JOURNAL OF MATERIALS SCIENCE 17 (1982) 247–254

Transformation toughening

Part 4 *Fabrication, fracture toughness and strength of Al_2O_3-ZrO_2 composites*

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Three Al_2O_3–ZrO_2 composite series, containing 0, 2 and 7.5 mol % Y_2O_3, were fabricated for fracture toughness determinations. Without Y_2O_3 additions, tetragonal-phase ZrO_2 could only be retained up to approximately 10 vol % ZrO_2; additions of 2 mol % Y_2O_3 allowed full retention of the tetragonal phase up to 60 vol % ZrO_2. Cubic ZrO_2 was produced with additions of 7.5 mol % Y_2O_3. Significant toughening and strengthening was achieved when tetragonal ZrO_2 was present.

1. Introduction

In Part 1 [1] of this series of papers, the thermodynamics of a constrained phase transformation was presented, with particular reference to the size-effect associated with retention of the high temperature phase. Part 2 [2] presented the theory concerning the contribution of the stress-induced transformation to fracture toughness. Part 3 [3] reported experimental observations concerning the retention of tetragonal-phase ZrO_2 and its contribution to fracture toughness for a series of materials fabricated in the ZrO_2–Y_2O_3 system. The theory shows that both the critical inclusion size and the contribution to fracture toughness can be increased by choosing a constraining matrix with an elastic modulus higher than that of ZrO_2.

The Al_2O_3–ZrO_2 system was chosen for this study because Al_2O_3 has approximately twice the elastic modulus of ZrO_2 (390 compared with 207 GPa) and both phases are chemically compatible with one another [4]. Claussen [5] has already demonstrated that Al_2O_3–ZrO_2 polycrystalline composites could be fabricated, and he also has demonstrated [6] that tetragonal-phase ZrO_2 could be retained in volume-fractions up to 0.17. The intent of the present work was to fabricate a series of Al_2O_3–ZrO_2 composite materials from one end-member to the other and to retain the ZrO_2 in its tetragonal state. Initial studies indicated that, within the range of fabrication parameters investigated, "pure" tetragonal ZrO_2 could only be retained in volume-fractions less than 0.10. Based on theoretical considerations (from Part 1 [1]) and retention studies in the ZrO_2–Y_2O_3 system (Part 3 [3]), it was found that additions of 2 mol% Y_2O_3 to the composite powders would allow the retention of the tetragonal phase to much greater volume-fractions of ZrO_2. Thus, this series of materials formed the principal base for investigating the contribution of the stress-induced phase transformation to fracture toughness and strength.

2. Experimental procedure

2.1. Fabrication and phase identification

Three Al_2O_3–ZrO_2 composite series were fabricated for this study: one containing ZrO_2 volume-fractions of up to 0.20, one containing ZrO_2 + 2 mol% Y_2O_3 in which tetragonal-phase ZrO_2 was retained, and one containing ZrO_2 + 7.5 mol% Y_2O_3 in which cubic ZrO_2 was obtained. The latter composite series was used for base-line information where transformation toughening was not a phenomena associated with the fracture mechanics of the material.

Powders with sub-micrometre particle size were used*. Y_2O_3 was introduced as soluble yttrium

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*Al_2O_3 from Lindy B, Union Carbide Corp.; ZrO_2 from Zircar Corp.

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nitrate*. Composite powders were mixed by ball-milling with methanol and Al_2O_3 balls in a plastic container. All powders were dried; those containing yttrium nitrate were calcined at 400° C for 4 h. Densification was achieved by hot-pressing. Most Y_2O_3-containing compositions were hot-pressed at 1600° C for 2 h; compositions containing 80 and 100 vol % ZrO_2 (plus 2 mol % Y_2O_3) were hot-pressed at 1400° C in order to achieve a smaller grain size which would allow the retention of the tetragonal-phase ZrO_2. The non-yttria composites were hot-pressed at 1500° C, for the purpose, again, of achieving a smaller grain size in order to optimize the retention of tetragonal-phase ZrO_2. The pure Al_2O_3 end-member was hot-pressed at 1400° C to achieve a grain size comparable with the two-phase materials (the introduction of one end-member into the other limited grain growth).

