JOURNAL OF MATERIALS SCIENCE 20 (1985) 2711–2718

Multicomponent toughened ceramic materials obtained by reaction sintering

Part 3 *System ZrO_2–Al_2O_3–SiO_2–TiO_2*

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Very dense zirconia-toughened ceramics with a mullite matrix based on the quaternary system ZrO_2–Al_2O_3–SiO_2–TiO_2 in the temperature range 1450 to 1550° C have been obtained by reaction sintering of zircon/alumina/titania mixtures. The reaction mechanism, advance of reaction, microstructure and mechanical properties of different compositions are reported. The results are explained in terms of a transitory liquid phase that appears at ~ 1400° C.

1. Introduction

As mentioned in parts 1 and 2 [1, 2] reaction sintering between zircon and alumina in order to produce zirconia-toughened mullite has received much attention in earlier publications. This paper concerns the effect of titania additions on the reaction sintering of $ZrSiO_4/Al_2O_3$ mixtures. In this system there are solid solutions of TiO_2 in mullite, and of TiO_2 in ZrO_2. This fact, together with the possible appearance of a transitory liquid phase, can play an important role in the reaction sintering process.

2. The phase equilibrium diagram ZrO_2–Al_2O_3–SiO_2–TiO_2

The system ZrO_2–Al_2O_3–SiO_2–TiO_2 has been studied by Pena and de Aza [3, 5]. Figs. 1a and b show the compatibility relationships of this quaternary system and the projection from the zirconia corner on to the opposite face of the composition tetrahedron.

Taking into account the compatibility in the solid state (Fig. 1a) and the experimental results obtained in previous works [1–5], $ZrSiO_4/Al_2O_3/TiO_2$ compositions with the following molar proportion were studied:

$$2ZrSiO_4 + 3Al_2O_3 + x(Al_2O_3 + TiO_2)$$

where x is variable. These compositions are located on the straight line defined by the equation

$$\underset{\text{zircon}}{2ZrSiO_4} + 3Al_2O_3 + x(Al_2O_3 + TiO_2) \rightarrow 2ZrO_2 + \underset{\text{mullite}}{Al_6Si_2O_{13}} + x\underset{\substack{\text{aluminium}\\\text{titanate}}}{Al_2TiO_5} \quad (1)$$

According to the system ZrO_2–Al_2O_3–SiO_2–TiO_2 the compositions studied were located in the subsolidus compatibility plane zirconia–mullite–aluminium titanate (Fig. 1b), and consequently the initial liquid formation takes place at 1595° C. From the projection of the primary phase volume of ZrO_2 from the zirconia corner on the opposite face of the composition tetrahedron (Fig. 1b) it can be stated that both compositions with $x \geqslant 0$ are situated in the primary phase field of ZrO_2.

However, in the case of $x = 1$ the secondary phase is Al_2O_3 and in the case of $x = 0.25$ the corresponding secondary phase is mullite. It should be emphasized that TiO_2 forms stable solid solutions with ZrO_2 and mullite. According to Pena and de Aza [3, 4] the solubility of TiO_2 into ZrO_2 and $Al_6Si_2O_{13}$ is about 4 wt %.

Taking into account these solid solutions, the two compositions just given have been studied. The composition with $x = 0.25$ is located inside

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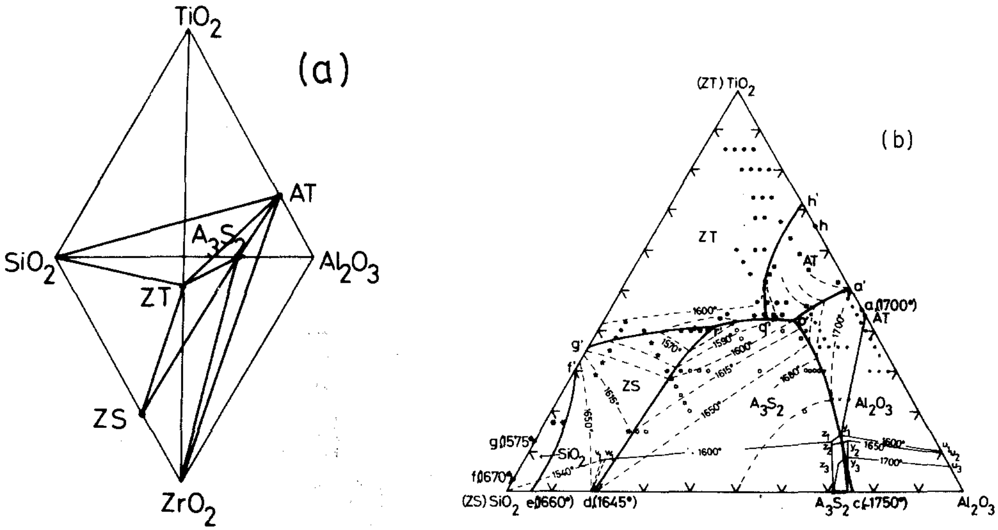


