

Effects of heteroflocculation of powders on mechanical properties of zirconia alumina composites

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Zirconia-toughened alumina (ZTA) composites colloidally processed from dense aqueous suspensions (>50 vol % solids) had ZrO₂ content varying from 5 to 30 vol %. Tetragonal zirconia (TZ) was used in the unstabilized, transformable form (0Y-TZ), in the partially transformable form, partially stabilized with 2 mol % yttria (2Y-TZ), and in the non-transformable form stabilized with 3 mol % yttria (3Y-TZ). After sintering in air to ~99% theoretical density, the elastic properties, flexure strength and fracture toughness were examined at room temperature. Dynamic moduli of elasticity of fully deagglomerated compositions did not show the effects of microcrack formation during sintering, even for materials with unstabilized zirconia. In all compositions made from submicron powders and with low content of dispersed phase (less than 10 to 20 vol %), the strength increased with increasing ZrO₂ content to a maximum of ~1 GPa, irrespective of the degree of stabilization of t-ZrO₂. With increasing content of the dispersed phase (>20 vol %), heteroflocculation of powder mixtures during wet-processing led to the formation of ZrO₂ grain clusters of increasing size. Residual tensile stresses built within cluster/matrix interfaces upon cooling not only facilitated the t→m ZrO₂ phase transformation in final composites with transformable t-ZrO₂, but also led to lateral microcracking of ZrO₂/Al₂O₃ interfaces. This enhanced fracture toughness, but at larger ZrO₂ contents the flexure strength always decreased due to intensive microcracking, both radial and lateral. The important microstructural aspects of strengthening and toughening mechanisms in ZTA composites are related in discussion to the effects of heteroflocculation of powder mixtures during wet-processing.

1. Introduction

The intimate dispersion of powders is a critical issue in the fabrication of ceramic composites from dense aqueous suspensions, and it depends primarily on their surface potentials. Recent systematic studies of the electrokinetic behaviour of ZrO₂-Al₂O₃ mixtures in aqueous suspensions [1] indicated that the points of zero charge (pzc) of these two oxides did not coincide, and that the values of their ζ -potentials differed by almost 30% at the pH for best dispersion. These results proved that the mixtures of Al₂O₃ and ZrO₂ were colloidally incompatible in aqueous suspensions, i.e. they were unstable against flocculation [2]. Moreover, it appeared that the additions of oxides stabilizing the tetragonal polymorph of ZrO₂, such as Y₂O₃, introduced their own strong flocculating effects into aqueous suspensions of zirconia-alumina mixtures [3].

Microscopic dispersion studies of the same materials [4] revealed that the intensity of heteroflocculation of ZrO₂-Al₂O₃ mixtures increased with increasing ZrO₂ content, and led to the formation of ZrO₂ clusters (groups of contiguous grains) of increasing size within the flocs (soft agglomerates) of mixed Al₂O₃ and ZrO₂ powders. Formation of these flocs and their particular structure, was shown to affect significantly the properties of dense aqueous suspensions [4, 5], consolidated [4, 6], and sintered [7, 8] zirconia-toughened alumina (ZTA) composites.

The appearance of contacts among ZrO₂ grains, i.e. their clustering in ZTA composites, is also dictated by geometrical factors, although this has not been studied extensively. The existing theoretical models related to dense packing of spheres [9, 10] indicate that their binary mixtures can have the "percolation threshold"

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for smaller particles not exceeding 16 vol% [11]. Microscopic observations of various ZTA microstructures indicate that this geometrical threshold for packing of non-contacting zirconia grains will be situated at its volume contents between 10 and 15%. These observations enable us to note that at larger contents of ZrO_2 dispersed phase (10 to 15 vol% and more), its clustering in ZTA microstructures may be regarded as unavoidable for both electrochemical and geometrical reasons. The size of these clusters will always increase with increasing ZrO_2 content, and following the conclusions of Zok *et al.* [12], at volume fractions exceeding 20 vol% clusters of the dispersed phase might be acting as "touching inclusions".

The presence of ZrO_2 grain clusters in real ZTA microstructures may have important practical consequences; in particular, for analysis of the state of internal stresses due to differences of thermal expansion of the components. The average coefficient of thermal expansion of polycrystalline alumina is known [13] to be $\alpha = 8.34 \times 10^{-6} K^{-1}$, while single crystals of α -alumina have $\alpha_{11} = 7.94 \times 10^{-6} K^{-1}$, and $\alpha_{33} = 9.15 \times 10^{-6} K^{-1}$. Tetragonal zirconia has the coefficient of thermal expansion along its *c*-axis $\alpha_c = 16.8 \times 10^{-6} K^{-1}$, and along the *a*-axis $\alpha_a = 6.8 \times 10^{-6} K^{-1}$ [14]. According to Schubert [14], increasing the content of a stabilizing solute brings about the decrease of this anisotropy in zirconia. For Y_2O_3 content of 4.5 mol% the expansion behaviour becomes isotropic (cubic), and the values of α are very close to the average value of $\alpha = 10.7 \times 10^{-6} K^{-1}$.

It is now well known [15, 16] that in ZrO_2 - Al_2O_3 microstructures, upon cooling from sintering temperatures, tensile stresses arise in dispersed ZrO_2 particles due to the mismatch of thermal expansion of the components, and they promote tetragonal-to-monoclinic martensitic transformation of ZrO_2 grains. Becher [17] analysed the ability of tetragonal ZrO_2 grains to undergo phase transformation depending on the content of stabilizing solute and grain size. Becher and Swain [18] pointed out recently that internal thermal stresses in ZrO_2 (CeO₂) grains increase with increasing grain size at a given content of the stabilizing solute.

