Journal of the European Ceramic Society 20 (2000) 1085–1090

Zirconia toughened aluminas by hydro-thermal processing

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Received 3 March 1999; received in revised form 27 September 1999; accepted 6 October 1999

Abstract

Zirconia toughened alumina materials have been produced by a hydro-thermal powder synthesis route. The resultant sols were concentrated using filtration to form extrudable pastes. The extruded products when dried and sintered had uniform microstructures with improved mechanical properties compared to pure mono-phase rods produced by a similar route. The zirconia particles produced by hydro-thermal synthesis were too small to give the optimum toughening effect, as the zirconia phase is undoped. Two alternative methods were investigated in order to increase the zirconia grain size in the finished body. The hydrothermally synthesized zirconia was freeze-dried to increase the flock size before mixing with the alumina sol and a commercial monoclinic zirconia powder was added to the alumina sol prior to concentration. The improvements in mechanical performance correlated well with theoretical predictions. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3, ZrO_2; Composites; Extrusion; Hydro-thermal processing

1. Introduction

Interest in nano-composites has increased over recent years as authors claim greater resistance to corrosion and increased mechanical properties. Nano-composites that have perhaps a longer history than most are chemical zirconia toughened alumina (ZTA) "nano-composites". The methods for forming such a system are wide and varied. Traditional methods of mixing and milling have been commonly applied, but tend not to yield ideal phase distributions. There are a number of methods available to create finer powders and to produce ZTA materials from combined precursor treatments. Co-precipitation[1] and sol–gel synthesis[2] methods have emerged as the front runners for such preparations. Problems have arisen with many preparations because of the intermediate processing steps, which follow the initial formation of the powders. Some processes, in particular milling, increase the impurity level. Rabih et al.[3] suggested that these problems can be overcome by combining hydro-thermal processing with co-precipitation. Here, the potential of producing effective ZTAs by the use of hydro-thermally prepared alumina and zirconia sols is reported. Hydro-thermal synthesis of alumina and zirconia has been reported previously.[4] Though it is most common to dry the powders produced and then process by conventional methods, it may be advantageous, to produce the ceramic from the precursor without resorting to this intermediate drying process. In this study we concentrated on the development of a totally wet process to obtain the green component, in an attempt to improve mechanical properties. Initially studies were carried out on how to combine the two sols most effectively, then on the control of the zirconia grain size.

2. Materials formulations

ZTA research[5] has shown that the optimum composition lies in the range of 10–20 vol% zirconia. Two compositions can be considered. The zirconia can either be unstabilized or partially stabilized with another oxide, normally Y_2O_3. The grain size of zirconia is critical to the selection of the formulation, the powders must typically be below 1 μm for unstabilized and below 5 μm for stabilized zirconia (depending on composition).[6] It has been shown by modelling and experimental work that the optimum grain size for unstabilized zirconia is 0.45 μm.[2,7] For this series of

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PII: S0955-2219(99)00274-5

experiments the preparation method was designed to give unstabilized zirconia particles with grain sizes of below 1 μm in the finished product, present at a concentration of 15 vol%. The process route is summarized in the block diagram shown in Fig. 1.

3. Powder precursor formation

3.1. Alumina

The alumina phase was prepared from basic aluminium acetate (Aldrich Chemical Co. Ltd.) following the work of Kilbride and Barker[8] and Conder et al.[9] Modifications to their process were made in order to minimize the size of the particles produced. Three hundred and seventy-five grams of aluminium acetate were mixed with 2765 ml of de-ionized water and 235 ml of ammonia (BDH, Analar, sp. gr. 0.88) and heated for 50 min at 200°C at autogenous pressure in a 4 l Baskerville Hasteloy C-276 autoclave. Thermocouples and pressure transducers instrumented the equipment. In order to give optimal results the material had to be stirred during the reaction. A boehmite (γ-AlOOH) gel resulted with pH 6.8 after cooling. It was analyzed by TEM to establish that the required particle size and dispersion had been achieved.

