Development of ZrO_2–ZrB_2 composites

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Abstract

Yttria-stabilised tetragonal zirconia (Y-TZP) composites with 30 vol.% ZrB_2 are prepared by hot pressing in vacuum for 1 h at 1450°C. Different commercial zirconia starting powders as well as a range of ZrO_2 'powder mixture' grades, based on co-precipitated powders were used for the composite production. The measured differences in the mechanical properties of the obtained composites is explained in terms of the microstructure, the residual stresses due to the presence of ZrB_2, and the stabiliser content and its distribution. While the stabiliser content and distribution remained significant, the residual stress in the zirconia matrix is found to be an important additional factor influencing the tetragonal zirconia transformability. Crack deflection by the ZrB_2 phase was identified as an active toughening mechanism in the composites. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Since the discovery of transformation toughening in zirconia ceramics [1], extensive efforts have been made to develop tough ceramic composites exploiting the excellent toughness of the tetragonal zirconia [2,3]. One of the research topics in our laboratory is the development of ZrO_2-based composites with increased hardness, while maintaining the excellent toughness of the monolithic tetragonal ZrO_2 materials [4]. Because of the strong covalent bonding, transition metal borides have an attractive combination of a high melting point, high hardness, high elastic modulus, chemical inertness, as well as thermal and electrical conductivity [5,6]. The low fracture toughness and strength, coupled with a poor sinterability however limit the application of monolithic borides as structural materials. Recently, the densification behaviour of Al_2O_3 composites containing ZrB_2 (up to 20 vol.%) has been investigated by performing pressureless sintering experiments in argon atmosphere in the temperature range 1200–1900°C [7]. Literature reports indicate that electrically conductive, wear and corrosion resistant ceramic composites can be fabricated for example in the ZrB_2–B_4C [6,8] and TiB_2–B_4C [6] system.

According to the best of the authors' knowledge, no work has been reported on the development of zirconia toughened ZrB_2 composites. In this perspective, the present paper reports on the first results on yttria-stabilised tetragonal zirconia (Y-TZP) toughened ZrB_2 composites. Commercially available Y_2O_3 co-precipitated ZrO_2, Y_2O_3-coated ZrO_2, as well as several zirconia powder mixtures were used for the fabrication of composites with 30 vol.% ZrB_2 particles as hard second phase. The microstructures of the composites were characterised and the mechanical properties were compared with those of the zirconia matrix materials.

2. Experimental procedure

The zirconia starting powders used in this work are listed in Table 1. The commercially available powders are 2.8 mol% yttria-coated zirconia (Tioxide grade YZ5N), 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) in such a ratio that the starting powder mixture has an overall Y_2O_3 stabiliser content of 2.5 (2.5Y-TZP) and 2 mol% (2Y-TZP) respectively. The TM grades are referred

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Table 1
Commercial and experimental ZrO_2 starting powder grades

Powder source	Ceramic code	Particle size (nm)	Y_2O_3 mol%
Commercial zirconia powders			
Tioxide (YZ5N)	Tio3	90	2.8
Tosoh (TZ-3Y)	T3	27	3.0
Tosoh (TZ-0)	T0	27	0.0
Experimental zirconia powder mixtures			
T3+T0	TM2.5	–	2.5
T3+T0	TM2	–	2.0