It may be expected, therefore, that heteroflocculation of ZrO_2 - Al_2O_3 mixed powders will accelerate t-m phase transformation due to the build-up of internal thermal stresses within ZrO_2 clusters upon cooling. However, due to the differences of thermal expansion coefficients of the components, clustering of ZrO_2 grains at higher contents of the stabilizer may also result in development of lateral microcracks within the ZrO_2 - Al_2O_3 interfaces before nucleation of phase transformation. These lateral cracks may increase the fracture toughness in a way similar to that due to radial cracks resulting from transformation [19], and theoretical models for this type of toughening are well established [20].

Rühle *et al.* [21] mentioned the occurrence of lateral microcracks within the components' interfaces in ZTA composites but did not examine them systematically. Microcracking of this nature was theoretically

predicted as a principal toughening mechanism in SiC/TiB₂ composites [22] and cracks of very fine size, formed due to differences of thermal expansion of the components, were directly observed under the transmission electron microscope [23]. Recently similar lateral microcracks within ZrO_2 - Al_2O_3 interfaces have been directly observed under the high-resolution scanning electron microscope [19].

The purpose of the present study is to assess the effects of heteroflocculation of colloidal mixtures of alumina-zirconia powders on the mechanical properties of ZrO_2 - Al_2O_3 composites processed from highly concentrated aqueous suspensions, with particular reference to the role of ZrO_2 grain clustering in the development of thermal residual stresses and subsequent microcracking in ZTA microstructures. It will be shown that fracture toughness can be increased in zirconia-alumina materials containing non-transformable ZrO_2 due to lateral microcracking within ZrO_2 - Al_2O_3 interfaces.

2. Experimental procedure

2.1. Powders

Three grades of commercial zirconia (Tosoh USA Inc., Bridgewater, NJ, formerly Toyo Soda) were used: (a) without stabilizer (0-TZ); (b) with an amount of yttria small enough (2 mol%) to ensure the partial transformability of the tetragonal zirconia phase (2Y-TZ); and (c) with yttria content (3 mol%) allowing for non-transformability of t- ZrO_2 (3Y-TZ) in the final sintered composites. All three zirconia powders were attrition milled (model 1-S, Union Process, Akron, OH) in water for 4 h, centrifuged (model CU 5000, Damon, Neetham Hts., MA) to submicron size ($d_{50} = 0.19 \mu m$), and redispersed with HNO₃ (ACS Reagent Grade, Fisher Scientific).

Commercial alumina powder (RCHP-DBM, Malakoff Industries, Malakoff, TX), with the addition of MgO as a sintering aid was used in the as-received state only in one composition, with (3Y) zirconia. The reported median particle size of this powder was $d_{50} = 0.48 \mu m$. Particle size distribution analysis (Capa-700, Horiba Instruments, Irvine, CA) of as-received alumina indicated the presence of agglomerates of the orders of 10 μm in this powder. In all other compositions the alumina used did not contain MgO, and was centrifugally classified (fractionated) to the maximum particle size setting of 1 μm , which resulted in a final powder with $d_{100} < 1.18 \mu m$, and $d_{50} = 0.39 \mu m$.

Electrokinetic behaviour of the powders used was determined by microelectrophoresis (Mark II, Rank Brothers, Cambridge, UK) in detailed studies as described elsewhere [1, 3]. The point of zero charge (pzc) of alumina in water was found at $pH 8.3 \pm 0.2$, and that of pure zirconia at $pH 6.3 \pm 0.2$, which is in good agreement with the values reported in other published works [24]. The values of pzc's of alumina-zirconia mixtures were found to decrease towards the pzc of pure ZrO_2 with increasing ZrO_2 content, which confirmed the occurrence of heteroflocculation in this system.

2.2. Dense aqueous suspensions

All $\text{ZrO}_2\text{-Al}_2\text{O}_3$ aqueous suspensions examined in this study were prepared in distilled water, and were electrostatically stabilized with HNO_3 (ACS Reagent Grade, Fisher Scientific). Solid content of individual aqueous suspensions of zirconia powders varied from 77 wt % (3Y-TZ) to 81 wt % (0-TZ), which corresponded to 35.6 and 41.1 vol %, respectively. The pH value of best dispersion was determined by the measurements of viscosity of concentrated slurries (model LVTD, Brookfield Eng. Labs, Inc., Stoughton, MA), as a function of pH varying by small intervals in the acidic range. Aqueous suspensions of alumina powder with as-received (unclassified) grains containing MgO as a sintering aid had the solid content of 77 wt % (45.7 vol %), and they reached minimum viscosity at pH 5.0. A highly concentrated aqueous suspension of size-classified alumina powder without MgO contained 85 wt % (58.8 vol %) of solids and showed a minimum of viscosity at pH 4.05.

Individual slurries of alumina and zirconia were mixed slowly to yield the series of compositions with 5, 10, 20 and 30 vol % ZrO_2 with respect to the total solid content for each content of the stabilizing solute Y_2O_3 . The pH of the composite suspension was adjusted to the value corresponding to conditions of best electrostatic dispersion of the major component, alumina. Final composite suspensions of (3Y) zirconia and unclassified Al_2O_3 had the solid content of 44.0 vol % and all other suspensions were adjusted to contain 51 vol % solids. Each dense suspension was homogenized for 12 h in a planetary mixer (model 2TC, Turbula, Glenmills Inc., Maywood, NJ) and then subjected to ultrasonic agitation (model W-385, Heat Systems Inc., Farmingdale, NY) for 10 min at 90% of output power level (ranging from 190 to 300 W, depending on the composition), before further processing steps.

