

## Zirconia–mullite ceramics by reaction-sintering

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**Abstract.** Zirconia–mullite composites were prepared by *in situ* reaction between zircon and alumina. Stabilizers like yttria and magnesium carbonate were used. Almost vitrified bodies were obtained by sintering at 1465–1535°C. Flexural strength increased on annealing at 1040°C.

**Keywords.** Zirconia ceramics; mullite; zirconia composites; sintering.

### 1. Introduction

Mullite ceramics have high chemical resistance, low thermal expansion and low thermal conductivity but inherently low strength as compared to other materials like alumina (Humenik 1981). The weaknesses of the sintered mullite can be reduced by incorporation of zirconia in the mullite matrix which promotes densification and also substantially reduces the glassy phase (Prochazka *et al* 1983) and improves the strength (De Portu and Henny 1984). It has been reported that better results are obtained if mullite–zirconia composites are prepared by *in situ* reaction of zircon and alumina (Di Rupo and Anseau 1980). Both these raw materials are available in India. In this paper, results on microstructure, phases of reaction products and mechanical properties of zirconia–mullite composites are presented.

### 2. Experimental

Ground zircon and technical alumina were mixed in stoichiometric ratio (54.4:45.5) with LR grade additives. It was milled for 24 h in a pot mill in an aqueous medium, sieved and dried.

Chemical analysis showed that zircon had almost stoichiometric proportions of silica and zirconia (32.8:67.2) and alumina was a low alkali material. The batch compositions are given in table 1. All samples were pressed into rectangular bars by uniaxial dry pressing at 650 kg cm<sup>-2</sup>. The samples were fired in an oil-fired furnace in the temperature range 1465–1535° depending upon the amounts of flux in the batches. The soaking time was 90 min. Samples were annealed (heat-treated) at 1040° with 120 min soaking and quenched to ambient temperature. A Philips diffractometer, a scanning electron microscope and an Instron were used to study phase composition, microstructure and flexural strength respectively. To measure modulus of rupture, a three-point bending test was carried out with a span length of 5 cm. The samples were approximately 79 mm × 20 mm × 6 mm before firing. Firing shrinkage was about 27%.

### 3. Results and discussions

#### 3.1 X-ray studies

The various phases present as seen by X-ray diffraction are given in table 1.

**Table 1.** Batch compositions and properties of the materials after firing.

Materials (Wt%)	Batches		
	A	B	C
Al <sub>2</sub> O <sub>3</sub>	47.81	46.00	43.95
Zircon	48.02	46.05	44.23
Ytria	4.17	4.07	6.00
MgCO <sub>3</sub>	—	—	3.82
Cryolite	—	—	2.00
Firing temperature (°C)	1535	1480	1465
Phases present	<i>t</i> -ZrO <sub>2</sub> , <i>m</i> -ZrO <sub>2</sub> , mullite, $\alpha$ Al <sub>2</sub> O <sub>3</sub>	<i>t</i> -ZrO <sub>2</sub> , $\alpha$ Al <sub>2</sub> O <sub>3</sub> , mullite, <i>C</i> -ZrO <sub>2</sub> , <i>m</i> -ZrO <sub>2</sub>	ZrO <sub>2</sub> , $\alpha$ Al <sub>2</sub> O <sub>3</sub> , mul- lite, <i>C</i> -ZrO <sub>2</sub> and some unidentified lines
Water absorption (%)	0.81	0.5	0.16
Bulk density (g cm <sup>-3</sup> )	3.70	3.54	3.55
Modulus of rupture (average) (kg cm <sup>-2</sup> )	1048	1098	1109
Modulus of rupture annealed at 1040°C for 120 min (average) (kg cm <sup>-2</sup> )	1198	1966	1602

The presence of alumina shows that reaction is not complete, but zircon could not be detected because it gets dissociated into zirconia and silica. The latter thus obtained becomes part of the glass formed with fluxes (Pena and De Aza 1984; Pena *et al* 1984). Formation of glass (liquid phase) helps in the densification process in the sintering of zirconia (McCartney 1987). The same may hold true in reaction-sintered zirconia–alumina mixtures. Table 1 shows the presence of monoclinic, tetragonal and/or cubic zirconia. Since some of the peaks of mullite and alumina overlap with those of zirconia, careful examination is needed. The *d* values of cubic zirconia depend on the extent of solid solution formation (Dietzel and Tober 1953). The distinction between tetragonal and cubic zirconia is rather difficult to determine because the *c/a* value of the tetragonal phase is about 1.02. For tetragonal zirconia,  $a_0 = 5.07 \text{ \AA}$  and  $C_0 = 5.16 \text{ \AA}$  and for cubic zirconia  $a_0$  value varies from 5.05 to 5.07  $\text{\AA}$ . The range is due to solid solution formation, especially when several components are present in the starting powder mixtures. The problem of differentiating cubic and tetragonal phases is solved by examining high angle (400)<sub>c</sub> and (400)<sub>t</sub> peaks which have slightly different *d* values due to slight difference in lattice constants of two phases in this case.

Mullite and alumina do not interfere with (400) lines. In all the batches, split peaks due to (400) diffraction were found to be (1.269)<sub>c</sub> and (1.279)<sub>t</sub>  $\text{\AA}$ . A small (004)<sub>t</sub> peak at 1.29  $\text{\AA}$  was also present. Because of the presence of more than one stabilizing agent (either coming from batch composition or impurities) the possibility of the formation of cubic zirconia cannot be ruled out. The presence of the cubic phase has also been reported by other workers (Dongare and Sinha 1984; Mondal *et al* 1987).

