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Microstructure and mechanical properties of mullite/ZrO_2 composites

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The sintering, microstructure and toughness of mullite/ZrO_2 composites with increasing amount of ZrO_2 (0 to 20 vol %) have been studied. A very active premullite powder has been used as matrix. The K_{IC} values increase from 2.1 to 3.2 MN m$^{-3/2}$ as the volume fraction of zirconia increases from 0 to 0.2. The realtive fraction of tetragonal zirconia decreases as the volume fraction of ZrO_2 increases to reach ~ 0.1 in the sample with 0.2 volume fraction of ZrO_2. The presence of ZrO_2 enhances the sintering rate and end-point density of the composites. Finally, the increasing toughness in mullite/ZrO_2 composites has been explained by a grain boundary strengthening mechanism produced by a metastable solid solution (~ 0.5 wt %) of ZrO_2 in mullite.

1. Introduction

It is known that the addition of a dispersed tetragonal phase of ZrO_2 to a matrix enhances its resistance to crack propagation [1–3]. In the present work mullite has been chosen as matrix to study the effect of different quantities of ZrO_2 on the microstructure, sintering rate and toughening.

The few works in the literature devoted to mullite/ZrO_2 composites have been mainly done on samples obtained by reaction sintering [4–6]. In this work a very active premullite powder [7] obtained from a kandite of a high degree of purity has been used as the starting material.

Due to the important physical and chemical properties of mullite – such as low thermal expansion (4 to 5×10^{-6} °C^{-1}), creep resistance [8], and high chemical stability [9] – improvement of the mechanical performance of mullite-based materials in order to exploit fully its potential capabilities is a goal of great technological interest.

2. Experimental procedure

Very fine premullite powder* (SEM, BET ~ 250 m^2 g^{-1}) was obtained by thermal and chemical treatment of a kandite [7].

Powders with different additions of ZrO_2† (0, 10, 15 and 20 vol %) were attrition milled with alumina balls in isopropyl alcohol for 1 h. These powders were isostatically pressed (200 MPa) and sintered at 1570° C for 2.5 h.

The sintering behaviour was observed using a dilatometer furnace in samples with (15 vol %) and without ZrO_2.

For examination in the scanning electron microscope (SEM) the specimens were polished and thermally etched (at 1350° C for 2 h). The average gain size was calculated by measuring the average intercept length [10].

The indentation test, made with a diamond Vickers pyramid on polished samples, was used for K_{IC} determinations. The load ranged from 50 to 70 N for the mullite samples and from 100 to 120 N for the mullite/ZrO_2 composites. The Young's modulus for each composition was determined considering the relative tetragonal content of zirconia. The K_{IC} values were obtained using the Evans [12] analysis. Finally the flexural strength (three-point bend test) of the different compositions was measured in cylindrical bars of ~ 3 mm diameter obtained by isostatic pressing and heated at 1570° C for 2.5 h. Each strength datum is an average over 5 samples.

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*Chemical analysis of premullite: Al_2O_3 72.20 wt %; SiO_2 26.92%; CaO 0.20 %; Fe_2O_3 0.15%; Na_2O 0.05%; MgO 0.02%; K_2O 0.02%.

†Magnesium Elektron Ltd, Manchester, UK.

0022–2461/84 $03.00 + .12

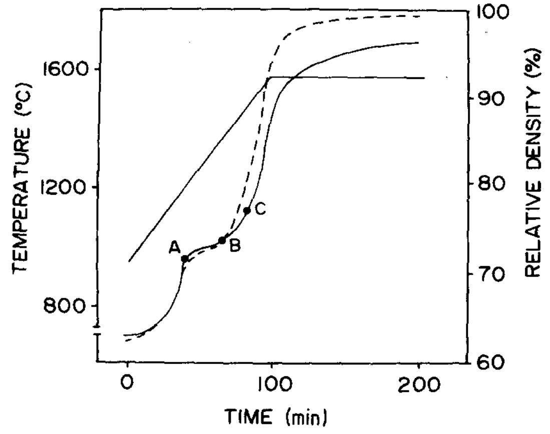

Figure 1 Sintering curves for (——) mullite and (— —) mullite + 15 vol% ZrO_2.