2.3. Consolidation and densification

Highly concentrated aqueous suspensions of ZTA composites with varying proportions of dispersed phase and the stabilizing oxide were consolidated by colloidal filtration into rectangular moulds (8×10 cm) placed on plaster of Paris plates. Smaller samples for density measurements were slip cast into plastic rings (4×2 cm) also placed on plaster of Paris plates. Densities of both consolidated and sintered composites were determined using the standard mercury displacement technique (mercury densitometer Fairey Tec-tramics Ltd, Filleybrooks, UK). Samples were sintered for 2 h at 1600°C in an electrical furnace in air, with a heating rate of 400°C h^{-1} . Samples with (3Y) zirconia and as-received Al_2O_3 matrix grains were sintered at 1550°C for 3 h. Final composites achieved an average of 99% of theoretical density.

2.4. Characterization of sintered ZTA composites

Samples selected for microscopic observations were polished to diamond finish, and thermally etched for

5 min at 1400°C . They were then sputtered with Au-Pd and observed under the scanning electron microscopes (models JXA-35C, Jeol 820 and Jeol 6000, Jeol, Tokyo) in SEI mode at 15 kV. Grain sizes of alumina and zirconia were determined from the SEM micrographs by the standard line intercept method [25].

The dynamic moduli of elasticity and the Poisson's ratios of sintered composites were calculated from the velocities of ultrasonic longitudinal and transverse waves (model NDE 5000, Ultrason, State College, PA) determined on test bars before fracture stress measurements [26]. The values of static Young's moduli were calculated from load-deflection curves obtained during strength determinations.

The fracture stress was evaluated in three-point bending on rectangular bars machined (Bomas Machine, Sommerville, MA) to size of $1.5 \times 2 \times 25$ mm, according to US Mil. Std. 1942 (type A) specifications. All composite samples containing (2Y) zirconia, as well as the series of composites with (3Y) zirconia made of as-received alumina powders were machined to type B size ($3 \times 4 \times 45$ mm). The three-point bending method was selected to obtain a large number of samples with well defined fracture surfaces produced due to more localized stress concentration. Since the examined materials were of very high average strength, in many instances they ruptured into a multitude of small blocks under more uniform loading, such as in the case of four-point bending. This made the subsequent analysis of primary fracture surfaces impossible. Fracture stress tests were performed in air and at room temperature (model 1125, Instron Corp., Canton, MA) with a cross-head speed of 0.2 mm min^{-1} . For compositions containing zirconia without stabilizer (5 to 30 vol % 0Y-TZ) an average of 10–12 samples were tested for each ZrO_2 content. Materials with (2Y) zirconia had 10 samples tested for each zirconia content, and finally, ZTA composites with (3Y) zirconia had 9–12 samples examined for each specific composition.

The fracture toughness of each series of the examined composites was determined by loading the single-edge-notched-beam (SENB) specimens in three-point bending. This method was chosen for its simplicity, despite known restrictions regarding its accuracy, and the only aim of the measurements was to define the differences among the various compositions. The SENB tests for each composition were performed on 3–6 samples similar to those used in the fracture stress measurements, with a central notch of $100 \mu\text{m}$ width, and depth of $a/w = 0.4$. After notching, samples were annealed for 0.5 h at 1300°C . They were then loaded at room temperature with a cross-head speed of $0.005 \text{ mm min}^{-1}$ in a standard testing machine (model 1125, Instron Corp., Canton, MA). The fractions of ZrO_2 grains transformed to monoclinic were determined using X-ray diffraction technique (model PW 1840, Phillips, Eindhoven, Netherlands, and Scintag XDS 2000 diffractometer, Scintag Inc., Sunnyvale, CA). The analyses were performed on lateral surfaces of coarsely ground, polished and annealed, and also where possible on selected fracture surfaces.

3. Results and discussion

3.1. Microstructures

The properties of highly concentrated aqueous suspensions of alumina varied very strongly with increasing zirconia content, indicating an increasing degree of heteroflocculation of $ZrO_2-Al_2O_3$ powder mixtures (Fig. 1). The size increase of the mixed powder flocs affected directly the density of the composites consolidated from these suspensions [4, 6, 8]. For example the densities of $ZrO_2-Al_2O_3$ green bodies slip-cast from dense slurries with (2Y) zirconia decreased from 71% T.D. for a composition with 5 vol% ZrO_2 to 66% T.D. for a composition with 30 vol% ZrO_2 . These results are in excellent agreement with the results of De Liso *et al.* [27] analysing similar effects of flocculation on the density of consolidated ZTA composites. Clusters of zirconia grains formed within the flocs of mixed composite powders remained in the final microstructures of the sintered materials, which is reflected in the measured grain sizes (Table I).