to as 'powder mixture' grades. Commercial ZrB_2 powder (99.5% pure, particle size <45 μm, Alpha Co., Germany) was used as second phase. Then, 50–100 g powder, with a ZrO_2/ZrB_2 volume ratio of 70:30, was mixed in a multidirectional mixer (type Turbula) for 24 h in 1 l 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 cylindrical graphite die with a diameter of 30 mm. After cold pressing at 30 MPa, the samples were sintered in a hot press (KCE Sondermaschinen, Rödental, Germany) in vacuum (≈0.1 Pa) for 1 h under a mechanical load of 28 MPa. The samples were separated from the furnace atmosphere by the graphite hot press set-up, whereas the sliding contacts were sealed by boron nitride. The powder mixtures 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 discs 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 (H_{V10}) was measured using a hardness tester (model 3202, Zwick, Ulm, Germany) with a load of 10 kg. The fracture toughness (K_{IC10}) calculations were based on the crack length measurements of the radial crack pattern produced by Vickers H_{V10} indentations, according to the formula of Anstis et al. [9]. The reported values are the average of data obtained from five indentation tests. The elastic modulus (E) was measured by the resonance frequency method according to ASTM C 1259-94. The resonance frequency was measured using the impulse excitation technique (Grindosonic and Lemmens, Leuven, Belgium). Microstructural investigation was performed by means of scanning electron microscopy (SEM, Philips XL-30-FEG) and X-ray diffraction (XRD, Philips, The Netherlands). Additionally, the transformability, i.e. the ability of the tetragonal zirconia to transform to monoclinic in the crack tip stress field, is defined as the difference in the monoclinic zirconia phase content (%) calculated from the XRD patterns obtained from fractured and polished surfaces. The volume fraction of the m-ZrO_2 (V_m) is calculated by

measuring intensities of (111) and (11$\bar{1}$) reflections of the monoclinic phase and the (111) peak of the tetragonal (+cubic) phase according to the formula of Toraya et al. [10]:

$$V_m = \frac{1.311 X_m}{1 + 0.311 X_m} \tag{1}$$

$$X_m = \frac{I_m(111) + I_m(11\bar{1})}{I_m(111) + I_m(11\bar{1}) + I_t(111)} \tag{2}$$

with X_m the summed intensity ratio, I_m and I_t the peak intensities of the monoclinic and tetragonal zirconia, respectively.

3. Results and discussion

3.1. Microstructural characterisation

A representative microstructure of the ZrO_2–ZrB_2 (70/30) composite is given in Fig. 1a. Due to the small difference in the mean atomic number of ZrO_2 and ZrB_2, the backscattered electron contrast between the boride particles and the zirconia phase is very small. The fracture surface of the composite, as shown in Fig. 1a, clearly reveals the relatively large size of the ZrB_2 phase, i.e. 4–8 μm with an average aspect ratio of 1.5–2.0. The grain size of the ZrO_2 matrix is below 1 μm. The microstructure also shows a uniform ZrB_2 distribution. The black phase in the microstructure is the residual porosity or the Al_2O_3 crystals, which originated from the milling medium during mixing.

XRD analysis on smoothly polished composite surfaces revealed a fully tetragonal zirconia matrix in the T3, TM2.5 and Tio3 composites. A large amount (60.9%) of monoclinic zirconia was recorded in the TM2–ZrB_2 (70/30) ceramic. Considering the fact that only 2.7% monoclinic zirconia is detected in the polished TM2 monolith, this result indicates that the presence of ZrB_2 causes significant tetragonal ZrO_2 phase transformation during cooling from the sintering temperature.

3.2. Mechanical properties

The mechanical properties and density of the Y-TZP matrix materials and the ZrO_2–ZrB_2 (70/30) composites, hot pressed for 1 h at 1450°C, are given in Table 2. The ZrO_2 monoliths can be considered as fully dense, whereas the apparent density of the hot pressed composites is 96–98% of the theoretical density, assuming a theoretical density of 6.08 and 6.10 g/cm^3 for ZrB_2 and ZrO_2, respectively. The actual density level in the composites however is higher as the presence of alumina (density of 3.89 g/cm^3) is not considered in the density calculations. A comparatively lower density is measured for the TM2 based composites (see Table 2).

