

Microstructure and Properties of Spark Plasma-Sintered ZrO₂–ZrB₂ Nanoceramic Composites

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In a recent work,¹ we have reported the optimization of the spark plasma sintering (SPS) parameters to obtain dense nanostructured 3Y-TZP ceramics. Following this, the present work attempts to answer some specific issues: (a) whether ZrO₂-based composites with ZrB₂ reinforcements can be densified under the optimal SPS conditions for TZP matrix densification (b) whether improved hardness can be obtained in the composites, when 30 vol% ZrB₂ is incorporated and (c) whether the toughness can be tailored by varying the ZrO₂-matrix stabilization as well as retaining finer ZrO₂ grains. In the present contribution, the SPS experiments are carried out at 1200°C for 5 min under vacuum at a heating rate of 600 K/min. The SPS processing route enables retaining of the finer t-ZrO₂ grains (100-300 nm) and the ZrO_2 - ZrB_2 composite developed exhibits optimum hardness up to 14 GPa. Careful analysis of the indentation data provides a range of toughness values in the composites (up to 11 MPa \cdot m^{1/2}), based on Y₂O₃ stabilization in the ZrO₂ matrix. The influence of varying yttria content, t-ZrO₂ transformability, and microstructure on the properties obtained is discussed. In addition to active contribution from the transformation-toughening mechanism, crack deflection by hard second phase brings about appreciable increment in the toughness of the nanocomposites.

I. Introduction

A MONG the important structural ceramics, stabilized zirconia ceramics, in particular yttria-stabilized tetragonal zirconia ceramics (Y-TZP), are widely investigated, because of their excellent combination of fracture toughness and strength. Since the pioneering work of Garvie *et al.*, research on Zirconia ceramics has been triggered rapidly during the last three decades.^{1–8} The high toughness of the tetragonal Zirconia monoliths originates from the stress-induced transformation of the tetragonal (*t*) phase to the monoclinic (*m*) phase in the stress field around the propagating cracks, a concept widely known as "Transformation toughening."^{4,5} Various dopants like yttria, ceria, magnesia, calcia, etc., play a major role in the stabilization of the high-temperature tetragonal phase in the sintered microstructure.^{2,7,8}

In spite of having better fracture toughness, the moderate hardness ($\approx 10-12$ GPa) of the TZP monolith, in comparison with other structural ceramics (Si₃N₄ or SiAlON ~ 16–22 GPa; Al₂O₃ ~ upto 19 GPa), limits their use in several structural applications.^{9–11} Various attempts^{11–12} have been made to exploit

the toughness of tetragonal ZrO_2 and to improve hardness by the composite approach, in which hard reinforcements are incorporated into the ZrO_2 matrix. Among various hard phases, a transition boride like ZrB_2 is used in the present work, because of its excellent hardness and wear properties. In view of its importance as a structural material, toughness tailoring and enhancement of the hardness are considered as important issues in developing ZrO_2 -based composites.

ZrB₂, a potential high-temperature material, is characterized by a high meting point, high hardness, and resistance to molten metals, and good electrical and thermal properties.^{13–15} Despite having such advantages, the difficulty in densification of boride ceramics arises from a high melting point, highly directional covalent bonds, and a low self-diffusion coefficient. Basu *et al.*¹¹ developed zirconia-toughened 30 vol% ZrB₂ composites (~95– 97% dense) by hot pressing in vacuum at 1450°C for 1 h. Optimum combination of mechanical properties, i.e., fracture toughness of ~9 MPa · m^{1/2} and a hardness of ~13 GPa, was obtained with the optimized hot-pressed ZrO₂–ZrB₂ composite. While the addition of ZrB₂ can potentially improve the hardness of the composites, achieving full density in ZrO₂–ZrB₂ composites requires adoption of a high processing temperature of ~1400°–1500°C in hot pressing^{T1} or Sinter-HIPing,¹⁶ and the total processing time in either route is usually 3–4 h or longer.

To this end, spark plasma sintering (SPS) has the potential to achieve maximum densification at a lower temperature in a shorter time. In our recent research, we have been able to demonstrate that fully dense nanostructured Y-TZP monoliths can be obtained after SPS processing at 1200°C for 5 min.¹ Following this, the present work is taken up to incorporate 30 vol% ZrB₂ particulate Y-TZP matrix in order to develop a hard and tough TZP nanoceramic composite using the SPS route. This contribution also analyzes the microstructure-mechanical property relationship of the newly developed materials.