3.2. Zirconia

The zirconia phase was prepared in the PTFE liner of a smaller autoclave (Berghof GmbH) with a capacity of 250 ml. One hundred millilitres of a zirconium acetate solution (MEL Chemicals, 22.5 wt% Zr-acetate in acetic acid) was diluted with an equal volume of de-ionized water. The solution was heated for 2 h at 200°C. After cooling the resultant sol had a pH of 2.3.

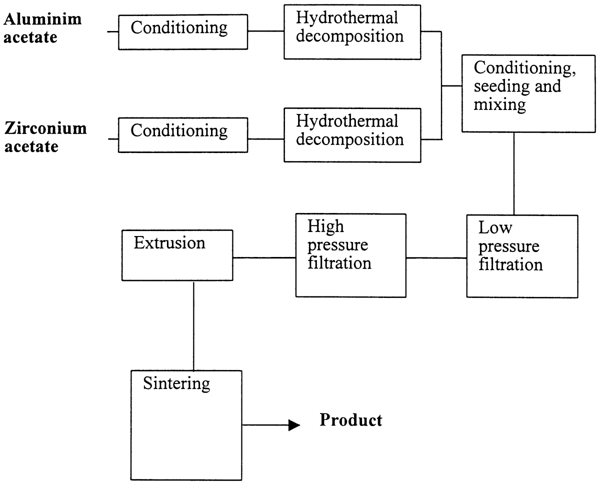


Fig. 1. Process diagram.

4. Mixing and sintering trials

Preliminary trials were carried out to establish the optimum conditions for mixing the two hydro-thermally derived components:

1. Both sols were mixed without further conditioning giving a suspension of pH 5.9. The two components were mixed by hand with a spatula or ball-milled for 2 h in a polypropylene bottle with zirconia media.
2. Both sols were adjusted to pH 9.5 before mixing and then ball-milled for 2 h.
3. The boehmite sol was adjusted to pH 3.1, mixed with the zirconia sol, then ball-milled for 2 h.

The optimum procedure was found to be the conditioning of the two sols to pH 9.5 by the addition of ammonia solution and mixing by ball mill.

The boehmite was seeded with 5 wt% fine α-alumina (Baikalox, SM8, d_{50} <1 μm) to prevent the formation of a vermicular structure during sintering.[8] In addition, it was found that adding 1% of glycerol (BDH, Analar) to the blend improved the surface finish of the later formed extrudate.

Sintering temperatures of 1250, 1400, 1500, 1550 and 1600°C in air with heating rates of 3°C/min and dwell times of 1 h were tried. The most uniform microstructure and highest strength resulted from sintering at 1550°C. This temperature was chosen for the following work.

5. Preparation of extrudable pastes

From the initial trials it was established that the fracture toughness of the ZTA had not improved to the degree reported by some workers. In order to establish the influence of the zirconia morphology on the composite properties, three ZTA compositions and a control alumina were prepared.

The selected ZTA compositions all contained 15 vol% unstabilized zirconia. ZTA(1) contained the products as prepared in the autoclaves conditioned to pH 9.5. The solids content of each sol was established by drying representative samples and calculating the slurry ratios. For ZTA(2), hydro-thermally derived zirconia sol was freeze-dried in an attempt to increase its agglomerate size. ZTA(3) consisted of a commercial unstabilized zirconia (Mandoval, DK2) milled with zirconia media for 36 h to a d_{50} of $\sim$1 μm.

After dispersing the α-alumina phase in a small amount of water and mixing it and the glycerol into the boehmite sol, the resultant blend was divided into four equal parts. The conditioned zirconia sol, the freeze-dried and the commercial zirconia were each added to one of the parts, leaving the fourth as a comparative alumina control. The four compositions were ball-milled for 2 h using zirconia media in propylene bottles to produce homogeneous blends.

As much liquid as possible was removed by conventional vacuum filtration using No. 1 Whatman filter paper in a Büchner funnel. This produced a soft extrudable material in all cases containing about 40 wt% solids, but the extrudates had poor shape retention properties. Further liquid was removed by high pressure filtration. A schematic of the equipment used is shown in Fig. 2. Load was applied cyclicly to a maximum of 70 kN for a period of 20 min with a cross-head speed of 1 mm/min. The filter cakes were turned over and repressed to give more uniform moisture distributions. The resultant filter cakes contained around 30 wt% liquid and were extruded into rods of about 3.3 mm diameter. After drying at room temperature, they were sintered at 1550°C for 1 h in all cases.

