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Processing and mechanical properties of ZrO_2–TiB_2 composites

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Abstract

In this paper, a strategy is described to develop high toughness yttria-stabilised tetragonal zirconia polycrystalline (Y-TZP) composites reinforced with hard TiB_2 particles. The experimental results revealed that fully dense Y-TZP composites with 30 vol.% TiB_2 can be obtained with a moderate hardness of 13 GPa, a high strength up to 1280 MPa and an excellent indentation toughness up to 10 MPa m$^{1/2}$ by hot pressing in vacuum at 1450 °C. The toughness of the composites can be tailored between 4 and 10 MPa m$^{1/2}$ by varying the yttria stabiliser content of the ZrO_2 matrix between 3 and 2 mol%. An optimum composite toughness was achieved for a ZrO_2 matrix with an overall yttria content of 2.5 mol%, obtained by mixing pure monoclinic and 3 mol% Y_2O_3 co-precipitated ZrO_2 starting powders. An important observation is that the thermal residual tensile stress in the ZrO_2 matrix due to the TiB_2 addition, needs to be taken into account when optimising the transformability of the ZrO_2 matrix in order to develop high toughness Y-TZP composites.

Keywords: Hot pressing; Toughness; Phase transformation; ZrO_2; TiB_2; Composites

1. Introduction

Yttria-stabilised tetragonal zirconia polycrystalline (Y-TZP) monoliths exhibit excellent mechanical properties such as bending strength and fracture toughness.[1] The rather modest hardness of Y-TZP materials, however, limits their use in demanding tribological applications, especially under high abrasive loads. Titaniumdiboride (TiB_2), on the other hand, has an excellent hardness, high thermal and electrical conductivity, but suffers from a moderate fracture toughness and bending strength.[2] Therefore, composites combining the excellent toughness of Y-TZP with the high hardness and thermal conductivity of TiB_2, can be promising candidate materials for tribological applications.

The high toughness of the zirconia monoliths originates from the stress-induced transformation of the stabilised tetragonal phase in the stress field of propagating cracks, a phenomenon known as transformation toughening.[3] Since the discovery of this concept some decades ago,[4] this approach was exploited to toughen several intermetallic,[5] glass[6] and ceramic[7] microstructures using the addition of the tetragonal zirconia (t-ZrO_2) phase. The incorporation of t-ZrO_2 was reported to increase the fracture toughness of nickel aluminides, used extensively for high temperature structural applications.[5] An example of a widely investigated zirconia-toughened oxide ceramic is zirconia-toughened alumina (ZTA).[7] Research efforts have also been made to incorporate non-oxide hard phases such as borides, carbides, nitrides, carbonitrides, etc. into a zirconia matrix in order to increase the hardness of Y-TZP monoliths.[8–10] Reviewing the mechanical property data of several zirconia-toughened composites, Swain observed that the hardness and toughness followed opposite trends as a function of the reinforcement content.[11] The influence of the yttria stabiliser content on the fracture and transformation behaviour of zirconia reinforced $MoSi_2$ composites was also reported.[12] In one of the early works, Watanabe and Shoubu developed TiB_2 composites with a m-ZrO_2 reinforcement content of 20–100 wt.%.[9] A considerable amount of t-ZrO_2 phase was observed to be stabilised in TiB_2–ZrO_2 composites, hot pressed at and above 1800 °C in vacuum. A high indentation toughness of

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8.4 MPa m$^{1/2}$ together with a moderate strength of 640 MPa was measured for 40 wt.% ZrO_2 addition to a TiB_2 matrix. Later, Shoubu et al. developed TiB_2 composites reinforced with varying amount of ZrO_2 (0–100 wt.%) stabilised with 1.94 mol% yttria.[13] The fracture toughness was observed to increase with increasing t-ZrO_2 content and a maximum indentation toughness of 8 MPa m$^{1/2}$ was measured for the TiB_2–75 wt.% ZrO_2 composites, hot pressed at 1500 °C. Muraoka et al. obtained dense TiB_2–(0–50 mol%) ZrO_2 composites, stabilised with 2 mol% Y_2O_3 and processed by hot isostatic pressing (HIP).[14] An attractive combination of mechanical properties, e.g. indentation toughness of 11.2 MPa m$^{1/2}$ and bending strength of 680 MPa, was obtained for TiB_2–30 mol% ZrO_2, stabilised with 2 mol% yttria.

Vleugels and Van Der Biest investigated hot pressed ZrO_2–TiB_2 composites with up to 50 vol.% TiB_2 based on a 3 mol% yttria-coated ZrO_2 starting powder.[10] A very high indentation toughness up to 10 MPa m$^{1/2}$, excellent bending strength up to 1237 MPa and increased hardness with respect to the Y-TZP matrix material could be achieved. The nature of the 3 mol% yttria stabiliser distribution in the ZrO_2 starting powder was found to be very important as revealed by the superior toughness achieved for ZrO_2–TiB_2 (70/30) composites with 3 mol% yttria-coated powder as compared to the conventional 3 mol% co-precipitated powder.[15] Although all the above-mentioned results demonstrated the possibility of increasing fracture toughness of TiB_2 ceramics by incorporating ZrO_2, none of the studies investigated the influence of the ZrO_2 matrix stabilisation by varying the dopant content on the toughening of ZrO_2–TiB_2 composites to obtain an optimum combination of hardness and toughness for tribological applications.

The toughness optimisation of yttria-stabilised tetragonal zirconia by tuning the yttria dopant content by means of mixing monoclinic and co-precipitated Y_2O_3-stabilised ZrO_2 starting powders was recently reported.[16] In this paper, a similar strategy is adopted in order to develop high toughness Y-TZP composites reinforced with hard TiB_2 particles. In this perspective, the present paper is focused on the toughness optimisation of ZrO_2 with 30 vol.% TiB_2 addition, hereafter referred to as ZrO_2–TiB_2 (70/30) composites.

