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Ageing effect on microstructural and mechanical properties of mullite–ZrO_2–TiO_2 composites

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The microstructural and mechanical properties of mullite–zirconia composites with TiO_2 (0.25 and 1.0 mol) additions have been studied, after ageing the samples over a wide temperature range (1000 to 1500° C) for long periods of time (100 to 200 h). In the sample with 0.25 mol TiO_2 addition, changes in mullite composition and in the solid state compatibility at temperatures below 1450° C were detected. In the sample containing 1 mol TiO_2, decomposition of Al_2TiO_5 occurs at $T \leqslant 1200°$ C. Both compositions exhibit no increment in zirconia average grain size during ageing and, concomitantly, there is no strength degradation until higher temperatures (>1400° C) are reached, which become more drastic when Al_2TiO_5 is present.

1. Introduction

Mullite–zirconia reaction-sintered composites with TiO_2 additions have proved to be [1–3] low-cost materials with reasonable high strength (300 to 350 MPa) and toughness (≈ 5 MPa m$^{1/2}$) values.

It has been shown in the literature [4–6] that higher temperature mechanical performance of zirconia-based ceramics is very dependent on microstructure as well as on microchemistry changes during ageing treatments. In order to understand the higher temperature microstructural and chemical stability of mullite–zirconia containing TiO_2 composites and how these parameters affect the mechanical behaviour, a study was made of the microstructural changes in these multicomponent composites as well as their effect on the mechanical properties during high-temperature ($\geqslant 1000°$ C) ageing treatments.

2. Experimental procedure

Taking into account the compatibility relationships in the ZrO_2–SiO_2–Al_2O_3–TiO_2 system [7], two different kinds of composition were formulated, according to the equations and the following molar proportions

$$2ZrSiO_4 + (3 + X)Al_2O_3 + XTiO_2 \rightarrow 2ZrO_{2(ss)} + Al_6Si_2O_{13(ss)} \quad (1)$$

with $X = 0.25$

$$2ZrSiO_4 + (3 + X)Al_2O_3 + XTiO_2 \rightarrow 2ZrO_{2(ss)} + Al_6Si_2O_{13(ss)} + Al_2TiO_5 \quad (2)$$

with $X = 1$

These are the (a) and (b) in Fig. 5.

Appropriate quantities of zircon (Zircon Opazir-S Quiminsa S.A., Spain), Al_2O_3 (Al_2O_3 CT 3000 SG Alcoa, USA) and titania (Titania Merck, West Germany) required to produce mullite–zirconia and mullite–zirconia–aluminium titanate composites as indicated by Reactions 1 and 2, were used. In both cases the powders were homogenized by attrition milling in a teflon-coated attritor using alumina balls in an isopropyl alcohol suspension. After drying and sieving, the raw compositions were isostatically pressed at 200 MPa.

The resulting cylindrical green bars were sintered at 1500° C, 2 h ($X = 1$ composition) and 1550° C 2 h ($X = 0.25$) in air. Sintered bars were subsequently aged at 1000, 1200, 1400, 1450 and 1500° C for times ranging from 0 to 200 h.

Powdered samples ($d < 35\,\mu$m), after sintering and ageing, were then analysed by X-ray diffraction (XRD) using CuKα radiation.

The final density of the sintered and aged material was determined by the Archimeds method using distilled water.

The sample microstructure was observed by reflected light optical microscopy (RLOM) and by scanning electron microscopy–energy dispersive spectrometry (SEM–EDS) after polishing and thermal etching. The zirconia average grain size was estimated in samples submitted to different heat treatments, by measuring lineal intercepts on scanning electron micrographs according to the Fullman and Richmon technique [8].

Bending strength (σ_F) was determined by the three-point bend method on cylindrical bars with ≈ 4 mm diameter and ≈ 80 mm length. The toughness (K_{IC}) value of different samples was determined by the indentation method [9].