Micrographs of the examined ZTA composites with (3Y) zirconia seen in Fig. 2 reveal that as long as the content of ZrO_2 is low (i.e. below 10 vol%), its grains

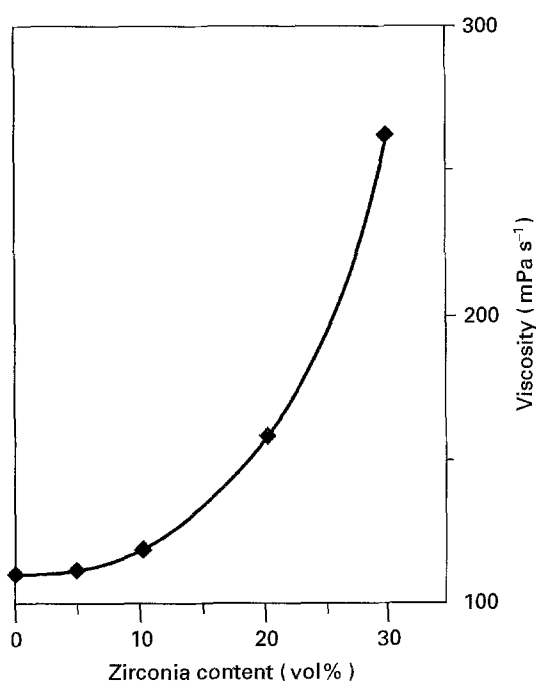


Figure 1 Increase of viscosity of highly concentrated aqueous suspensions of (3Y) $ZrO_2-Al_2O_3$ colloidal mixtures at pH 4 (optimal dispersion of alumina powder).

are well dispersed. In compositions with 30 vol% ZrO_2 large zirconia grain clusters are readily visible (Fig. 2b). The martensite start-up temperature M_s was not experimentally assessed on materials examined in this study, but the observed changes in the ability of ZrO_2 grains to undergo the t-m phase transformation seem to follow the principles presented by Becher and Swain [18]. Namely, in composites with unstabilized zirconia (0Y-TZ), the martensite start-up temperature M_s appeared to be close to the testing temperature, because the ZrO_2 phase transformation occurred upon cooling in all compositions (Table II). It is notable though, that the fraction of ZrO_2 grains transformed upon cooling from sintering temperatures increased proportionally to the size of zirconia grain clusters, which depends on ZrO_2 content. Since increasing grain size brings about the increase in M_s temperature, at larger zirconia contents, a larger number of ZrO_2 grains (clusters) may undergo stress-induced t-m phase transformation during strength test.

As pointed out by Becher and Swain [18], introduction of the stabilizing solute decreases significantly the M_s temperature of t- ZrO_2 dispersed particles. This effect may be seen from Table II for ZTA composites with (2Y) zirconia. No transformation occurred in these samples on cooling and none of their lateral surfaces showed the presence of monoclinic zirconia. It is notable, however, that the size increase of ZrO_2 grain clusters offset the effect of the solute on M_s . This promoted the stress-induced transformation upon loading in some of the larger ZrO_2 grain clusters within the flexure samples with 30 vol% ZrO_2 . In the series of ZTA composites with (3Y) zirconia the amount of solute stabilizer (Y_2O_3) appeared to sufficiently decrease the M_s temperature to prevent the phase transformation, either upon cooling or during external loading. There was no m- ZrO_2 observed in fracture and lateral surfaces of these samples (Table II).

3.2. Elastic properties

The values of dynamic and static moduli of elasticity and of Poisson's ratios versus zirconia content are plotted in Fig. 3 for ZTA composites containing unstabilized, transformable ZrO_2 (0Y-TZ), and non-transformable at room temperature zirconia (3Y-TZ). Materials with unstabilized zirconia were made of powders of both components centrifugally classified to submicron size, whereas composites with

TABLE I Variations of grain sizes of Al_2O_3 and ZrO_2 * in ZTA composites with non-transformable zirconia (3Y-TZ)

Composition	ZrO_2 size-classified	Al_2O_3 as-received	ZrO_2 size-classified	Al_2O_3 size-classified
A	—	2.48 ± 0.1	—	1.42 ± 0.08
5 Z/A	0.45 ± 0.11	1.42 ± 0.15	0.30 ± 0.07	1.01 ± 0.09
10 Z/A	0.57 ± 0.09	1.29 ± 0.13	0.38 ± 0.05	0.81 ± 0.09
20 Z/A	1.21 ± 0.34	1.09 ± 0.26	1.06 ± 0.10	0.78 ± 0.10
30 Z/A	1.24 ± 0.29	0.98 ± 0.08	1.05 ± 0.32	0.61 ± 0.1

*Contiguous ZrO_2 grains (clusters) were considered as entities.