II. Experimental Procedures

(1) Starting Powders

In the present investigation, commercially available co-precipitated nanosized-zirconia (average primary particle size 27 nm) starting powders (Tosoh grade: 3 mol% Y-ZrO₂, TZ-3Y) were mixed with varying amounts of yttria-free monoclinic powders (Tosoh grade: 0 mol% Y-ZrO₂, TZ-0Y) to obtain "mixed grades" having an overall yttria content of 2, 2.25, and 2.5 mol%, respectively. Additionally, co-precipitated 2 mol% Y-ZrO₂ powders (Tosoh TZ-2Y grade, Tosoh Corporation, Minato-Ku, Tokyo, Japan) were also used in composite production. Details of the starting powder nomenclature are given in Table I. ZrB₂ starting powder is synthesized in the laboratory by a Selfpropagating High-temperature Synthesis process (SHS). In the SHS process, commercial ZrO₂ powders (99% purity, particle

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 Table I.
 Nomenclature Assigned for the Nanoceramic Composites Developed

Sample designation	Mol% yttria in ZrO ₂ matrix	Comments
TM2B	2 mol% yttria	Mixed grade
TM2.25B	2.25 mol% yttria	Mixed grade
TM2.5B	2.5 mol% yttria	Mixed grade
T3B	3 mol% yttria	Co-precipitated grade
T2B	2 mol% yttria	Co-precipitated grade

B stands for ZrB₂

size $<5 \,\mu\text{m}$), boron (99% purity, particle size $<40 \,\mu\text{m}$), and Mg (99% purity, particle size $<100 \ \mu m$) were taken in a stoichiometric amount and mixed thoroughly in a planetary ball mill (PM400-Retsch, Haan, Germany). The mixture was ignited from the top by an electric arc in argon atmosphere and the velocity of the combustion wave has been calculated to be as high as 25 cm/s. The reaction was carried out in a closed chamber, flushed, and filled with IOLAR-1 argon. After the completion of the SHS reaction, the reacted product consisted of ZrB₂, MgO, and unreacted Mg. The reaction by-product, i.e., MgO, was removed by dissolving in dilute HCl and washing with distilled water, and subsequently metallic Mg was leached out. No further milling was required to yield fine ZrB₂ powders. The as-synthesized ZrB₂ powders were observed to be spherical, with a uniform size distribution (average size $\sim 0.3-0.6 \ \mu m$). X-Ray diffractometer (XRD) analysis (not shown) of the powders obtained showed the predominant presence of ZrB₂. More details of the synthesizing route of ZrB₂ powders and sintering of ultra fine ZrB₂ powders can be found elsewhere.¹⁷ The "mixed-grade" yttria-doped zirconia powders as well as TZ-3Y and TZ-2Y powders are further mixed with ZrB₂ powder in the required proportion (70:30 volume ratio) on a planetary mill using WC balls on WC vials in acetone milling media. The milling was carried out for 24 h and the ratio of milling balls to powder was 4:1.

(2) SPS Processing

Appropriate amounts of dried premixed powders were placed in a graphite die having 10 mm internal diameter, and proper dressing with a graphite sheet was performed inside the die to avoid contamination. Lower and upper graphite punches were inserted into the central hole of the graphite die. This whole die assembly was transferred carefully into the SPS chamber (SPS, Eltech Co., Ulsan, Korea) and placed in between the graphite electrodes. These electrodes transfer pressure and current to the die assembly. A vacuum of 70 mtorr and a pressure of 40 MPa was maintained throughout the experiment. A DC current of 1-1.5 kA and a DC voltage of 5-10 V was applied during the SPS experiments. The pulse frequency during spark sintering varies around 30–40 KHz. The sintering of ZrO₂–ZrB₂ nanocomposite was carried out at 1200°C at a heating rate of 600 K/min and a holding time of 5 min. The selection of the processing parameter was based on our earlier experience in obtaining fully dense Y-TZP nanoceramics in the SPS route.¹ At the end of the experiment, the current flow was stopped and the pressure was released gradually. The temperature during the entire SPS processing was monitored by focusing an optical pyrometer on the graphite die. The graphite die used was of high-quality commercial graphite, and a temperature calibration revealed that the temperature difference between the graphite die and the powder sample was limited to a maximum of 100°C in the temperature range of 1200°–1300°C. The final thickness of the spark plasma-sintered composite was around 2–3 mm. The removal of the graphite sheet around the sample was ensured before further characterization.

