

# Thermal processing and properties of highly homogeneous alumina-zirconia composite ceramics

WILLIAM C. MOFFATT\*, H. KENT BOWEN

*Ceramics Processing Research Laboratory, Materials Processing Center,  
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA*

Alumina-zirconia composites were made using a novel processing technique involving nonsolvent precipitation of a dilute polymer solution containing dispersed ceramic powder particles. Seven identical alumina-nominally 15 wt% zirconia composite green bodies were fired at different temperatures. An optimal firing temperature of 1500°C was found, above and below which sample fracture strengths, densities, and tetragonal zirconia contents were lower. Fracture strengths correlated well with porosity. An alumina-14.06 wt% (zirconia-1.35 mol% yttria) composite had excellent resistance to abnormal grain growth upon high-temperature annealing. The tetragonal zirconia content increased with increasing annealing time; this was attributed to the equilibration of zirconia particles with widely varying yttria concentrations.

## 1. Introduction

Many studies of the processing of composite materials have had the goal of uniformly distributing second-phase particles in a matrix material. This is because uniform particle distribution is thought to lead to better properties and higher reliability than would be achieved with less uniform distribution.

Various paths have been taken to produce composite ceramics in the past. Techniques used in the alumina-zirconia system, in particular, have included the milling of powders in air, water, or other liquids [1-7]; oxidation or decomposition of soluble, often organic, ceramic precursors [1, 8-11]; heterocoagulation of sols [12]; and the high-shear mixing of flocced sols [13]. Some powders have been consolidated wet, using slip casting [13, 14] or centrifugal casting [12]; others have been consolidated dry [1, 3-8, 11], often by hot pressing [1, 6-8]. Consolidation techniques have generally not been well integrated with powder production or mixing techniques.

A rapid, flexible technique for producing uniform composite ceramics has been developed at the Ceramics Processing Research Laboratory, based on nonsolvent precipitation of dilute polymer solutions containing co-dispersions of ceramic powders. Preliminary results for the alumina-zirconia system are given by Moffatt and Bowen [15]. The effects of varying the zirconia content and zirconia phase chemistry of alumina-zirconia composites produced in this way on the composites' mechanical properties are described by Moffatt *et al.* [16].

This paper describes the effects of variations in the thermal processing of alumina-zirconia composites produced using this nonsolvent precipitation tech-

nique in their microstructures, phase structures, and mechanical properties. The paper is divided into two parts, the first of which details the effects of variations in firing temperature on the properties of a series of identical green bodies. The second part details the effects of high-temperature anneals of varying duration on the properties of a fired body.

## 2. Experimental details

### 2.1. Specimen production and characterization

Alumina-zirconia composite ceramics were made in the following way. A 0.333 wt% water solution of polyvinyl alcohol (mol. wt = 14 000, Aldrich Chemical Co., Milwaukee, Wisconsin) was filtered through a 10 to 20  $\mu\text{m}$  glass frit. Some of the filtered solution, 400 ml, was poured into a polypropylene bottle under a laminar-flow hood, and 40 g of an appropriate mixture of alumina (Sumitomo AKP-HP, Sumitomo Chemical America, New York), zirconia (Toyo Soda TZ-O, Toyo Soda USA, Atlanta, Georgia), and zirconia-yttria (Toyo Soda TZ-3Y) powders was then added. The bottle's contents were adjusted to pH 2 to 3 with 0.3 ml concentrated nitric acid, and ultrasonically agitated (Model W-220F Sonicator Cell Disruptor, Heat Systems Ultrasonics, Inc., Farmingdale, New York) at high power (100 W) for 8 min. This agitation significantly warmed the slurry. The bottle containing the slurry was resealed, and the contents were allowed to gravitationally settle for 24 h.

The middle 300 ml of the supernatant was removed using a cannulation procedure at a rate of about 5 ml  $\text{sec}^{-1}$ . Filtered air (0.1  $\mu\text{m}$  filter) was used as the cover gas during cannulation. The cannulated supernatant

\*Present address: Superconductivity Research Laboratory, Shinonome 1-10-13, Koto-Ku, 135 Tokyo-To, Japan.