Archimedes' technique was used to measure the density of the 5 cm diameter billets. Specimens were cut, ground and polished† prior to phase identification by X-ray diffraction analysis. 2θ-scans between 27 and 33° were used to estimate the tetragonal/monoclinic ZrO_2 ratio; 2θ-scans between 55 and 62° were used to confirm either the tetragonal or the cubic ZrO_2 phase.

2.2. Mechanical measurement

Young's modulus, E, of selected compositions was measured at room temperature by the resonance technique with two modes of vibration: flexural (9 k Hz) and extensional (60 kHz).

The critical stress-intensity factor, K_c, was measured on polished specimens using the identation technique (20 kg load) developed by Evans and Charles [7]. Hardness, H, data was also obtained. Three measurements were made for each material.

Flexural strength measurements were obtained in four-point bend testing (inner span: 1.22 cm; outer span: 2.54 cm) on diamond-cut specimens (of cross-section approximately 0.32 cm x 0.32 cm) finished with a 220 grit diamond grinding wheel.

3. Results

3.1. Fabrication and phase identification

Table I lists the fabrication conditions for the compositions reported here and their respective average properties. In the series which excluded Y_2O_3, high proportions of the tetragonal-phase ZrO_2 could only be retained up to approximately 10 vol% ZrO_2. In the series containing 2 mol% Y_2O_3, tetragonal-phase ZrO_2 was fully retained up to about 60 vol% ZrO_2. Cubic ZrO_2 was the only ZrO_2 structure observed in the series containing 7.5 mol% Y_2O_3. No Y–Al oxide compounds were observed.

Lattice-parameter measurements reported by Scott [8] are confirmed in the present work: $a = 0.5090$ nm, $c = 0.5174$ nm for the tetragonal (plus 2 mol% Y_2O_3) structure and $a = 0.5135$ nm for the cubic structure. Using these values and the formulation $Zr_{1-x}Y_xO_{2-(x/2)}$, the theoretical densities for the tetragonal and cubic structures were calculated as 6.09 and 5.97 cm^{-3}, respectively. Measured densities, ρ, for the two composite series containing either the tetragonal or the cubic phases obeyed the Rule of Mixtures for the end-members (Al_2O_3: $\rho = 3.98$ g cm^{-3}), indicating that theoretical density was achieved during fabrication.

Fig. 1 illustrates microstructures of the polished surfaces typical of the Al_2O_3–ZrO_2 composites (cracks present were purposely propagated from hardness indents). The observed agglomeration of the minor phase in occasional groups of 2 to 5 grains indicates that the dispersion could be improved. The average ZrO_2 grain-size, d, for the composite materials was dependent on the fabrication temperature: $d \sim 0.2\,\mu m$ at 1400° C, $d \sim 0.5\,\mu m$ at 1500° C and $d \sim 1\,\mu m$ at 1600° C. The average grain-size for the single-phase end-members was approximately 2 μm for Al_2O_3 and approximately 0.5 μm for ZrO_2.

As reported in the Appendix, hot-pressed billets containing greater than 30 vol% Al_2O_3 contained large surface cracks, as observed by fluorescent-dye penetration. Although small crack-free specimens could be cut and polished for K_c measurements, larger bar specimens invariably contained one or more cracks, which restricted meaningful strength measurements to composites containing $\leqslant 30$ vol% ZrO_2.

3.2. Hardness

Fig. 2 illustrates the Vickers hardness (20 kg) for the Al_2O_3–ZrO_2 (plus 2 mol% Y_2O_3) series,

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*Research Chemicals Inc.

†Surface damage caused by cutting and grinding causes the surface to transform. Polishing decreases the depth of the transformed surface layer.