3. Results and discussion

3.1. Sintering

The sintering curves of mullite and mullite/ZrO_2 are plotted in Fig. 1. It can be observed that the end-point density is first reached in the mullite/ZrO_2 specimen. At the starting point of the isothermal treatment (1575° C) the theoretical density, ρ_{th}, of the mullite/ZrO_2 sample is 93.7% ρ_{th}, while that of the mullite is only 87.3% ρ_{th}. Therefore, the presence of ZrO_2 enhances the sintering rate of the composite and also the end-point relative density is greater in the mullite/ZrO_2 composite (99% ρ_{th}) that in the pure mullite (97% ρ_{th}). Fig. 1 shows a step in the sintering behaviour of both curves in the temperature range 1100 to 1300° C. To explain this behaviour X-ray diffraction (XRD) analysis of samples heated at 1200, 1350 and 1470° C was performed (following the same heating schedule as Fig. 1); the corresponding charts are shown in Fig. 2. The observed change corresponds to an ordering process in which the premullite transforms to mullite [13].

It is is interesting to point out that a dense pure mullite (⩽ 3% porosity) is obtained at very low temperature (1570° C) and low isostatic pressure (200 MPa) without using special methods such as hot-pressing techniques [14], sol–gel processes [15] or coprecipitation methods [16].

3.2. Microstructure

SEM microphotographs of the microstructures observed on the mullite sample are shown in Fig. 3. Specimens present a narrow grain size distribution with equiaxial shape and an average grain size of 0.4 μm.

In the mullite/ZrO_2 composites the mullite grains are more angular and larger (0.8 μm) than in the corresponding mullite sample. The ZrO_2 grains are mainly located at the grain boundaries (Fig. 4).

In Fig. 5 the dependence of the mullite grain size ($\bar{d}_M$) on annealing time is plotted for mullite

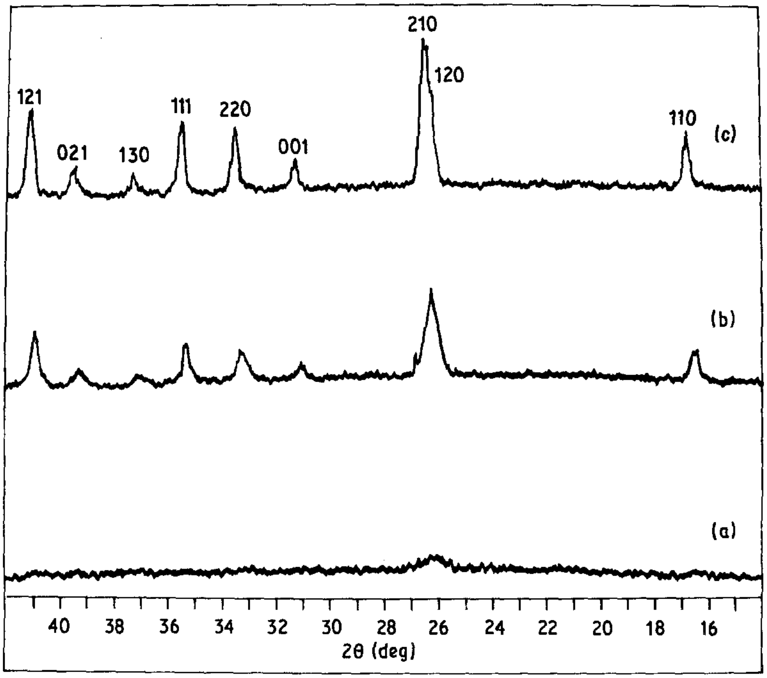

Figure 2 XRD profiles of mullite obtained at the three points indicated in Fig. 1: (A) 1200° C; (B) 1350° C; and (C) 1470° C.

