Improvement in the mechanical properties of polycrystalline beta-alumina via the use of zirconia particles containing stabilizing oxide additions

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Polycrystalline beta-alumina ceramics containing yttria-doped zirconia particles have been produced by hot-pressing and "two-peak" sintering schedules. With the former fabrication process, both a chemical reaction involving sodium meta-zirconate and α-alumina, and a direct mixing route were employed. The mechanical properties of the ceramics produced by the direct mixing route were superior to those produced by the chemical route.

The maximum amount of tetragonal zirconia retention, and thus fracture toughness, obtained using direct mixing occurred for additions of 4 wt % yttria-doped zirconia. An increase of $\sim 124\%$ in the fracture toughness was obtained compared with the pure beta-alumina ceramic. Transfer of this fabrication route to a pressureless sintering schedule was less successful owing to difficulties in attaining full densification. The increases in strength observed with introduction of second phase zirconia could be attributed to an improvement in the degree of densification achieved, and the maximum increase in toughness was only $\sim 27\%$.

1. Introduction

The production of polycrystalline beta-alumina containing unstabilized zirconia as a dispersed second phase, by both hot-pressing and zone sintering, has been described earlier [1, 2]. One of the routes by which zirconia was introduced into the beta-alumina matrix was via a chemical reaction involving the dissociation of sodium meta-zirconate,

$$xAl_2O_3 + Na_2ZrO_3 \rightarrow Na_2O \cdot xAl_2O_3 + ZrO_2$$
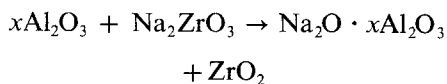
however, this resulted in low retention of tetragonal zirconia. This was caused by the metazirconate decomposing at particularly low temperatures (400 to 700° C) in the presence of α-alumina [3], whereas it did not decompose at temperatures over 1400° C when α-alumina was not present. A finely divided and hence highly reactive form of zirconia was produced by the low temperature decomposition, which was capable of significant growth during the remainder of the firing process.

In an attempt to increase the fraction of zirconia retained in the tetragonal form, the pure zirconia powders hitherto used were replaced by zirconia powders containing 3 to 4 wt % (1.33 to 1.77 mol %) additions of yttria as a stabilizing oxide (Fig. 1). The presence of such an oxide lowers the chemical free energy (ΔG^c) and hence lowers the transformation temperature [5] enabling larger zirconia particles to be retained with the metastable tetragonal symmetry in a given constraining matrix.

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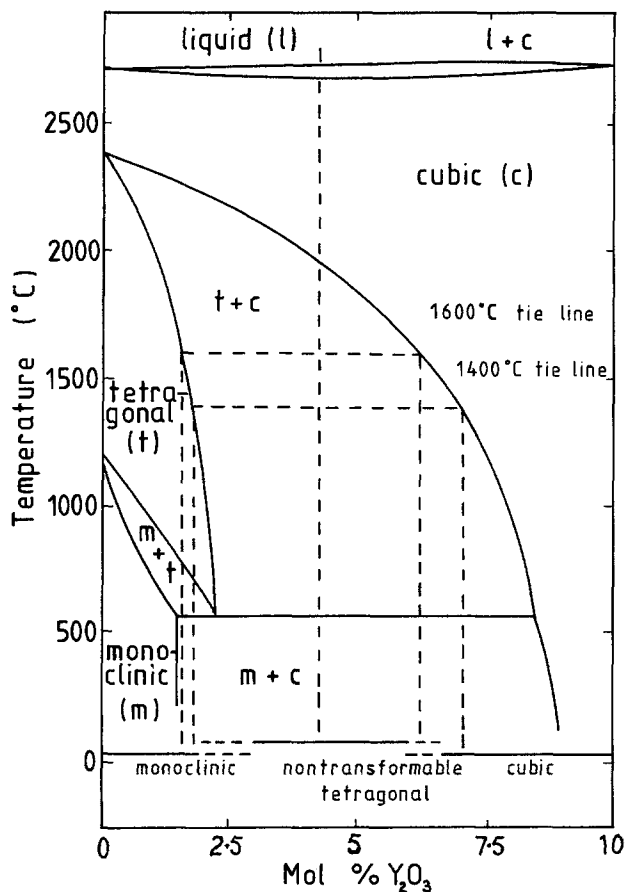
Figure 1 Low yttria region of the ZrO_2–Y_2O_3 phase diagram [4].