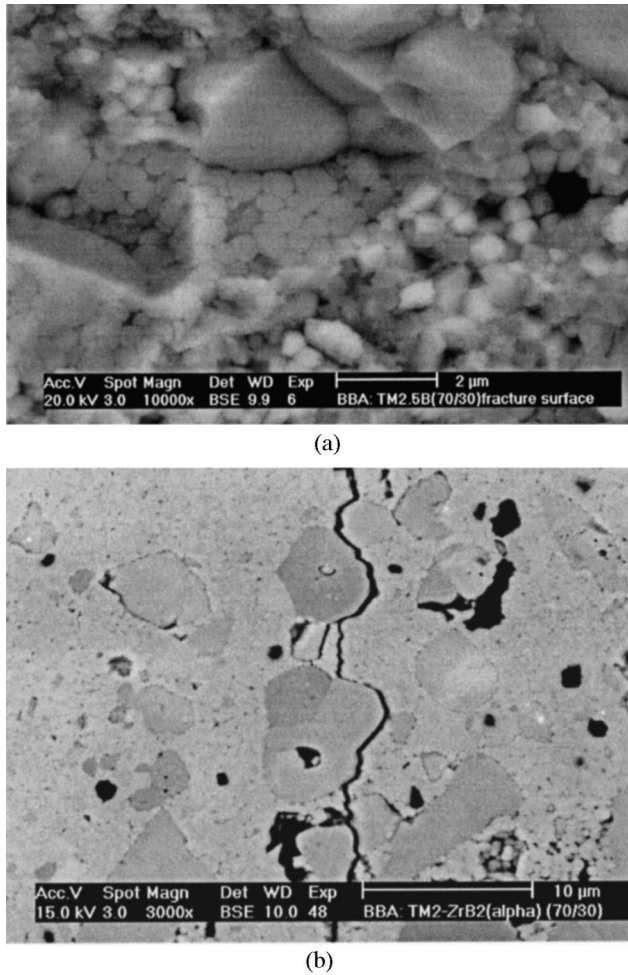From Table 2, it is clear that the addition of ZrB_2

(a)

(b)

Fig. 1. SEM micrograph of the fractured surface showing the distribution of different phases (a) and the crack deflection (b) in the polished surface of a ZrO_2–ZrB_2 (70/30) composite, hot pressed at 1450°C. The large darker grains are ZrB_2, the small brighter grains are ZrO_2 and the black phase is the residual porosity of the Al_2O_3 particles from the alumina milling cylinders.

increases the E-modulus of the Y-TZP materials. The Vickers hardness of the investigated composites varies from 12 to 13 GPa. A maximum hardness of 13 GPa was

Table 2
Mechanical properties of Y-TZP monoliths and TZP-ZrB_2 (70/30) composites, hot pressed at 1450°C for 1 h

Material designation[a]	ρ (g/cm^3)	E (GPa)	H_{V10} (GPa)	K_{IC} (10 kg) (MPa m$^{1/2}$)	$\Delta K_{Ic}/K_m$ (%)
Tio3	6.07	205	12.2±0.2	4.7±0.3	–
Tio3B	5.95	259	12.2±0.2	10.1±0.8	114.5
T3	6.08	194	11.9±0.2	2.5±0.1	–
T3B	5.98	255	12.6±0.3	4.3±0.4	72.0
TM2.5	6.05	203	12.6±0.1	5.7±0.1	–
TM2.5B	5.96	261	13.0±0.2	8.7±0.9	52.6
TM2	6.07	215	11.9±0.1	10.3±0.5	–
TM2B	5.88	247	10.8±0.1	7.8±0.7	−24.3

[a] B refers to the ZrB_2 composites. ΔK_{Ic} represents the difference between the composite and the matrix toughness (K_m).

measured with the TM2.5B material. The hardness increase by the addition of ZrB_2 is limited due to the low ZrB_2 content and the relatively large grain size of the ZrB_2 phase. The hardness of the TM2B composite is even lower than that of the TM2 matrix. This has to be related to the presence of monoclinic ZrO_2 in this composite. It is well known that the transformation from tetragonal to monoclinic zirconia is accompanied by the formation of microcracks. These microcracks actually reduce the density, the E-modulus as well as the hardness of the composite [11].