3. Results and discussion

In Fig. 1 the phase evolution plotted against ageing

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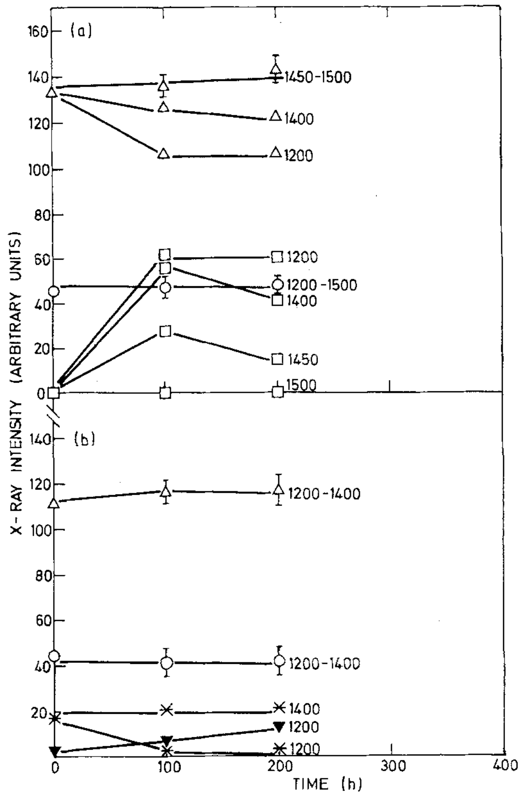


Figure 1 Phase evolution plotted against ageing time at different temperatures for (a) $X = 0.25$, (b) $X = 1$. (○) Mullite (1 1 0), (□) $ZrSiO_4$ (2 0 0), (△) m-ZrO_2 (1 1 1), (⁎) Al_2TiO_5 (1 1 0), (▼) rutile (1 1 0).

time at different temperatures for $X = 0.25$ and $X = 1$ compositions is shown. The RLOM micrographs corresponding to $X = 0.25$ and $X = 1$ samples are given in Fig. 2. Scanning electron micrographs corresponding to $X = 0.25$ as-sintered and after 100 h ageing at 1200° C, and $X = 1$ indicating the presence of zircon grains, are shown in Fig. 3. Fig. 4 shows the σ_f–time plots at different temperatures for $X = 0.25$ and $X = 1$ compositions.

The density and K_{IC} values for the different samples are reported in Table I. For $X = 1$ composition (Fig. 1) the only change observed in the initial starting phases, during ageing at different temperatures occurs at 1200° C as a consequence of aluminium titanate eutectoid decomposition into rutile plus alumina [10].

Conversely, when the composition is located in the solid solution region ($X = 0.25$), the appearance of zircon during the ageing treatment at $T \leqslant 1400°$ C without the simultaneous appearance of α-Al_2O_3 could be related to the shift of mullite composition from that as-sintered (fired at 1550° C) towards others with high alumina content. The Al/Si ratio in the samples as-fired (1550° C, 2 h) and after 100 h ageing at 1200° C changes from 2.90 to 3.41 which is in agreement with previous statement (Fig. 3). Okada *et al.* [11] reported a large chemical composition change in mullite formed at different temperatures. The mullite formed at ≈ 1000° C showed higher alumina content