### 3.2 SEM studies

In the fractographs, zirconia grains were more or less egg-shaped or elliptical in shape (figures 1 and 2). This is due to the formation of mullite and zirconia during the *in situ* reaction of zircon and alumina. Zircon particles dissociate into smaller

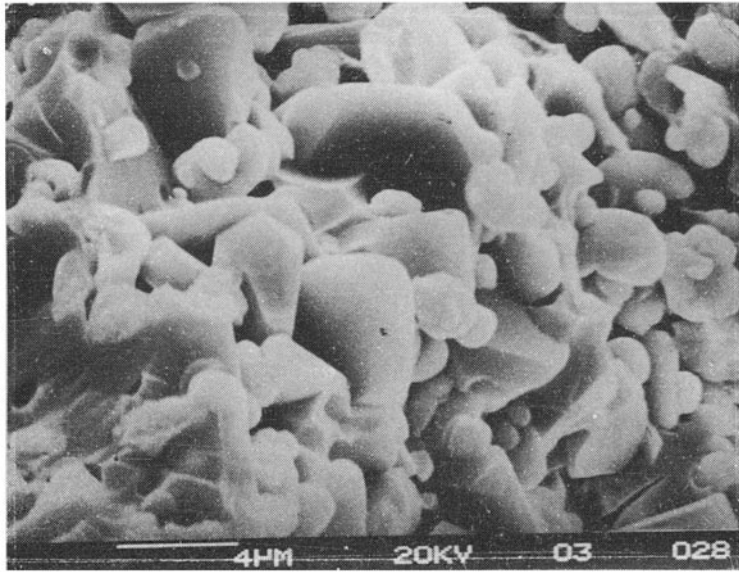


Figure 1. SEM of sample B.

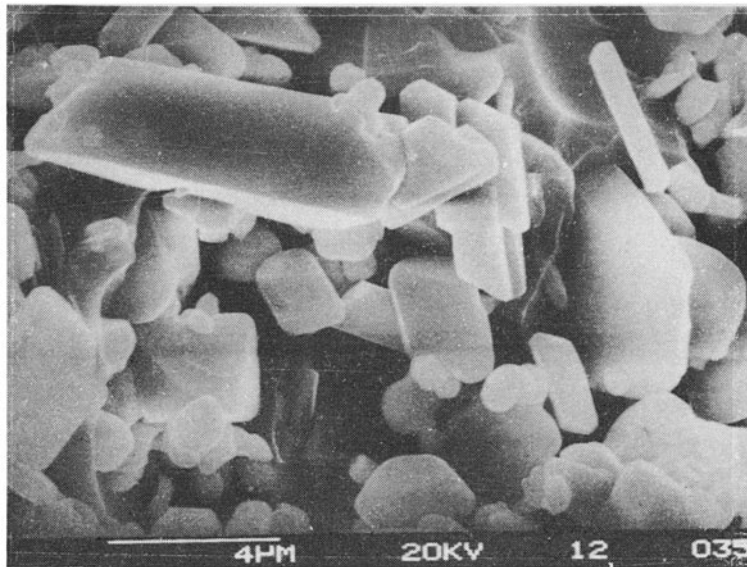


Figure 2. SEM of sample C.

zirconia particles and silica (Cambier *et al* 1984). The latter in turn reacts with alumina and forms mullite. Thus smaller zirconia particles are formed from larger zircon particles. These particles grow in a non-crystalline glassy phase and so no facets are formed (Wallace *et al* 1983; Cambier *et al* 1984; McCartney 1987). The rounded corners of the grains in the milled samples indicate little growth anisotropy for zirconia in the presence of excess liquid phase. This morphology can be

compared with silicon nitride which has a high degree of preference in certain growth planes. Alpha alumina having a significant growth anisotropy displays faceted grain boundaries (Hansen and Phillips 1983). There is also a possibility of zirconia being present in mullite solid solution (Moya and Osendi 1983). Two fractographs of sample B+C (figures 1 and 2) are shown. The grain size is much larger in sample C because of the presence of large amounts of flux which encourages crystal growth in the liquid phase.

### 3.3 Mechanical properties

Table 1 presents the flexural strength, water absorption and bulk density of the materials. The bulk density is within  $3.5\text{--}3.6\text{ g cm}^{-3}$ . MOR is a function of water absorption and bulk density. The presence of tetragonal zirconia increases strength due to transformation toughening of the composites (Claussen and Wallace 1981). Other mechanisms of strengthening also play an important role, considering the results of other workers (Claussen and Wallace 1981; De Porter and Henney 1984; Moya and Osendi 1983). The flexural strength values are lower in this work. The initial powders were coarse and the samples were prepared by uniaxial pressing. If isostatic pressing (or hot isostatic pressing) is utilized then strength values will certainly increase. Annealing (heat treatment) has increased the strength values. In most cases, the number of X-ray diffraction lines increased on annealing, thus showing crystallization of phases which perhaps increase the strength properties at relatively lower temperatures as compared to that observed by other workers (De Portu and Henny 1984).

## 4. Conclusions

Strength properties of mullite matrix containing zirconia is improved compared to mullite. In this work, this was achieved at relatively lower temperatures  $1465\text{--}1535^\circ\text{C}$ . Also, low purity zircon material can be useful where the environmental temperature is not very high.

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