A broad range of toughness values were obtained for the different Y-TZP materials, hot pressed for 1 h at 1450°C (see Table 2 and Fig. 2a). The fracture toughness of the yttria-coated 3Y-TZP material grade Tio3 is significantly higher than that of the yttria co-precipitated powder based T3 ceramic. The fracture toughness of the co-precipitated
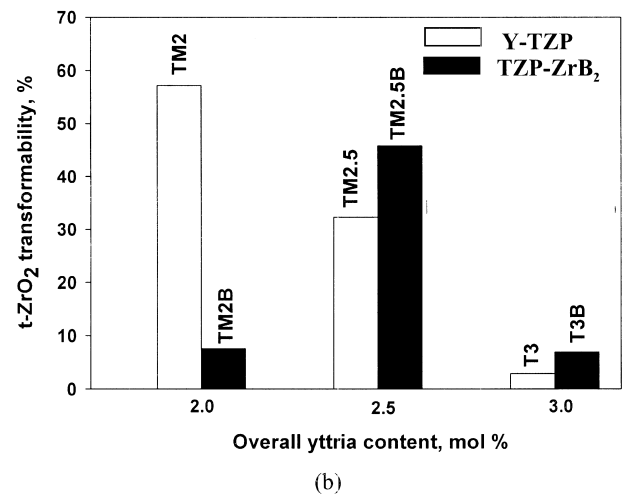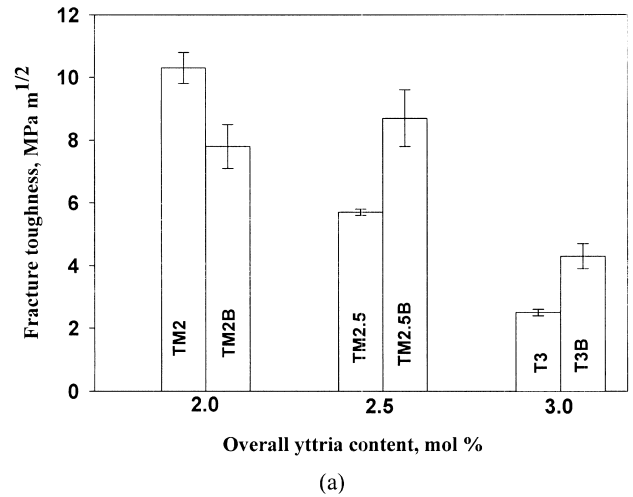

(a)

(b)

Fig. 2. (a) Comparison of the toughness obtained in the TM grades Y-TZP monoliths and composites. (b) The tetragonal zirconia transformability, as defined by the difference in m-ZrO_2 content between fractured and polished surfaces, in both Y-TZP monoliths and composites.

powder based material can however be tuned, by the addition of monoclinic ZrO_2 powder to the starting mixture, from 2.5 MPa m$^{1/2}$ for the 3Y-TZP (T3 grade) up to 10.3 MPa m$^{1/2}$ for the 2Y-TZP (TM2 grade). The toughness data of the monoliths clearly indicate that the tetragonal phase transformability in the crack tip stress field increases with the increasing addition of the monoclinic zirconia particles in the 3 mol% powders. The highest value here is recorded at an overall Y-content of 2 mol%. This is clearly revealed in the transformability data, as presented in Fig. 2b.

A different picture arises in the presence of ZrB_2. The data, shown in Table 2 and Fig. 2a, clearly indicate that addition of 30 vol.% of ZrB_2 improves the fracture toughness of the 3Y-TZP and 2.5Y-TZP materials. The toughness of the 2Y-TZP composite however is lower than that of the corresponding matrix material. A clear maximum in toughness (around 9 MPa m$^{1/2}$) is measured in the TM2.5B composite with the yttria stabilisation level of 2.5 mol% (see Fig. 2). This also corresponds to a maximum in the transformability of the tetragonal phase among the composites (Fig. 2b). It can be noted from Table 2 here that significant toughness improvement ($\Delta K_{Ic}/K_m$) is also recorded in the Tio3B composite (10 MPa m$^{1/2}$).