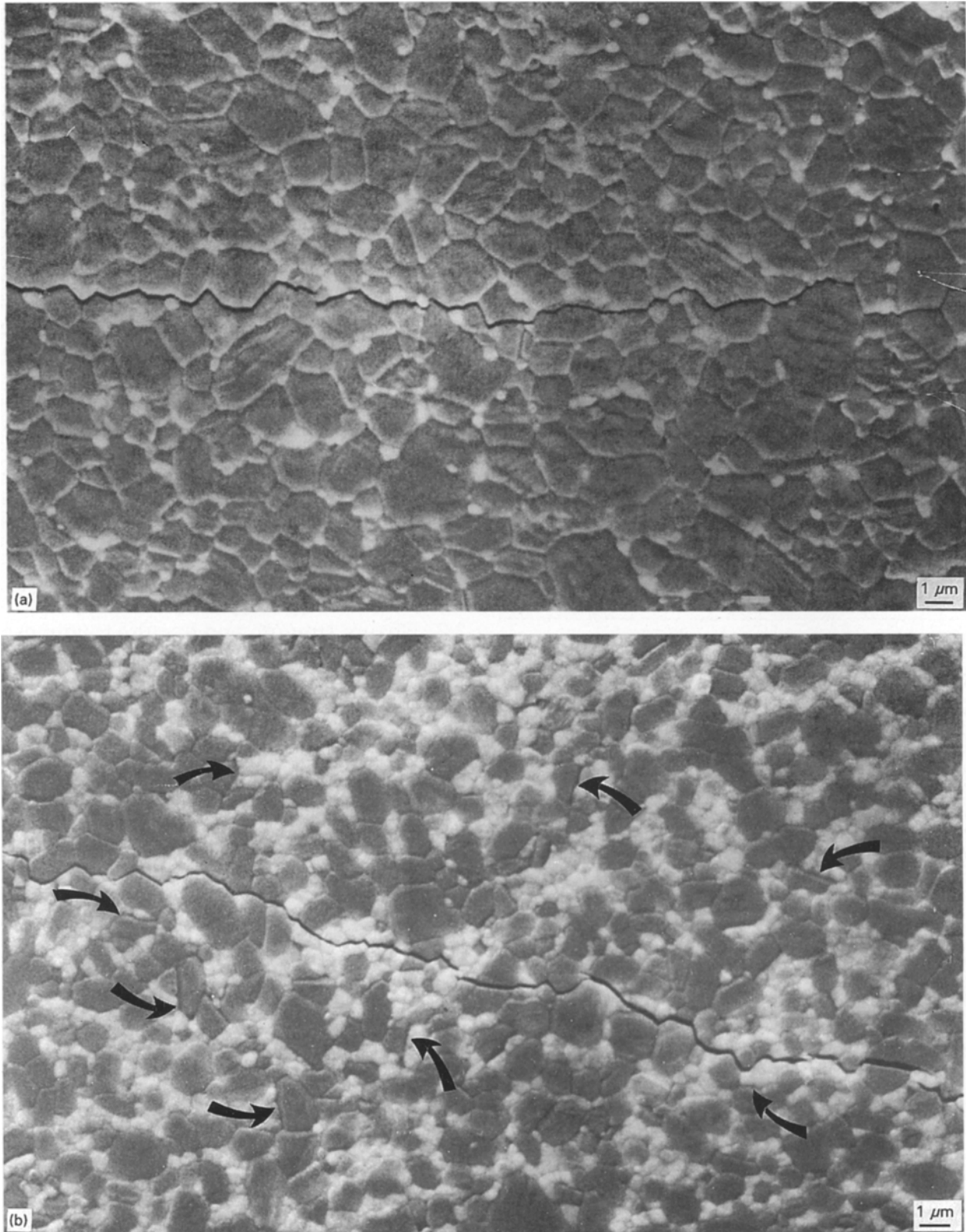


Figure 2 Microstructures of examined ZTA composites containing (a) 5 vol % (3Y) ZrO_2 and (b) 30 vol % (3Y) ZrO_2 . The presence of large ZrO_2 flocs (white phase) in the composition with 30 vol % ZrO_2 is evident. Arrows indicate the sites of formation of lateral microcracks within ZrO_2 - Al_2O_3 interfaces, due to thermal residual stresses at the vicinity of the indentation crack.

non-transformable zirconia were made using the as-received alumina matrix powder. The decrease of composite Young's moduli with increasing zirconia content follows the rule of mixtures in both cases, and the values of static moduli are some 12% lower than the dynamically measured values. The results for ma-

terials containing partially transformable zirconia (2Y-TZ), and non-transformable (3Y-TZ) zirconia made of all-submicron powders of both components were very similar to the values presented in Fig. 3 for composites with unstabilized ZrO_2 . They were not included in Fig. 3 for reasons of legibility.

The most remarkable differences of elastic properties seen from Fig. 3 appear between the ZTA materials made of deagglomerated centrifugally classified powders, and composites made of as-received matrix powders, containing hard agglomerates from the calcination process. It is known that commercial powders, even those with nominally submicron median grain sizes, contain hard agglomerates of up to several dozens of micrometres in diameter. These agglomerates may introduce large (50 μm and more) crack-like voids into the microstructures upon sintering [28], which decrease the modulus of elasticity most dramatically. As long as these agglomerates exist in microstructures (and they always do, unless powders are size classified), the attempts to detect the effects of microcracks related to phase transformation or thermal expansion mismatch might be unsuccessful.

TABLE II Monoclinic zirconia content in the examined ZTA composites as determined by X-ray diffraction technique

Content of stabilizer*	Surface	m-ZrO ₂ content (%) in different compositions (vol % zirconia)			
		5	10	20	30
0Y-TZ	fracture	15	35	81	—
	lateral	15	35	74	88
2Y-TZ	fracture	0	0	0	5

*No monoclinic zirconia was found in composites with 3Y-TZ, neither on lateral, nor on fracture surfaces.