TABLE I Fabrication conditions, phase content and properties of Al_2O_3–ZrO_2 composites

ZrO_2 content (vol%)	Y_2O_3 content (mol%)	Fabrication conditions		Density (gm cm^{-3})	Volume-fraction ZrO_2 phase* (%)	Hardness, H (GPa)	Young's modulus, E (GPa)	K_c (MPa $m^{1/2}$)
		Temperature (°C)	Time (h)					
Al_2O_3–ZrO_2 (*plus* 2 mol% Y_2O_3) *series*								
0	–	1400	2	3.98	–	17.6	390	4.89
6	2	1600	2	4.12	100t	16.8	–	5.97
12.3	2	1600	2	4.26	100t	15.9	–	6.22
18.2	2	1600	2	4.38	100t	16.1	356	6.58
23.9	2	1600	2	4.50	100t	16.4	–	6.38
29.5	2	1600	2	4.62	100t	15.7	–	7.43
45.0	2	1600	2	4.89	tr–m	15.1	291	8.12
60.0	2	1600	2	5.24	~ 95t	13.7	–	7.45
80.0	2	1400	2	5.57	~ 85t	12.6	237	6.79
100.0	2	1400	2	6.01	~ 80t	11.6	210	6.62
Al_2O_3–ZrO_2 (*pure*) *series*								
7.5	–	1500	2	4.12	~ 90t	17.2	–	5.88
10.0	–	1500	2	4.15	~ 80t	15.8	–	6.73
12.5	–	1500	2	4.22	~ 70t	16.9	–	6.21
15.0	–	1500	2	4.25	~ 50t	17.3	–	5.71
20.0	–	1600	2	–	< 20t	10.1	–	(5.25)
Al_2O_3–ZrO_2 (*plus* 7.5 mol% Y_2O_3) *series*								
20.0	7.5	1600	2	4.46	100c	15.8	–	4.54
40.0	7.5	1600	2	4.89	100c	15.9	–	3.75
60.0	7.5	1600	2	5.28	100c	15.0	–	3.50
80.0	7.5	1600	2	5.63	100c	14.3	–	3.14
100.0	7.5	1600	2	5.95	100c	11.4	–	3.90

*t = tetragonal; c = cubic; tr–m = trace monoclinic.

suggesting that the hardness obeys a linear Rule of Mixtures. The 20 vol% ZrO_2 (pure) composition had an exceptionally low hardness (see Table I). Its high monoclinic-phase content and friable nature suggested that it contained a high density of microcracks. Scanning electron microscope observations adjacent to the hardness indent in this material indicated that the indenter pushed the microcracked material aside as it extended.

3.3. Young's modulus

Fig. 3 reports the Young's modulus values of the Al_2O_3–ZrO_2 (plus 2 mol% Y_2O_3) series obtained from the two resonance techniques.

3.4. Critical stress-intensity factor

Fig. 4a reports K_c as a function of composition for the two series containing Y_2O_3. A considerable increase in fracture toughness could be achieved with the addition of the tetragonal-phase ZrO_2 (series containing 2 mol% Y_2O_3). In contrast, the addition of cubic-phase ZrO_2 lowered the fracture toughness (the series containing 7.5 mol% Y_2O_3). Fig. 4b shows that the peak in K_c for the series that excluded Y_2O_3 corresponds to the maximum retention of the tetragonal phase in this series.

3.5. Strength

Flexural-strength determinations for the series containing 2 mol% Y_2O_3 are shown in Fig. 5. Since it is known that surface grinding can result in compressive surface stresses in these types of materials, a set of specimens were annealed at 1300° C prior to testing to eliminate the transformed surface-layer. Annealing resulted in a lower average strength. It is interesting to note that significant strengthening of Al_2O_3 can be achieved by adding the tetragonal-phase ZrO_2 toughening agent.