2. Experimental procedure

Details on the commercial starting powders and experimental zirconia powder mixture grades used in the present investigation are given in Table 1. The commercial powders are yttria-free monoclinic ZrO_2 (Tosoh grade TZ-O) and 3 mol% yttria co-precipitated ZrO_2 (Tosoh grade TZ-3Y). The mixed zirconia powder grades, TM2.5 and TM2, are powder mixtures of Tosoh TZ-3Y (T3) and Tosoh TZ-O (T0) with an overall Y_2O_3 content of 2.5 (2.5Y-TZP) and 2 mol% (2Y-TZP), respectively.

Table 1
ZrO_2 starting powder compositions, as obtained from the suppliers and ICP analysis

Powder source	Material code	Y_2O_3 (mol%)	SiO_2 (wt.%)	Al_2O_3 (wt.%)[a]
Commercial powders				
Tosoh (TZ-3Y)	T3	3.0	0.007	0.020
Tosoh (TZ-0)	T0	0.0	0.006	0.050
Powder mixtures				
T3 + T0	TM2.5	2.5	ND	ND
T3 + T0	TM2	2.0	ND	0.450

ND: not determined.
[a] Al_2O_3 content, as obtained by ICP analysis.

Two different TiB_2 grades, H.C. Starck grades E and F with an average particle size of 1.5–2.0 and <0.9 μm, respectively, were used as secondary phase. According to the supplier, the non-metallic impurities in the TiB_2 powders include C, O and N with a maximum amount of 0.25, 2.0 and 0.25 wt.% respectively, a metallic Fe impurity content of maximum 0.25 wt.%, and a maximum other metallic impurity content of 0.2 wt.%. The impurity level is similar for both grades.

Fifty to one hundred grams of powder, with a ZrO_2/TiB_2 volume ratio of 70/30, was mixed in a multidirectional mixer (type Turbula) for 24 h in one litre of *n*-propanol in a polyethylene bottle. To break the agglomerates in the starting powders, 200 g alumina milling cylinders were added to the container. After mixing, the propanol was removed by means of a rotating evaporator. The dry powder mixture was inserted into a boron nitride coated graphite die of 30 mm diameter. After cold compaction at 30 MPa, the samples were hot pressed in a FCT hot press (FCT Systeme, Rauenstein, Germany) in vacuum (≈0.1 Pa) for 1 h under a mechanical load of 28 MPa. The ceramic samples were hot pressed at 1450 °C, with a heating rate of 50 °C/min and a cooling rate of 10 °C/min. The final thickness of the hot pressed disc was about 5 mm.

The density of the specimens was measured in ethanol, according to the Archimedes method (BP210S balance, Sartorius AG, Germany). The Vickers hardness (HV_5 and HV_{10}) was measured on a Zwick hardness tester (model 3202, Zwick, Ulm, Germany) with an indentation load of 5 and 10 kg. The indentation toughness, K_{Ic5} and K_{Ic10}, was based on the crack length measurements of the radial crack pattern produced by Vickers HV_5 and HV_{10} indentations, and calculated according to the formula of Anstis et al.[17] The reported values are the mean and standard deviation of the data obtained from five indentations.

The elastic modulus (*E*) of the ceramic specimens was obtained by the resonance frequency method, as measured by the impulse excitation technique (Grindosonic, J.W. Lemmens N.V., Leuven, Belgium). The flexural strength at room temperature was measured in a three-point bending test. The test specimens (25.0 mm × 5.4 mm × 2.1 mm) were machined out of the hot pressed discs. All surfaces were ground with a diamond-grinding wheel (type MD4075B55, Wendt

Table 2
Mechanical properties of ZrO_2 monoliths and ZrO_2–TiB_2 (70/30) composites, hot pressed in vacuum for 1 h at 1450 °C

Material grade[a]	HV_5 (GPa)	HV_{10} (GPa)	E (GPa)	ρ (g/cm^3)	K_{Ic} (5 kg) (MPa m$^{1/2}$)	K_{Ic} (10 kg) (MPa m$^{1/2}$)	$\Delta K_{Ic}/K_m$ (10 kg) (%)	Flexural strength (MPa)	M_s (°C)
TM2	11.9 ± 0.1	11.9 ± 0.1	215	6.07	10.2 ± 0.4	10.3 ± 0.5	–	1269 ± 150	301
TM2E	10.5 ± 0.1	10.6 ± 0.1	264	5.39	5.3 ± 0.6	5.1 ± 0.4	−55.0	715 ± 62	323
TM2F	11.2 ± 0.3	10.9 ± 0.1	244	5.33	6.5 ± 0.5	6.7 ± 0.3	−34.0	–	–
TM2.5	12.6 ± 0.1	12.6 ± 0.1	203	6.05	6.2 ± 0.4	5.7 ± 0.1	–	1085 ± 35	<RT
TM2.5E	12.7 ± 0.1	12.4 ± 0.2	244	5.37	11.4 ± 0.5	10.6 ± 0.4	86.0	–	330
TM2.5F	13.1 ± 0.3	13.0 ± 0.2	258	5.43	10.3 ± 0.5	9.7 ± 0.6	70.2	1283 ± 79	–
T3	11.9 ± 0.2	11.6 ± 0.1	194	6.08	2.5 ± 0.1	2.5 ± 0.1	–	1007 ± 126	<RT
T3E	13.0 ± 0.2	13.2 ± 0.1	281	5.39	4.9 ± 0.4	4.4 ± 0.1	77.0	–	<RT

[a] The material grade indicates the zirconia matrix code with the overall yttria stabiliser content (e.g. TM2, TM2.5, etc.), whereas E or F refers to the TiB_2 powder grade. ΔK_{Ic} represents the difference between the composite toughness and the ZrO_2 matrix toughness (K_m).

