

Strength improvement in beta'' alumina by incorporation of zirconia

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Beta'' alumina ceramic electrolytes for use in Na/S batteries are inherently weaker than most engineering ceramics due to the presence of weakly-bonded conduction planes in the crystal structure and to difficulties in controlling grain growth during firing. Substantial improvement in microstructural control is obtained by incorporation of monoclinic zirconia (m-ZrO₂) or partially stabilized zirconia (PSZ) resulting in increases in strength and fracture toughness to around 350 MPa and 4 MPam^{1/2}, respectively. PSZ may adversely influence the electrical resistivity of the ceramic owing to the presence of impurities. With most zirconia powders a high level of retention of tetragonal zirconia (t-ZrO₂) is obtained at levels of addition up to 15% by weight ZrO₂. At these levels ZrO₂/β''-Al₂O₃ ceramics show low resistivity and stable resistance in Na/S cells.

1. Introduction

A number of attempts have been made to obtain transformation toughening of beta alumina. Good results have been obtained by hot pressing or slip casting [1-3] but not in the context of a viable production process [4]. The present paper describes the addition of ZrO₂ to β/β'' alumina at levels that are sufficiently high to cause substantial increases in mechanical strength and fracture toughness, but not high enough for the electrical properties of the ceramic to be degraded.

2. Experimental details

Composite ZrO₂/β''-Al₂O₃ ceramic tubes of diameter 33 mm and wall thickness 1 to 2 mm were fabricated by electrophoretic deposition [5] and sintered at 1600°C for 10 min. Phase contents were determined

using a Philips 1720/1050 diffractometer and electrical conductivity measurements obtained using a four-probe axial direct current method. Strength measurements were obtained by diametrical compression testing of 10 mm width C rings cut from the tube, and microstructures obtained by polishing to 1 μm finish followed by thermal etching.

3. Results

3.1. Ionic conductivity

Zirconia is non-conductive to sodium ions at Na/S battery operating temperatures (300 to 350°C) and in adding zirconia to β'' alumina it is important not to degrade the conductivity of the ceramic. In previous literature [2, 3] some variations in resistivity with ZrO₂ content were found, but few values have been reported and this property is likely to be sensitive to choice of composition, impurity levels and processing. With some types, especially PSZ, the presence of impurities such as Y₂O₃, CaO or SiO₂ may lead to an increase in resistivity. With m-ZrO₂ it is possible to add up to 10% by weight before significant increases in resistivity are

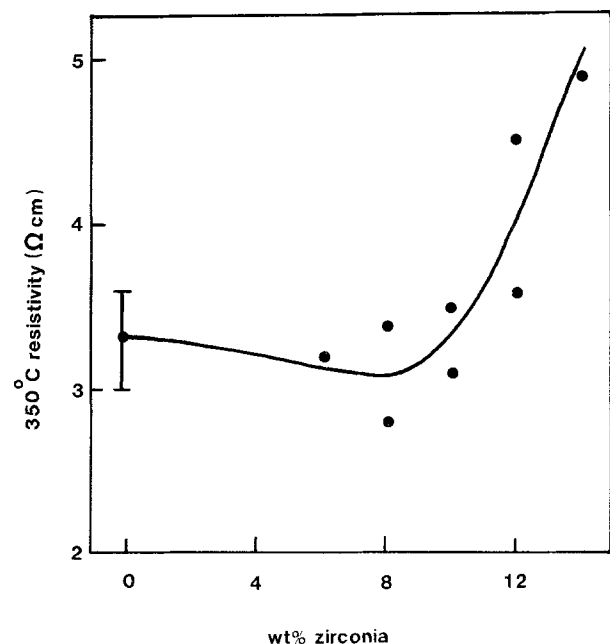


Figure 1 Effect of ZrO₂ on ceramic resistivity at 350°C.

