however limits their use in tribological applications. Titaniumdiboride (TiB<sub>2</sub>) on the other hand has an excellent hardness, but a limited fracture toughness [2]. Therefore, composites combining the excellent toughness of Y-TZP with the high hardness of TiB<sub>2</sub>, are promising materials for tribological applications. According to the best of our knowledge, no work is carried out to investigate and optimise the mechanical behaviour of ZrO<sub>2</sub>-TiB<sub>2</sub> composites with high volume fractions of tetragonal zirconia to elucidate the role of transformation toughening in these composites. This paper is focussed on the toughness optimisation of ZrO<sub>2</sub>-TiB<sub>2</sub> composites with 30 vol % of TiB<sub>2</sub>.

### **Experimental Procedure**

The commercial zirconia powders used are 3 mol % yttria co-precipitated ZrO<sub>2</sub> (Tosoh grade TZ-3Y (T3)) and monoclinic yttria-free ZrO<sub>2</sub> (Tosoh grade TZ-O (T0)). The mixed zirconia powder grades, TM2.5 and TM2, are powder mixtures of Tosoh TZ-3Y and TZ-O in such a ratio that the starting powder mixture has an overall Y<sub>2</sub>O<sub>3</sub> content of 2.5 (2.5Y-TZP) and 2 mol % (2Y-TZP) respectively. H. C. Starck grade E TiB<sub>2</sub> powder with an average particle size of 1.5-2.0 µm was used as secondary phase. The ceramic powders were mixed on a multidirectional mixer for 24 hours in propanol, using alumina milling cylinders to break the agglomerates, and hot pressed at 1450°C for 1 h in vacuum.

The Vickers hardness (HV<sub>10</sub>) was measured on a Zwick hardness tester with an indentation load of 10 kg. The indentation fracture toughness (K<sub>Ic</sub>) was calculated from the measured radial cracks around HV<sub>10</sub> indentations, according to the formula of Anstis et al. [3]. The E-modulus of the ceramics was measured by the resonance frequency method using a Grindo-Sonic. The density of the specimens was measured in ethanol. Microstructural investigation of polished and fractured specimens was performed using SEM and XRD. The transformability, i.e. the ability of the

tetragonal zirconia to transform to monoclinic, is defined as the difference in the m-ZrO<sub>2</sub> content calculated from the XRD patterns obtained from fractured and polished surfaces. The m-ZrO<sub>2</sub> volume fraction is calculated according to the formula of Toraya et al. [4].

## Results and Discussion

A representative backscattered electron micrograph of a hot pressed ZrO<sub>2</sub>-TiB<sub>2</sub> composite is shown in Fig. 1a. The different phases that can be distinguished are ZrO<sub>2</sub> (white), TiB<sub>2</sub> (grey) and Al<sub>2</sub>O<sub>3</sub> (black). The alumina particles originate from the milling balls used during mixing. The microstructures of all investigated composites display a homogeneous TiB<sub>2</sub> phase distribution. The fractured surface, shown in Fig. 1b, reveals the presence of coarser TiB<sub>2</sub> particles (3–4 μm) in a sub-micron particle sized ZrO<sub>2</sub> matrix. SEM observations on polished cross-sections revealed that all composites were fully dense, except the TM2E composite.

The mechanical properties of the Y-TZP ceramics and their composites are listed in Table 1. The hardness of the 3Y-TZP and 2.5Y-TZP based composites, T3E and TM2.5E, is comparable or slightly higher than that of the corresponding ZrO<sub>2</sub> matrix materials T3 and TM2.5, whereas the hardness of the 2Y-TZP based composite (TM2E) is inferior to that of the ZrO<sub>2</sub> matrix ceramic (TM2). The hardness increase aimed at by the addition of TiB<sub>2</sub> however is very limited, due to the relatively coarse grain size of the TiB<sub>2</sub>.

