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Toughening mechanisms in duplex alumina–zirconia ceramics

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A series of Al_2O_3–ZrO_2 ceramics has been fabricated using both conventional sintering and a hot-pressing route, which results in various microstructures including (i) Al_2O_3 with well-dispersed ZrO_2 single crystals; (ii) Al_2O_3 with TZP (tetragonal zirconia polycrystals) agglomerates (20 to 50 μm); and (iii) Al_2O_3–ZrO_2 duplex structures, in which both well-dispersed ZrO_2 single crystals and TZP agglomerates are dispersed. The fracture strength of the composites has been measured by means of three-point bending and the fracture toughness by means of the micro-indentation technique. The microstructural characterization was carried out using scanning and transmission electron microscopy, and phase analysis of the zirconia by means of X-ray diffraction. The high toughness values of $\sim 12\,\mathrm{MPa\,m^{1/2}}$ measured for the duplex structure have been correlated with the toughening mechanisms operative and the fracture strength with the matrix grain size and with larger defects present in the structure. A combined toughening process is proposed to account for the improved properties, including transformation toughening, microcrack toughening and crack deflection, which are discussed in context with the property measurements and the microstructural observations.

1. Introduction

In the last few years, increasing attention has been paid to enhancing the mechanical properties of ceramics by dispersion of a second phase [1–5].

Recently published research on the fracture toughness of zirconia-based ceramics has indicated that various toughening mechanisms can work synergetically, resulting in a more effective toughening process. The mechanisms associated with zirconia-based ceramics include stress-induced transformation toughening, stress-induced microcrack toughening, spontaneous microcrack toughening, and crack deflection. The toughening mechanisms differ in that

(i) stress-induced transformation toughening and crack deflection can give a positive effect on both toughening and strengthening;

(ii) microcracks, on the other hand, give a positive effect on toughening and a negative effect of strengthening.

Recently, Evans and Cannon [6, 7] have discussed combined or multiple toughening mechanisms in zirconia-based ceramics and observed that several such mechanisms can operate simultaneously. However, this could result in either additional or counteracting influences on the net toughness. In particular, it was suggested that transformation toughening and crack deflection are strictly additive, whereas with the combination of transformation toughening and microcrack toughening, this is not the case due to the presence of microcracks decreasing the elastic modulus.

In the present work, a series of alumina–zirconia composites were designed and fabricated for the purpose of combining various toughening mechanisms in order to study their influence on the toughness. The composites utilizing the individual mechanisms involved in the duplex structures were also fabricated for comparison. The mechanical property measurements have been correlated with the microstructural characterization. A combined toughening process is proposed to the duplex structures, including transformation toughening, microcrack toughening, crack deflection, etc.

2. Experimental procedure

The starting materials, alumina and zirconia, were obtained from commercial sources (Alumina, Alcan Chemicals Ltd, UK; ZrO_2, Toyo Soda Manufacturing Co. Ltd, Japan). Three groups of composites were fabricated:

(i) Al_2O_3 matrix with dispersed ZrO_2 single crystals (Structure I);

(ii) Al_2O_3 with TZP (tetragonal zirconia polycrystals) agglomerates (20 to 50 μm) (Structure II);

(iii) A duplex structure consisting of Al_2O_3 matrix with both ZrO_2 single crystals and TZP agglomerates (20 to 50 μm) (Structure III).

It is apparent that Structure III is a a combination of Structures I and II.

The experimental route detailed in Fig. 1 was employed to fabricate the composites. The fabrication started with preparation of the matrix component (Structure I) [8], that is, Al_2O_3 with dispersed ZrO_2 single crystals, the volume fraction of which varied from 2 to 20%. The next stage involved the calcination of the as-received ZrO_2–2.5 mol % Y_2O_3 powder,