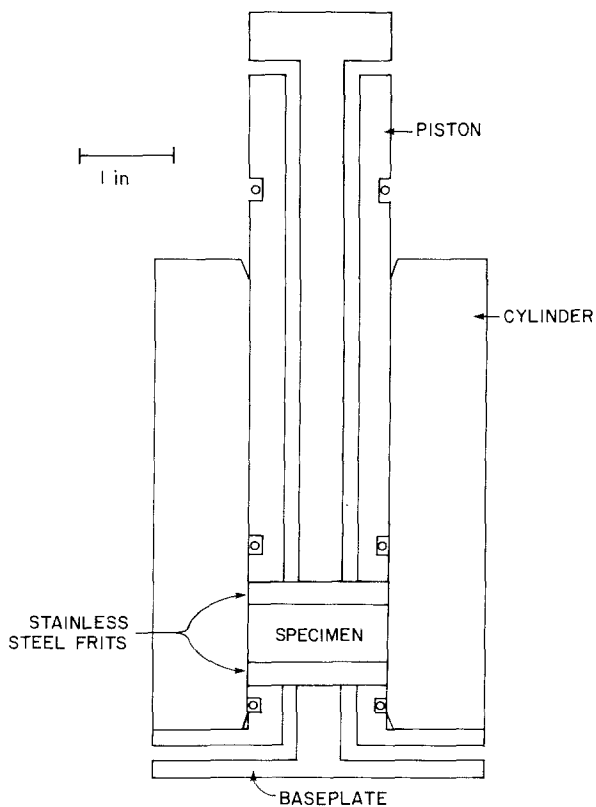


Figure 1 Fritted press.

was homogenized before further use. It was then flocculated with 375 ml filtered reagent-grade acetone. The flocculated slurry was allowed to stand for 15 min, and was then poured onto a 100-mesh stainless steel screen.

The retained flocs were scooped into a colloid press (Fig. 1), where they were consolidated at a pressure of 35 MPa over a period of 15 to 30 min. The sample was held in the press for 30 min after the press came to equilibrium, then was ejected from the press, dried at 60 to 80°C in laboratory air, and cold isostatically pressed at 280 MPa. The green density was typically 57 to 58% of theoretical, and the volume of the green body was typically 15% of the volume of the flocs from which it was pressed. Binder burnout and bisque firing were accomplished by ramping the specimen at 2°C min<sup>-1</sup> from room temperature to 600°C and at 5°C min<sup>-1</sup> from 600 to 1200°C. A flow chart of this processing route is given in Fig. 2.

Some fired samples were machined into 2 mm × 1.5 mm × 25 mm bend specimens, which were mechanically tested using a four-point jig having an inner span of 10 mm and an outer span of 20 mm. The cross-head displacement rate was 0.025 cm min<sup>-1</sup> (stress rate ~ 50 MPa sec<sup>-1</sup>). Weibull plots and probability of failure–fracture strength plots were constructed from the fracture data. Fracture toughnesses of the specimens were determined for polished surfaces using the microindentation technique described by Evans and Charles [17]. Surface-grinding alumina–zirconia composite ceramics can result in residual compressive surface stresses as high as 1 GPa [18], which can interfere with fracture toughness determinations [19–21]. The normal grinding and polishing stresses in this study were kept to < 50 kPa to mini-

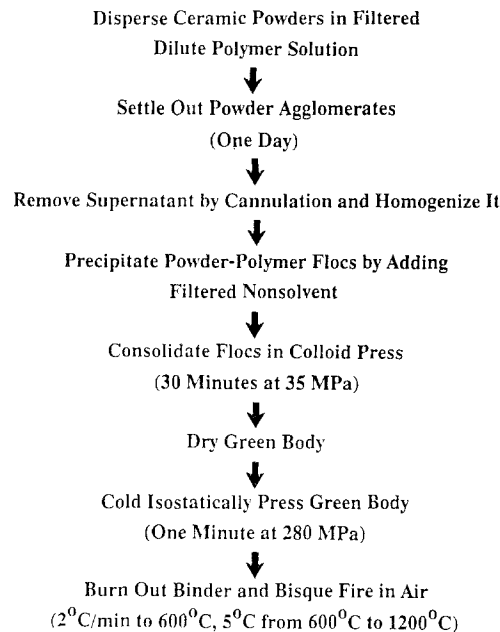


Figure 2 Flow chart of defect-resistant processing technique.

mize surface damage, and an indentation load of 10 kg was applied to ensure fully developed cracks. Indentations were made using a Vickers diamond pyramid indenter attached to an Instron machine with an indenter displacement rate of 0.005 cm min<sup>-1</sup> and a hold time after loading of 1 min; the load typically relaxed less than 10% during the hold period. Five indents were made on each sample. The tetragonal zirconia fractions were determined from X-ray diffraction analysis, which involved the relative monoclinic and tetragonal phase integrated X-ray peak areas [22] as determined from samples with polished surfaces. Chemical analyses of the specimens were obtained using a Hitachi S-530 scanning electron microscope (Hitachi Scientific Instruments, Nissei Sangyo America, Rockville, Maryland) fitted with an EG&G ORTEC Model 7938-4ST Si (Li) X-ray Detector, and EG&G ORTEC System 5000 spectral analysis software (EG&G ORTEC, Inc., Oak Ridge, Tennessee).