The fracture toughness of the Y-TZP ceramics can be increased from 2.5 MPa m<sup>1/2</sup> for the 3Y-TZP up to 10.3 MPa m<sup>1/2</sup> for the 2Y-TZP by the powder mixing approach. The increased toughness correlates well with an increased t-ZrO<sub>2</sub> phase transformability, the difference in m-ZrO<sub>2</sub> content between fractured and polished surfaces, as shown in Fig. 2.a.

The toughness of the 2.5 and 3Y-TZP based composites is higher than that of their ZrO<sub>2</sub> matrix materials. The toughness of the TM2E composite however is significantly lower than that of the TM2 ceramic, revealing that the optimum composite toughness is obtained with 2.5 mol % yttria.

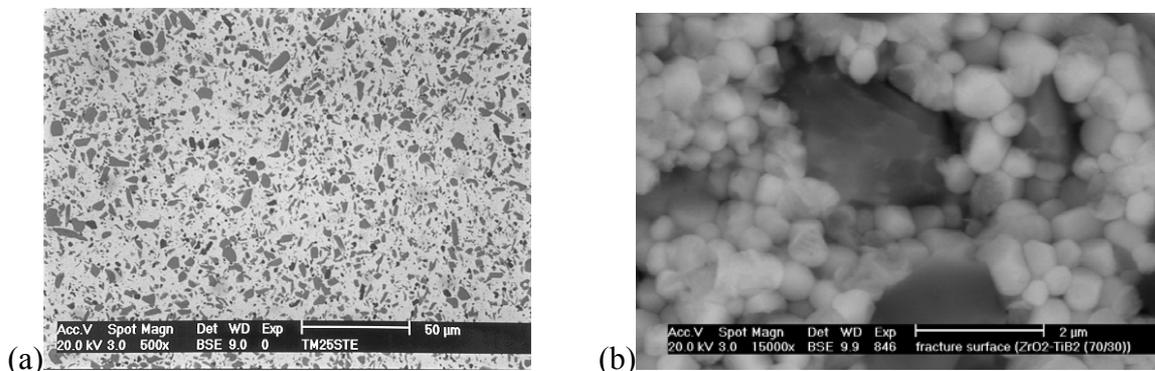


Fig. 1. Backscattered electron micrographs of a polished cross-section and a fracture surface of a ZrO<sub>2</sub>-TiB<sub>2</sub> (70/30) composite. The phases are: ZrO<sub>2</sub> (white), TiB<sub>2</sub> (grey) and Al<sub>2</sub>O<sub>3</sub> (black).

| Material                                   | Code   | HV <sub>10</sub> [GPa] | E [GPa] | ρ [g/cm <sup>3</sup> ] | K <sub>IC</sub> [MPa m <sup>1/2</sup> ] |
|--------------------------------------------|--------|------------------------|---------|------------------------|-----------------------------------------|
| ZrO <sub>2</sub> (3 Y-TZP)                 | T3     | 11.9 ± 0.2             | 194     | 6.08                   | 2.5 ± 0.1                               |
| ZrO <sub>2</sub> (2.5Y-TZP)                | TM2.5  | 12.6 ± 0.1             | 203     | 6.05                   | 5.7 ± 0.1                               |
| ZrO <sub>2</sub> (2 Y-TZP)                 | TM2    | 12.9 ± 0.1             | 215     | 6.07                   | 10.3 ± 0.5                              |
| ZrO <sub>2</sub> -TiB <sub>2</sub> (70/30) | T3E    | 13.2 ± 0.1             | 281     | 5.39                   | 4.4 ± 0.1                               |
| ZrO <sub>2</sub> -TiB <sub>2</sub> (70/30) | TM2.5E | 12.4 ± 0.2             | 249     | 5.46                   | 10.6 ± 0.4                              |
| ZrO <sub>2</sub> -TiB <sub>2</sub> (70/30) | TM2E   | 10.6 ± 0.1             | 264     | 5.39                   | 5.1 ± 0.4                               |