4. Discussion

4.1. Retention of tetragonal ZrO_2

Part 1 [1] of this series of papers showed that the critical grain-size for retention of the high-temperature tetragonal structure of ZrO_2 could be increased by increasing the elastic modulus of the constraining matrix and by alloying to decrease

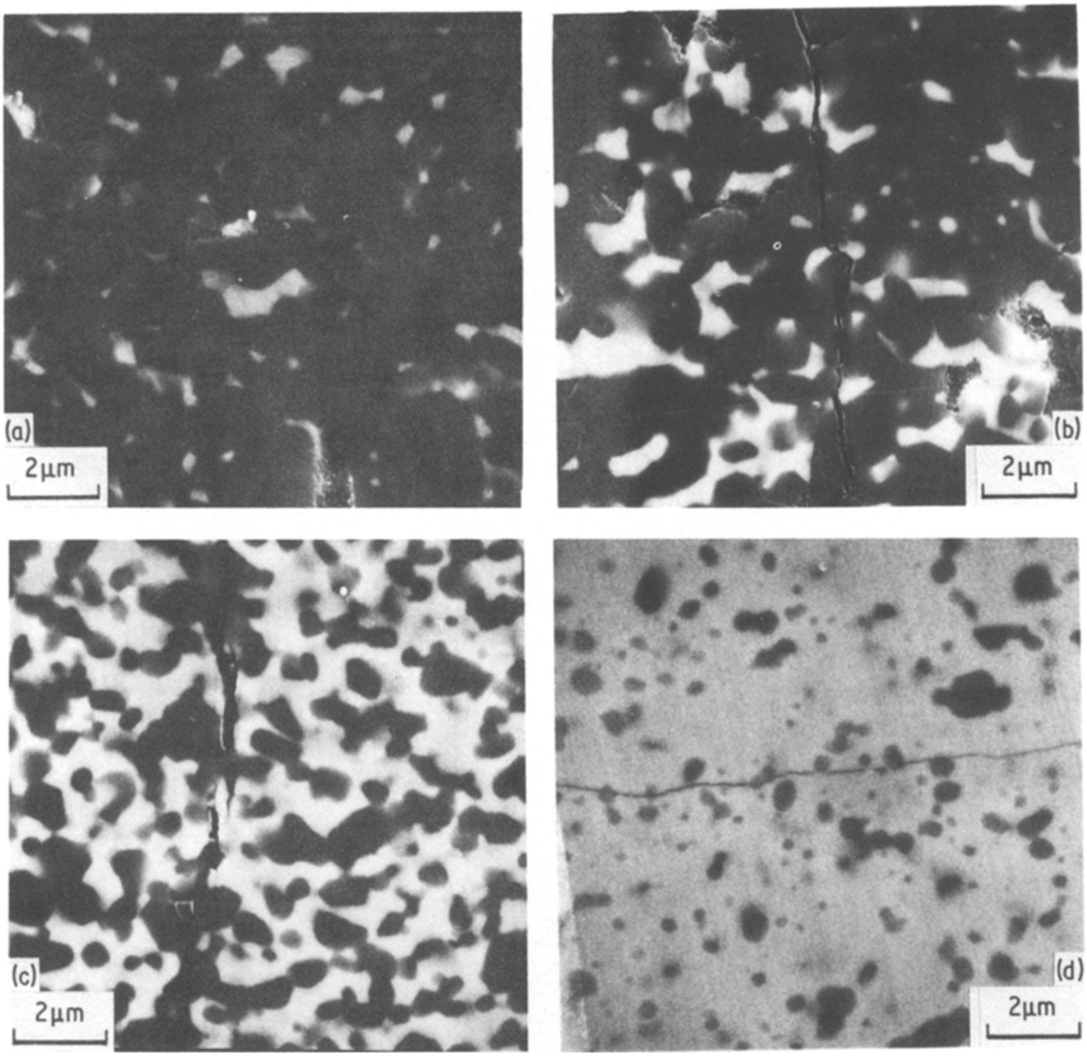

Figure 1 SEM micrographs of polished surfaces of Al_2O_3–ZrO_2 (plus 2 mol% Y_2O_3) composites at ZrO_2 volume-fractions of (a) 0.063, (b) 0.123, (c) 0.45 and (d) 0.80. Al_2O_3 is dark-phase.