## 2.2. Effect of thermal history on properties

Seven billets containing 14.98 wt % zirconia were produced using the procedure described above. These were fired in vacuum for 2 h at 1300, 1350, 1400, 1450, 1500, 1550, and 1600°C, respectively. Ten bend bars were machined from each of the fired specimens. The fracture strength, indentation fracture toughness, and tetragonal zirconia fraction were determined as described above.

Weibull plots of the specimens tested are shown in Fig. 3a for the fired billets; probability of failure/fracture strength plots for the same billets are shown in Fig. 3b. Fig. 4 shows the average fracture strengths and Weibull moduli for the samples tested. The fracture strengths are quite high for alumina–zirconia composites produced without hot-pressing. The maximum in Fig. 4 may be interpreted as follows: below 1500°C the specimens are probably not fully densified; above 1500°C rapid grain growth may stop sintering short of theoretical density.

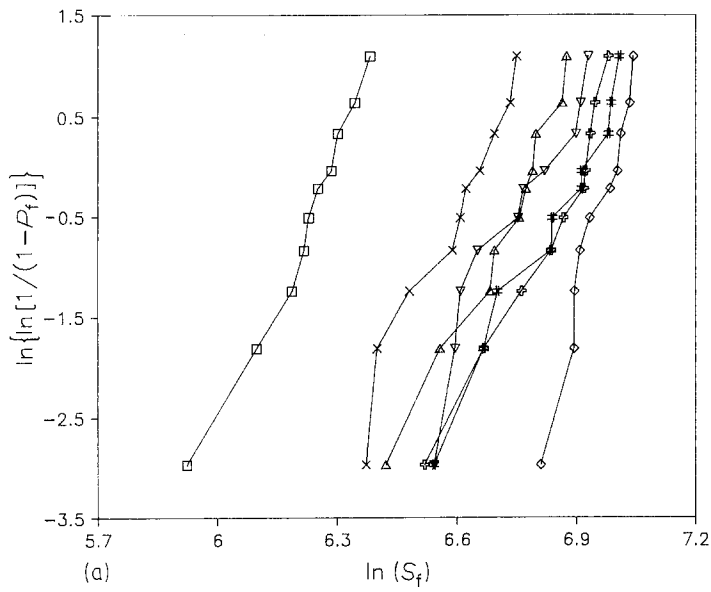


Figure 3 Alumina-nominally 15.0 wt % zirconia composites fired at various temperatures: (a) Weibull plots, and (b) probability of failure/fracture strength plots. Time 2 h, temperature: (□) 1300°C, (×) 1350°C, (▽) 1400°C, (#) 1450°C, (◇) 1500°C, (⊖) 1550°C, (△) 1600°C.