6. Dispersion analysis

TEM analysis of the three ZTAs before sintering showed that the alumina morphology had been unaffected by the conditioning. The average alumina grain size being platelets of 30 nm diameter and 5–10 nm thickness. The zirconia in ZTA(1) formed 80–150 nm diameter clusters of very fine equi-dimensional particles (~3 nm). ZTA(2) showed similar but possibly larger clusters, while ZTA(3), as expected, showed dense crystalline fragments of zirconia particles. These three powder dispersions are shown in Fig. 3.

7. Micro-structural evaluation

Sintered extrudates of the four batches were polished parallel and perpendicular to the extrusion direction and thermally etched at 1400°C for 1.5 h to make the

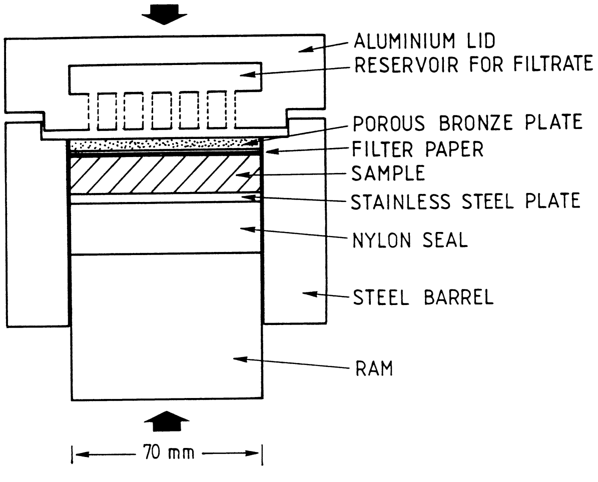


Fig. 2. High pressure filtration unit used in the concentration of the mixed sols produced by hydrothermal decomposition.