the chemical free-energy change. Data presented here are consistent with these theoretical conclusions. Namely, without Y_2O_3 additions, retention of tetragonal ZrO_2 became increasingly more difficult as the elastic modulus of the composite decreased. Additions of 2 mol% Y_2O_3 resulted in tetragonal-phase retention to much larger ZrO_2 volume-fractions, despite the decreased modulus and larger grain-size. Part 3 [3] of this series of papers showed that the critical grain-size for ZrO_2 (plus 2 mol% Y_2O_3) was approximately 0.2 μm when the constraining matrix was ZrO_2. The current study shows that the critical grain-size can be increased to at least 1 μm with the higher modulus of the Al_2O_3–ZrO_2 constraining matrix. In addition, as the composition approached the ZrO_2 end-member, the fraction of tetragonal-phase retained decreased.

4.2. Fracture toughness

Fracture-toughness data presented in Fig. 4 clearly illustrate that the tetragonal-phase is the toughening agent. When cubic ZrO_2 is incorporated into Al_2O_3, the toughness decreases. This may be a result of residual stresses associated with differential thermal expansion. Data for the series which excluded Y_2O_3 indicate that the toughness decreased with increasing monoclinic content.

Part 2 [2] of this series presented an expression for K_c:

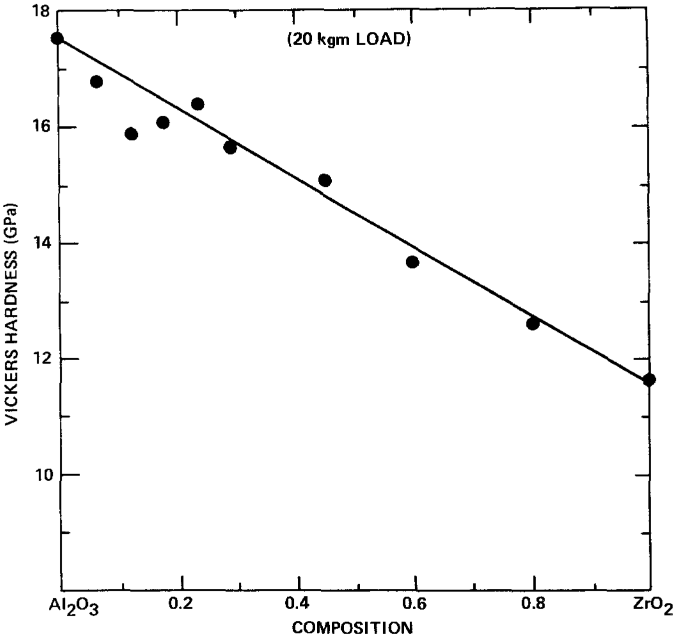

Figure 2 Vicker's hardness (measured at 20 kg) for the Al_2O_3–ZrO_2 (plus 2 mol% Y_2O_3) composite series.

$$K_c = \left[K_0^2 + \frac{2(|\Delta G^c| - \Delta U_{se}f)E_c V_i R}{(1-\nu_c^2)}\right]^{1/2}, \tag{1}$$

where K_0 is the critical stress-intensity factor for the composite without the transformation toughening phenomena, $(|\Delta G^c| - \Delta U_{se}f)$ is the work done per unit volume to stress-induce the transformation, E_c and ν_c are the elastic properties of the composite, V_i is the volume-fraction of the tetragonal-phase ZrO_2 and R is the size of the transformation-zone adjacent to the crack. By using the measured values of K_c for the series containing the tetragonal-phase ZrO_2, the values of K_0 obtained from the series containing cubic-phase ZrO_2, the E_c value from Fig. 3, $\nu_c = 0.25$ and assuming that $R = 1\,\mu m$ (i.e., the average grain-size for this series when $V_i < 60$ vol% ZrO_2), the average value of