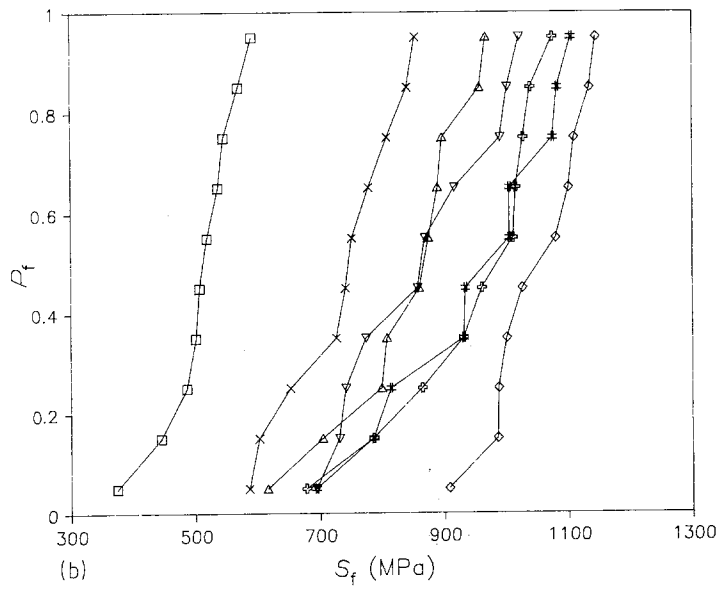
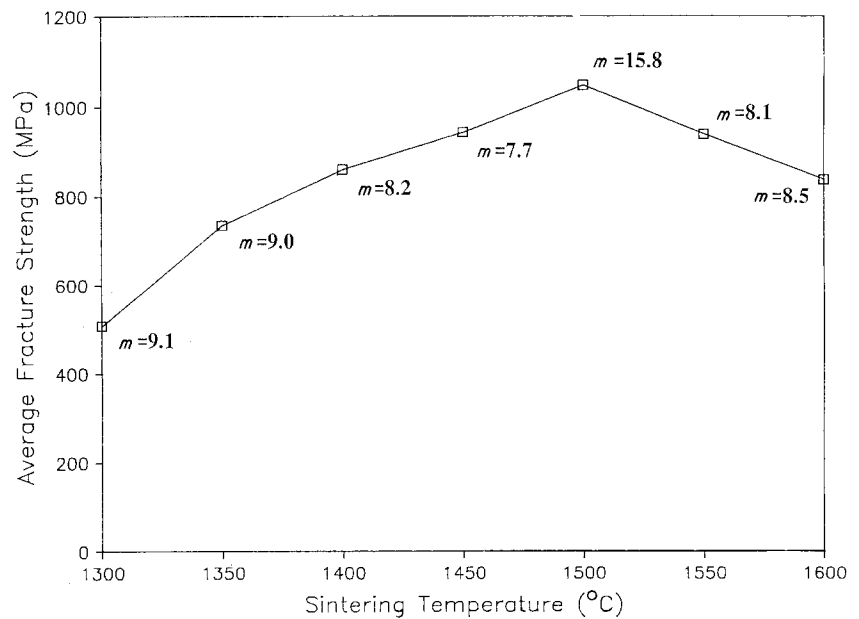


Figure 4 Average fracture strength plotted against sintering temperature for alumina-nominally 15.0 wt % zirconia samples ( $m$  = Weibull modulus).