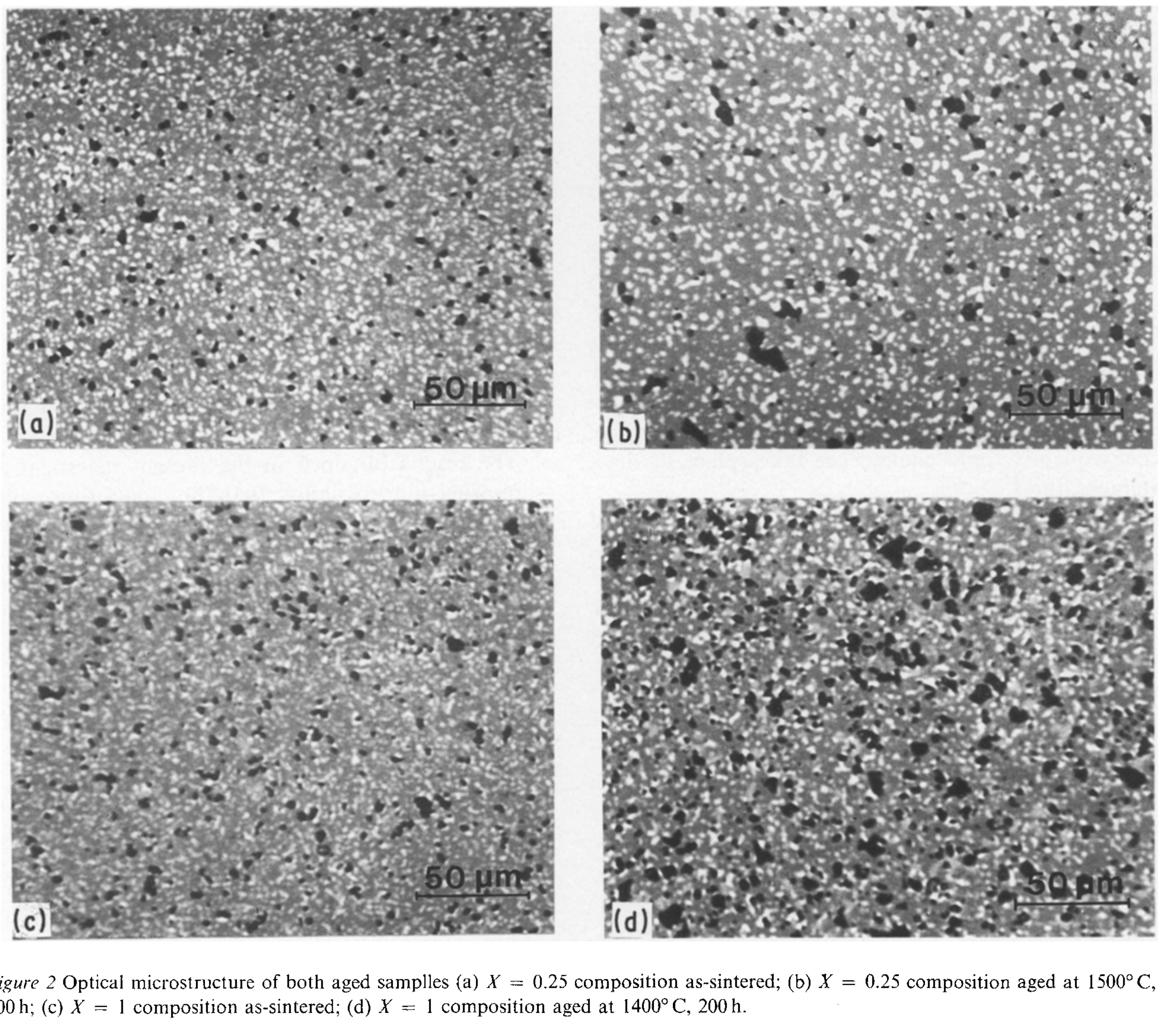
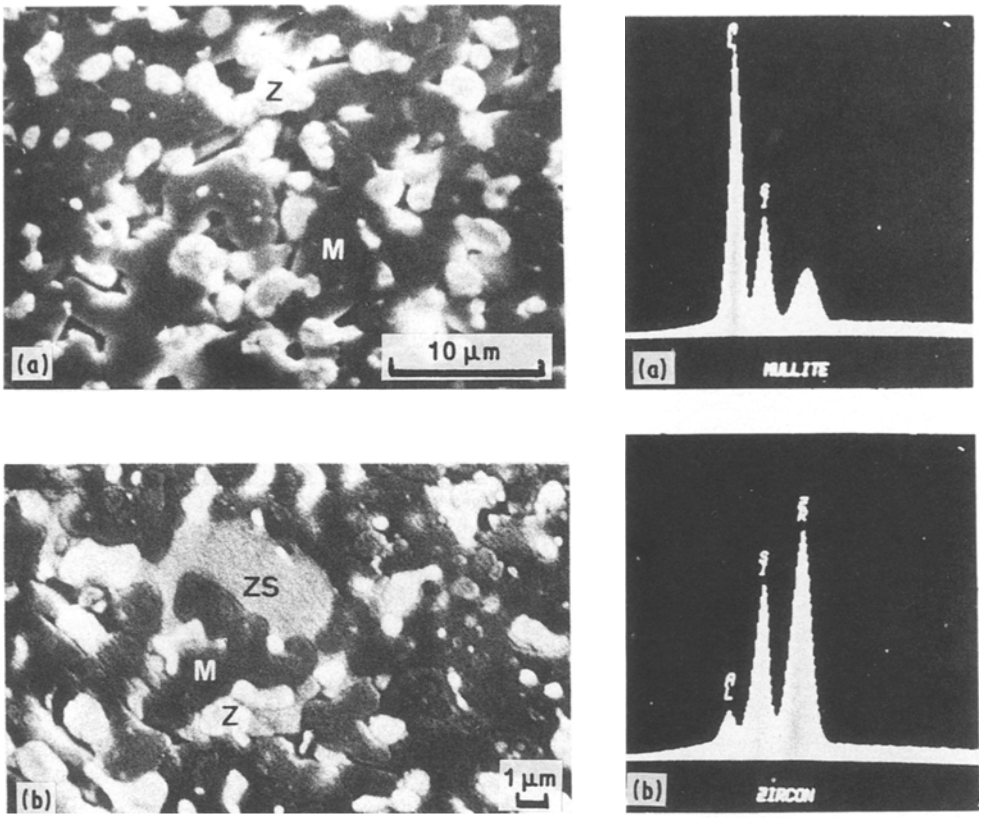