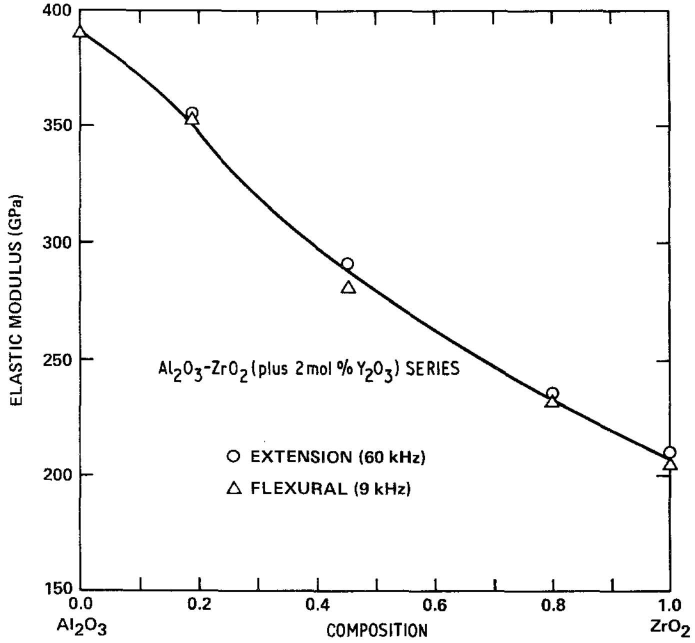

Figure 3 Young's modulus plotted against composition for the Al_2O_3–ZrO_2 (plus 2 mol% Y_2O_3) series.