(3) Characterization

The density of all the SPS-processed materials was measured according to the Archimedes principle in distilled water. All the samples were smoothly polished using a diamond paste. The phase identification of starting powders as well as polished and fractured samples was performed using an XRD (Isodebyeflex 2002 and 1001, Rich Seifert & Co., Ahrensburg, Germany). XRD data were collected using a diffractometer (Intel CPS-120, Santa Clara, CA), equipped with a copper-rotating anode. The XRD patterns were collected at a scan rate of 0.05°/min with a fixed counting time of 3 s. The volume fraction of the m-ZrO₂ $(V_{\rm m})$ was calculated by measuring intensities of (111) and (111) reflections of the monoclinic phase as well as the (111) peak of the tetragonal phase and following the formula of Toraya et al.¹⁸ In order to estimate quantitatively the ability of t-ZrO₂ to transform to m-ZrO₂ in the crack tip stress field, the transformability, defined as the difference in the *m*-ZrO2 phase content (%) calculated from the XRD patterns obtained from fractured and polished surfaces, is computed. Further, the microstructural characterization of all polished and fracture surfaces was carried out using scanning electron microscopy (FE-SEM, JSM-6330F, Philips, Eindhoven, The Netherlands). The elastic modulus (E) was measured using the pulse-echo resonance frequency method (Tektronix TDS 200, Panametrics Model 5800). The Vickers hardness measurements were performed on smoothly polished surfaces at a load of 10 kg for a dwelling time of 15 s, using a Universal Hardness tester. The reported hardness values are the average of five indentation measurements.

As far as the toughness measurement is concerned, it should be noted that the toughness of brittle materials is dependent on the test techniques, $^{19-25}$ which are widely classified into long crack and short crack methods. Long crack methods include the single edge-notched beam (SENB) and single edge V-notched beam (SEVNB) techniques.²⁰ Short crack techniques involve measurement of the crack lengths (radial/median) around hardness indentations, from which the toughness data can be approximated using various reported models.¹⁹⁻²⁵ Note that the absolute toughness values of brittle materials cannot be measured by the indentation technique, for which one has to adopt the long crack fracture toughness measurement techniques, e.g., SENV, SEPVB, Cheveron notch beam (CNB), etc. However, in order to compare the toughness property of the newly developed composites, the indentation technique has been used in the present work. Additionally, it is now widely recognized that careful use can yield reproducible results for indentation toughness measurements.

In the present work, the fracture toughness of the SPSed composites was calculated by measuring the crack lengths originating from the corners of the Vickers indents. At least five indentations were taken on smoothly polished surfaces to measure hardness and toughness. It should be mentioned here that the indentation method is now routinely used for convenience to compute the fracture toughness of small and relatively brittle specimens, which are otherwise hard to machine into standard test samples (for example, SENB, SEVNB, etc.). A critical summary of the toughness values of various Y-TZP monoliths, presented in a recent review article,⁸ also indicates that the indentation method is, by far, the most widely used method in measuring the toughness of transformation-toughened ceramics.

III. Results and Discussion

(1) Densification

SPS processing of the ZrO_2-ZrB_2 composites was carried out at 1200°C for a holding period of 5 min in vacuum at a heating rate of 600 K/min, and the density data are provided in Table II. The developed composites exhibit maximum densification (~95%–99% ρ_{th}) under the selected SPS conditions. The theoretical density is calculated following the rule of mixture, assuming a theoretical density of 6.10 and 6.09 g/cm³ for ZrO₂ and ZrB₂, respectively. The mixed-grade 2 mol% yttria-stabilized grade (TM2B) exhibited a slightly lower densification of around 95%

Table II. Overall Properties, i.e., Relative Density (RD), Elastic Modulus (*E*), Hardness (H_{v10}), and Fracture Toughness (K_{Ic}), of the ZrO₂–ZrB₂ nanocomposites, SPSed at 1200°C

Material designation	Relative Density $(\% \rho_{th})$	Elastic Modulus (<i>E</i> , GPa)	Vickers Hardness (<i>H</i> v ₁₀ , GPa)	
TM2B	95.4	250	12.3 ± 0.1	
TM2.25B	97.8	260	13.1 ± 0.2	
TM2.5B	98.4	257	13.7 ± 0.1	
T3B	98.4	266	13.9 ± 0.3	
T2B	98.5	261	13.9 ± 0.2	

The standard deviation in the hardness data measured is also shown.