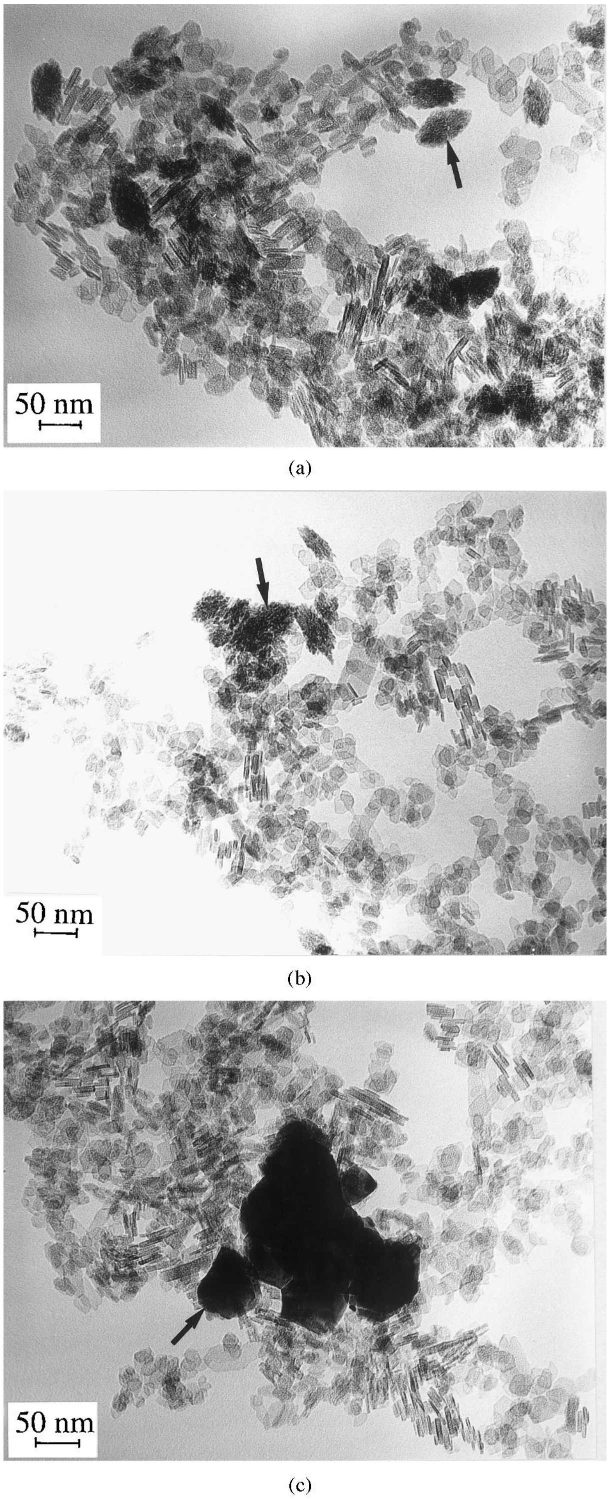


Fig. 3. TEM micrographs of the ZTA precursor powders, (a) being produced from a mixture of hydrothermally processed alumina and zirconia, (b) being formed from a mixture of the alumina sol and the freeze dried zirconia sol and (c) being a mixture of the alumina sol and a commercial zirconia powder. Arrows indicate Zirconia clusters or particles, the boehmite formed platelets.

grain boundaries visible. The SEM images of Fig. 4 show uniform distribution of zirconia in the three ZTA compositions and low porosity in formulations ZTA(1) and ZTA(2). A lower magnification of ZTA(3) is shown in Fig. 5. In all cases, grain growth of alumina was much reduced compared to the pure alumina system due to the blocking of alumina grain growth by the well-dispersed zirconia. Others[1,10] report this phenomenon. The grain sizes of the products were determined using the linear intercept method[11] and the results are given in Table 1. The pure alumina extrudate had a mean particle size of 3.17 μm while in the ZTAs the alumina grain sizes averaged 0.86 μm. The zirconia grain size followed the desired increase with the variations in addition method, ranging from 0.38 μm in the hydro-thermal sol preparation to 0.61 μm in the commercial preparation. No discernable difference was found in the microstructure with respect to direction of extrusion.

The change in the microstructure between the pure alumina and the ZTA materials brings about notable differences in the fracture surface morphology as shown in Fig. 6. The pure alumina shows a coarse fracture pattern with trans- and inter-granular breakage. The ZTAs all show much finer morphologies reflecting their grain size. In all cases the fracture seems to be predominantly inter-granular. The slightly coarser nature of ZTA(3) is seen in the fracture and was associated with an increase in porosity. This increased porosity was more evident in polished sections (Fig. 5).

The surface finish of the extrudates was generally very good, both after extrusion in the green state and after sintering. The shape retention and shrinkage were much improved by the reduced liquid content. The linear shrinkage, reflecting the level of filter pressing rather than material differences, between wet and sintered products is given in Table 2, as well as the densities determined in a density bottle. The densities of the three ZTAs appear similar although ZTA(3) has larger pores