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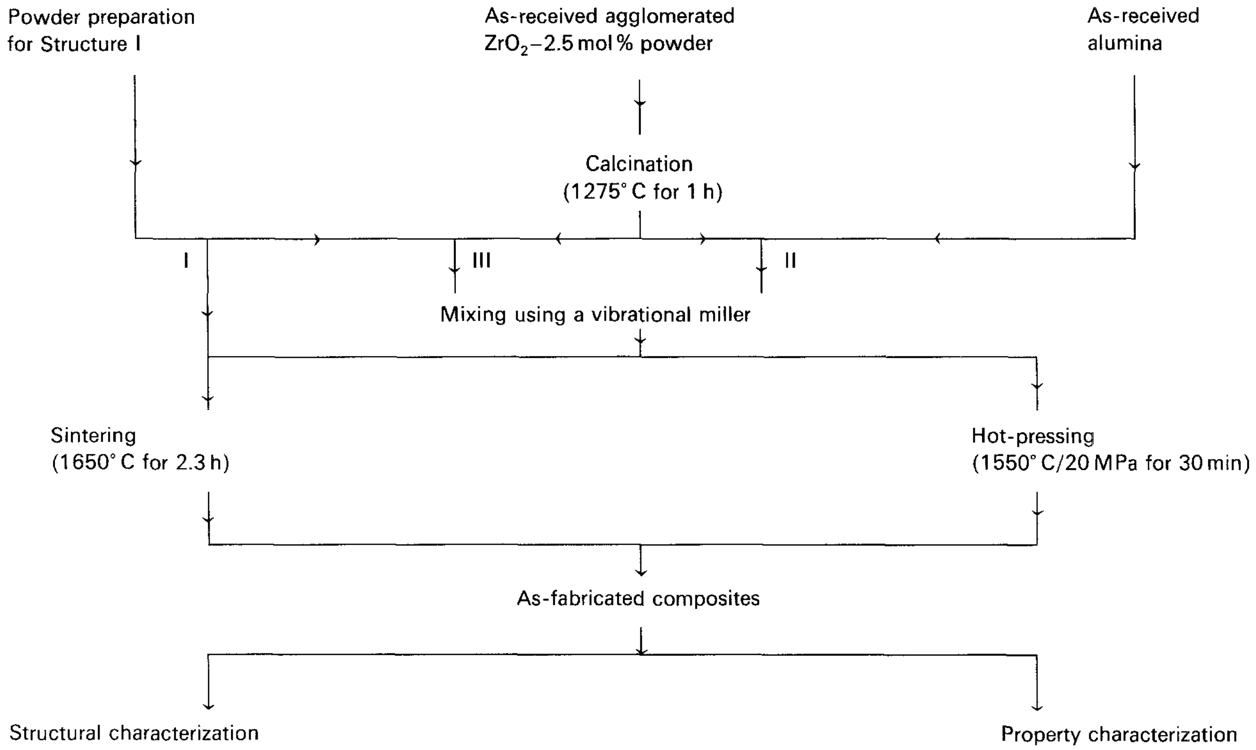

Figure 1 Experimental route for specimen preparation and characterization.

with an agglomerate size of 20 to 50 μm. The calcination of the agglomerated powder for 1 h at 1275° C was considered to be necessary for two purposes: (i) to complete the stabilization of ZrO_2 by Y_2O_3; and (ii) to strengthen the agglomerates by partial sintering in order for them to survive the subsequent mixing process. The calcined agglomerated ZrO_2 powder was then mixed with the Al_2O_3 (for Structure II) and the matrix in which ~ 12 vol % of ZrO_2 single crystals had been incorporated (for Structure III) using vibrational milling, with ZrO_2–2.5 mol % Y_2O_3 addition from 5 to 40 vol %. The desired powders, in which 3 wt % of polyethylene glycol binder was introduced, were then pressed into pellets at a pressure of 30 MPa in a steel die of 45 mm diameter, resulting in a compact having a green density of 52%. The sintering of the compacts were carried out at 1650° C for 2.3 h.

Certain specimens were made by a hot-pressing route and for this the powders were directly poured into a graphite die, and hot-pressed at 1550° C and 20 MPa for 30 min. Density measurement of the sintered and hot-pressed composites was made using a water-immersion method. Property characterization was carried out using the indentation technique for fracture toughness and hardness [9], and an Instron testing machine for fracture strength. Finally, the microstructural characterization was made using such techniques as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD).