Therefore, the experimental data indicate that the engineering of the zirconia matrix in terms of the overall Y-content, pursued in the 'powder mixing' route, is effective to optimise the toughness of the Y-TZP based composites. Additionally, a range of toughness in both the zirconia monoliths and composites can be achieved in the powder mixing route, by changing the ratio of the monoclinic to tetragonal particles in the starting powder mixture.

3.3. Toughening mechanisms

The radial crack profiles at the edges of Vickers indentations as observed by SEM, clearly revealed the presence of a crack deflection toughening mechanism in all composites (see Fig. 1b). Due to the coarser boride particles, significant crack deflection is observed. Following the well-known crack deflection model of Faber and Evans [12], a toughness increase of 15% can be predicted for ceramic composites with 30 vol.% of secondary phase, assuming uniform distribution of ZrB_2 phase with an average aspect ratio of 2.0. Table 2 shows that the toughness enhancement in the composites with more than 2 mol% yttria is much higher than 15%. This indicates that transformation toughening contributes significantly to the overall toughness. For these composites the tetragonal phase is fully retained after cooling from the hot pressing temperature. This is not the case in the TM2B composite where a large amount of monoclinic zirconia was detected.

Tensile residual stresses are developed in the ZrO_2 matrix during cooling from the sintering temperature due to the lower coefficient of thermal expansion (CTE) of ZrB_2 ($\alpha_{298-1773\ K} = 7.4 \times 10^{-6}\ K^{-1}$) [5] when compared to

Y-TZP ($\alpha_{300-2000\ K} = 10.0 \times 10^{-6}\ K^{-1}$) [2]. Taya's model [13] is used to evaluate residual stress level in the zirconia matrix. The estimated tensile residual stress in zirconia is 261 MPa. In the residual stress calculation, the E-modulus of ZrO_2 and ZrB_2 is taken as 215 GPa and 500 GPa respectively. Looking at the data presented in Fig. 2, it is clear that the thermal residual stress has a significant influence on the tetragonal zirconia transformability and hence the toughness of the investigated composites. This is quite reasonable from the fact that the tensile stress reduces the critical transformation stress and thereby promotes the stress induced tetragonal zirconia phase transformation at a much lower crack tip stress [2,3]. However, the tensile residual stress in the TM2B composite makes the tetragonal phase extremely transformable leading to transformation during cooling from the sintering temperature and to a lower toughness compared with the monolith (see Table 2). Thus, the above discussion clearly indicates that the zirconia matrix should be tuned taking into account the additional influence of residual stress in the composites.

Looking at Fig. 2, it is clear that the TZP–ZrB_2 composites could be optimally toughened by controlling the overall yttria content in the zirconia matrix. In the compositional window of 2–3 mol% yttria, a maximum in the t-ZrO_2 transformability and the toughness is measured for the 2.5 mol% Y_2O_3 composite. The importance of the yttria distribution as one of the key factors determining the transformation toughness of the Y-TZP monoliths is reported elsewhere [14]. A narrow uniform yttria distribution is obtained in sintered ceramics obtained from coprecipitated powders, whereas a much broader yttria distribution is achieved in Y-TZP materials based on yttria-coated powders and in the TM grade powder mixtures [14]. Comparing the differences in the yttria distribution with the obtained toughness of the composites, it is clear that a relatively higher toughness could be achieved with a zirconia matrix having an inhomogeneous yttria distribution. In the composites with an yttria level near 3 mol%, a significantly higher toughness is measured in the Tio3B composite where the zirconia matrix has an inhomogeneous Y-distribution compared to the T3B composite based on co-precipitated powder with a homogeneous Y-distribution. From the above, it can be stated that the overall yttria content and the yttria distribution are the important factors in the toughness optimisation of the Y-TZP based composites at a fixed ZrB_2 level.