2. Effect of yttria partially stabilized zirconia

Sodium meta zirconate was produced by calcining stoichiometric mixtures of sodium carbonate and yttria doped zirconia powders* at 1250° C for 2.5 h [3]. Three different batches were manufactured, incorporating yttria levels of 3, 3.5 and 4 wt % (the 3.5 wt % dopant level was achieved by mixing equal proportions of the 3 and 4 wt % powders). All the yttria-doped zirconia powders were pre-heat treated at 1600° C for 10 min and subsequently air quenched prior to production of the metazirconate. This allowed the yttria rich surface coating on the as-received powders (Fig. 2) to diffuse into the zirconia to produce a homogeneous solid solution.

Each of the three sodium metazirconate powders produced was micronized in propanol with α-alumina and spinel in the weight ratios 1:3.48:0.29. to produce an intimate mixture

ready for hot-pressing after filtering and drying.

A further three batches of the yttria partially stabilized zirconias (3, 3.5 and 4 wt %) were heat-treated to the same schedule and then mixed directly with magnesia stabilized beta-alumina powder and spray dried.[†] All six powder mixes were hot-pressed at 1500 ± 20° C for 1 min with a pressure of 20 ± 0.5 MPa; the apparatus used has been described previously [2]. The densities of the resultant discs were measured using a water immersion technique and the fraction of tetragonal zirconia determined by X-ray diffraction [6]. One surface of each of the discs was subsequently ground to remove the surface α-alumina present and then polished to a 1 μm finish [7]. The toughness of the discs was measured using the indentation technique of Anstis et al. [8].

Further batches of two 3 wt % yttria-doped zirconia powders[‡] were mixed with beta-alumina

*SCY3 and SCY4 from MEL, Swindon, Manchester.
[†]Performed by Chloride Silent Power Ltd.
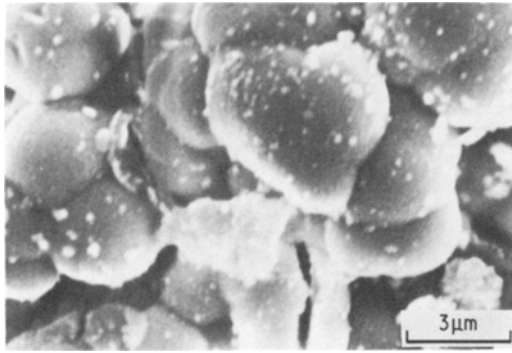[‡]SCY3, from MEL, Swindon, Manchester and TSK-3Y, from Toyo-Soda, Japan.

Figure 2 Yttria rich surface coating on as-received yttria-doped zirconia powder.

precursor powders to prepare samples containing 2, 5, 7, 10 and 15 wt % zirconia additions. (The SCY3 powder was pre-heat treated by the schedule described above.) Pellets of the zirconia-bearing beta-alumina powders were prepared by die pressing using a 32 mm diameter die (to enable strength measurements to be made) and subsequently sintered in an electrically heated furnace using a magnesia saggar with an alumina oxygen lance providing an enriched atmosphere[§] [9]. The sintering schedule developed was "two-peak firing" [10] which allowed the sluggish conversion of β-alumina to the lower resistivity β''-alumina to continue while densification was stopped. A cool-down of 170 to 200° C between the firing peaks controlled the development of a duplex microstructure. The main disadvantage with this sintering process was an increase in the overall crystallite size; however this was of negligible importance owing to the lack of exaggerated grain growth.