Boart, Brussels, Belgium). The span width was 20 mm with a crosshead speed of 0.1 mm/min. The reported values are the mean of at least five bending experiments.

Microstructural investigation of the phase assembly was performed by means of X-ray diffraction (XRD, Philips, The Netherlands), scanning electron microscopy (SEM, XL30-FEG, FEI, The Netherlands) and a 200 kV transmission electron microscope (TEM, CM-200 FEG, FEI, The Netherlands) equipped with an EDAX energy dispersive system for compositional analysis. TEM samples were prepared by the standard preparation technique including laser cutting of 3 mm discs, grinding, dimpling and subsequent ion-milling at 5 kV under an angle of 12° till perforation. Coating of the TEM samples with a thin layer of carbon was necessary to prevent charging under the electron beam.

The transformability, i.e. the ability of t-ZrO_2 to transform to m-ZrO_2 in the crack tip stress field, is defined as the difference in the m-ZrO_2 phase content (%) calculated from the XRD patterns obtained from fractured and polished surfaces. The monoclinic and tetragonal ZrO_2 volume fractions are calculated according to the formula of Toraya et al.[18]

The M_s temperatures of the hot pressed samples are measured by dilatometry experiments in air in the temperature range between room temperature (RT) and 650 °C, using commercial thermo-mechanical analysis equipment (model TMA 800, Dupont 943, USA). The furnace was heated and cooled at a rate of 2 °C/min.

3. Results

3.1. Densification and microstructure

The density of the ZrO_2–TiB_2 (70/30) composites and their corresponding pure matrix materials, all hot pressed at 1450 °C for 1 h, are compared in Table 2. The ZrO_2 monoliths with 2–3 mol% Y_2O_3 stabiliser are fully densified, whereas the density of the hot pressed composites is lower than the calculated theoretical density of 5.61 g/cm^3, assuming a theoretical density of 4.52 and 6.08 g/cm^3 for TiB_2 and ZrO_2, respectively. Optical and scanning electron microscopy investigation of polished cross-sections of the hot pressed ZrO_2–TiB_2 composites, however, revealed no residual porosity. The lower density of the composites has to be fully attributed to the presence of a significant amount of alumina that is calculated to be about 11 vol.%. This is not so surprising due to the extremely abrasive character of the TiB_2 powder in contact with the Al_2O_3 milling medium during powder mixing.

The lower density of the TM2-based composites is due to the presence of m-ZrO_2 in the TM2E and TM2F composites, as mentioned further. A 1.75 mol% of Y_2O_3 stabiliser was not enough to prevent spontaneous transformation of the tetragonal ZrO_2 phase in the pure ZrO_2 monolith and related composites. Due to the formation of micro- and macrocracks in these materials, they were not further investigated.

Representative scanning electron micrographs of fully dense ZrO_2–TiB_2 (70/30) composites with two different TiB_2 starting powder grades are presented in Fig. 1. Three phases, ZrO_2 (white), TiB_2 (grey) and Al_2O_3 (black), can be differentiated on the backscattered electron contrast pictures. The grain size of TiB_2 grade E in the composite is significantly larger than that of grade F, in agreement with the larger average grain size of the starting powder. The TiB_2 phase is homogeneously distributed in the ZrO_2 matrix.

In order to investigate the influence of the addition of TiB_2 on the grain size of the t-ZrO_2 phase, the microstructure of ZrO_2–TiB_2 composite grade TM2.5E and the corresponding ZrO_2 matrix grade TM2.5 are compared in Fig. 2. The average ZrO_2 grain size in the TM2.5E composite is around 0.4–0.5 μm, whereas that in the TM2.5 monolith is around 0.3–0.4 μm, indicating that only limited grain growth occurred in the TiB_2 containing composite.

Representative bright field TEM micrographs showing the morphology and size of the zirconia grains and TiB_2 phase in the TM2.5E composite are shown in Fig. 3a. The ZrO_2 grains in the composite are clearly submicrometer sized with an average particle size of 0.3–0.4 μm. Occasionally, some monoclinic zirconia grains reveal the typical martensite laths as a result of the martensitic transformation, as shown in Fig. 3b.