Figure 2 Optical microstructure of both aged sampIles (a) $X = 0.25$ composition as-sintered; (b) $X = 0.25$ composition aged at 1500° C, 100 h; (c) $X = 1$ composition as-sintered; (d) $X = 1$ composition aged at 1400° C, 200 h.



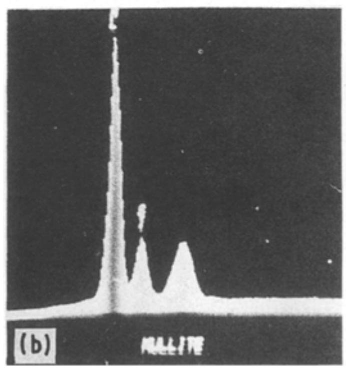


Figure 3 Scanning electron micrographs and corresponding EDX spectra for $X = 0.25$ composition, (a) as-sintered, A/Si = 2.90; (b) aged at 1200° C, 100 h, A/Si = 3.41.

in the sample $X = 0.25$ (Figs 3 and 5) at temperatures below 1450° C the new compatibility tetrahedra for this composition could be A_3S_2(ss)–$Z_{(ss)}$–ZS.

On the microstructural evolution of both samples during ageing, the following points can be made.

1. In both compositions, the porosity appears to be constant over all ageing treatments. No noticeable variation in the final density was detected (Table I).

2. A significant increase in the average pore size was detected in compositions $X = 0.25$ and $X = 1$ after ageing at 1450 and 1400° C, respectively. This effect was more evident in composition $X = 1$ (Fig. 2), consequently, pore coalescence takes place at these temperatures.

3. At ageing temperatures $\geqslant 1400°$ C, zirconia and aluminium titanate (in $X = 1$) grain growth takes place, as can be observed in Figs 2 and 6.