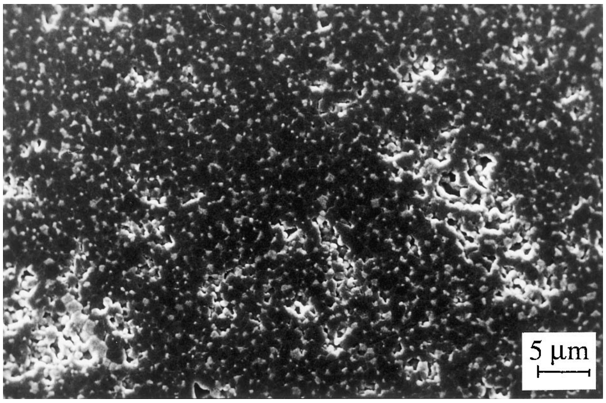
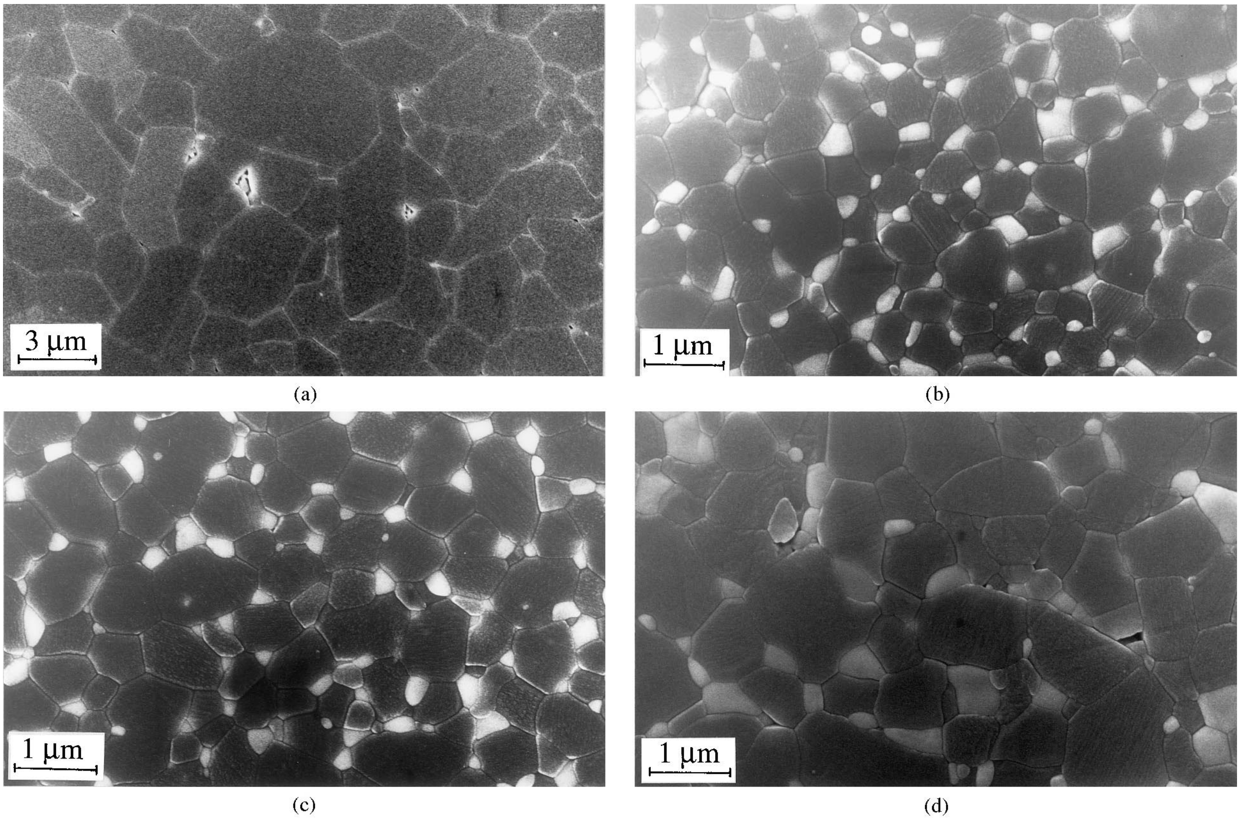


Fig. 5. Lower magnification SEM micrograph of ZTA(3) showing porosity.



(a) (b) (c) (d)

Fig. 4. SEM micrographs of polished sections of (a) alumina, (b) ZTA(1), (c) ZTA(2) and (d) ZTA(3), the light grains being zirconia.

evident in the microscopy studies. This indicates a difference in pore distribution.

8. Mechanical evaluation

Flexural strengths were determined in three point bend tests using 30 sintered rods of each composition. The span widths were set at a minimum of 10 times the rod diameter. The rollers had a diameter of 5 mm. Loading was standardized at 0.5 mm/min and the standard formula for rods of circular cross-section was applied. The strengths are reported in Table 2, Weibull statistics on the specimens are shown in Fig. 7 The strengths of ZTA(1) and ZTA(2) were greater than the pure alumina while ZTA(3) was weaker due to the porosity of the body. Addition of the zirconia improved reliability only in ZTA(2), where the structure was most uniform and defect free.