 ρ_{th} when compared with the co-precipitated powder-based composites. The sintering of nanocrystalline 3Y-ZrO₂ powders to full density via the SPS route was effectively carried out at 1200° C for a holding period of 5 min at a heating rate of 600 K/ min in vacuum.¹ Recent work in our research group indicated that the full density in a similar composite could be obtained after sinter-HIP at $1400^\circ C$ for 1 h under a 110 MPa argon pressure.¹⁶ Also, Basu *et al.*¹¹ reported ~97% ρ_{th} in ZrO₂–ZrB₂ (70/ 30) composites after hot pressing (HP) at 1450°C for 1 h in vacuum. Therefore, it can be stated that the full density in ZrO₂- ZrB_2 (70/30) composites can be obtained by the SPS route at 200°–250°C lower temperatures with reduced overall processing time of 30 min, which is much less than that by the HP or HIP route. The reduction of the total processing time is a useful advantage of the SPS process. The fact that the ZrO₂ composite containing 30 vol% of difficult-to-sinter powder particulates, i.e., ZrB₂, is sintered to near-theoretical density under optimal SPS conditions for ZrO₂ matrix densification further reconfirms such an advantage.

From the SPS point of view, the passage of current depends on the electrical conductivity property of the powder compact. In case of a powder compact containing only ZrO₂ powders, the major part of current passes through the graphite die, with a smaller fraction passing through insulating ZrO₂ particles. In a recent work of Vanderbiest and co-workers, finite-element (FE) calculations²⁶ of the temperature field during the field-assisted sintering technique (FAST) have revealed that the temperature distribution in case of ZrO₂ is more homogeneous, while that of conducting ceramic particle compacts like TiN is non-homogeneous in the presence of more thermal gradients. In the present case, because of the presence of a larger amount of conducting ZrB₂ phase, a comparatively larger fraction of the total current will pass through the powder compact and therefore, spark discharges in the void spaces become more frequent in the composite powder compact. We believe that this will enhance the mass transport, leading to increased neck growth and hence, enhanced densification is obtained for the composites at a much lower temperature by the SPS route. It can be mentioned here that the driving force in the case of conductive ceramics (ZrB_2) is joules heating effect.²⁷ As has been well established, the oxide layers on the non-oxide particle surfaces, like borides, are formed as a result of selective oxidation of base transition metal. However, the surface cleaning of ZrB₂ particles, during plasma sintering might possibly have occurred and this could enhance the densification of the composite material at a much lower temperature. Moreover, due to the use of finer starting powders of ZrO_2 (average particle size ~27 nm) and ZrB_2 (average particle size $\sim 0.3-0.6 \,\mu\text{m}$), the increase in sintering driving force, i.e., the decrease in surface-free energy, triggers densification, ensuring grain boundary diffusion as the dominant mass transport path.

From the above discussion, the enhancement of the driving force for sintering because of the electric field-assisted faster heating, pressure application, and surface activation, combined with grain boundary diffusion as the dominant mass transport mechanism, enable rapid densification of the developed $ZrO_{2^{-}}ZrB_{2}$ nanocomposite in the SPS process.

(2) Microstructure

XRD phase analyses of the starting powders and polished surfaces of the SPS-processed materials are shown in Fig. 1. The XRD spectra obtained clearly indicate the predominant phase for the ZrO_2 matrix as t- ZrO_2 . However, there is also an indication for the presence of m- ZrO_2 in the TM2B composite. Otherwise, the addition of ZrB_2 is found to have no observable influence on t- ZrO_2 retention. Note the apparently lower relative density of the TM2B composites as compared with other composites (see Table II), which is due to the fact that the presence of m- ZrO_2 is not taken into account while calculating the theoretical density. Therefore, the amount of porosity would be, in fact, less in the TM2B composite as otherwise could be expected from the density data of Table II.

Selected SEM fractographs of both mixed and co-precipitated ZrO₂ powder-based composites are shown in Fig. 2. Based on SEM images, the microstructure is characterized by the presence of coarser tabular/elongated ZrB₂ particles ($\sim 2-3 \mu m$) and equiaxed nano-ZrO₂ particles ($\sim 100-300 nm$). A schematic illustration of the phase assemblage in the microstructure is presented in Fig. 2(d). A comparison of Figs. 2(a)–(c) indicates that the ZrO₂ grain sizes in T3B composite are relatively finer (100– 150 nm) than T2B and TM2.25B composites. The average ZrO₂ grain size in the T2B composite appears to be around 200–300 nm, while the presence of few coarser ZrO₂ grains of sizes 300



Fig. 1. XRD spectra obtained with starting powder (a) and SPS-synthesized nanocomposites, sintered at 1200° C at a heating rate of 600 K/min and holding period of 5 min in vacuum (b).