The strength degradation observed for compositions $X = 0.25$ and $X = 1$ at $T \geqslant 1450°$ C and (75 mol %) than that obtained at $T > 1400°$ C (65 mol %). The authors explained these results as a problem of metastability.

The results obtained in the present investigation supported the possibility that the equilibrium solid solution region in the SiO_2–Al_2O_3 system [12] below 1200° C shift toward the higher alumina region.

Fig. 5 represents the different sections of the compatibility tetrahedra over the plane ZS–Al_2O_3–TiO_2 at ≈ 1600° C. Considering the phase evolution observed

TABLE I Final density and toughness values

	Sample	As-sintered	1200° C, 200 h	1400° C 200 h	1450° C 200 h	1500° C 100 h
Final density ($g\,cm^{-3}$)	$X = 0.25$	3.65 (±0.01)	3.64 (±0.01)	3.66 (±0.00)	3.66 (±0.01)	3.63 (±0.02)
	$X = 1$	3.58 (±0.02)	3.54 (±0.11)	3.62 (±0.01)	–	–
K_{IC} ($MPa\,m^{1/2}$)	$X = 0.25$	4.4 (±0.1)	4.5 (±0.2)	4.5 (±0.2)	4.7 (±0.3)	4.8 (±0.4)
	$X = 1$	4.0 (±0.2)	4.1 (±0.2)	4.4 (±0.2)	–	–

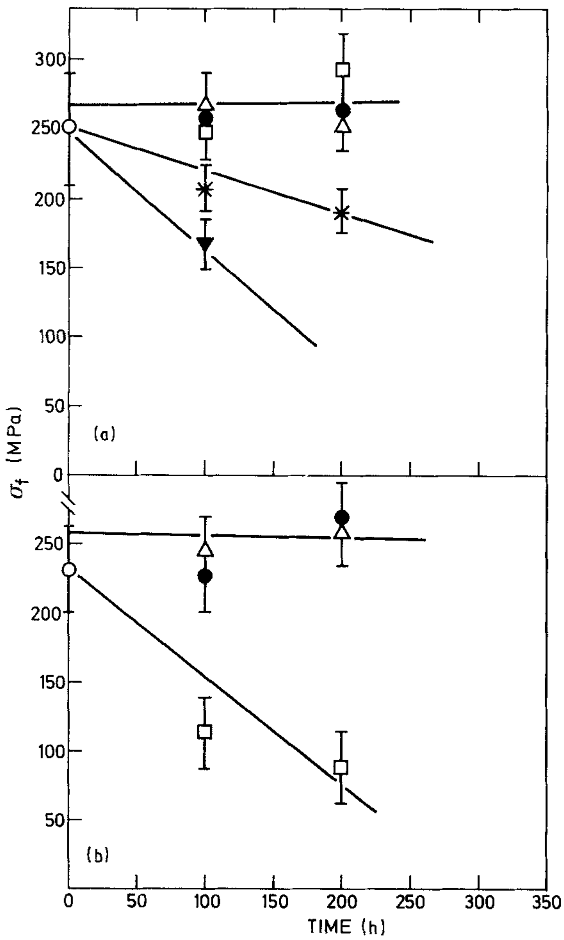


Figure 4 Bending strength plotted against time at different ageing treatments for (a) $X = 0.25$, (b) $X = 1$. (○) As-sintered, (●) 1000° C, (△) 1200° C, (□) 1400° C, (×) 1450° C, (▼) 1500° C.