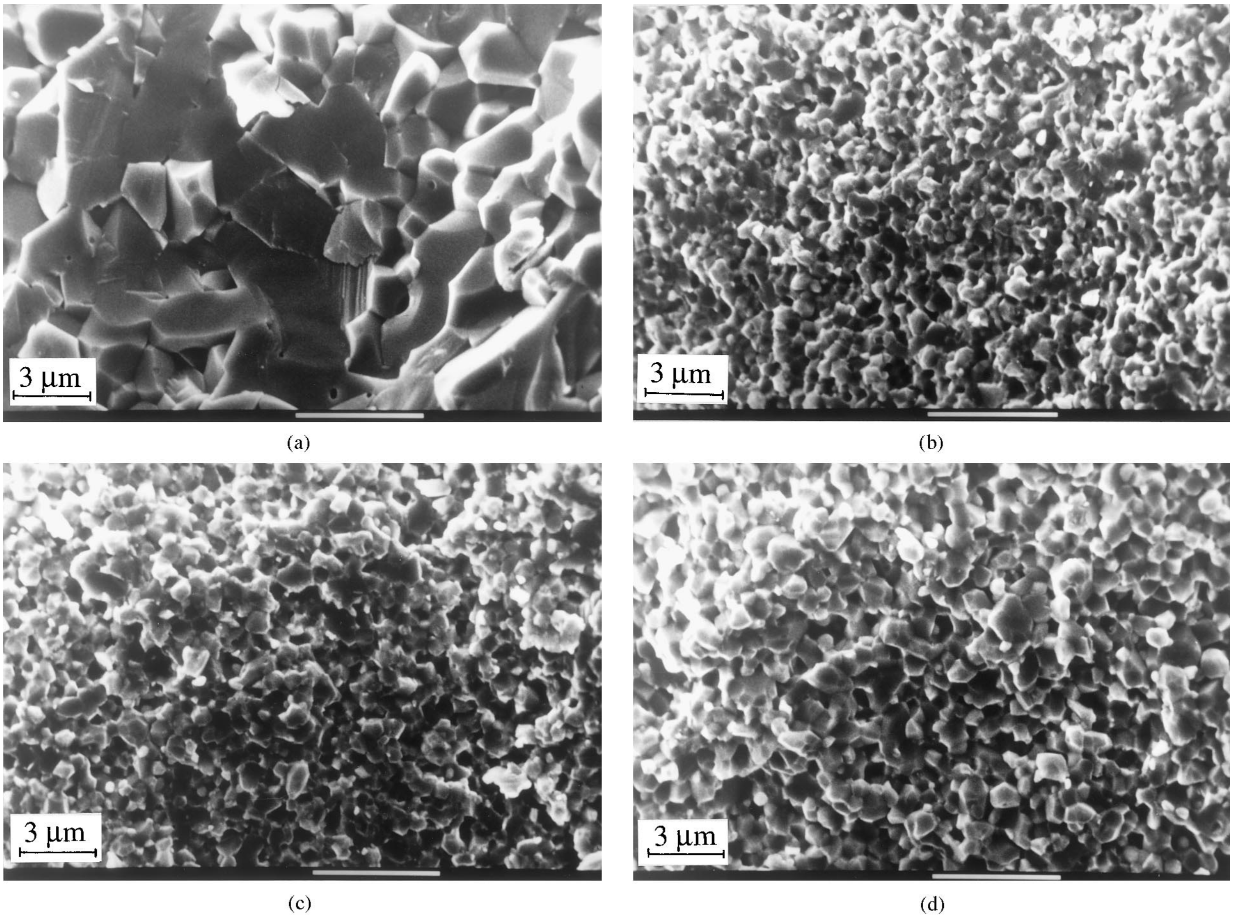
Table 1
Grain size analysis (µm)

	Al_2O_3	ZTA(1)	ZTA(2)	ZTA(3)
Al_2O_3	3.17	0.79	0.80	0.99
ZrO_2	–	0.38	0.50	0.61

Fracture toughness was determined by the indentation method. The polished specimens were micro-indented using a Zeiss micro-hardness tester with a 500 g load. The indents and their crack development were measured by SEM shortly after indentation, ~1 h, and again 3 months later. There were no significant differences in the results. The measurements were used in the equation of Liang et al.,[12] as this appears commonly accepted in the current literature. The fracture toughness, K_{1C} was calculated for comparative analysis using:

$$\left(\frac{K_{1c}\phi}{Ha^{1/2}}\right)\left(\frac{H}{E\phi}\right)^{0.4}\alpha=\left(\frac{c}{a}\right)^{(c/18a)-1.51} \quad (1)$$

where H is the hardness (GPa), a is half the diagonal length of the indent, c is the crack length and ϕ is the constraint factor, which was taken to be 3. The Young's modulus, E, taken from the flexural strength data was used in the calculation of K_{1C}, a Poisson's ratio of $\nu=0.27$ taken from Liang's original paper. It is noted in the calculation that K_{1C} is very sensitive to the values of ν which is a component of α given by:



(a) (b) (c) (d)

Fig. 6. Fracture surface morphologies (SEM) of (a) alumina, (b) ZTA(1), (c) ZTA(2) and (d) ZTA(3).

Table 2
Mechanical property data

	Linear shrinkage (%)	Density (g/cm^3)	Bending strength (MPa)	Weibull modulus	Young's modulus (GPa)	Hardness (HV)	Fracture toughness (MPam$^{0.5}$)	Improved toughness (%)
Alumina	35.0	3.91	645.4 ± 123.6	6.07	362.4 ± 14.9	1641 ± 89	3.73 ± 0.29	–
ZTA (1)	39.0	4.18	754.4 ± 148.3	5.74	338.2 ± 6.4	1792 ± 53	5.90 ± 0.80	58
ZTA (2)	36.0	4.12	755.6 ± 109.9	8.06	363.8 ± 9.8	1653 ± 270	5.79 ± 0.57	55
ZTA (3)	34.6	4.14	331.6 ± 66.8	5.98	300.3 ± 24.4	1586 ± 91	6.17 ± 0.89	65

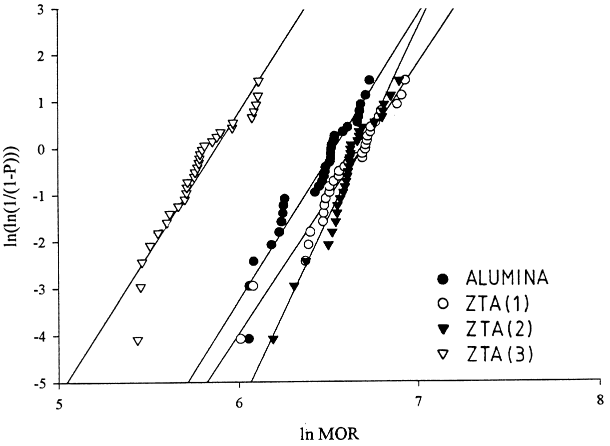


Fig. 7. Weibull plots of the four compositions.

$$\alpha = 14\left[1 - 8\left(\frac{4\nu - 0.5}{1 + \nu}\right)^4\right] \qquad (2)$$

Results show (Table 2) that there is an improvement in fracture toughness of 58% in ZTA(1) compared to the pure alumina and that a similar result was achieved in ZTA(2) due to it having a slightly larger zirconia grain size. The performance in terms of toughness is the same for the three ZTAs within the statistics of the test. ZTA(3) possibly shows enhanced results, which are contrary to the data presented by Srdic and Radonjic[2] for such a size distribution, but this may only reflect the difficulty in discerning the crack tips in the more porous structure. Within the limits of the work carried out here, the improvement in mechanical properties is restricted by the materials' inherent behaviour. It is suggested, therefore, that if toughness values are to be improved still further that doped zirconia will have to be substituted into the structure.

9. Conclusions

A route to produce zirconia toughened alumina extrudates has been developed. The powders were synthesized by hydro-thermal decomposition of acetates. Four routes for the formation of dispersions of zirconia were studied. The most important was the mixing of the two sols after conditioning to pH 9.5, followed by first low and then high pressure filtration to yield extrudable pastes. Following this route the drying of the sol to give powders was avoided along with the concomitant difficulties with the formation of hard agglomerates. The improvement in toughness correlated well with the expected behaviour reported in the literature.

Acknowledgements

The authors would like to thank Dr. I. MacLaren for his help with the autoclave and TEM work and Dr. C. B. Ponton for his help with hydro-thermal synthesis. Thanks are also due to the EPSRC for supporting this work.

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