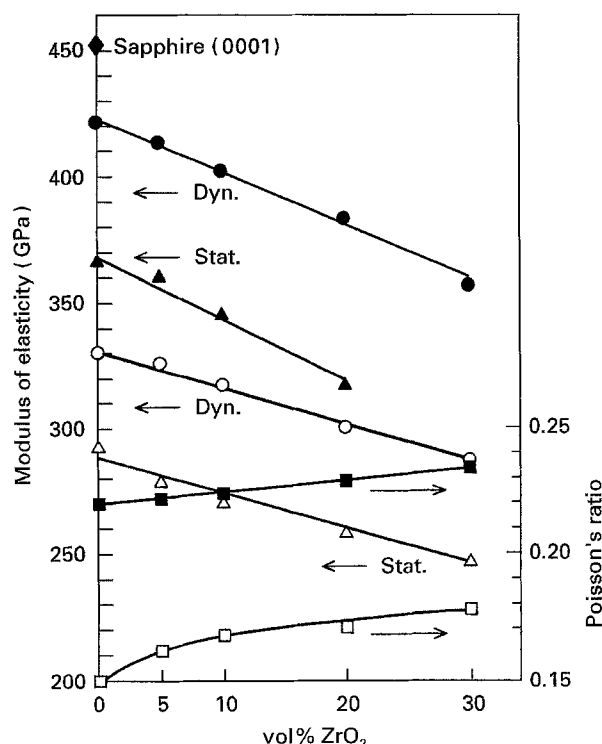


Figure 3 Elastic properties of ZTA composites. Materials containing transformable, unstabilized zirconia (0Y-TZ) were made of centrifugally classified to submicron size powders of both components. Materials containing non-transformable zirconia (3Y-TZ) were made of classified ZrO₂ and as-received (not deagglomerated) Al₂O₃. The presence of hard agglomerates appears to have the strongest effect on reducing the measured values of the elastic properties. ●▲■ OTZ/A classified powders; ○△□ 3TZ/A as-received powders.

The results of dynamic measurements of the modulus of elasticity for ZTA composites with unstabilized ZrO₂ did not show the occurrence of spontaneous radial microcracking accompanying phase transformation of zirconia grains (which took place indeed, see Table II), even at ZrO₂ content of 30 vol %. At this zirconia content, the plates of sintered composites contained surface "macrocracks" of up to several centimetres in length preventing cutting of the flexure bars. These macrocracks were recently related [5] to variations in surface tension of the slurries with increasing ZrO₂ content, also due to heteroflocculation of powder mixtures in dense aqueous suspensions. Bearing this in mind, the dynamic moduli of elasticity of ZTA composites containing 30 vol % of unstabilized ZrO₂ were measured in this work on smaller samples, cut out from homogeneous parts of the sintered plates, separated by optically visible macrocracks. As a result, a continuous monotonic decrease of modulus of elasticity versus zirconia content was registered, similar to the decrease of modulus of hot-pressed ZTA with partially stabilized ZrO₂ reported earlier by Lange [29].

3.3. Flexure strength and fracture toughness

3.3.1. Composites with unstabilized, transformable zirconia

The results of fracture stress determinations shown in Fig. 4 indicate that as long as the content of unstabilized ZrO₂ grains within the ZTA microstructure is low (i.e. less than 10 vol %), they are well dispersed and even if part of them can undergo phase transformation upon cooling from sintering temperatures (Table II), they are still too small to induce the spontaneous microcracking at the time of transformation. Therefore, the grains of dispersed ZrO₂ phase act at this level of concentration mainly as the inhibitors of

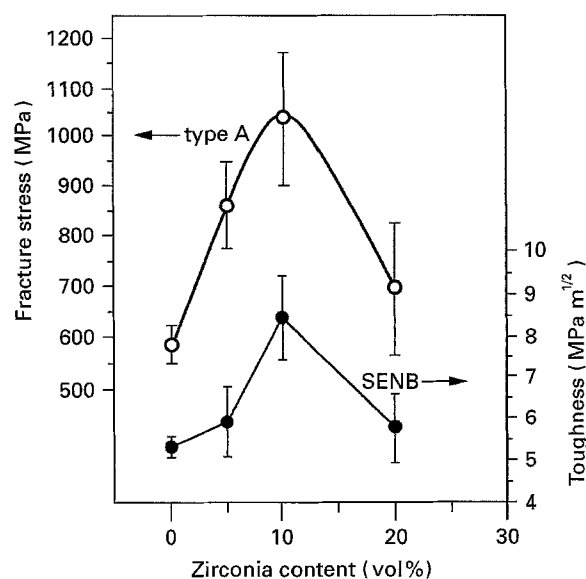


Figure 4 The fracture stress (three-point bending) and fracture toughness (determined by SENB) of ZTA composites containing unstabilized, transformable ZrO₂ (0Y-TZ), and made of centrifugally classified powders of both components.

Al_2O_3 grain growth during sintering [30], which results in a significant increase in strength of the composite, as can be seen from Fig. 4. The accompanying increase in fracture toughness probably originates in localized stress-induced radial microcracking [31], since there is no increase in m- ZrO_2 content at fracture surfaces of these samples (Table II).

Formation of ZrO_2 grain clusters at higher zirconia contents (≥ 10 vol %) during wet-processing may increase the M_s temperature enough to facilitate the t-m phase transformation of larger ZrO_2 clusters upon cooling from sintering temperatures, which results in a larger m- ZrO_2 content in these compositions. On the other hand, clustering of ZrO_2 grains may also bring them closer to the critical size for microcracking due to thermal expansion mismatch of the components [32,33]. The modulus of elasticity of (0Y) ZrO_2 - Al_2O_3 composites did not drop sharply with the increasing ZrO_2 content, which proved that neither spontaneous radial microcracking due to phase transformation, nor the lateral microcracking due to thermal residual stresses occurred upon cooling from sintering temperatures, even at higher ZrO_2 concentrations.

Since not all t- ZrO_2 grains were subjected to phase transformation during cooling (Table II), a very complex state of localized residual stresses around zirconia particles may be expected in these composites at room temperature. The analysis of these stresses was beyond the scope of the present study and it was not determined if massive stress-induced radial microcracking due to t-m ZrO_2 phase transformation, or rather lateral, due to thermal residual stresses, played the dominant role in the observed decrease of strength at ZrO_2 content of 20 vol %. Simultaneous decrease of fracture toughness might have occurred for the same reasons.