Figure 1 (a) Solid-state compatibility relationships in the $ZrO_2-Al_2O_3-SiO_2-TiO_2$ system; (b) Projection through the ZrO_2 corner showing secondary phases crystallizing during freezing from $ZrO_2-Al_2O_3-SiO_2-TiO_2$ mixtures containing 60 wt % ZrO_2. The various symbols represent experimental compositions.

the solid solubility limit of the compatibility volume $(ZrO_2)_{ss}-Al_6Si_2O_{13}$, whereas the $x = 1$ composition is in the compatibility plane $(ZrO_2)_{ss}-(Al_6Si_2O_{13})_{ss}-Al_2TiO_5$. $(\ )_{ss}$ = solid solution.

3. Experimental procedure

3.1. Materials

The raw materials used were zircon opacifier supplied by Quiminsa, Castellion, Spain, (Opazir S), a finely milled mineral zircon: USA Al_2O_3 R.C. 172 DBM; and Merck AR Grade TiO_2 (99.9%).

3.2. Sample preparation and firing

$ZrSiO_4/Al_2O_3/TiO_2$ mixtures were made up in the molar proportions of Equation 1 where x took the values 0.25 and 1. The mixtures were then subjected to the treatment reported in Part 1 [1]. Finally the samples were fired in an electrical temperature-controlled furnace heated by Kanthal elements in the temperature range 1300 to 1550° C, and subsequently air-quenched.

3.3. Density measurements

Using the same procedure as before [1], the sample densities after different heat treatments were measured by both water and mercury displacements and theoretical densities were calculated, considering the phase compositions of the product as well as the true density values of zircon (4.68 $Mg\,m^{-3}$), mullite ($3.16\,Mg\,m^{-3}$) and Al_2TiO_5 ($3.702\,Mg\,m^{-3}$).

3.4. X-ray analysis

The samples were examined by X-ray analysis as before [1] and (1 1 3) Al_2O_3, $(1\,1\,\bar{1})$ ZrO_2, (2 0 0) $ZrSiO_4$ and (1 1 0) mullite lines were used to estimate the extent of the chemical reactions in terms of α and β expressions.

3.5. Microstructural analysis

Sample microstructure was observed in a reflected light microscope and after thermal etching (2 h at 1350° C) or chemical etching (10% HF) by SEM (JEOL) and energy dispersive X-ray microanalysis (EDAX).

3.6. Mechanical properties

The critical intensity factor (K_{IC}) was determined by the indentation method [6] and the bend strength (σ_f) by the three point method on cylindrical samples with diameter ~4 mm and length 8 mm, using an Instron machine.

4. Results and discussion

The reaction of zircon and alumina powders in the presence of titania takes place during firing to produce mullite/zirconia and mullite/zirconia/aluminium titanate composites.

X-ray diffraction (XRD) analysis of the compositions studied, after different temperatures and times, showed (Fig. 2) that the reaction between the components proceeds, in the case of $x = 1$, in two steps which can be described by the following