The specimens were characterized by the density, toughness, proportion of tetragonal zirconia present and the bend strength. This latter property was measured by three-point loading to fracture of bars cut from the pellets, the faces being ground on an $\sim 35\,\mu m$ diamond wheel. The formula used to calculate the fracture strength was:

$$\text{fracture strength (MPa)}, \sigma_f = \frac{1.5\,lP}{bd^2}$$

where P is the fracture load (N), l is the distance between the loading anvils, b is the specimen breadth and d is the specimen depth.

A second series of smaller pellets (diameter $\sim 7\,mm$) were also produced by a similar preparation route. These specimens developed a greater degree of densification during sintering and were characterized in the above manner.

3. Results and discussion

Table I shows the results obtained from the hot-pressed discs manufactured using yttria-doped zirconia powders via the sodium metazirconate and direct mixing production routes. In all cases more than 50% of the zirconia initially present was retained in the tetragonal form leading to increased toughness compared with hot-pressed pure beta-alumina ($\sim 2.2\,\text{MPa m}^{1/2}$ [2]). It can be seen that the toughness values obtained from the specimens produced via direct mixing were consistently higher than for the chemical route, even when the fraction of tetragonal zirconia retained was the same. No explanation for this phenomenon can be offered, although it was observed that the average zirconia particle size was slightly larger with the sodium metazirconate route, contrary to expectations. Figs. 3a and b show scanning electron micrographs for the metazirconate and direct mixing routes respectively.

The results obtained for the sintered

TABLE I

Production route	Hot-pressing conditions			% ϱ_{th}	% ZrO_2	% t-ZrO_2	K_c
	T (° C)	P(MPa)	t(min)				(MPa m$^{1/2}$)
Na_2ZrO_3 (SCY3)	1500	20	1	99.01	13.99	55	2.91
Na_2ZrO_3 (SCY3/SCY4)	1520	20	1	99.07	13.98	57	3.31
Na_2ZrO_3 (SCY4)	1520	20	1	98.99	13.99	60	3.76
Mechanical mix (SCY3)	1500	20.5	1	98.92	15.02	55	4.61
Mechanical mix (SCY3/SCY4)	1500	20.5	1	99.09	14.99	63	4.76
Mechanical mix (SCY4)	1520	20	1	98.25	15.00	84	4.98

[§]The production of zone sintered tubes, as in [2] was no longer feasible owing to a change in fabrication techniques at Chloride Silent Power Ltd.
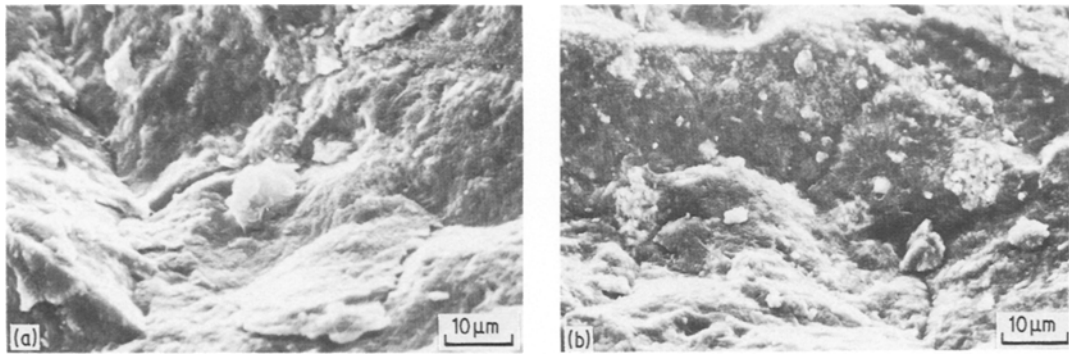
Figure 3 (a) Hot-pressed beta-alumina disc produced via the sodium metazirconate rote. (b) Hot-pressed beta-alumina disc produced via the direct mixing route.