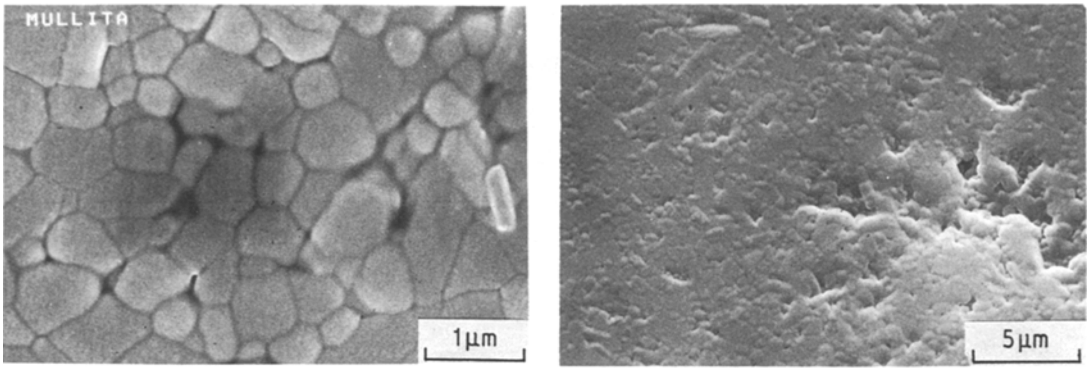

Figure 3 SEM microphotographs of a mullite sample heated at 1570° C for 2.5 h at two magnifications.

and mullite + 15 vol% ZrO_2 composites. At 0 annealing time (i.e. 2.5 h at 1570° C) $\bar{d}_M$ of the mullite/ZrO_2 composite is about twice that corresponding to the mullite compact. With increasing time (16 h annealing) both samples reach a similar average grain size. The initial difference in the grain size may be explained by the existence of a solid solution of ZrO_2 into mullite [17].

After 16 h annealing a noticeable change in the microstructure is observed (Fig. 6). In the case of the mullite sample, large grains of about 4 μm coexist with areas of small grains ($\leqslant 1\,\mu$m) which show a very angular shape. Conversely in the mullite/ZrO_2 composite these kinds of small grain do not appear.

Considering the ionic radii relations Si^{4+}/Zr^{4+} (0.53) and Al^{3+}/Zr^{4+} (0.65), the substitution of Zr^{4+} for Al^{3+} is the most probable mechanism for the solid solution. This solid solution would enhance the diffusional mechanisms by the creation of aluminium vacancies increasing the grain-boundary mass transport and consequently the sintering rate, as observed in mullite/ZrO_2 composites (Fig. 1).

The $(1\,1\,\bar{1})_M ZrO_2$ peak corresponding to premullite + 5 wt% ZrO_2 heated at 1570° C for 2.5 h (b), and to mullite* + 5 wt% ZrO_2 homogeneous mixture (a), are recorded in Fig. 7. The area of the peak (b) is 22.5% lower than the corresponding peak (a), due to the above-mentioned ZrO_2(ss). This ZrO_2(ss) was found to be 0.5 ± 0.1 wt% by a careful quantitative XRD analysis [17]. In the case of equilibirum, Pena and Aza [18] found that the extension of the ZrO_2(ss) into mullite at 1600° C was $\leqslant 0.1$ wt%.

The value of 0.5 wt% determined in the present work must be considered metastable as a consequence of the small grain size of mullite and ZrO_2 ($\sim 1\,\mu$m) in the samples.

3.3. Mechanical properties

The toughness (K_{IC}) has been measured on samples with 0, 10, 15 and 20 vol% of ZrO_2 (Fig. 8). The relative tetragonal content of ZrO_2

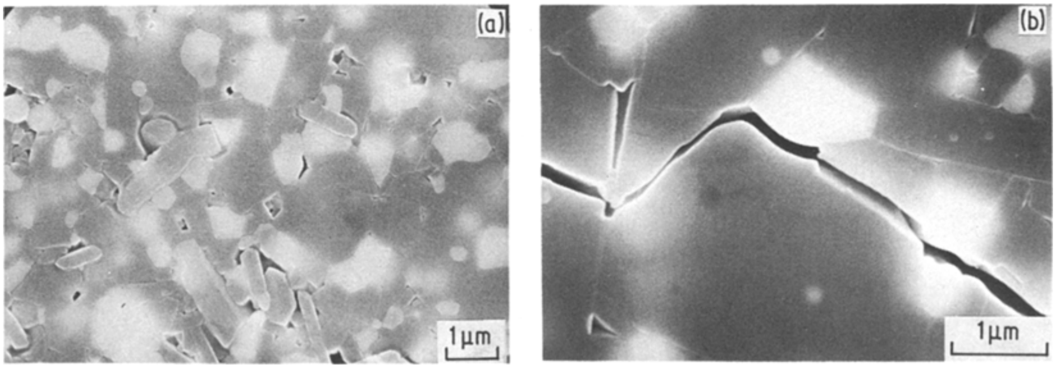

Figure 4 SEM microphotographs of: (a) mullite + 15 vol% ZrO_2 composite; (b) indentation crack.