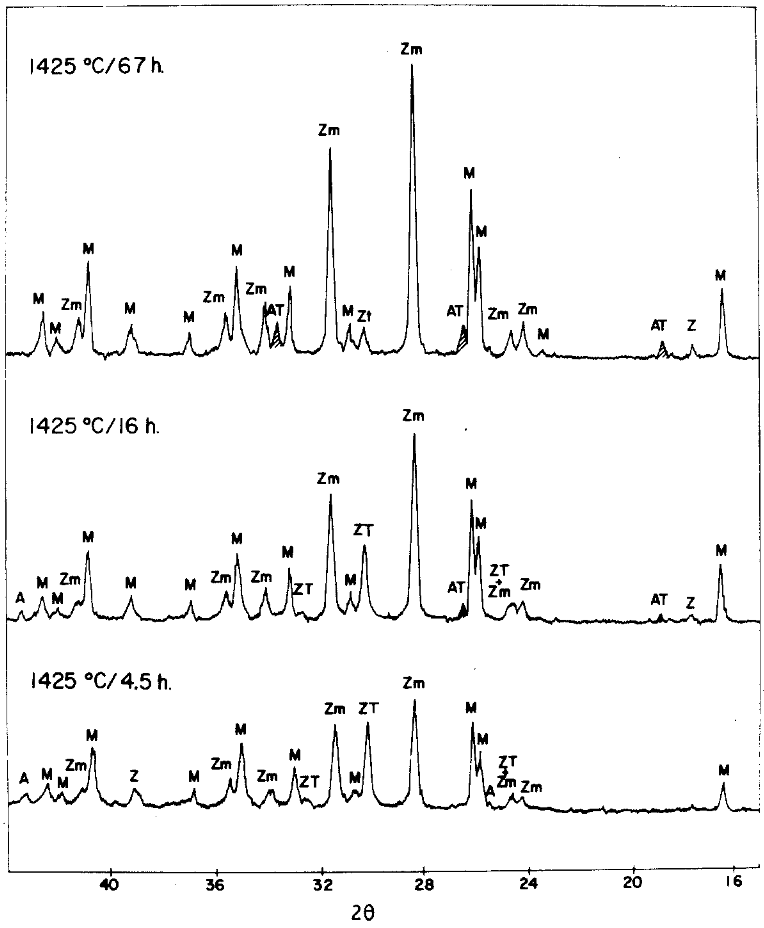


Figure 2 XRD patterns corresponding to $x = 1$ after different times at 1425° C. ZT = $ZrTiO_4$; M = $Al_6Si_2O_{13}$; A = Al_2O_3; Zm = ZrO_2 (*m*); Zt = ZrO_2 (*t*) AT = Al_2TiO_5.

equations at 1425° C:

$$2ZrSiO_4 + 4Al_2O_3 + TiO_2 \rightarrow Al_6Si_2O_{13} + ZrO_2 + ZrTiO_4 + Al_2O_3 + \text{transient liquid phase} \quad (2)$$

$$Al_6Si_2O_{13} + ZrO_2 + ZrTiO_4 + Al_2O_3 + \text{transient liquid phase} \rightarrow (Al_6Si_2O_{13})_{ss} + (ZrO_2)_{ss} + Al_2TiO_5 \quad (3)$$

For $x = 0.25$ the aluminium titanate does not form even after long periods (70 h) at 1425° C, which is in agreement with the prediction of the corresponding quaternary phase diagram [3, 5].

In order to elucidate the true mechanism for the appearance of the transitory liquid phase referred to in the above equations, long (20 h) heating experiments at lower temperatures (1300, 1350 and 1400° C) were carried out. The corresponding XRD patterns are shown in Fig. 3. As can be seen, at 1300° C no sign of reaction is detected. However at 1350° C TiO_2 (rutile) has completely disappeared, a considerable amount of $ZrTiO_4$ (ZT) is present and a small amount of mullite is formed. At 1400° C no sign of zircon is present, but $ZrTiO_4$ coexists with $Al_6Si_2O_{13}$, ZrO_2 and Al_2O_3. At 1425° C (Fig. 2) the expected equilibrium phases ZrO_2, $Al_6Si_2O_{13}$ and Al_2TiO_5 are reached after 67 h.

The fact that at 1350° C mullite, zircon, and ZT coexist confirms that the transitory liquid phase must correspond to the quaternary invariant point $ZrSiO_4 + Al_6Si_2O_{13} + ZrTiO_4 + SiO_2$. This is the lowest invariant point of the ZrO_2–Al_2O_3–SiO_2–TiO_2 system [7], being the zircon present.