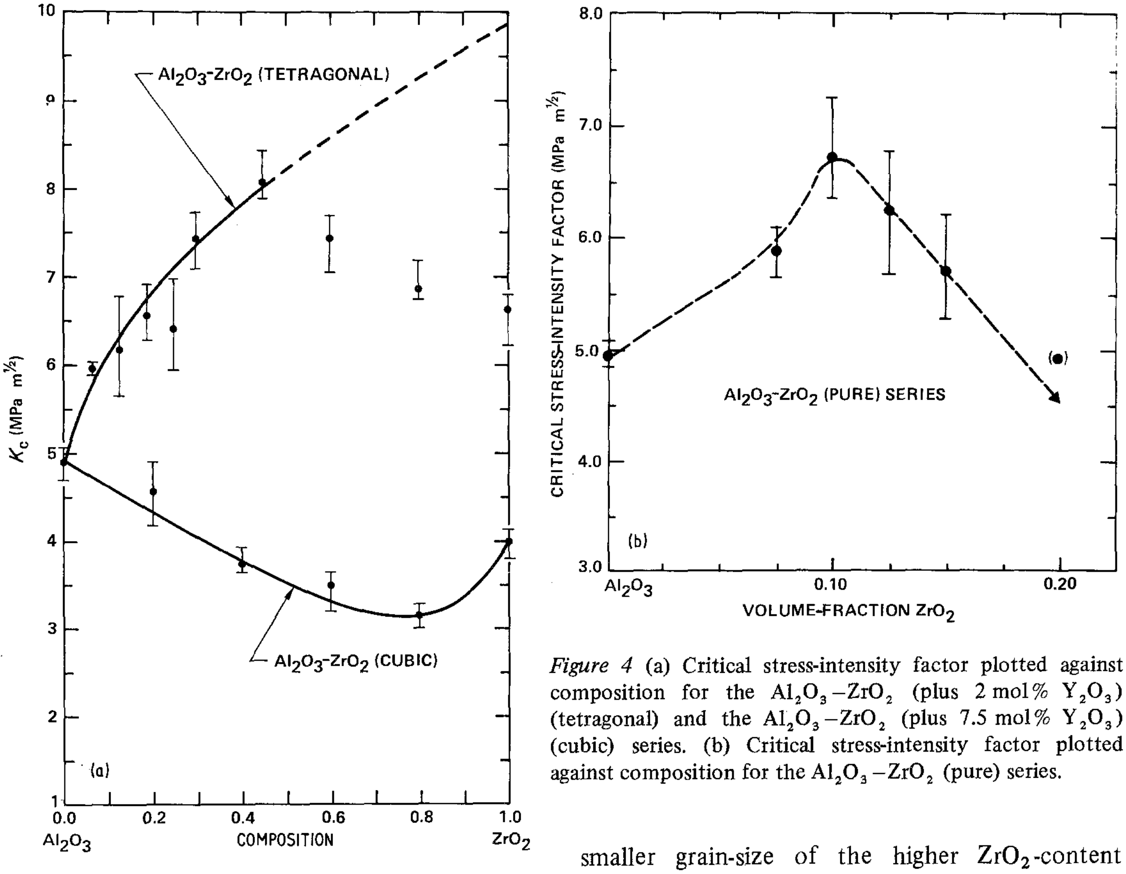

Figure 4 (a) Critical stress-intensity factor plotted against composition for the $Al_2O_3-ZrO_2$ (plus 2 mol% Y_2O_3) (tetragonal) and the $Al_2O_3-ZrO_2$ (plus 7.5 mol% Y_2O_3) (cubic) series. (b) Critical stress-intensity factor plotted against composition for the $Al_2O_3-ZrO_2$ (pure) series.

$(|\Delta G^c| - \Delta U_{se} f)$ was calculated as 188 MJ m^{-3} for compositions containing less than 60 vol% tetragonal-phase ZrO_2. The agreement of the experimental data with this value is shown by the solid line drawn through the $Al_2O_3-ZrO_2$ (tetragonal-phase) data. Although this value is in good agreement with that calculated in Part 3 for the ZrO_2 + 3 mol% Y_2O_3 material (188 compared with 176 MJ m^{-3}), this agreement may be fortuitous since the magnitude of the terms in $(|\Delta G^c| - \Delta U_{se} f)$ are expected to be different for the two systems. Namely, $|\Delta G^c|$ should be greater for the ZrO_2 + 2 mol% Y_2O_3 composition relative to the ZrO_2 + 3 mol% Y_2O_3 composition, and ΔU_{se} should be greater for the higher modulus $Al_2O_3-ZrO_2$ constraining matrix relative to constraint with ZrO_2 alone.

As shown in Fig. 4a, good agreement between theory (Equation 1) and the experimental data is obtained for compositions containing $\leqslant 0.45$ vol% ZrO_2. Poor agreement is obtained at higher volume-fractions. This lack of agreement may be due to the lack of total retention of the tetragonal-phase ZrO_2 when V_i is greater than 60 vol%, the smaller grain-size of the higher ZrO_2-content compositions and/or a compositional difference due to the apparent oxygen deficiency of the ZrO_2 phase (see the Appendix).

4.3. Strength

The strength data presented in Fig. 5 have been analysed to determine their dependence on the experimental K_c values. In this analysis, it was assumed that the crack-size distribution responsible for failure remained unchanged from material to material. With this assumption, the strength of each material should be related to that of any other by a relation that is dependent of their respective critical stress-intensity factor such that

$$\sigma_2 = \frac{K_2}{K_1}\sigma_1, \qquad (2)$$

where σ_1 and σ_2 and the strengths of any two materials and K_1 and K_2 are their respective critical stress-intensity factors. This relation was used, with the average strength and K_c values for the pure Al_2O_3, to obtain the broken line in Fig. 5. As shown, three of the five original sets of data were in good agreement with this

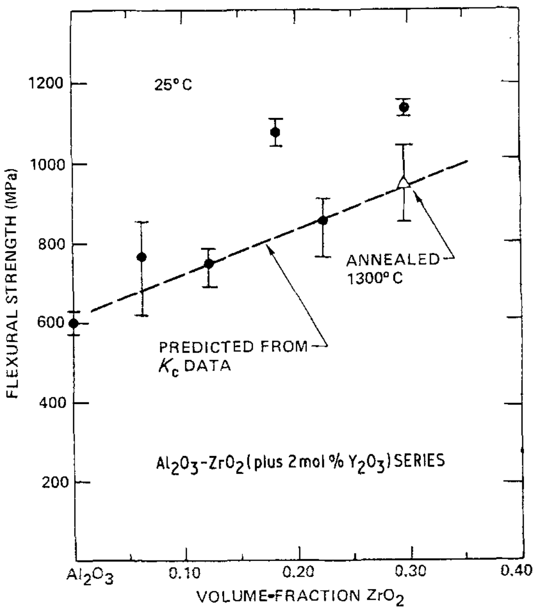

Figure 5 Flexural strength plotted against composition for the Al_2O_3–ZrO_2 (plus 2 mol% Y_2O_3) series.

analysis; however, two of the data sets (V_i = 0.182 and 0.295) were higher than predicted.