specimens containing additions of 3 wt % yttria-doped zirconia introduced by mechanical mixing are shown in Table II. Use of a large die to press pellets resulted in fabrication problems, notably the absence of full densification. This restricted the possibility of measuring the toughness to the smaller diameter pellets, the presence of extensive porosity with the large diameter discs interfered with the formation of an indent and its radiating cracks. The results obtained on such specimens were not thought representative and have not been quoted. It can be seen from results on the smaller discs, however, that increases in toughness were obtained with the higher zirconia levels using SCY3 powder. Fig. 4 is a scanning electron micrograph of the small disc prepared incorporating 15 wt % of the SCY3 powder. The zirconia particles can be seen to range in size from submicron to $\sim 5 \mu m$.

The much finer Toyo-Soda powder (crystallite size ~ 25 nm, aggregate size $\sim 0.5 \mu m$) produced no increase in toughness below 15 wt % additions, and then only $\sim 7\%$. This is believed to result from the TSK-3Y powder being too fine for the level of stabilizer involved; using X-ray diffraction analysis no decrease in tetragonal zirconia content was noted with grinding of the specimen surface. On the contrary, what appeared to be a slight *increase* in tetragonal level was noted with abrasion of the surface; however this was attributed to the possible formation of sodium aluminate where its strong (2 0 4) diffraction peak at 0.294 nm would interfere with the tetragonal zirconia (1 1 1) peak at 0.296 nm. Raising the temperature of the material to 1300° C and cooling restored the original values.

Table II reveals an apparent increase in

TABLE II

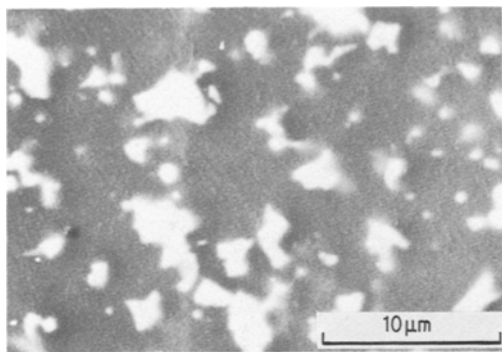| Zirconia	Sintering conditions T (° C)	Pellet diameter 32 mm			Pellet diameter 7 mm	
		% ϱ_{th}	% t-ZrO	σ_f(MPa)	% ϱ_{th}	K_c (MPa m$^{1/2}$)
None	1640	–	–	180	–	–
	1650	93.2	–	212	–	–
	1660	93.5	–	238	–	–
	1620	–	–	–	97.1	2.25
TSK 3Y	1620					
2%		97.0	81	211	99.4	2.27
5%		98.0	91	256	99.5	2.23
7%		98.1	87	264	99.7	2.26
10%		97.0	89	256	99.4	2.27
15%		96.0	89	257	98.4	2.41
SC Y3	1620					
2%		–	–	–	99.3	2.26
5%		–	–	–	99.0	2.55
7%		–	–	–	99.1	2.58
10%		–	54	259	97.8	2.81
15%		–	53	262	98.1	2.82

Figure 4 Small sintered beta-alumina disc containing 15 wt % SCY3 zirconia powder.

mechanical strength with addition of partially stabilized zirconia to beta-alumina. However when the low densities attained with the pure beta-aluminate compositions are considered it can be seen that any increase observed could justifiably be attributed to removal of porosity. The presence of zirconia does however have another important effect in that it appears to improve the sinterability of beta-alumina, and it can thus be used to allow the use of lower sintering temperatures.

Lange *et al.* [11] have carried out similar work using 15 vol % ($\sim$ 24 wt %) additions of 1, 2, 3 and 4 mol % yttria-doped zirconia powders to beta-alumina. With 3 mol % (5.66 wt %) yttria added to the zirconia as a stabilizer, increases in fracture toughness of $\sim$ 100% and in strength of $\sim$ 60% were measured compared to pure beta-alumina. The conclusion that these improvements were due to transformation toughening mechanism however, is open to question. The high stabilizer level (3 mol % Y_2O_3) incorporated in the zirconia is sufficient to stabilize the cubic phase in addition to the tetragonal polymorph (Fig. 1). No results were reported with respect to measurement of the amount of cubic zirconia present, or of the level of transformable tetragonal zirconia. It is quite feasible, therefore, for the improvements in the mechanical properties to have been caused by a crack deflection and branching mechanism, in addition to the possibility of the transformation toughening mechanism.