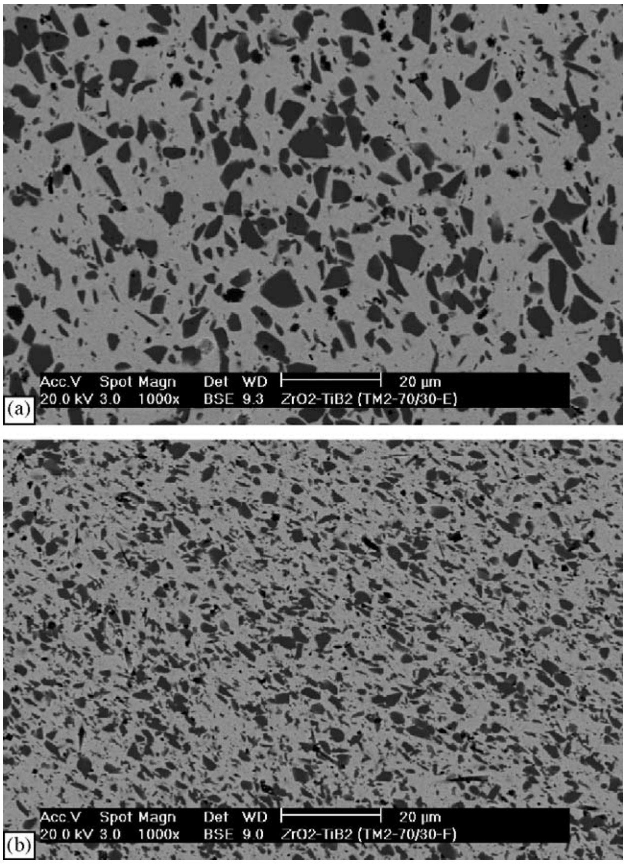
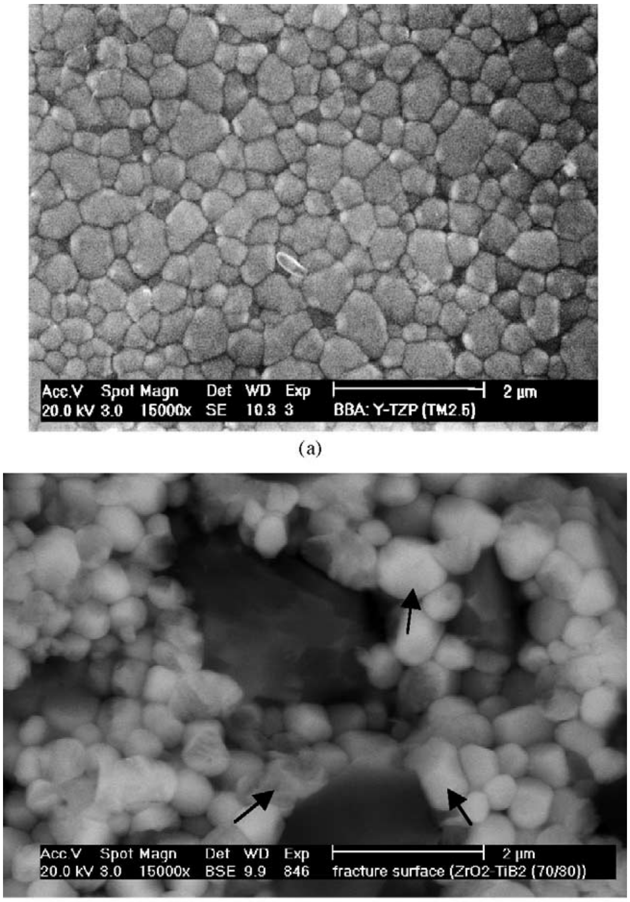


Fig. 1. Backscattered electron micrographs revealing the microstructures of 2 mol% Y_2O_3-stabilised (TM2) ZrO_2–TiB_2 composites with 30 vol.% of TiB_2 grades E (a) and F (b). Three phases can be distinguished: ZrO_2 (white), TiB_2 (grey) and Al_2O_3 (black).

Since no m-ZrO_2 is measured within the detection limit of the XRD analysis, the partial tetragonal zirconia transformation is believed to be caused either by the mechanical stress during the thin foil preparation or due to the thermal stress developed during the high voltage electron beam irradiation. These observations indicate a high transformation potential or transformability of the ZrO_2 grains in the composite. The TiB_2 particles are much coarser, about 2–5 µm for grade E, than the ZrO_2 grains and have irregular grain edges rather than sharp facets.

XRD spectra obtained from the polished composite grades T3E, TM2.5E and TM2E are presented in Fig. 4. While the predominant presence of the t-ZrO_2 phase is achieved in the T3E and TM2.5E composites, significant transformation of t-ZrO_2 to m-ZrO_2 occurred in the TM2E composite, as indicated by the presence of 67.4% m-ZrO_2 on the polished TM2E sample. Full retention of the tetragonal zirconia phase was achieved in the T3 and TM2.5 monoliths, whereas only 2.7% m-ZrO_2 was recorded on the polished TM2 monolith. These results clearly indicate that the presence of TiB_2 in the TM2 monolith increases the transformability of the tetragonal phase, causing a considerable amount of t-ZrO_2 to transform during cooling from the sintering temperature.



(a)

(b)

Fig. 2. SEM micrographs showing the tetragonal zirconia grains of the polished and thermally etched Y-TZP grade TM2.5 (a) and a fracture surface of the ZrO_2–TiB_2 composite grade TM2.5E (b). ZrO_2 grains are indicated by arrows.

3.2. Mechanical properties of the hot pressed composites

The mechanical properties of the composites are compared with those of the Y-TZP monoliths, all hot pressed in vacuum for 1 h at 1450 °C, in Table 2.

A modest hardness of 13 GPa was obtained for the 3Y-TZP (T3E)- and 2.5Y-TZP-based composites (TM2.5F). The hardness of the TM2.5F composite is slightly higher than for the TM2.5E due to the finer TiB_2 particle size. A relatively lower hardness is measured for the 2Y-TZP grade (TM2) composites due to the microcracks formed upon spontaneous t-ZrO_2 phase transformation, as revealed in Fig. 4. The obtained hardness for the ZrO_2–TiB_2 (70/30) composites, however, is lower than what one can expect from the rule of mixtures. A HV_{10} hardness of 14.4 GPa is calculated assuming the hardness of TiB_2 to be 20 GPa, as measured on a hot pressed (4 h at 1900 °C) H.C. Starck grade F TiB_2 monolith with 5 vol.% SiC as sinter additive, whereas the hardness of ZrO_2 was taken as 12 GPa. The presence of the alumina contamination from the milling media is not considered in the hardness calculation. It should be mentioned here that the hardness increase by the TiB_2 addition is limited due to the relatively coarse grain size of the TiB_2 phase.

The bending strength of the TM2.5F composite is higher than that of the TM2.5 matrix material and comparable to that of the 2Y-TZP (TM2), whereas the strength of the TM2E composite is significantly lower than that of the TM2 ceramic. The latter is due to the formation of microcracks as a result of the spontaneous transformation of part of the t-ZrO_2 phase in the TM2E composite.