Pascoe and Garvie [9] have shown that surface compressive stress arises in materials containing metastable tetragonal ZrO_2 when the transformation at the surface is induced by an abrasion process. The volume increase associated with the transformed surface-layer gives rise to the compressive stresses. Since each set of specimens was independently surface ground it was suspected that several of these sets (the two that resulted in the higher values) may have received sufficient surface damage to impart enough surface compressive stress to increase their strength. To test this hypothesis, the effect of surface abrasion on strength was examined. Although the principal results of this work will be reported elsewhere [10], it was shown that when the abrasively-ground specimens were annealed at 1300° C to eliminate the transformed surface layer, the average strength was lowered to that expected from Equation 2. These data are shown by the open triangle in Fig. 5.

It can be concluded that the strength of the Al_2O_3–ZrO_2 (plus 2 mol% Y_2O_3) composite materials increases in a way proportional to their increase in K_c values, as expected. Additional strengthening can be obtained by compressive stressing the surfaces through abrasion. Studies are currently underway to characterize and optimize the abrasion phenomena.

Acknowledgements

The careful technical services of Mr M. G. Metcalf are deeply appreciated. The author also wishes to acknowledge the valuable discussions with Dr D. R. Clarke and Dr D. J. Green. Thanks are due to Dr B. R. Tittmann and Mr E. H. Cirlin for the elastic modulus measurements. This work was supported by the Office of Naval Research under Contract number N00014-77-C-0441.

Appendix: Formation of surface cracks during the hot-pressing of Al_2O_3–ZrO_2 composites

As indicated in the text, Al_2O_3–ZrO_2 composites containing greater than 30 vol% ZrO_2 hot-pressed in graphite dies were observed to contain large surface cracks. Although the exact cause of the stresses that give rise to these cracks is beyond the scope of the present work, the experimental observations indicate a probable cause.

The colour of hot-pressed Al_2O_3–ZrO_2 composite billets changes from a light grey to black as the ZrO_2 volume-fraction increased to 1. A colour gradient also exists within a sectioned billet, darker on the outside, lighter near the centre. This colour gradient indicates a compositional gradient. Black ZrO_2 can also be produced at high temperatures in vacuum and ZrO_2 is known to lose oxygen in high-temperature low-oxygen content environments [11].

X-ray diffraction examination did not reveal phases other than the ZrO_2 structures indicated in the text (Table I). Surface and interior phases were the same (precise lattice-parameter measurements were not performed).

Oxidation in air at 1300° C transformed the grey-to-black specimens to pure white. Specimens oxidized for short periods revealed, when sectioned, a dark core. Oxidation resulted in moderate to severe surface spalling for compositions containing greater than 30 vol% ZrO_2. The 100 vol% ZrO_2 specimens could be completely oxidized in 15 min at 750° C due to severe cracking.

The above evidence suggests that the dark colour is consistent with an oxygen-difficient ZrO_2-phase. Ruh and Garrett [12] have shown that the oxygen-difficient ZrO_2 has a smaller molar volume. Thus, a gradient in the oxygen-content of the ZrO_2-phase from the billet surface to its interior would result in surface tensile stresses at the fabrication temperature. With a sufficient volume-fraction of ZrO_2 (e.g.,

> 30 vol%), these tensile stresses could be significant enough to produce surface cracks. Similarly, oxidation would increase the molar volume of the depleted phase to produce surface compressive stresses and surface spalling [12].

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Received 12 May
and accepted 18 June 1981