3. Results and discussion

Figs 2 and 3 show the dependence of the fracture strength and toughness on the volume fraction of dispersed ZrO_2 single crystals for the sintered composites (Structure I). It can be noted from Fig. 2 that the strength of the composites decreases with increasing volume fraction of ZrO_2 additions only slightly at low ZrO_2 content (< 10 vol %) and there is a fall when the ZrO_2 addition is ~ 10 vol %. The toughness of the composites increases linearly with increasing volume fraction of ZrO_2 single addition at low ZrO_2 content (< 10 vol %) and increases only slightly for those containing high (> 10 vol %) ZrO_2 content up to 20 vol %.

X-ray traces indicated that ~ 73 wt % of ZrO_2 single crystals were in the monoclinic form, estimated using

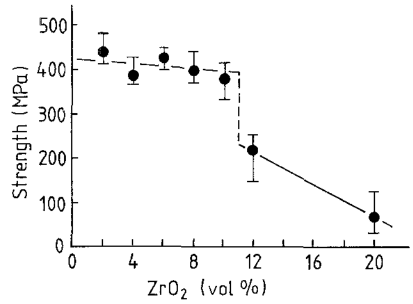

Figure 2 The dependence of fracture strength on the volume fraction of ZrO_2 single crystals for Structure I.

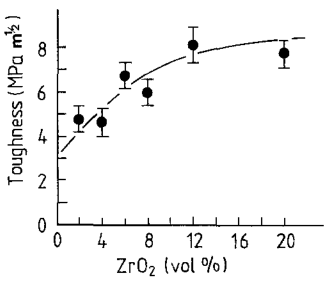

Figure 3 The dependence of fracture toughness on the volume fraction of ZrO_2 single crystals for Structure I.

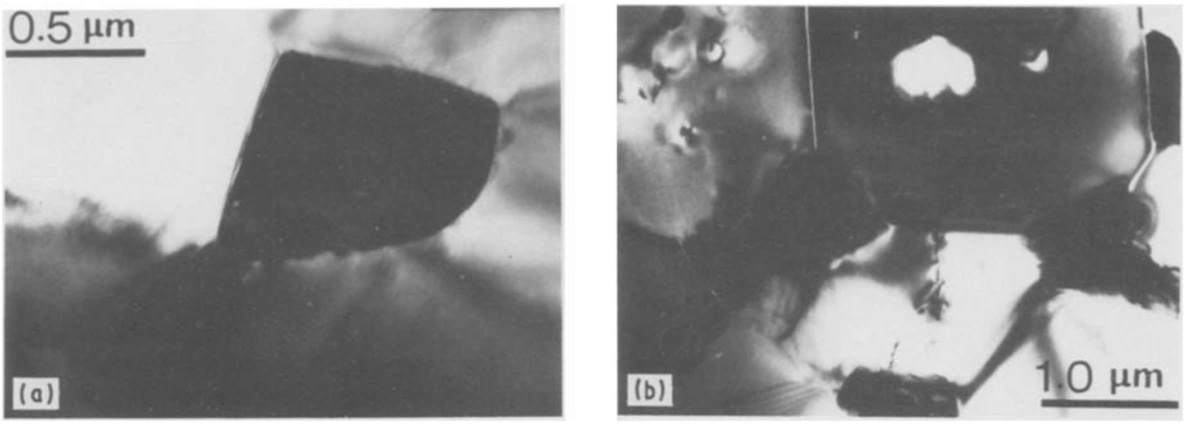

Figure 4 (a) A bright-field TEM image showing strain fields and microcracks associated with transformed ZrO_2 grains for the composite containing 8 vol % ZrO_2; (b) A bright-field TEM image showing serious cracks for the composite containing 20 vol % ZrO_2.

the method given by Evans *et al.* [10]. It was therefore concluded that the main toughening effects of the composites were from microcrack toughening, although the metastable tetragonal zirconia could also contribute to toughening to some extent, since ~ 27 wt % of the dispersed ZrO_2 single crystals were in the tetragonal form.