$T \geqslant 1400°$ C, respectively, can be associated with pore coalescence and zirconia particle coarsening. These effects are more marked in sample $X = 1$, where, in addition, aluminium titanate grain growth is also present to produce a negative effect in the σ_f/ value (Fig. 4). K_{IC} increases in the samples treated at temperatures $\geqslant 1400°$ C for both compositions as shown in Table I. This is probably due to the contribu-

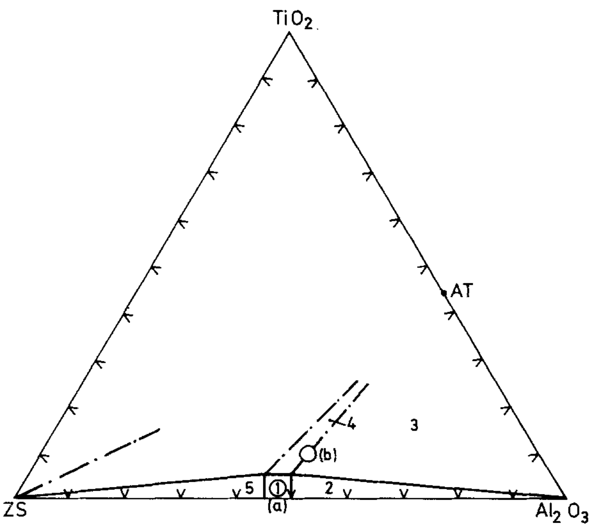


Figure 5 Compatibility tetrahedra sections corresponding to $\approx 1600°$ C with the inherent solid solutions. 1, A_3S_{2ss}–Z_{ss}; 2, Z_{ss}–A_3S_{2ss}–A; 3, Z_{ss}–A_3S_{2ss}–A–AT_{ss}; 4, Z_{ss}–A_3S_{2ss}–AT_{ss}; 5, A_3S_{2ss}–Z_{ss}–ZS.

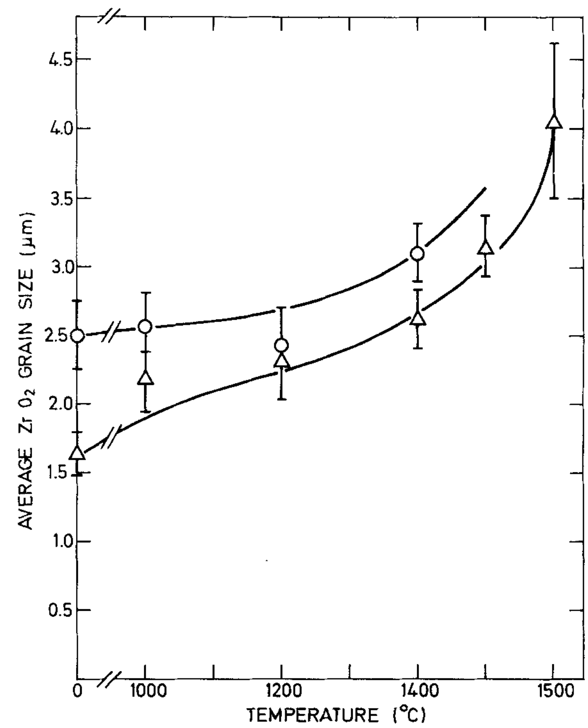


Figure 6 Plot of average grain size against temperature. (△) $X = 0.25$, (○) $X = 1$, after 100 h ageing.

tion of microcracking–toughening as a consequence of the higher average grain size of zirconia particles. This fact agrees with data previously reported by Srikrishna *et al.* [12].

4. Conclusions

1. No microstructural or mechanical degradation is observed for $X = 0.25$ and $X = 1$ compositions at temperatures below 1450 and 1400° C, respectively.

2. Degradation is present in both composites at temperatures higher than 1450 and 1400° C and is related to pore coalescence and particle coarsening. Both effects are more evident in composition $X = 1$.

3. Because of the change in mullite composition and in solid state compatibilities which take place at $T < 1450°$ C, the zircon is compatible with mullite (ss) and zirconia (ss), in $X = 0.25$ composition. This change does not substantially affect the mechanical properties of the samples.

4. An increase in K_{IC} values is seen for both composites during ageing treatments at higher temperatures ($> 1400°$ C).

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