3.3.2. Composites with partially transformable zirconia

Mechanical behaviour of examined ZTA composites with partially transformable ZrO_2 (2Y-TZ) is different from that of ZTA with unstabilized zirconia (0-TZ). However, the effects of heteroflocculation of powder mixtures are also evident in this case. Fig. 5 shows a significant increase of flexure strength for composites with low ZrO_2 content, while the fracture toughness values increase slowly when compared to materials with unstabilized zirconia grains. Monoclinic ZrO_2 was not found on the lateral surfaces of test bars, nor on their fracture surfaces within this range of compositions (Table II). These results suggest that ZrO_2 grains also act here mainly as inhibitors of Al_2O_3 grain growth, and thus increasing the strength. The addition of 2 mol % Y_2O_3 solute decreases the martensitic start-up temperature M_s enough for t- ZrO_2 to remain untransformable under the stresses developed upon cooling, as well as under mechanical loading.

At ZrO_2 content of 20 vol % microscopic observations revealed significant clustering of the dispersed phase. However, the size of these clusters was prob-

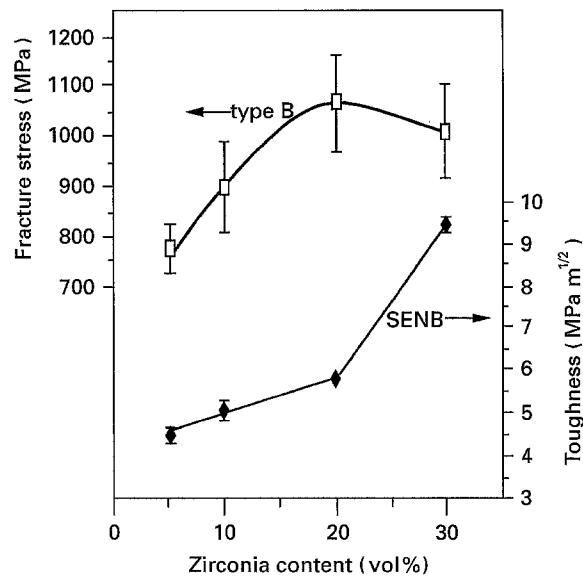


Figure 5 Strength (three-point bending) and fracture toughness (SENB) of ZTA composites with partially transformable zirconia (2Y-TZ). Materials made using deagglomerated powders of both components (centrifugally size-classified). Fracture stress determined only on type B samples, according to US Mil.Std 1942.

ably not sufficient to offset the decrease of M_s and cause the t-m ZrO_2 phase transformation. It was also insufficient to increase thermal residual stresses enough to affect the fracture toughness by lateral microcracking. An observed slight increase in toughness, with ZrO_2 increasing from 5 to 20 vol %, could be related to the increase of overall heterogeneity of the microstructure. It was found recently [7] in similar ZTA compositions, that a systematic increase of heterogeneity can bring about a 20 % increase in fracture toughness. This was achieved only by varying the size of flocs of mixed ZrO_2 - Al_2O_3 powders by varying parameters of ultrasonic agitation.

Samples with 30 vol % ZrO_2 show substantial increase in fracture toughness, which coincides with the occurrence of stress-induced t-m phase transformation of (small) part of ZrO_2 particles, as can be seen from Table II. This limited phase transformation cannot fully account for the observed increase of fracture toughness, because it is not accompanied by a simultaneous increase in strength. Instead, a slight decrease in flexure strength was observed which could be considered as statistically insignificant for the number of samples tested here, but it might be also indicative of the increasing role of residual stresses at this zirconia content. Clustering of ZrO_2 grains content may be sufficient to promote stress-induced lateral microcracking within alumina-zirconia interfaces, which contributes to the enhancement of the measured fracture toughness. On the other hand, this intensified microcracking brings about the observed slight decrease in flexure strength.

3.3.3. Composites with non-transformable zirconia

In the series of ZTA composites with (3Y) ZrO_2 the addition of 3 mol % yttria stabilizing solute decreases the martensitic start-up temperature so efficiently that

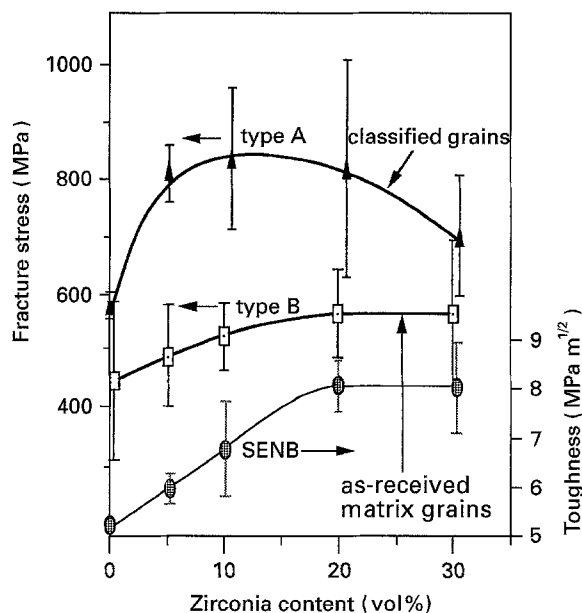


Figure 6 Strength (three-point bending) and fracture toughness (SENB) of ZTA composites containing non-transformable zirconia (3Y-TZ). Type B samples (US Mil.Std 1942) were made only of the material containing as-received (not deagglomerated) alumina matrix powder. Type A samples were prepared from powders of both components centrifugally size-classified.

it cannot be offset by the clustering of ZrO_2 grains at larger zirconia contents (> 20 vol %), and the dispersed phase remains untransformable in all compositions. The flexure strength values determined on larger samples (type B, Mil.Std 1942), cut out from ZTA materials made of as-received alumina matrix grains show practically no effect with increasing zirconia content (Fig. 6). As in many other ceramic composites made of as-received commercial powders, mechanical properties are dominated here by the presence of hard agglomerates, and modifications introduced by microstructural features smaller than these principal defects are undetectable.