Fig. 2. SEM fractographs of spark plasma-sintered ZrO_2 – ZrB_2 nanoceramic composites, sintered at 1200°C for a holding period of 5 min in vacuum: T3B grade (a), T2B grade (b), and TM2B grade (c). The presence of finer ZrO_2 grains (100–300 nm) and coarser ZrB_2 particulates (2–3 μ m) can be distinguished. A model ceramic nanocomposite microstructure with nanosized matrix particles reinforced with microsized reinforcement particulates, as observed in the newly developed materials, is shown in (d).

nm or more can be critically noted in the TM2B composite. As far as ZrB_2 size is considered, a closer observation of Figs. 2(a)-(c) indicates that considerable grain growth occurs for boride particles from 500 to 600 nm (starting particle size) to 2-3 µm (SPSed material). Qualitatively, the grain growth appears to be more in the case of conductive particles than insulating ZrO₂ in our SPSed composites. The fractographs further reveal the transgranular fracture of ZrB_2 particles, and predominantly intergranular fracture of nano-ZrO2 grains. The ZrB2 particulates are well bonded in the nano-ZrO₂ matrix in all the composites. The fact that a finer microstructure ($ZrO_2 \sim 100-300$ nm and $ZrB_2 \sim 2-3 \mu m$) is obtained after SPS processing indicates that the spark plasma processing route is effective in retaining of a fine-grained microstructure in a dense nanocomposite. The correlation between microstructure and properties will be discussed in the subsequent sections.

(3) Mechanical Property

The mechanical property data, presented in Fig. 3, Tables II and III, provide some interesting facts regarding the mechanical behavior of the Zirconia nanoceramic composites developed. The E-modulus data, as presented in Table II, reveal that the addition of ZrB_2 increases modulus up to ~266 GPa. The measured E-modulus varies between 250 and 266 GPa. Also, the lower elastic modulus of 250 GPa, as measured with the TM2B composite, can be attributed to the presence of *m*-ZrO₂ and/or porosity than that in other composites. As far as the hardness is considered (see Table II), SPS-processed nanoceramic composites exhibit moderate hardness varying in the range of 12–14 GPa. Higher hardness is measured with the composites, synthesized using co-precipitated ZrO₂ powders (Table II).

Importantly, it should be pointed out here that no observable hardness improvement is recorded, despite incorporating 30

vol% of harder ZrB₂ particulates into a nanosized zirconia matrix. Such an observation can be explained based on similar observations made in other ceramic systems, including monolithic ZrB₂.^{28–30} In an earlier study, Green also measured a substantially lower hardness of 10–12 GPa in Al₂O₃ composites, containing more than 10 vol% ZrO₂.²⁸ Such an observation was attributed to the presence of microcracks, which were either



Fig. 3. Plot of hardness and toughness versus yttria stabilization ZrO_2 matrix for spark plasma-sintered (1200°C, 5 min) nanocomposites. Different symbols represent the mechanical property measured with various composites based on the ZrO_2 matrix processed from either co-precipitated or mixed-grade ZrO_2 powders: \blacksquare , H_{v10} of the mixed grades; \Box , H_{v10} of the co-precipitated grades; \blacktriangle , K_{Ic} of the co-precipitated grades (using the Palmqvist formulae); and \triangle , K_{Ic} of the mixed grades (using the Palmqvist formulae).

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formed because of postfabrication cooling or developed because of indentation stresses. In a recent work, Chamberlain et al.² measured a lower hardness of 14.5 GPa in a pressureless-sintered (2150°C, 9 h, helium atmosphere) monolithic ZrB₂. In contrast, a much higher hardness of 23 GPa was measured in hotpressed monolithic ZrB₂ (1900°C, 45 min, vacuum). Such a significant difference in hardness was attributed to the differences in the ZrB₂ grain sizes, which are expectedly much coarser (average size $\sim 9.1 \,\mu\text{m}$) in the pressureless-sintered material. A similar observation was also made by Lee and Speyer,³⁰ who measured a decrease in hardness from 18.3 to 16.5 GPa, as a result of an increase in the grain size from 2.2 to 3.1 µm, respectively, in case of pressureless-sintered (90% theoretical density) monolithic B₄C. From the mechanistic point of view, it is quite likely that the frequency with which the movement of dislocations is impeded will decrease with an increase in grain size and this would lower the stress required for deformation.^{29,30} Therefore, at a given indent load, more deformation zone around the indented region can be expected in coarser-grained material.