In the present investigation, the indentation toughness method was chosen, as it is an easy and effective way to make a ranking of the materials based on their toughness. The observed indentation crack profiles closely follow the well-established radial or Palmqvist crack pattern. Therefore, the indentation toughness data are thought to be reliable as far as ranking of the investigated materials is concerned. The toughness measured by the conventional indentation technique is reported to be lower than that of the long crack toughness of transformation toughened materials.[1] This is due to the fact that the conventional indentation theory neglects the effect of stress-induced transformation on the volume expansion of the plastic zone beneath the indentation, that forms an additional driving force for the indentation cracking in materials containing transformable phase. In order to check for "*R*-curve" effects, the indentation toughness was measured for different crack lengths by increasing the indentation load. The measured hardness and toughness values, obtained with an indentation load of 5 and 10 kg, are reported in Table 2. For all investigated ZrO_2 and ZrO_2–TiB_2 composites, the indentation toughness is found to have reached the steady state value even with an indentation load of 5 kg. It is also clear from the data presented in Table 2 that the relative ranking of the investigated Y-TZP materials in terms of indentation toughness is the same, irrespective of the indentation loads.

The indentation toughness of the pure Y-TZP material can be increased by reducing the overall Y_2O_3 stabiliser content by the addition of Y_2O_3-free m-ZrO_2 particles to the 3 mol% yttria-stabilised co-precipitated starting powder. The toughness increases with decreasing overall yttria content from 2.5 up to 10.3 MPa $m^{1/2}$ for an yttria content of 3 and 2 mol%, respectively. Below 2 mol% yttria, the tetragonal ZrO_2 phase spontaneously transforms. For the ZrO_2–TiB_2 (70/30) composites, however, the toughness was found to increase up to a maximum of about 11 MPa $m^{1/2}$ at 2.5 mol% yttria. At lower yttria contents, the toughness was significantly lowered. The toughness of the TM2.5E composite is relatively higher than that of TM2.5F. The mechanical properties of the TM2E and TM2F composites, however, are inferior to those of the TM2 matrix, revealing property degradation due to the TiB_2 addition. It should, therefore, be concluded that careful engineering of the ZrO_2 matrix composition in terms of dopant content is essential to optimise the toughness of Y-TZP-based composites. The relative toughness enhancement, $\Delta K_{Ic}/K_m$, with ΔK_{Ic} the toughness difference between the composite and the pure matrix material K_m, was calculated using the

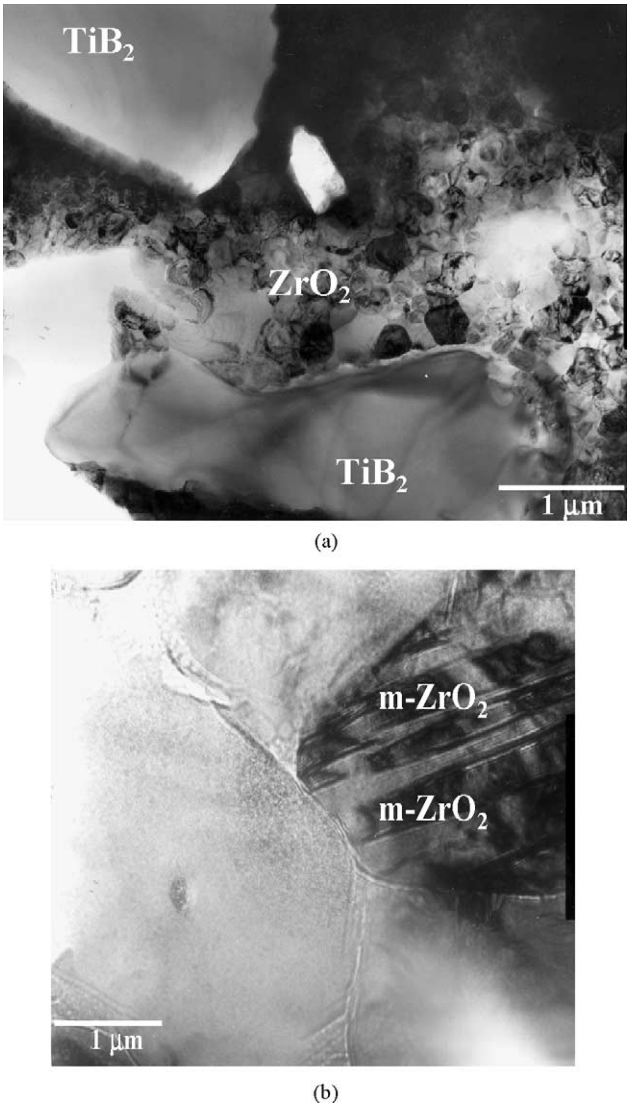


Fig. 3. TEM micrographs of ZrO_2–TiB_2 (70/30) composite grade TM2.5E showing coarser (2–3 µm) TiB_2 grains in a submicrometer grain sized ZrO_2 matrix (a). Typical martensite laths are observed in the transformed monoclinic ZrO_2 grains (b).

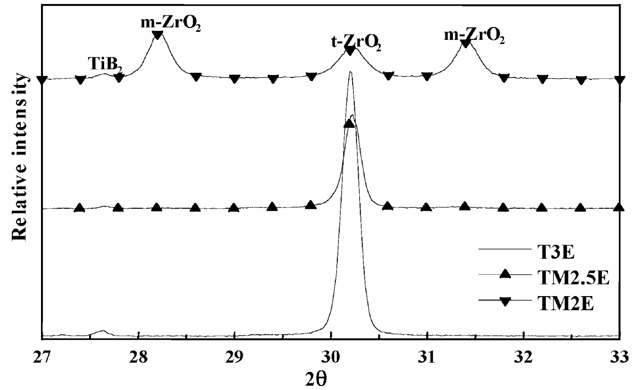


Fig. 4. XRD spectra of polished surfaces of the ZrO_2–TiB_2 (70/30) composite grades T3E, TM2.5E and TM2E.

indentation toughness data obtained with 10 kg indentations and is summarised in Table 2.