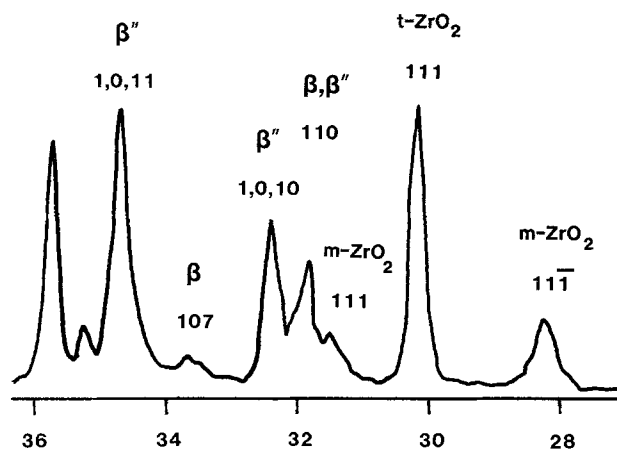


Figure 2 X-ray diffraction pattern (CuKα) of ZrO₂/β''-Al₂O₃.

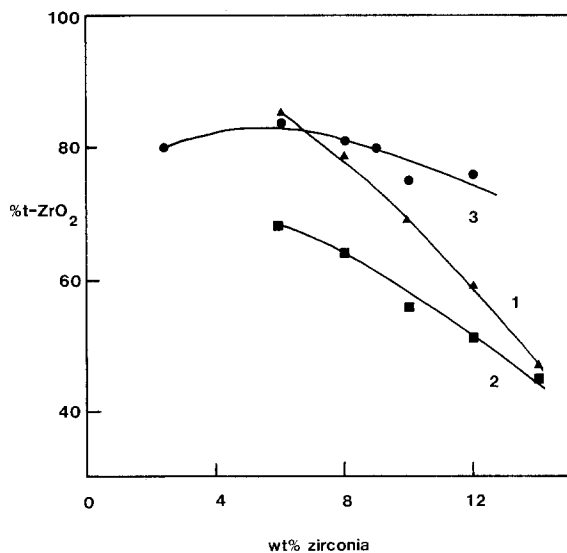


Figure 3 Proportion of t-ZrO₂ in the ZrO₂ phase, for three starting materials.

encountered. Fig. 1 shows the variation with zirconia content of electrical resistivity at 350°C.

3.2. Beta alumina phase content

Fig. 2 shows the X-ray diffraction (XRD) pattern (CuK α radiation) of a ZrO₂/ β'' -Al₂O₃ composite. In the β'' -Al₂O₃ matrix the proportion of β'' remained constant at $92 \pm 2\%$ at all levels of zirconia addition from 0 to 15% and with all ten zirconia powders investigated. Beta'' alumina content and lattice parameters were determined according to procedures described previously [6]. Sample lattice constant measurements are given in Table I, and indicate no significant change on addition of zirconia. These results suggest that there is essentially no chemical interaction between the β'' -Al₂O₃ and ZrO₂ phases.

3.3. Zirconia phase content

XRD patterns were analysed according to the procedure [4] that uses the $t(111)$ and $m(1\bar{1}\bar{1})$ reflections, avoiding the $m(111)$ that overlaps the β'' -Al₂O₃ (110) (Fig. 2). Measurements were made immediately following sintering, in order to avoid the spontaneous $t \rightarrow m$ conversion that occurs due to atmospheric moisture attack at the free surface. Fig. 3

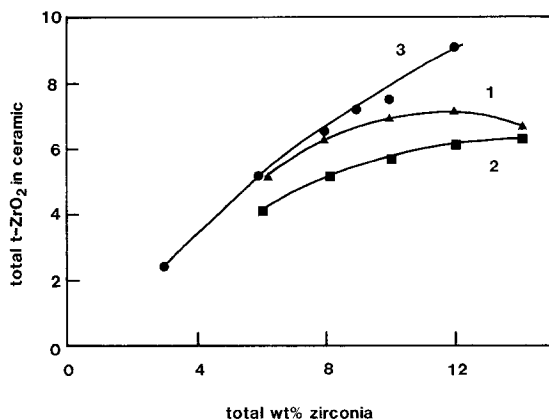


Figure 4 Quantity of t-ZrO₂ in the ceramic, for three starting materials.