In the present case, the absence of any observable hardness increment in SPSed composites can be attributed to both the microcracking effect and the coarser particle size of ZrB₂. The microcracking effect is quite probable, because of the presence of residual stress. In the ZrO₂–ZrB₂ materials developed, the thermal residual stress is developed due to two factors: the first one is the anisotropy in the coefficient of thermal expansion (CTE) of the tetragonal zirconia matrix ($\alpha_c = 11.4 \times 10^{-6} \,^{\circ}\text{C}^{-1}$)³¹ as well as that of ZrB₂ particulates ($\alpha_c = 6.7 \times 10^{-6} \,^{\circ}\text{C}^{-1}$)³¹ as well as that of ZrB₂ particulates ($\alpha_c = 6.7 \times 10^{-6} \,^{\circ}\text{C}^{-1}$)³¹ as the tensile residual stress in ZrO₂, the microcracking potentially takes place either during post-fabrication cooling or in the indented region. Besides possible contribution from microcracking, the coarser ZrB₂ particles can potentially, like in other ceramic systems, ^{28–30} contribute to low-ering the hardness of ZrO₂–ZrB₂ nanoceramic composites.

In order to compute the toughness data, SEM analysis of the Vickers indents (taken at 10 kg) was carried out and the crack lengths around the indentations were measured from the SEM images. Typical SEM images of the indented composites material surfaces, as shown in Fig. 4, clearly indicate the presence of radial cracks, which predominantly emanate from the indent corners. All the relevant indentation data, i.e., the indent diagonal length (2a) and total crack length (2c), used in hardness and toughness measurements are provided in Table III. The indentation data reveal that l/a varies in the range of 0.3-0.9.

In estimating the toughness values, we have considered various indentation fracture mechanics models, which can be broadly classified into two categories:

(a) The toughness can be measured using Anstis's model¹⁹ for brittle materials, exhibiting radial-median cracks (l/a > 2.5):

$$K_{Ic} = \eta (E/H)^{1/2} P/c^{3/2} \tag{1}$$

where E is the elastic modulus, H the Vickers's hardness, P the indent load, and c the half crack length:

(b) The toughness of brittle materials, exhibiting Palmqvist type cracks (0.25 < l/a < 2.5) can be computed by a different equation²⁵:

$$K_{\rm Ic} = \eta (E/H)^{2/5} P/(al^{1/2})$$
⁽²⁾

where 2a is the average indent diagonal length, 2c is the crack length, and l = c-a.

In both the above equations, the dimensionless quantity, η , is a constant for a given indenter geometry, provided the volume is conserved within the "plastic zone" (adjacent to indentation). In case of transformation-toughened materials, the crack driving force-induced *t*-ZrO₂ transformation additionally modifies the



Fig. 4. SEM topography images of the Vickers indents and indentation-induced radial crack pattern in the SPS-processed zirconia nanoceramic composites: T3B, T2B, TM2B.

value of the dimensionless quantity (η). It is worthwhile to note that Kaliszewski *et al.*²¹ have critically analyzed the transformation effect around the indented zone and reported that an appropriate value of $\eta = 0.019$ (instead of $\eta = 0.016$ as widely used for non-transforming ceramics) can be used when the transformation zone size as well as the volume fraction of *t*-ZrO₂ (transformed within the transformation zone) are both experimentally obtained for ZrO₂ materials. As such measure-

Table III. Indentation Data, i.e., Average Indent Diagonal Length (2*a*) and Total Crack Length (2*c*), as well as the Fracture Toughness Values for the SPSed ZrO₂–ZrB₂ Nanocomposites

Material designation	Indent diagonal (2 <i>a</i>) (µm)	Crack length (2c) (µm)	l/a	Indentation toughness $(MPa \cdot m^{1/2})$
TM2B TM2.25B TN2.5B T3B T2B	122 118 115 115 115 114	158 185 197 210 166	0.3 0.6 0.7 0.9 0.4	$11.4 \pm 1.0 \\ 8.7 \pm 0.9 \\ 7.8 \pm 0.3 \\ 6.9 \pm 0.7 \\ 10.0 \pm 1.2$

The crack length parameter (*l*) is defined as l = c-a. The standard deviation in the measured toughness data is also shown.

ments have not been performed, Anstis's formulation has not been used in the present work. It should now be realized that the choice of dimensionless constant (η) from various models can considerably influence the value of K_{Ic} , calculated using Eq. (1) or (2). In an earlier work, Niihara et al.²² experimentally obtained the value of η to be 0.0089 and 0.0122 for l/a ratios varying in the range of 0.25–2.5 and 1–2.5, respectively. In the present study, we have chosen Eq. (2) with $\eta = 0.0089$, because the l/a ratio lies in the range of 0.3–0.9 (see Table III). Besides the above-mentioned reason, the use of Anstits's formula would be inappropriate as the l/a ratio (measured in our work) is much less than 2.5, a value characterizing the radial-median crack pattern. A similar analysis in using the toughness equations has been performed in a recent work, reporting the mechanical properties of the SPS-processed zirconia-containing composites.