4. Discussion

4.1. Active toughening mechanisms

SEM observations of the radial crack patterns generated at the corners of Vickers indentations clearly reveal the presence of a crack deflection toughening mechanism in all composites, as illustrated in Fig. 5 for the TM2F composite. The crack deflection model of Faber and Evans[19] predicts a toughness increase of about 15% for ceramic composites with 30 vol.% of secondary phase, assuming an aspect ratio of 2. The relatively higher toughness obtained with the coarser TiB_2 starting powder in the TM2.5E composite compared to TM2.5F, can be attributed to the larger contribution of the crack deflection toughening mechanism to the overall toughness in the grade E composites.

Looking at the relative toughness enhancement in the composite with respect to the matrix toughness, $\Delta K_{Ic}/K_m$, given in Table 2, and considering the above estimate that crack deflection only accounts for a 15% increment in toughness of the composites, it is clear that enhanced transformation toughening contributes significantly to the overall toughness of the 3Y-TZP- and 2.5Y-TZP-based composites.

Following the classical zirconia literature,[1,3] the overall toughness of a zirconia-toughened composites can be expressed as:

$$K_{Ic} = K_0 + \Delta K_{IcT} + \Delta K_{IcM} + \Delta K_{IcD} \qquad (1)$$

with K_0, the inherent matrix toughness, i.e. the zirconia matrix without or with negligible transformation toughening, ΔK_{IcT} is the transformation toughening contribution, ΔK_{IcM} is the contribution from microcrack toughening and ΔK_{IcD} is the toughening due to crack deflection by the TiB_2 phase.

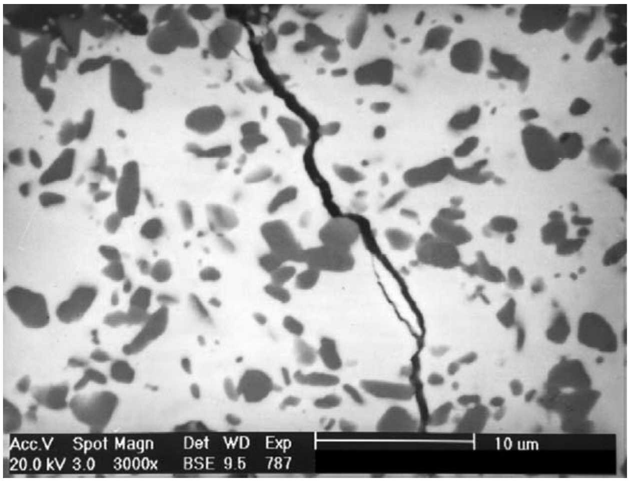


Fig. 5. Crack path revealing crack deflection by the TiB_2 grains in a ZrO_2–TiB_2 (70/30) composite.

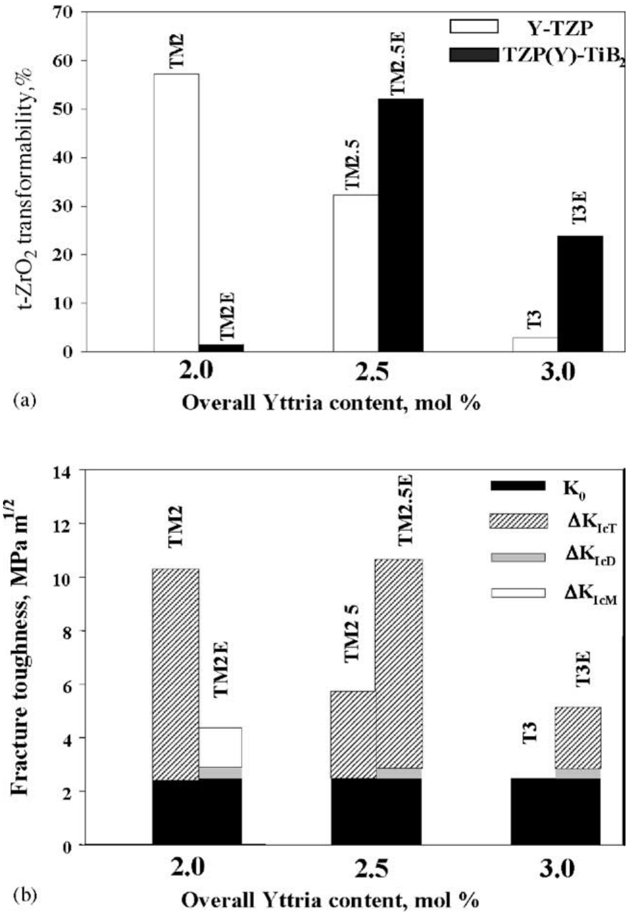


Fig. 6. The tetragonal ZrO_2 phase transformability as determined by the difference in m-ZrO_2 content between fractured and polished surfaces (a) and the contribution of different toughening mechanisms to the overall toughness of the Y-TZP monoliths and ZrO_2–TiB_2 (70/30) composites (b). K_0 is the inherent matrix toughness, ΔK_{IcT} is the transformation toughening contribution, ΔK_{IcM} is the contribution from microcrack toughening and ΔK_{IcD} is the contribution from crack deflection.

For the TM-based composites, the inherent matrix toughness, K_0, is 2.5 MPa $m^{1/2}$ since the T3 ceramic did only reveal a very small amount of m-ZrO_2 phase on a fractured surface.