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*Obtained heating the premullite at 1570° C for 2.5 h in order to avoid the matrix effect.

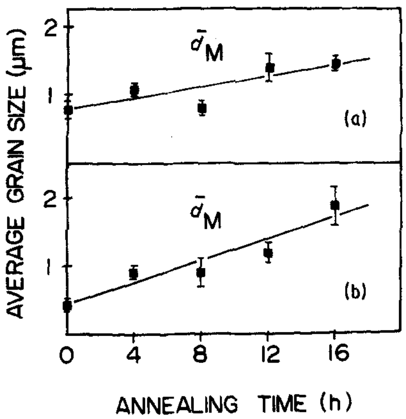

Figure 5 $\bar{d}_M$ against annealing time at 1570° C: (a) mullite + 15 vol% ZrO_2 composite; (b) mullite sample.

was determined on samples as-fired and after polishing; in both cases the fractional content of ZrO_2 (t) was found to be the same. Fig. 7 shows that the strength (σ_F) increases, the K_{IC} remains constant and the fraction of ZrO_2 (t) decreases as the ZrO_2 content increases.

It is evident that the transformation toughening mechanism is not the operative one in these composites because the K_{IC} value is independent of the tetragonal content of ZrO_2 [1]. Claussen and Wallace [19] also make doubtful the existence of transformation toughening in the mullite/ZrO_2 composite obtained by reaction sintering.

If the microcracking is the dominant toughening mechanism, as has been observed in Al_2O_3/ZrO_2 composites [20]: (a) the K_{IC} increases when the volume fraction of ZrO_2 increases; (b) the σ_F is kept constant; (c) the inclusions must be sharply angular rather than spherical; and (d) the thermal mismatch between the matrix and the particle $(\alpha_p - \alpha_M)$ should be minimum to allow maximum possible transformational stresses to build up [21].

The above conditions are not met in the present case, consequently microcracking does not appear to be the dominant toughening mechanism. Conversely, the increasing of toughness and flexural strength in mullite/ZrO_2 composites could be due to a strengthening–grain-boundary mechanism produced by a continuous metastable solid solution at the grain boundary between ZrO_2 and mullite. A similar effect has been observed in some metal alloys [22, 23]. The fact that a mainly transgranular fracture behaviour has been observed in this composite (Fig. 4) is additional support for this proposition. Scanning transmission electron microscope microanalyses performed on the sample mullite + 15 vol% ZrO_2 at the mullite–zircona grain boundary [24] showed the existence of an extensive solid solution of ZrO_2 in mullite (> 10 wt%). The amount of this solid solution decreases toward the centre of the grain. This preliminary result is in agreement with what has previously been stated.

4. Conclusions

1. A pure dense mullite has been obtained at low temperatures (1570° C) by isostatic pressure from a very active premullite powder.

2. The presence of a dispersed phase of ZrO_2 enhances the sintering rate, the K_{IC} from 2 to 3 MN m$^{-3/2}$ and the σ_F from 200 to 300 MPa. The fractional tetragonal content of ZrO_2 does not influence the K_{IC} and σ_F over the compositions tested.

3. A grain-boundary strengthening is proposed as the principal toughening mechanism of the mullite/ZrO_2 composites, produced by a meta-