The fracture toughness data are presented in Table III and plotted in Fig. 3. The toughness data can be interpreted in terms of the difference in ZrO₂ matrix stabilization. For the co-precipitated powder-based ZrO2 matrix, a decrease in overall yttria content from 3 to 2 mol% significantly increases the fracture toughness from 6.9 (T3B composite) to 10.0 MPa \cdot m $^{1/2}$ (T2B composite). It can be noted that nanocrystalline T3 monoliths, SPSed at 1200°C for 5 min, is reported to have a fracture toughness of ~4.5 MPa \cdot m^{1/2}.¹ This indicates that ZrB₂ addition increases the fracture toughness of the composites. For the mixedgrade composites (TM based), the decrease in overall Y content from 3 to 2 mol% increases the toughness from 6.9 MPa \cdot m^{1/2} (T3B composite) to 11.4 MPa \cdot m^{1/2} (TM2B composite). The toughness is also observed to increase systematically as the Y content is lowered from 3 to 2.5 mol% and finally to 2 mol%. Because of a greater increase in toughness by decreasing the Y content from 2.5 to 2 mol% rather than by decreasing in Y content from 3 to 2.5 mol%, an additional experiment was conducted to develop a composite with a ZrO₂ matrix having 2.25 mol% Y stabilization. The mechanical property measurement on the TM2.25B composite indicated the moderate toughness improvement as revealed by K_{Ic} data: 8.7 MPa \cdot m^{1/2} for the TM2.25B grade as compared with 7.8 MPa \cdot m^{1/2} for the TM2.5B grade. Broadly, the toughness data indicate that the toughness of the ZrO₂–ZrB₂ composites can be tailored by carefully optimizing the Y stabilization of the ZrO₂ matrix, when all are SPSed under identical sintering conditions. However, a higher toughness is measured with the mixed-grade TM2B composite, when compared with the co-precipitated powder-based T2B composite. This certainly indicates that although the hardness of TM2B (12.3 GPa) is inferior compared with that of T2B (13.9 GPa), the toughness property is better in the mixed-grade TM2B composite than T2B material.

(4) Toughening Mechanisms

XRD results, as mentioned in Section III(2), indicated that t-ZrO₂ is predominantly retained in all the SPSed composites (polished surfaces). Only in the TM2B composite, a trace amount of *m*-ZrO₂ content was also recorded. Furthermore,

the m-ZrO₂ content was also measured on the fracture surfaces in order to evaluate t-ZrO₂ transformation during fracture crack propagation. The transformability, the difference between the fracture and the polished surface m-ZrO₂ content (%), varies around 50%-60% for all the composites (see Fig. 5). A critical comparison of the toughness data (Table III) and the transformability data (Fig. 5) indicated that the toughness shows an almost linear correlation with transformability. In particular, the high-toughness TM2B composite also exhibits the highest transformability. However, the observation that both TM2.5B and TM2.25B composites experience a slightly higher transformability, but lower toughness, than the T2B composite should be attributed to the use of two different ZrO₂ starting powders used in the composite production. In the TM-grade composites, the mixed powders, i.e., a mixture of 0 mol% yttria and 3 mol% yttria-containing powders, are used, while T2B is processed from co-precipitated ZrO₂ starting powders. Such a difference in starting powders is reported to result in a difference in the toughness of sintered Y-TZP monoliths (all hot pressed under identical conditions), as reported elsewhere.³ Nevertheless, the toughness increase in both the TM-grade composites as well as co-precipitated powder-based composites (T2B and T3B) commensurate well with the increase in measured t-ZrO₂ transformability. This is expected as the toughness of the transformation toughened zirconia is directly proportional to the volume fraction of transformable $t-ZrO_2$.^{3,5,6} Also, a large amount of monoclinic ZrO₂, relative to that on the polished surface, with a maximum of 60% in the case of the TM2B composite, has been measured on fracture surfaces (Fig. 5). Such an observation should be attributed to the fact that t-ZrO₂ is largely transformable in the SPSed composites and hence transformation toughening is considered as a toughening mechanism. The increased transformability, an indication of a higher transformable t-ZrO₂ content, clearly implicates a higher transformation-toughening contribution in the SPSed ZrO₂ nanocomposites.