With increasing temperature (> 1400° C) reaction sintering progresses through the boundary line r′q′ (Fig. 1b) in which ZrO_2, $Al_6Si_2O_{13}$ and $ZrTiO_4$ coexist with a small amount of a transitory liquid phase which must disappear together with $ZrTiO_4$. In the present case, a permanent liquid phase appears at the invariant point of the compatibility plane Al_2TiO_5, ZrO_2, $Al_6Si_2O_{13}$ (1600° C).

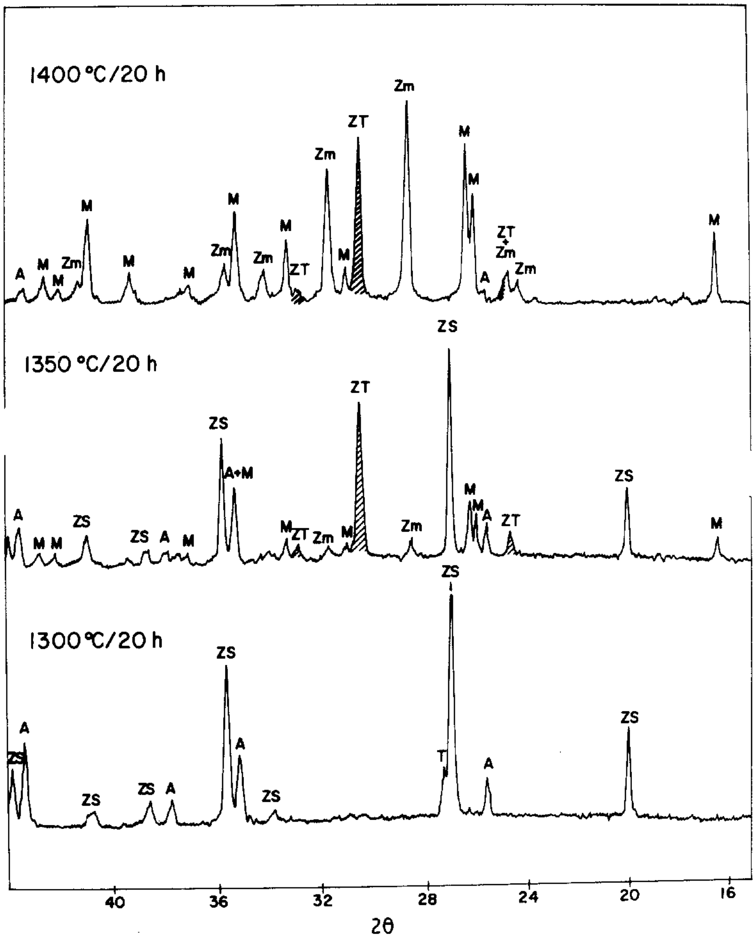


Figure 3 XRD patterns corresponding to $x = 1$ heated for 20 h at different temperatures. ZS = $ZrSiO_4$; A = Al_2O_3; T = TiO_2; ZT = $ZrTiO_4$; M = $Al_6Si_2O_{13}$; Z_m = ZrO_2 (*m*).

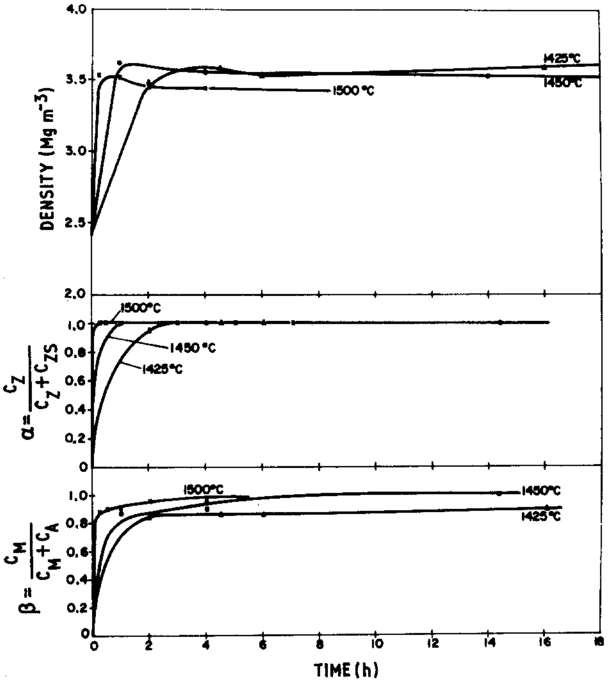


Figure 4 Densification and reaction rate against time at different temperatures for $x = 0.25$. C_m, C_A, C_z, C_{zs} are the concentration of mullite, alumina, zirconia and zircon respectively.