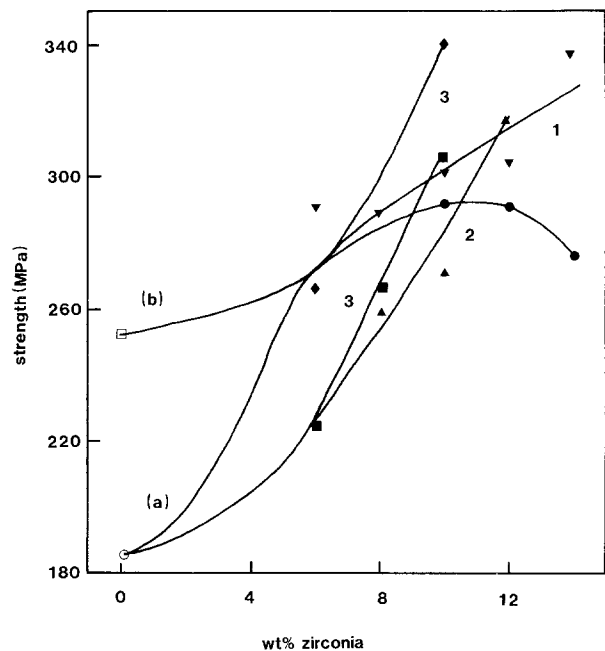


Figure 5 Strength of ZrO₂/ β'' -Al₂O₃ ceramics, for two processing routes a and b and three starting materials.

shows, for three types of zirconia powder, the proportion of t-ZrO₂ present. Curve 1 represents a Mg-PSZ, 2 and 3 represent unstabilized zirconias. As the quantity of ZrO₂ in the ceramic is increased, the proportion of t-ZrO₂ retained after firing tends to diminish, possibly as a result of particle growth during firing; for example, in one specimen overfired by 40°C the proportion of t-ZrO₂ fell from 56% to 34%. Fig. 4 shows the total amount of t-ZrO₂ present as a function of total ZrO₂ content. It is interesting that the highest levels of t-ZrO₂ are not necessarily obtained with PSZ; this suggests that particle size is the dominant factor in determining the amount of transformation toughening present.

3.4. Strength and fracture toughness

Weibull characteristic strength values for the diametrical compression C-ring test are shown in Fig. 5 for two processing routes (a and b) and three types of ZrO₂. Zirconia 1 was a PSZ. While in a few instances only a slight increase in strength was obtained, and even a decrease at higher levels of ZrO₂ addition, in most cases a sharp increase in strength was obtained. The highest strengths obtained were around 340 MPa with a Weibull modulus of 16. Higher levels of ZrO₂ addition were not investigated owing to their deleterious effect on the conductivity of the ceramic (Fig. 1). It is noteworthy that unstabilized zirconias can yield strength values as high as those obtained with PSZ; this indicates that the origin of the strength increase lies principally in microstructural control rather than transformation toughening.

Indentation fracture toughness measurements for one series of zirconia additions is shown in

TABLE I Lattice constants of the β'' -Al₂O₃ phase

	<i>a</i> (nm)	<i>c</i> (nm)
β'' -Al ₂ O ₃	0.56100 ± 0.00002	3.3449 ± 0.0002
ZrO ₂ / β'' -Al ₂ O ₃	0.56106 ± 0.00004	3.3451 ± 0.0003

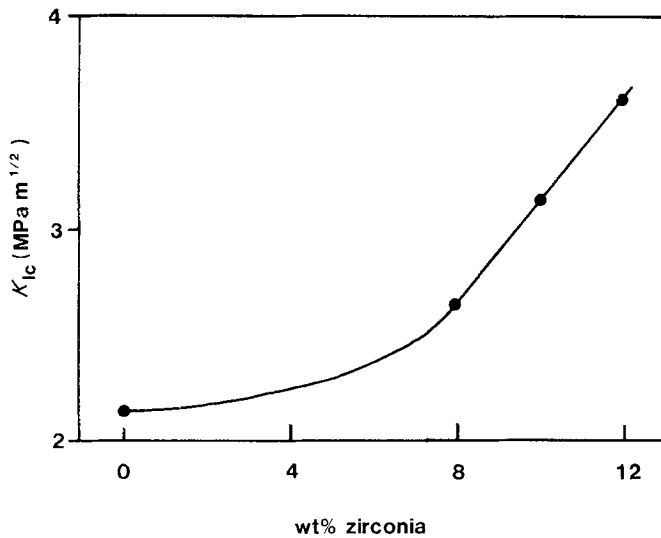


Figure 6 Fracture toughness of $ZrO_2/\beta''-Al_2O_3$ ceramic.