Regarding the microstructure–toughness relationship, the influence of grain size on toughness needs to be considered. It is noted in our work that finer t-ZrO₂ grain sizes (100–300 nm) are retained and such finer grains are also able to transform in the crack tip stress field, leading to a higher transformation toughness in the nanocomposites. To this end, it can be recalled that such a finer zirconia microstructure (in case of Y-TZP monoliths) should be extremely stable and should not transform at



Fig. 5. Percentage transformability of the Z_rO_2 matrix against the mol% of yttria content in that matrix at sintering temperatures of 1200°C. The *t*-ZrO₂ transformability is defined as: [% *m*-ZrO₂ on the fractured surface-% *m*-ZrO₂ on the polished surface]. The transformability data of various composite grades processed from the use of ZrO₂ powders are indicated by different symbols: ∇ , co-precipitated grades; and \blacktriangle , mixed grades.





Fig. 6. Crack deflection by the hard second-phase ZrB_2 particles (a) and crack wake debonding of the coarser ZrB_2 particles at the interface (b) in the T2B nanocomposite, SPSed at 1200°C for 5 min (heating rate: 600 K/min).

the crack tip, according to the earlier literature reports.^{3–6} Therefore, the attainment of higher fracture toughness (up to 10 MPa \cdot m^{1/2}) with the newly developed composites implicates that other factors, besides grain size, should also be considered.

As far as the transformation toughening is concerned, another important factor, apart from the yttria content and grain size, is the residual stress. Because of the CTE mismatch, as mentioned earlier, ZrO_2 grains are subjected to residual tension in a sintered microstructure. Therefore, the critical stress needed to induce the transformation of ZrO_2 grains in the crack tip would be reduced accordingly, as also predicted from the established literature.^{5,6,34} This increases the driving force for stress-induced t-ZrO₂ phase transformation. This should also contribute to the enhanced transformability of t-ZrO₂.

Coming to the other factors influencing toughness, the contribution of additional toughening mechanisms besides transformation toughening needs to be considered. The crack pathmicrostructure interaction in the SPSed nanocomposites is illustrated in Fig. 6. Figure 6(a) clearly reveals the increase in crack path tortuosity (more like a sinusoidal crack path) because of crack deflection by hard and coarser ZrB_2 particles. A closer observation of Fig. 6(b) also reveals the crack wake debonding of the ZrB_2 , as evident from the crack propagation around the ZrO_2/ZrB_2 interface. From the above observations, it can be predicted that in addition to deflection by boride particles, the crack tip stress field energy is utilized in debonding the ZrB_2 particles and thus provides less driving force for further crack propagation.

IV. Conclusions

(a) Near theoretical density of the yttria-stabilized tetragonal zirconia nanocomposites, reinforced with 30 vol% of ZrB_2 by the SPS route, is obtained at 1200°C with a holding time of 5 min and a heating rate of 600 K/min under vacuum. The sintering temperature, which is 200°–250°C less, as well as the total processing time (~20–25 min) are considerably less in comparison with established densification processes like hot pressing or sinter-HIPing.

(b) The composite materials developed exhibit a finer microstructure, with ZrB_2 exhibiting an average grain size of 2–3 µm and ZrO_2 in the range of 100–300 nm. Also, XRD results indicate that *t*-ZrO₂ is predominantly retained in all the SPSed materials. No noticeable hardness improvement, despite incorporating 30 vol% ZrB_2 particulates, is recorded in spark plasma-sintered ZrO_2 composites, and the hardness of the developed composites remains moderate, varying in the range of 12–14 GPa.

(c) Careful use of indentation data provides an estimate of toughness properties, and the computed toughness values of SPSed ZrO₂-ZrB₂ composites vary in the range of 6-11 MPa \cdot m^{1/2}, depending on the Y₂O₃ stabilization level of the ZrO₂ matrix. An important observation has been that the toughness can be tailored by varying the Y₂O₃ content, followed by mixing 3Y-ZrO₂ with undoped ZrO₂ in the starting powder mixture. Considerable amount of t-ZrO₂ is observed to transform to m-ZrO₂ on the fracture surface and the t-ZrO₂ transformability broadly increases with reduction in overall yttria stabilizer content of ZrO2 matrix. Such experimental observations suggest that the transformation toughening is an active toughening mechanism in the SPSed ZrO₂ nanocomposite. A critical observation is that a high transformation-toughening contribution is obtained with a ZrO₂ matrix having finer tetragonal grains (100-300 nm). The experimental observations also suggest that both crack deflection by ZrB2 particulates and crack wake debonding at ZrO2/ZrB2 interface contribute toward attaining the toughness obtained.

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