Table 1. Mechanical properties of Y-TZP monoliths and 30 vol % TiB<sub>2</sub> composites

XRD analysis on polished surfaces revealed that the t-ZrO<sub>2</sub> phase is fully retained in the T3E and TM2.5E composites, whereas a significant amount of m-ZrO<sub>2</sub> (67.4 %) was measured on the polished TM2E composite. Upon fracturing, only a small amount of transformable t-ZrO<sub>2</sub> was measured for the TM2E composite, whereas a maximum transformability was measured for the TM2.5E material, as shown in Fig 2.a. The high amount of m-ZrO<sub>2</sub> in the TM2E composite is a result of spontaneous transformation that should be attributed to the presence of TiB<sub>2</sub>. Microcrack toughening,  $\Delta K_{IcM}$ , should therefore be considered as the predominant toughening mechanism in the TM2E composite.

SEM observations of the crack pattern of the radial cracks generated at the corners of the Vickers indentations in the composites proved that crack deflection is an active toughening mechanism. Following the classical zirconia literature [1], the overall toughness of zirconia toughened composites can be expressed as:

$$K_{IC} = K_0 + \Delta K_{IcT} + \Delta K_{IcM} + \Delta K_{IcD} \quad (1)$$

with  $K_0$ , the inherent matrix toughness or the toughness of the non-transformable zirconia matrix,  $\Delta K_{IcT}$ , the transformation toughening contribution,  $\Delta K_{IcM}$ , the contribution from microcrack toughening and  $\Delta K_{IcD}$ , the toughening due to crack deflection by the secondary TiB<sub>2</sub> phase.

Based on the low transformability of the T3 ceramic, a toughness value of 2.5 MPa m<sup>1/2</sup> is considered to be a reasonable estimate of the inherent matrix toughness  $K_0$ . The contribution of the different toughening mechanisms to the total toughness of the Y-TZP monoliths and Y-TZP based composites is illustrated in Fig. 2.b. Since the crack deflection model of Faber and Evans [5] predicts a toughness increase of about 15 % for ceramic composites with 30 vol. % of secondary phase (assuming an aspect ratio of 2). The  $\Delta K_{IcD}$  contribution in the composites was calculated as a 15 % increase in  $K_0$ .

From Fig. 2.b, it is clear that transformation toughening remains the dominant toughening mechanism in the TM2.5E and TM2E composite. Moreover, the tetragonal transformability data shown in Fig. 2.a correlate very well with the transformation toughness in both the Y-TZP monoliths and composites. The higher the t-ZrO<sub>2</sub> transformability, the larger the  $\Delta K_{IcT}$  contribution.

Due to the lower coefficient of thermal expansion of TiB<sub>2</sub> ( $5 \times 10^{-6} \text{ K}^{-1}$ ) [6] when compared to Y-TZP ( $10 \times 10^{-6} \text{ K}^{-1}$ ) [7], tensile residual stresses are developed in the ZrO<sub>2</sub> matrix during cooling from the hot pressing temperature. The residual tensile stress in the zirconia matrix, calculated according to the model proposed by Taya et al. [8], is 263 MPa.