Fig. 6. Because with this material the proportion of $t-ZrO_2$ retained fell sharply with increasing ZrO_2 content, the sharp increase in fracture toughness suggests that some microcrack toughening is occurring. However, this result must be treated with caution, because atmospheric moisture attack may be a cause of microcracking.

3.5. Microstructure

Average fired densities of $ZrO_2/\beta''-Al_2O_3$ composites (10% ZrO_2) were around 3.42 g cm^{-3} , corresponding to a volume porosity of 0.5%. Fig. 7 shows an unetched micrograph indicating well-dispersed porosity and zirconia distribution, and Fig. 8 shows a corresponding etched microstructure indicating the general absence of grain growth and processing flaws. Fig. 9

shows a scanning electron micrograph, the white regions representing zirconia particles.

3.6. Durability of $ZrO_2/\beta''-Al_2O_3$ ceramics

These ceramics have shown stable long-term resistance in Na/S cells and good reliability, with over 3000 charge/discharge cycles being completed without premature failure.

4. Conclusions

In $ZrO_2/\beta''-Al_2O_3$ composite ceramics the two phases remain dispersed and there is essentially no chemical interaction between them. Resistivity, β'' content and lattice constant are unchanged by the addition of ZrO_2 to $\beta/\beta''-Al_2O_3$.

Monoclinic zirconias with a fine particle size can

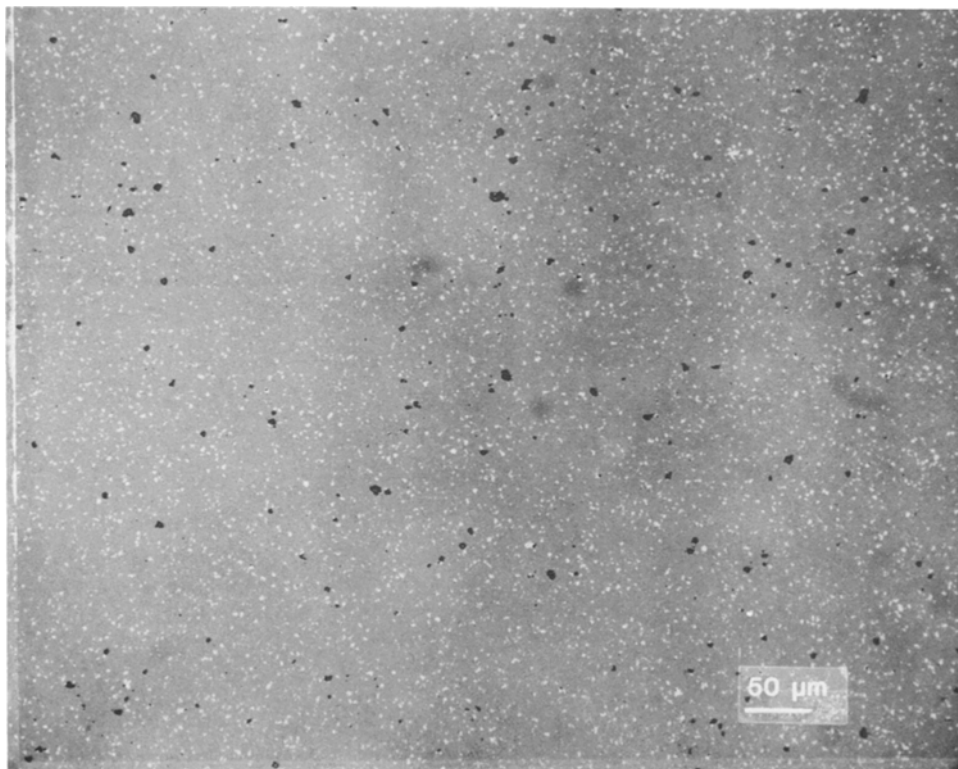


Figure 7 Unetched microstructure of $ZrO_2/\beta''-Al_2O_3$.