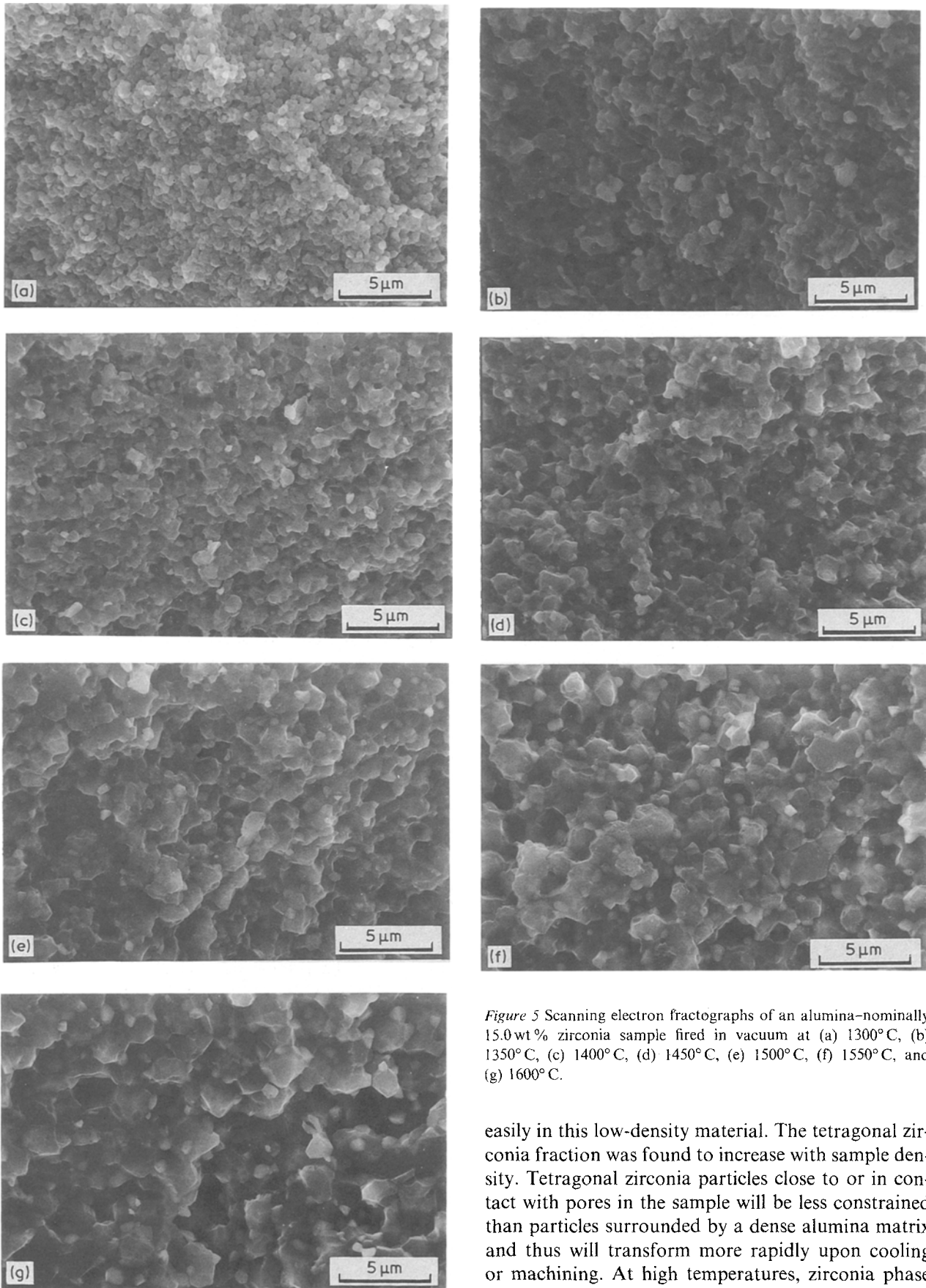


Figure 5 Scanning electron fractographs of an alumina-nominally 15.0 wt% zirconia sample fired in vacuum at (a) 1300°C, (b) 1350°C, (c) 1400°C, (d) 1450°C, (e) 1500°C, (f) 1550°C, and (g) 1600°C.

The fracture strengths, Weibull moduli, fracture toughnesses, and tetragonal zirconia fractions of these specimens are reported in Table I. No fracture toughness determination could be made for the sample fired at 1300°C because the cracks at the corners of the microindentations were too diffuse to be measured

easily in this low-density material. The tetragonal zirconia fraction was found to increase with sample density. Tetragonal zirconia particles close to or in contact with pores in the sample will be less constrained than particles surrounded by a dense alumina matrix and thus will transform more rapidly upon cooling or machining. At high temperatures, zirconia phase coarsening may lead to increased monoclinic zirconia content.

Figs 5a to g show scanning electron fractographs of samples sintered at selected temperatures ranging from 1300 to 1600°C. A scanning electron micrograph of a polished section of the material in Fig. 5e is shown in Fig. 6. It is clear from these figures that fine zirconia particles are located at grain corners, and that the distribution of these particles is very homogeneous.

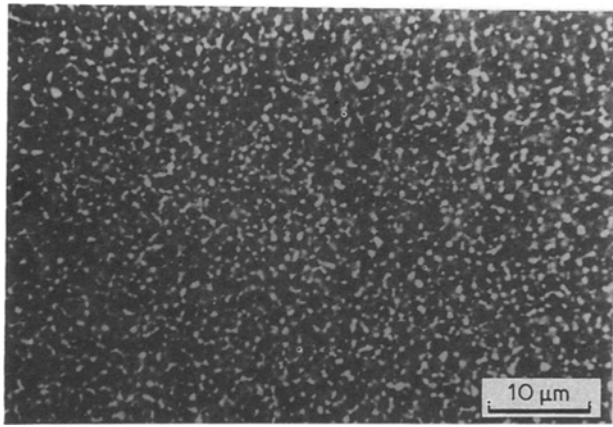


Figure 6 Scanning electron micrograph of a polished section of an alumina-nominally 15.0 wt % zirconia sample fired at 1500°C in vacuum.