Green and Metcalf [12] have also investigated β''-alumina–zirconia composite ceramics. The ceramic bodies were formed by casting from alcohol-based slips and subsequent sintering.

The slip-cast bodies could be densified at lower temperatures than usually reported; 1480° C for single phase β''-alumina and 1535° C for the β''-alumina–zirconia composites. The as-received powders were found to contain agglomerates up to $\sim$ 20 μm in size, which were found to be deleterious to the mechanical strength of the sintered composites. Such agglomerates could be removed either by a milling or sedimentation treatment prior to casting. Milling led to silica contamination which impaired the ionic conductivity, whilst the sedimentation process removed particles > 1 μm in size. The resulting fine grain size of the β''-alumina matrix may have given rise to the slight increase in the ionic conductivity observed with this route. It was postulated that both the milling and sedimentation routes could be optimized to produce superior results.

Addition of zirconia led to significant increases in fracture toughness and strength when compared to pure β''-alumina. It was found that, in addition to the reported transformation toughening, the strength of the materials was increased by the zirconia phase limiting the grain growth of the β''-alumina and hence eliminating failures from large β''-alumina grains. With 15 vol % ($\sim$ 24 wt %) zirconia additions (doped with 2 mol % yttria) typical strength increases were > 100%, the higher values being obtained on specimens made using the fabrication routes which involved removal of the large agglomerates from the as-received powders. The presence of powder agglomerates had a beneficial effect on the measured fracture toughness, however. With the agglomerates removed the maximum increase in toughness obtained was $\sim$ 30%, whereas with the agglomerates retained within the sintered body a toughness increase of nearly 70% was achieved.

This observation supports the view that deflection toughening is a significant toughening mechanism in β''-alumina–zirconia composites. The lower degree of constraint available from a β''-alumina matrix, owing to the similarity in the Young's modulus values ($\sim$ 207 GPa for both materials), prevents the larger zirconia particles being retained in the tetragonal polymorph, an effect enhanced by the elastic softness of β''-alumina in the c direction, perpendicular to conduction. This phenomenon thus rescues the contribution of the transformation toughening mechanism, whilst having no significant effect

on the deflection toughening mechanism which relies purely on the presence of second phase particles as obstacles to the passage of a crack.

4. Conclusions

The use of yttria partially stabilized zirconia as the precursor material for the production of sodium metazirconate resulted in an improvement in the fraction of tetragonal zirconia retained when used to toughen beta-alumina. Even with additions of 4 wt % yttria, however, the fraction of tetragonal zirconia retained was only ~ 60%, leaving a significant quantity of monoclinic zirconia which could not contribute to a transformation toughening mechanism. When the same partially stabilized zirconias were mixed with the beta-alumina powders directly and then hot-pressed, a further increase in tetragonal retention resulted with the higher yttria levels, together with a major increase (~ 124%) in the toughness values.

When the fabrication of specimens was via a sintering rather than a hot-pressing route the degree of densification was reduced and much of the increase in toughness also lost. It is suggested that use of a sintering route to develop full densification with ~ 15 wt % additions of ~ 4 wt % yttria-doped zirconia would produce toughness values approaching those reported for the hot-pressed material. The precursor powder particle size and level of stabilizer addition must be carefully controlled to achieve the maximum degree of transformation in the stress field of propagating cracks, and so maximize the contribution of the transformation toughening mechanism. It is further suggested that, at present, a significant proportion of the improvements observed in the mechanical properties of β''-alumina associated with the addition of second phase zirconia results from a deflection toughening mechanism.

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