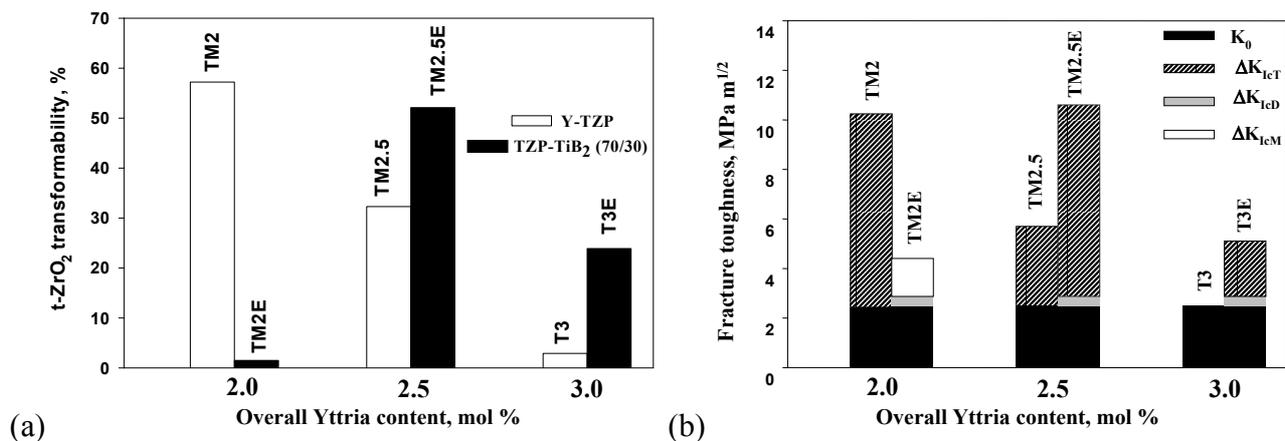


Fig. 2. t-ZrO<sub>2</sub> transformability in Y-TZP monoliths and composites (a), and the contribution of different toughening mechanisms to the overall toughness of the investigated materials (b).

The presence of the tensile residual stress reduces the critical stress to initiate the stress induced t-ZrO<sub>2</sub> transformation at a possible crack tip. Moreover, this actually increases the t-ZrO<sub>2</sub> transformability and the contribution of transformation toughening in the composites, what is indeed experimentally observed for the TM2E and T3E composite as shown in Fig. 2. On the other hand, a ZrO<sub>2</sub> matrix with a very high transformability such as TM2, will spontaneously transform during cooling because of this residual stress. In that case, microcrack toughening becomes an active toughening mechanism, as in the TM2E composite. It should be clear that the type and amount of secondary phase strongly influences the way to engineer the fracture toughness of ZrO<sub>2</sub>-based composites.

## Conclusions

The present work clearly demonstrated that the fracture toughness of ZrO<sub>2</sub>-TiB<sub>2</sub> (70/30) composites can be optimised by mixing of monoclinic and 3 mol % yttria co-precipitated ZrO<sub>2</sub> powders, allowing to carefully adjust the overall yttria content. An excellent indentation toughness of 10 MPa m<sup>1/2</sup> in combination with a HV<sub>10</sub> hardness of 12.5 GPa was obtained with 2.5 mol % yttria.

Transformation toughening was observed to be the major toughening mechanism in these composites, whereas crack deflection by the TiB<sub>2</sub> particles was identified as an additional active toughening mechanism. Beside the overall yttria content, the residual stress is identified as an important additional factor in optimising the toughness of the composites.

## References

- [1] R. H. J. Hannink, P. M. Kelly and B. C. Muddle: *J. Am. Cer. Soc.* Vol. 83 (2000), pp 461ff.
- [2] R. A. Cutler, *Engineering Properties of borides*, in *Engineered materials handbook*, vol. 4, ceramics and glasses, ASM international, USA, (1991), pp. 787ff.
- [3] G. R. Anstis et al.: *J. Am. Cer. Soc.* Vol. 64 (1981), pp. 533ff.
- [4] H. Toraya, M. Yoshimura and S. Somiya: *J. Am. Cer. Soc.* Vol. 67 (1984), pp. C119ff.
- [5] K. T. Faber and A. G. Evans: *Acta Metall.* Vol. 31 (1983), pp. 565ff.
- [6] M. Johnsson and L. Eriksson: *Z. Metallkd.* Vol. 89 (1998), pp. 478ff.
- [7] H. Schubert: *J. Am. Cer. Soc.* Vol. 69 (1986), pp. 270ff.
- [8] M. Taya, S. Hayashi, A. Kobayashi and H. Yoon: *J. Am. Cer. Soc.* Vol. 73 (1990), pp. 1382ff.