XRD analysis revealed that the t-ZrO_2 phase is fully retained in the sintered microstructure of the pure ZrO_2 ceramics stabilised with 2–3 mol% Y_2O_3 as well as in the 3Y-TZP- and 2.5Y-TZP-based composites, whereas a significant amount of m-ZrO_2 phase was measured on the polished 2Y-TZP composite. Additional information could be obtained by measuring the m-ZrO_2 content on fractured surfaces, allowing to calculate the transformability of the t-ZrO_2 phase in all investigated material grades. The experimental data are summarised in Fig. 6a, revealing that the transformability of the Y-TZP ceramics increases with decreasing stabiliser content. Moreover, the transformability of the t-ZrO_2 phase in the ZrO_2–TiB_2 (70/30) composites stabilised with 2.5 and 3 mol% yttria is higher than in the corresponding pure ZrO_2 matrix materials, indicating that the addition of TiB_2 increases the transformability of the t-ZrO_2 phase. It should also be clear that transformation toughening is the dominant toughening mechanism in these ceramics.

Because of the very high transformability of the t-ZrO_2 phase in the TM2 material, the addition of TiB_2 results in spontaneous transformation of the t-ZrO_2 phase resulting in microcracked TM2E and TM2F composites. This, however, implies that microcrack toughening should be taken into account as an active toughening mechanism in these composites.

The contribution of the different toughening mechanisms in the composites and their corresponding ZrO_2 matrix materials is graphically illustrated in Fig. 6b. The ΔK_{IcD} contribution in all composites is calculated as the 15% increase in K_0 due to crack deflection by the presence of 30 vol.% TiB_2, as predicted from the crack deflection model of Faber and Evans.[19] The remaining toughness in the Y-TZP materials and the TM2.5- and T3-based composites is attributed to transformation toughening, whereas the additional contribution to the toughness in the TM2-based composites is attributed to microcrack toughening. Typically, 5–10% deviation in the toughness and the transformability data was measured in the experiments.

Comparing Fig. 6a and b reveals that the t-ZrO_2 transformability data correlate very well with the transformation toughness in both the Y-TZP monoliths and composites. The higher the t-ZrO_2 transformability, the larger is the transformation toughening contribution. It should be clear that the transformation toughening contribution towards the overall toughness of the composites is strongly dependent on the ZrO_2 matrix composition and the residual stress due to the presence of TiB_2, as will be discussed in the following section.

4.2. *Influence of thermal residual stresses*

The residual thermal stress is considered to be one of the important design parameters in the fabrication of ceramic matrix composites. While the coefficient of thermal expansion (CTE) mismatch decides the tensile or compressive nature of the residual stress in the constituent phases, the magnitude of the residual stress is determined by the mismatch in CTE and elastic modulus. In general, if the residual stress is compressive, the far field applied stress necessary for the t-ZrO_2 phase transformation will increase. On the contrary, the existence of tensile residual stresses will trigger the t-ZrO_2 transformation at a much lower level of applied stress, since tensile stresses activate the t-ZrO_2 transformation in the crack tip stress field.[3]

Due to the lower CTE of TiB_2 ($\alpha_{300\text{–}800\,\mathrm{K}} = 5 \times 10^{-6}\,\mathrm{K}^{-1}$ and $\alpha_{950\text{–}2000\,\mathrm{K}} = 9 \times 10^{-6}\,\mathrm{K}^{-1}$)[20] when compared to Y-TZP ($\alpha_{300\text{–}2000\,\mathrm{K}} = 10 \times 10^{-6}\,\mathrm{K}^{-1}$),[21] tensile residual stresses are developed in the ZrO_2 matrix during cooling from the hot pressing temperature. Several theoretical models to calculate residual stresses in multi-phase ceramic composites are reported in literature.[22,23] In the present study, the residual stress is calculated according to the model proposed by Taya et al.,[22] assuming all zirconia particles have the tetragonal symmetry at the sintering temperature. The anisotropy in CTE of t-ZrO_2 as a function of the yttria content, and the anisotropic CTE of TiB_2 due to the hexagonal crystal symmetry were not considered in the calculations. The calculated residual tensile stress in the zirconia matrix is 263 MPa. The toughness data obtained in this work clearly show that the influence of the tensile residual stresses in the ZrO_2 matrix on the transformability and hence the transformation toughening of the ZrO_2 matrix is very pronounced for the 3Y-TZP- and 2.5Y-TZP-based composites, contributing effectively to an increased transformation toughness compared to the corresponding Y-TZP matrix materials, as shown in Table 2 and Fig. 6.

The influence of the residual stress on the transformation toughness can be explained from the existing transformation toughening literature.[3] In the presence of tensile residual stress (σ_{r}), the critical stress (σ_{c}) required to initiate the stress-induced transformation in the crack tip would be modified ($\sigma_{\mathrm{c}}^{\mathrm{m}}$) and reduced:

$$\sigma_{\mathrm{c}}^{\mathrm{m}} = \sigma_{\mathrm{c}} - \sigma_{\mathrm{r}} \tag{2}$$

The reduction in critical stress would actually contribute to the development of a larger transformation zone (h) according to the formula proposed by Budiansky et al.:[24]

$$h = \frac{\sqrt{3}(1+\nu)^2}{12\pi}\left(\frac{K_\infty}{\sigma_{\mathrm{c}}}\right)^2 \tag{3}$$

with ν the Poisson's ratio, K_∞ the stress intensity factor due to the applied (external) stress and σ_{c} the critical transformation stress.

The increased transformation zone size enhances the transformation toughening contribution according to the established formula of Evans and Cannon:[25]

$$\Delta K_{\mathrm{IcT}} = \frac{0.38\, f E \varepsilon^{\mathrm{t}} \sqrt{h}}{1-\nu} \tag{4}$$

with f the volume fraction of the t-ZrO_2 phase transformed within the transformation zone, ν the Poisson ratio, E the elastic modulus and ε^{t} the transformation strain.