The effect of variations in fired sample density on the fracture strengths of the materials in this series is shown in Fig. 7. Samples fired both above and below the optimal firing temperature are seen to have the same dependence of fracture strength on fired density. The sharp rise in strength at high fired densities is consistent with the reported exponential dependence of the fracture strength of alumina on porosity [23]. A semilogarithmic plot of fracture strength against porosity is shown in Fig. 8. The least squares data fit to the points given has a slope of  $-3.56$ , well within the range of values reported in the literature for pure alumina [24–26]. The strengths seen here are, however, substantially higher than those found in the studies on alumina. This may be due to the small grain size of the alumina-zirconia composites. It seems that the dependence of fracture strength on porosity arises from largely material-independent geometrical considerations.

### 2.3. Effect of high-temperature annealing on properties

An alumina-14.06 wt % (zirconia-1.35 mol % yttria) sample was made using the defect-resistance processing technique. The green body was broken into five

TABLE I Properties of  $\text{Al}_2\text{O}_3$ -14.98 wt %  $\text{ZrO}_2$  composites fired at various temperatures

Firing temperature (°C)	Fracture strength (MPa)	Weibull modulus	Fracture toughness ( $\text{MPa m}^{1/2}$ )	Tetragonal zirconia fraction
1300	508(10)*	9.1	—	$0.21 \pm 0.02$
1350	734(10)	9.0	$5.02 \pm 0.09(5)^\dagger$	$0.38 \pm 0.04$
1400	860(10)	8.2	$4.98 \pm 0.13(5)$	$0.49 \pm 0.05$
1450	943(10)	7.7	$5.13 \pm 0.20(5)$	$0.46 \pm 0.05$
1500	1048(10)	15.8	$4.69 \pm 0.16(5)$	$0.58 \pm 0.06$
1550	939(10)	8.1	$5.19 \pm 0.25(5)$	$0.58 \pm 0.06$
1600	838(10)	8.5	$4.92 \pm 0.15(5)$	$0.49 \pm 0.05$

\*Numbers in parentheses indicate the number of bend bars tested.  
 $^\dagger$  Numbers in parentheses indicate the number of indents made.

pieces, which were then prefired as described above and fired for 2 h at 1500°C under vacuum. The pieces were subsequently annealed at 1600°C for 0, 1, 3, 9, and 27 h, respectively. The fracture toughnesses and tetragonal zirconia fractions, determined as described above, are reported in Table II. Scanning electron micrographs of polished sections of these specimens are shown in Figs 9a to e. The microstructures were highly resistant to exaggerated grain growth and grain-boundary breakaway from second-phase particles upon high-temperature annealing.

The intermediate yttria content of this alumina-zirconia-yttria composite ceramic was achieved using a mixture of two zirconia powders: one with no yttria, the other with a high yttria content. As a result of this processing approach, the yttria content of the individual zirconia particles could be expected to vary between the two extremes of 0.0 mol % yttria and 3.0 mol % yttria. Only the high-yttria/zirconia particles are expected to retain the tetragonal structure upon cooling from the sintering temperature to room temperature. High-temperature annealing would cause the yttria in high-yttria/zirconia particles to diffuse to low-yttria/zirconia particles. In addition, grain growth in the alumina matrix would bring about zirconia particle impingement and coalescence. An increase in the volume fraction of zirconia particles containing enough yttria to resist transformation to

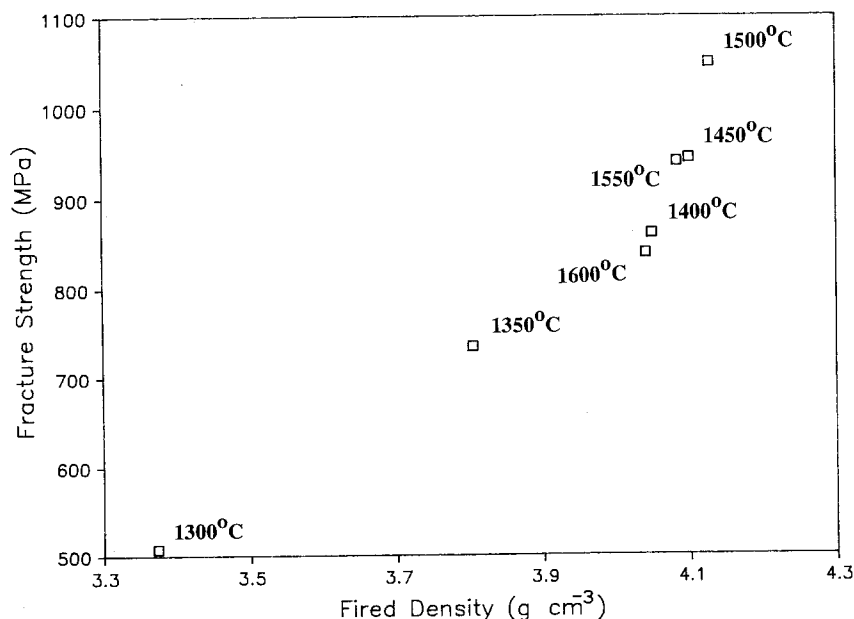


Figure 7 Dependence of fracture strength on density for alumina-nominally 15.0 wt % zirconia composites.