4. Summary and conclusions

(a) Dense tetragonal ZrO_2 composites with 30 vol.% ZrB_2 could be obtained by hot pressing in vacuum at 1450°C for 1 h. An excellent combination of mechanical properties with a fracture toughness of around 9 MPa m$^{1/2}$ and a hardness of 13 GPa could be obtained. The maxi-

mum composite toughness of 10 MPa m$^{1/2}$ is obtained with the use of yttria coated powders. Both the yttria coated powders and the powder mixture based 2.5Y-TZP are found to provide an attractive combination of hardness and toughness of the composites.

(b) A simple 'powder mixing' route is found to be effective to optimise the toughness of the ZrO_2–ZrB_2 composites. While the matrix toughness increases with a decrease in overall Y-content with the highest value at 2 mol% in the present work, the toughness of the composites is found to have a maximum at 2.5 mol% and then decreases with further reduction in yttria level. This indicates that engineering of the zirconia matrix is extremely important in the development of zirconia based composites.

(c) Transformation toughening is observed as the predominant toughening mechanism in the optimised composites. The residual tensile stress in the ZrO_2 matrix of the ZrO_2–ZrB_2 composites was found to have a considerable influence on the transformability of the tetragonal ZrO_2 matrix and the transformation toughness of the composites. The experimental results clearly indicate that the residual stress should be taken into consideration in optimising the transformation toughening contribution. The overall yttria content and distribution in the ZrO_2 matrix were identified as key factors in controlling the tetragonal zirconia transformability and the concomitant transformation toughness. All these factors should therefore be considered as the important design parameters in the development of Y-TZP based transformation toughened materials.

(d) Crack deflection by the ZrB_2 phase was identified as an active and additional toughening mechanism.

References

[1] R.C. Garvie, R.H. Hannink, R.T. Pascoe, Nature 258 (1975) 703.
[2] R.H.J. Hannink, P.M. Kelly, B.C. Muddle, J. Am. Ceram. Soc. 83 (2000) 461.
[3] M. Rühle, A.G. Evans, Prog. Mat. Sci. 33 (1989) 85.
[4] J. Vleugels, O. Van Der Biest, J. Am. Ceram. Soc. 82 (1999) 2717.
[5] R.A. Cutler, Engineering properties of borides, in: Engineered Materials Handbook, Ceramics and Glasses, Vol. 4, ASM International, The Materials Information Society, USA, 1991, p. 787.
[6] R. Telle, Boride and carbide ceramics, in: R.W. Cahn, P. Haasen, E.J. Kramer (Eds.), Materials Science and Technology, Vol. 11, Structure and Properties of Ceramics, VCH, Weinheim, Germany, 1994, p. 175.
[7] S. Postrach, J. Pötschke, J. Eur. Ceram. Soc. 20 (2000) 1459.
[8] G. Van De Goor, P. Sägesser, K. Berroth, Solid State Ionics 101–103 (1997) 1163.
[9] G.R. Anstis, P. Chantikul, B.R. Lawn, D.B. Marshall, J. Am. Ceram. Soc. 64 (1981) 533.
[10] H. Toraya, M. Yoshimura, S. Somiya, J. Am. Ceram. Soc. 67 (1984) C119.
[11] J.W. Hutchinson, Acta Metall. 35 (1987) 1605.
[12] K.T. Faber, A.G. Evans, Acta Mater. 31 (1983) 565.
[13] M. Taya, S. Hayashi, A.S. Kobayashi, H.S. Yoon, J. Am. Ceram. Soc. 73 (1990) 1382.
[14] B. Basu, J. Vleugels, O. Van Der Biest, J. Eur. Ceram. Soc. (submitted).