It has been reported by Claussen and co-workers [11, 12] and by Lange [1] that the fracture strength of Al_2O_3 with dispersed unstabilized zirconia was lower than that of unadulterated Al_2O_3, and they were convinced that the critical flaw size in the composites was increased by the introduction of ZrO_2 particles. It was considered that the increased critical flaw size was a result of microcracks coalescence, a consequence of the volume expansion associated with the $ZrO_2(t) \rightarrow ZrO_2(m)$ transformation.

It was observed in the present work that microcracks and strain fields were developed in the structures of composites containing low ZrO_2 additions (< 10 vol %), Fig. 4a. This is in comparison with the serious cracks in the structure of composites containing high ZrO_2 content (> 10 vol %), Fig. 4b. It is therefore considered that the effect on toughness of microcracks is critically dependent on their stability. Only those microcracks with high stability can result in a noticeable increase in the fracture toughness. On the other hand, the spontaneous propagation of microcracks can result in an increased critical flaw size and weaken the material.

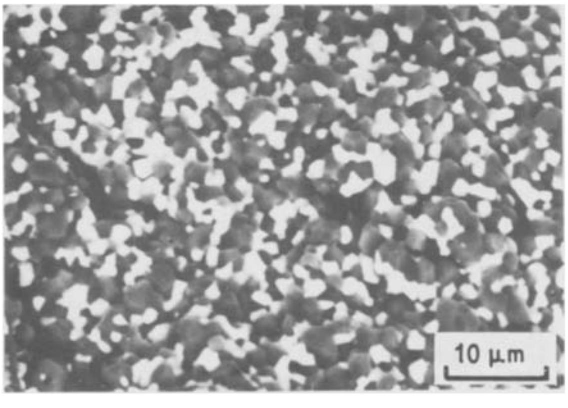

Figure 5 SEM micrograph showing fracture surface of the composite containing 10 vol % ZrO_2 single crystals.

The microstructural characterization using SEM, etc., indicated the features summarized in Table I. One example is shown in Fig. 5, which is a fracture surface of the composite containing 10 vol % of ZrO_2 single crystals.

Fig. 6 shows the toughness results for Structures II and III, prepared by sintering. It can be seen that both of the structures have been toughened by the presence of large ZrO_2 agglomerates. In particular the toughening of Structure III is more effective than that of Structure II.

It was confirmed by XRD phase analysis that the ZrO_2–2.5 mol % agglomerates were in the tetragonal form, and the phase presence of ZrO_2 single crystals in Structure III was similar to those in Structure I.

The explanation for these results can be made on the basis of toughening mechanisms operative in the structures. From the concept of a process zone [13], any stress-induced transformable tetragonal ZrO_2 particles in the process zone can contribute to toughening. The TZP agglomerates in Structure II can result in toughening via transformation. The inhomogeneous stress distribution at the interface between TZP agglomerates and the alumina matrix can give a resistance to advancing cracks and therefore contribute to toughening.

As both TZP agglomerates and ZrO_2 single crystals are present, the toughening processes in Structure III will be expected to be those of Structure I plus those of Structure II. The toughening process in this structure would be

(a) transformation toughening (TZP agglomerates);

(b) microcrack toughening and transformation toughening to a lesser extent (matrix);

(c) crack interaction, i.e. deflection (between the agglomerate and the matrix).

TABLE I Properties of composites

Sintered density	~ 98% theoretical density
ZrO_2 phases present	~ 27 wt % tetragonal, ~ 73 wt % monoclinic
Grain size of ZrO_2	~ 1 μm
Grain size of Al_2O_3	3 to 10 μm (15 to 2 vol % ZrO_2
Fracture	Intragranular → intergranular with increasing volume of ZrO_2 additions

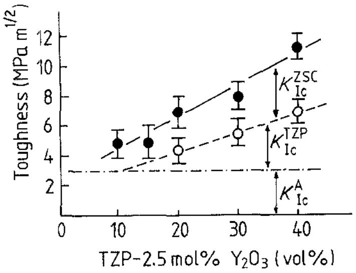

Figure 6 The dependence of fracture toughness on the volume fraction of TZP agglomerates for (○) Structure II and (●) Structure III, fabricated by sintering.