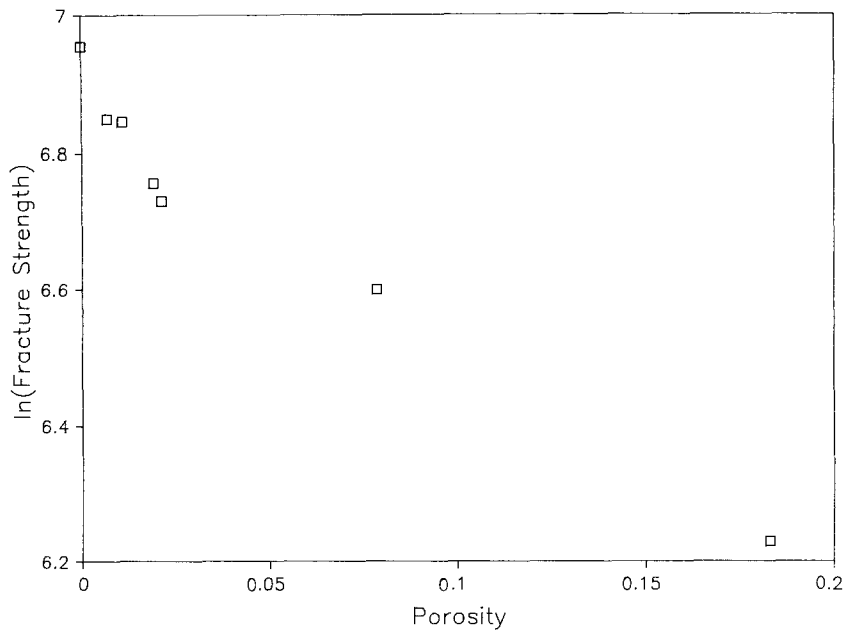
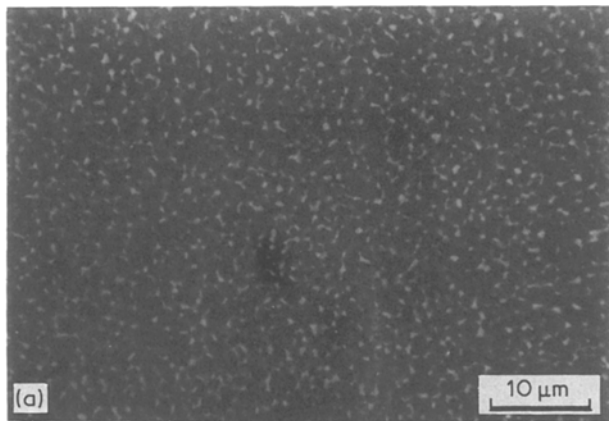


Figure 8 Dependence of fracture strength on porosity for alumina-nominally 15.0 wt % zirconia composites.



the monoclinic structure upon cooling to room temperature is thus expected. This is consistent with the tetragonal zirconia fractions found experimentally after high-temperature anneals of various lengths.

### 3. Conclusions

When alumina-15 wt % zirconia composites processed as described above were fired at different tempera-

Figure 9 Scanning electron micrograph of a polished surface of an alumina-14.06 wt % (zirconia-1.35 mol % yttria) sample fired at 1500°C (a), and annealed at 1600°C for (b) 1 h, (c) 3 h, (d) 9 h, or (e) 27 h.