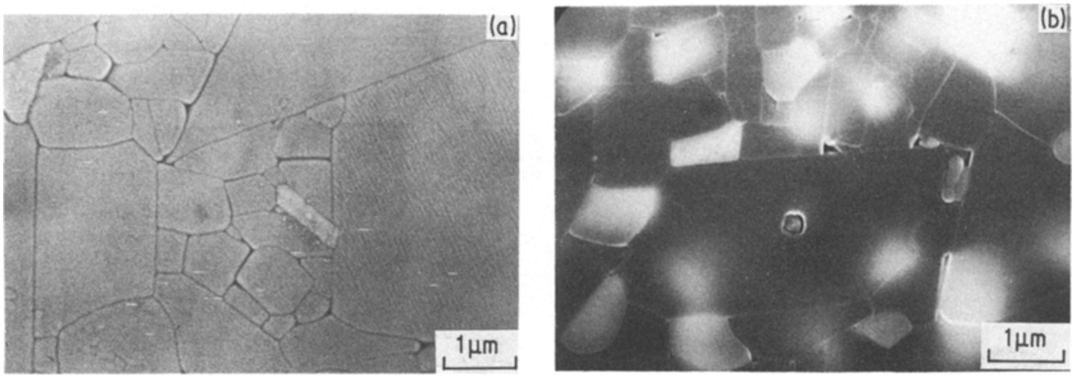

Figure 6 SEM microphotographs of: (a) mullite and (b) mullite/ZrO_2 composite annealed for 16 h at 1570° C.

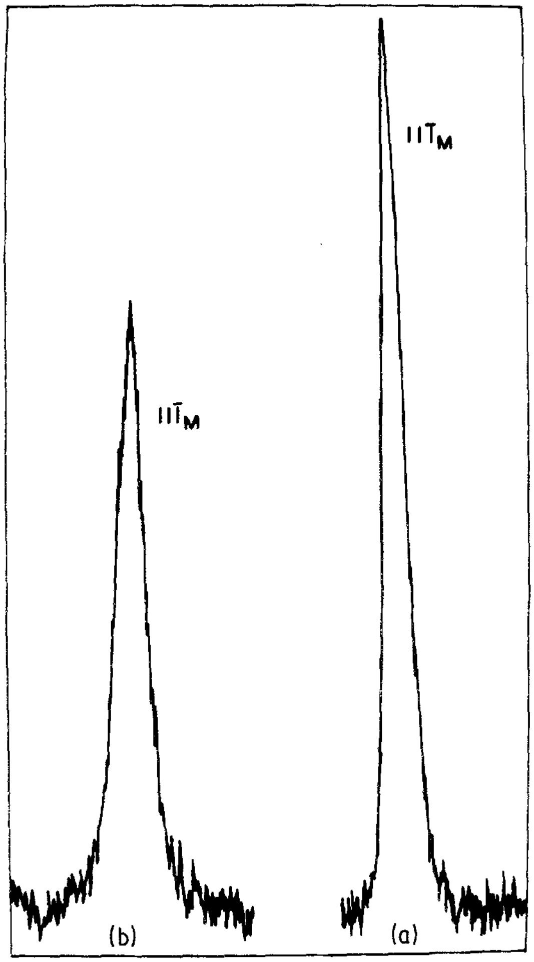

Figure 7 $(11\bar{1})_M ZrO_2$ peak for: (a) mullite + 5 wt% ZrO_2; (b) premullite + 5 wt% ZrO_2, heated at 1570° C for 2.5 h.

stable solid solution between mullite and ZrO_2 grains.

Acknowledgements

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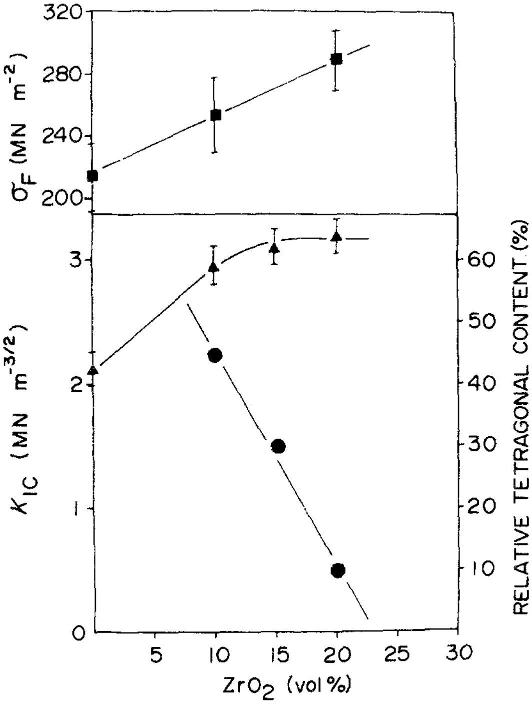

Figure 8 Toughness (K_{IC}), bending strength (σ_F) and relative tetragonal content against the additions of ZrO_2.

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