TABLE II Properties of Structures II and III

Property	Treatment	
	Hot-pressed	Sintered
Density, theoretical density %	~ 100	~ 97
Grain size of Al_2O_3 (μm)	~ 2	~ 4
Grain size of dispersed ZrO_2 single crystals (μm)	~ 0.5	~ 1
Grain size of TZP inside agglomerates (μm)	~ 1	4 to 5
Shape of TZP agglomerates	Ellipsoid	Spherical
Fracture of matrix	Intergranular	Intergranular
Fracture of TZP agglomerates	Intergranular	Intergranular

It is therefore very easy to understand why the toughness of Structure III is higher than that of Structure II in Fig. 6. It is considered that transformation toughening and crack deflection are additive from this work. The addition is evidenced by the toughness results in Fig. 6, in which the toughness increment due to the presence of TZP agglomerates is strictly proportional to the volume fraction of the TZP agglomerates in the structure.

The relationship between transformation toughening and microcrack toughening in Structure III is not exactly the same as in the case considered by Evans and Cannon [6, 7]. In the duplex Structure III, the toughening by TZP agglomerates via transformation and that by the microcracks in the matrix can be considered as separate processes. The tetragonal zirconia crystals inside the agglomerates can constrain each other and therefore retain the tetragonal form. This is in comparison with the situation considered by Evans and Cannon [6, 7], in which the retention of metastable tetragonal zirconia could be influenced critically by the presence of microcracks. On the basis of the consideration that toughening processes inside TZP agglomerates and those in the matrix for Structure III are separate, the net toughness of Structure III can be analysed as three components in Fig. 6:

(i) K_{Ic}^{A} is the intrinsic toughness of alumina, ~ 3 MPa m$^{1/2}$;

(ii) K_{Ic}^{TZP} is the toughness increment due to the presence of TZP agglomerates; and

(iii) K_{Ic}^{ZSC} is the toughness increment due to the presence of ZrO_2 single crystals.

The dependence of fracture strength on the volume fraction of TZP agglomerates for Structure III is shown in Fig. 7. According to

$$\sigma_f = K_{Ic}/(2\pi C)^{1/2}$$

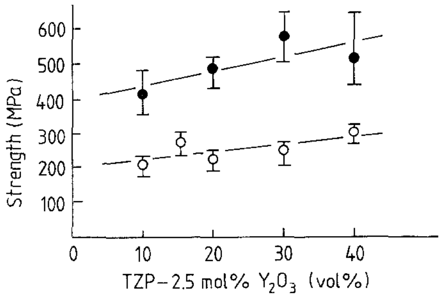

Figure 7 The dependence of fracture strength on the volume fraction of TZP agglomerates for (○) sintered and (●) hot-pressed Structure III.

the variables which affect strengthening of the duplex structures, in which there exist more than one toughening mechanism, include toughness values and critical flaw size (c).

The strengthening can be discussed on the basis of the individual toughening mechanisms. Transformation toughening always gives a strengthening [1]; crack deflection can also result in a strengthening process [14–16]. Microcracks, however, would diminish the strength of the ceramics as a consequence of increased critical flaw size. The strength of the composites is strongly influenced by the presence of processing defects, which result mainly from the differential sintering of the TZP agglomerates with respect to the matrix. The effects of these defects on the strength of composites is demonstrated by a comparison of strength results between sintered and hot-pressed specimens in Fig. 8

The microstructural characterization using SEM, etc., for Structures II and III is summarized in Table II. A typical example is shown in Fig. 8, which illustrates the polished surfaces of Structure III, fabricated by both a conventional sintering and a hot-pressing route.