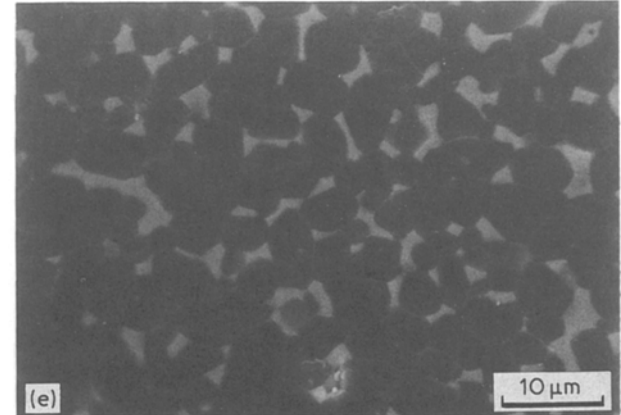
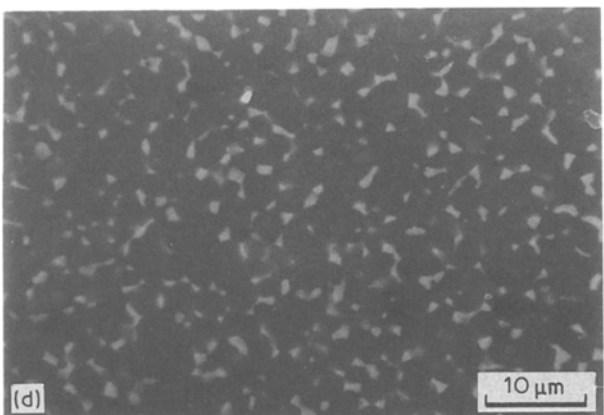
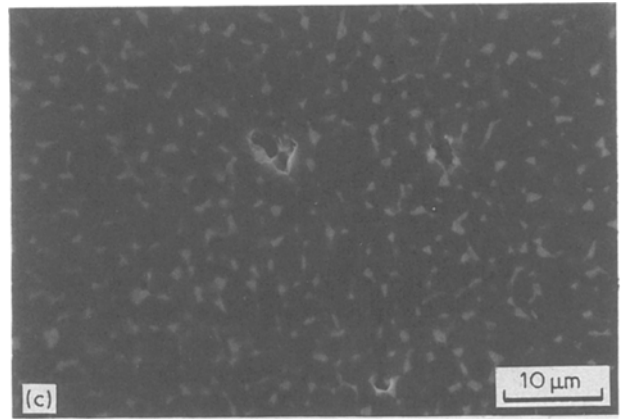
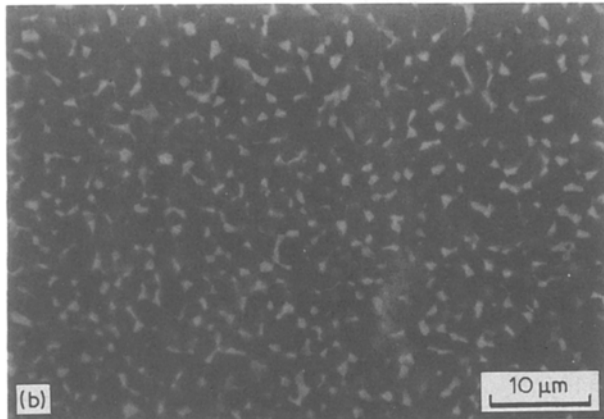


TABLE II Properties of Al<sub>2</sub>O<sub>3</sub>-14.06 wt % (ZrO<sub>2</sub>-1.35 mol % yttria) composites annealed at elevated temperature

Time (h) at 1600°C	Fracture toughness (MPa m <sup>1/2</sup> )	Tetragonal zirconia fraction
0	4.98 ± 0.20(5)*	-
1	4.98 ± 0.09(5)	0.35 ± 0.04
3	5.05 ± 0.16(5)	0.39 ± 0.04
9	5.04 ± 0.08(5)	0.57 ± 0.06
27	5.55 ± 0.25(5)	0.85 ± 0.09

\*Numbers in parentheses indicate the number of indents made.

tures, an optimal firing temperature of 1500°C was found. Fracture strengths, densities, and tetragonal zirconia contents were lower both above and below this temperature. Fracture strengths correlated well with porosity.

An alumina-14.06 wt % (zirconia-1.35 mol % yttria) composite processed as described above had excellent resistance to abnormal grain growth upon high-temperature annealing. The tetragonal zirconia content increased with increasing annealing time; this was attributed to the equilibration of zirconia particles with widely varying yttria concentrations.

### Acknowledgements

This research was supported by the Air Force Office of Scientific Research under Contract no. F4962-0084-0097. Portions of this paper were presented at the First International Conference on Ceramic Powder Processing Science (11/1-4/87, Orlando, Florida, pp. 645-53 in Proceedings) and at the World Congress on High-Tech Ceramics (6/86, Milan).

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Received 13 December 1988  
and accepted 31 January 1989