Furthermore, the experimental data also indicate that the transformability of the ZrO_2 matrix should be affected considering the presence of residual stress. The additional transformability due to the tensile residual stresses generated by the presence of TiB_2 in a high toughness 2Y-TZP matrix (highest tetragonal transformability among the monoliths) causes spontaneous transformation of the t-ZrO_2 matrix during cooling from the sintering temperature, resulting in the formation of microcracks and a degradation of the mechanical properties. The zirconia matrix of the 2Y-TZP composites contains both t-ZrO_2 and m-ZrO_2 phases, whereas the zirconia matrix of the 2.5Y-TZP- and 3Y-TZP-based composites is predominantly tetragonal, as shown in Fig. 4. The lower hardness, density and strength of the 2Y-TZP composites are a direct result of the formation of microcracks caused by

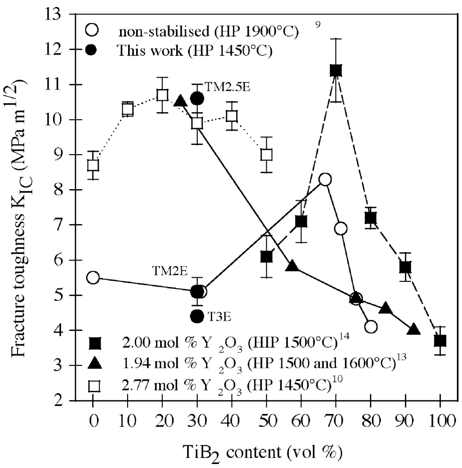


Fig. 7. Indentation toughness of ZrO_2–TiB_2 composites, literature data and preset work. Different processing techniques, e.g. hot pressing (HP) and hot isostatic pressing (HIP) are indicated.

spontaneous transformation. Therefore, the influence of the presence of a secondary phase should be taken into account when optimising the toughness of ZrO_2-based composites by means of the starting powder mixing route.

The influence of the residual stress on the increased t-ZrO_2 transformability is also reflected in a higher onset temperature (M_s) for the t-ZrO_2 to m-ZrO_2 transformation. The transformation data of all composites is compared with that of the monoliths in Table 2, and reported in detail elsewhere.[26,27] The M_s temperature of the TM2.5E composite is around 330 °C, whereas that of the TM2.5 monolith is below room temperature (RT). The increased M_s temperature clearly indicates that the presence of TiB_2 increases the t-ZrO_2 phase transformability in the investigated composites.

4.3. *Influence of the ZrO_2 matrix stabilisation*

Comparing the toughness increment ($\Delta K_{Ic}/K_m$) obtained in the composites (see Table 2 and Fig. 6) reveals that the TZP–TiB_2 (70/30) composites can be toughened by lowering the overall yttria content in a controlled manner by tailoring the ZrO_2 matrix composition. In the 2–3 mol% yttria compositional window, the highest toughness is recorded at an overall yttria content of 2.5 mol%, obtained by the addition of pure monoclinic zirconia to a 3 mol% Y_2O_3 co-precipitated ZrO_2 powder.

The indentation toughness of the TM2E and T3E composites is comparable to that reported for a ZrO_2–TiB_2 (70/30) composite obtained by hot pressing an unstabilised m-ZrO_2–TiB_2 powder mixture at 1900 °C,[9] as graphically presented in Fig. 7. The excellent toughness of the TM2.5E is comparable to that reported for a ZrO_2–TiB_2 (80/20) composite based on 3 mol% yttria-coated ZrO_2 starting powder, hot pressed at 1450 °C[10] and a ZrO_2–TiB_2 (75/25) composite based on 1.94 mol% co-precipitated ZrO_2 starting powder, hot pressed at 1500 °C.[13] It should be noted that the 3 mol% yttria-coated as well as the 2 mol% co-precipitated ZrO_2 starting powders are no longer available. It is, therefore, of high interest to see that a comparable toughness can be achieved by mixing pure monoclinic and 3 mol% co-precipitated ZrO_2 powders, which are commercially available from different sources.

The experimental work revealed that the overall yttria content and residual stress play a predominant role in optimising the toughness of TZP–TiB_2 composites. It should be mentioned that the formulated ZrO_2 powder mixing route has also been successfully exploited to develop ZrO_2–Al_2O_3,[28] ZrO_2–ZrB_2[29] and ZrO_2–WC[30] composites with a high toughness up to 9 MPa $m^{1/2}$.

5. Conclusions

A high indentation toughness of 10 MPa $m^{1/2}$ in combination with a HV_{10} hardness of 13 GPa and a high strength of more than 1 GPa was achieved for the ZrO_2–TiB_2 composites with 30 vol.% TiB_2 with a 2.5Y-TZP matrix, hot pressed for 1 h at 1450 °C.

The fracture toughness of Y-TZP–TiB_2 (70/30) composites can be optimised by adjusting the overall yttria content by means of the addition of pure monoclinic ZrO_2 to a 3 mol% yttria co-precipitated ZrO_2 starting powder. The formulated ZrO_2 powder mixing approach allows to tune the toughness of the composites as well as the Y-TZP ceramics between 2.5 and 10.5 MPa $m^{1/2}$.

The addition of TiB_2 results in thermal residual tensile stresses in the ZrO_2 matrix that increases the t-ZrO_2 transformability. Due to this residual tensile stress, a zirconia matrix with higher overall yttria content of 2.5 mol%, i.e. lower transformability, is essential to optimise the fracture toughness of the ZrO_2–TiB_2 composites. A 2 mol% yttria containing matrix resulted in spontaneous transformation of the t-ZrO_2 in the composites leading to microcracks and concomitant reduction of the hardness, toughness, strength, as well as the sintered density. Transformation toughening was observed to be the major toughening mechanism in the composites with 2.5 and 3 mol% yttria, whereas crack deflection was also active.

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