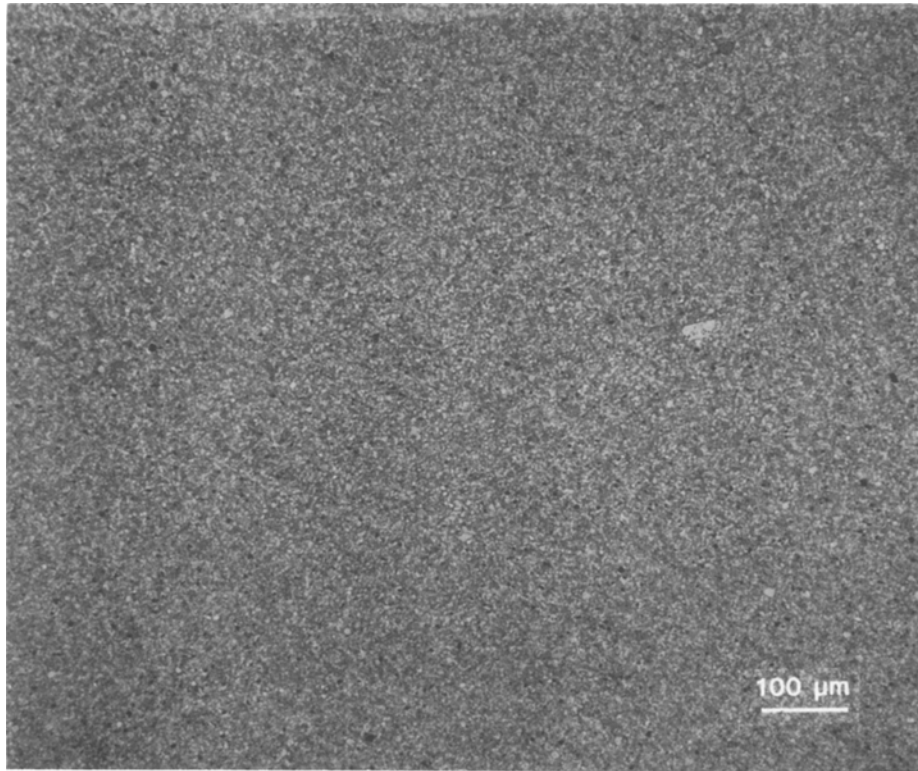


Figure 8 Etched microstructure of $ZrO_2/\beta''-Al_2O_3$.

yield a greater retention of t- ZrO_2 in the fired ceramic than with PSZ. In all cases, grinding of the ceramic indicated that a considerable amount of transformation toughening was present. However, the increases

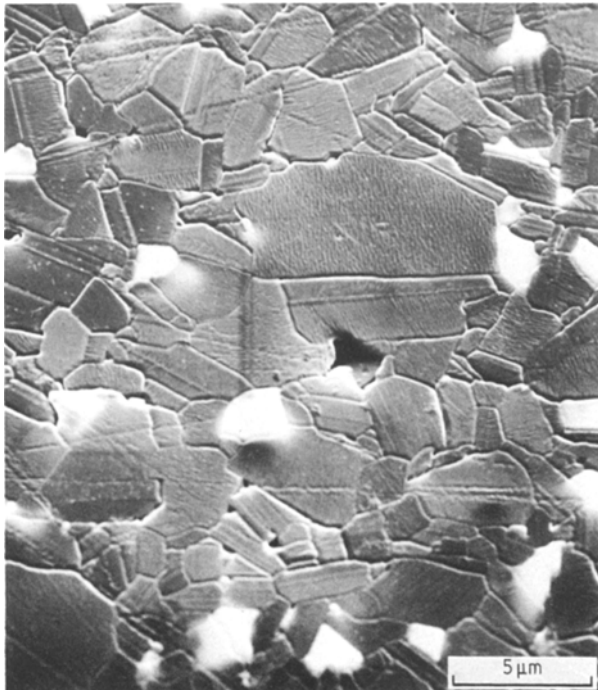


Figure 9 Scanning electron micrograph of $ZrO_2/\beta''-Al_2O_3$ ceramic.

in mechanical strength reported are due primarily to the improvement in microstructural control.

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