The concurrence of various toughening mechanisms in the duplex structures was evidenced by TEM observation. Fig. 9 shows an example of the combined toughening mechanism, in which microcrack toughening, crack deflection and transformation toughening occur together.

In summary, the toughening mechanisms in the composites studied are as follows:

(i) in Structure I, transformation toughening and microcrack toughening;

(ii) in Structure II, transformation toughening and crack deflection;

(iii) in Structure III, transformation toughening, microcrack toughening and crack deflection.

The higher toughness values of Structure III over either Structure I or Structure II indicates that the more effective combined processes can be achieved by a combination of various structures.

4. Conclusions

The ability of microcracks to toughen by way of dissipating the energy of a propagating crack is dependent on their stability.

A duplex structure which combines more than one toughening mechanism has been successfully designed

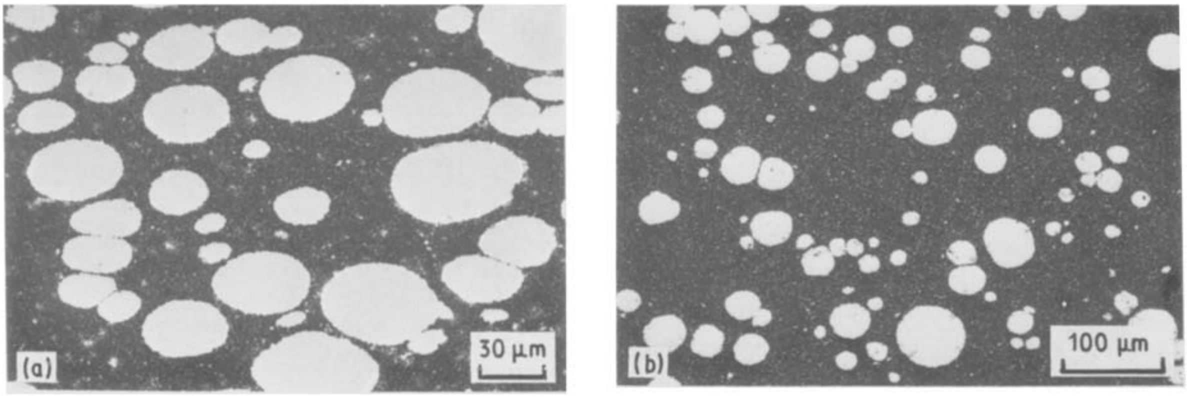

Figure 8 SEM micrographs showing polished surfaces of (a) hot-pressed and (b) sintered Structure III (30 vol % TZP agglomerates).

and fabricated. The toughening processes in the duplex structure are related to the individual mechanisms due to the relevant toughening agents. The concurrence of transformation toughening and microcrack toughening can result in a more effective process. The promising mechanical properties of the duplex structures were demonstrated. The parameters which influence the strength of the duplex structure include individual toughening mechanisms and the residual process defects. In particular, transformation toughening is the most effective term to cause strengthening, and the defects as a consequence of differential sintering of TZP agglomerates with respect to the surrounding matrix are the most critical source of failure.

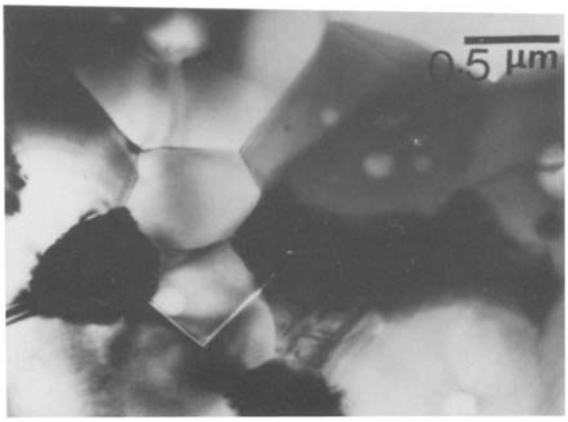

Figure 9 A bright-field TEM image showing a combined toughening process in Structure III: a crack interacts with microcracks, is then deflected and eventually stopped by a TZP agglomerate via transformation toughening.

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