The results of strength measurements on smaller samples (type A), cut out of ZTA composites made of size-classified powders of both components show the most pronounced increase of strength at small ZrO_2 contents (up to 5 vol %). Strength reaches a maximum between 10 and 20 vol % ZrO_2 content, and as previously, this increase can be related to the enhanced control of Al_2O_3 grain size. A slight decrease of three-point bending strength of composites with 30 vol % ZrO_2 is statistically insignificant for the number of samples tested, but as before (composites with 2Y-TZ), it might be indicative of the increasing role of thermal residual stresses around ZrO_2 grain clusters, facilitating the formation of lateral microcracks within the interfaces. This effect should become more evident at larger zirconia contents than those used in the present study.

It has been found recently [4] that microcrack formation in ZTA composites with non-transformable ZrO_2 can be facilitated by heteroflocculation of powder mixtures during processing not only by increasing the size of ZrO_2 clusters to a critical value for microcracking from thermal stresses, but also by the generation of very fine crack-like voids (few μm) around the

flocs of mixed powders in a consolidated (green) body. These defects are believed to sinter into "weaker boundaries" within the final microstructures and then, under load, they become the preferential sites for microcrack formation due to thermal residual stresses, whenever they coincide with Al_2O_3/ZrO_2 interfaces. This concept was supported by an experiment in which some of the ZTA consolidated samples were isopressed after drying, which eliminated crack-like voids around the flocs within the green bodies. These samples showed no dependence of fracture toughness on ZrO_2 content. In contrast, "cast only" samples contained crack-like voids around the flocs of mixed powders, and as a consequence, "weaker boundaries" in a sintered composite. Fracture toughness of these composites doubled with the increase in ZrO_2 content to 30 vol %. This work proved that fracture toughness of ZTA composites with non-transforming dispersed ZrO_2 phase may increase uniquely due to stress-induced lateral microcracks resulting from thermal residual stresses.

The above described model for the effects of heteroflocculation of powder mixtures during processing on the mechanism of microcrack formation due to thermal residual stresses may appear to be universal for all ceramic composites having sufficient colloidal incompatibility of the components during processing on one hand, and a mismatch of their thermal expansions on the other. The existence of a microcracking process zone has been confirmed experimentally in SiC/TiB_2 composites [22], where the difference of average thermal expansion coefficients was similar to that existing in ZrO_2/Al_2O_3 systems. Lateral microcracks resulting from thermal expansion mismatch observed directly in ZrO_2/Al_2O_3 materials under the SEM [19] were of the same nature as those observed under TEM in SiC/TiB_2 composites [22, 23].

4. Conclusions

1. Clustering of ZrO_2 grains in suspension-processed zirconia-alumina microstructures is unavoidable for geometrical (particle packing), as well as electrochemical reasons (heteroflocculation of components).

2. At low content of dispersed phase (less than 10 to 20 vol %), individual ZrO_2 grains act primarily as grain growth inhibitors for Al_2O_3 matrix grains during sintering. In composites free of hard agglomerates and made of grains classified to submicron size, this leads to an increase in fracture stress with increasing ZrO_2 content, irrespective of the degree of stabilization. In ZTA compositions where t-m ZrO_2 phase transformation does not occur, the fracture toughness may increase slowly with increasing ZrO_2 content due to the increase of overall heterogeneity of the microstructure. Where (even limited) transformation is possible, increase in fracture toughness is steeper, and may additionally enhance the strength as long as it is not offset by excessive microcracking.

3. At larger contents of the dispersed phase (> 10 to 20 vol %), formation of ZrO_2 grain clusters during wet-processing may facilitate the t-m phase trans-

formation around the cracks propagating in the final composites with transformable, or partially transformable ZrO₂, depending on the value of the martensitic start-up temperature M_s. In ZTA compositions where transformation related radial microcracking and/or thermal stress related lateral microcracking is limited, fracture toughness increase with increasing ZrO₂ content is accompanied by a slight decrease of strength (such as in alumina with 2Y-TZ). Where microcracking is more intensive (possibly both radial and lateral, such as in alumina with 0Y-TZ), both fracture toughness and strength decrease rapidly with increasing zirconia content, i.e. degree of clustering of ZrO₂.

4. In ZTA materials with a sufficient content of non-transformable zirconia (> 20 vol %), residual stresses built within composite interfaces due to thermal expansion mismatch of the components may promote the formation of lateral microcracks in the process zone of a crack propagating in material under external load. This leads to the enhancement of fracture toughness of these composites proportional to the degree of clustering of ZrO₂ grains (i.e. zirconia content), which is accompanied by a decrease of strength. Further decreases of both strength and fracture toughness of composites containing non-transformable ZrO₂ may be expected at larger contents of zirconia phase.

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