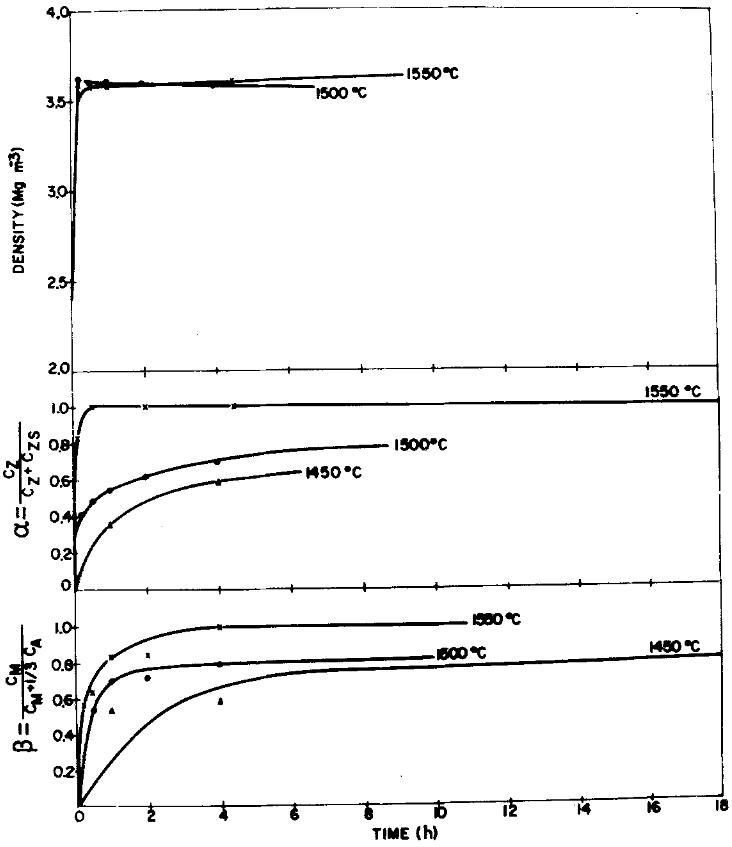


Figure 5 Densification and reaction against time at different temperatures for $x = 1$.

Figs. 4 and 5 show plots of density, advance of zircon dissociation (α) and mullite formation (β) against time at different temperatures. From these figures it can be stated:

(a) For $x = 1$ (Fig. 5) the two reactions take place almost at the same time. After four hours of treatment even at the lowest temperature studied, all zircon was dissociated and the value of β was about 80%.

(b) From the density and reaction curves it can be stated that reaction and sintering go together.

(c) The presence of titania increases the reaction rate. This effect is drastic in the case of $x = 1$, as can be deduced by comparing Fig. 6 with Figs. 4 and 5.

Contrary to what has been observed in CaO and MgO-containing compositions [1, 2], in the present case zircon dissociation and mullite formation occur simultaneously.

Fig. 7 shows SEM micrographs corresponding to $x = 0.25$ heated for 1 h at 1550° C and $x = 1$ heated for 2 h at 1500° C. As can be seen in the

TABLE I Properties of zircon/alumina/titania mixtures

Molar composition*	T (° C)	Time (h)	X_t (%)	σ_f† (MPa)	K_{IC} (MPa m$^{1/2}$)
2 ZS/4 A/T	1500	1	49	250 ± 21 Max = 280	4.7 ± 0.1
	1500	2	16	240 ± 10 Max = 250	4.5 ± 0.1
2 ZS/3.25 A/0.25 T	1500	2	5	310 ± 23 Max = 350	4.9 ± 0.1
	1550	1	6	270 ± 17 Max = 300	4.9 ± 0.1

*ZS = $ZrSiO_4$, A = Al_2O_3, T = TiO_2

†Average value over 5 measurements

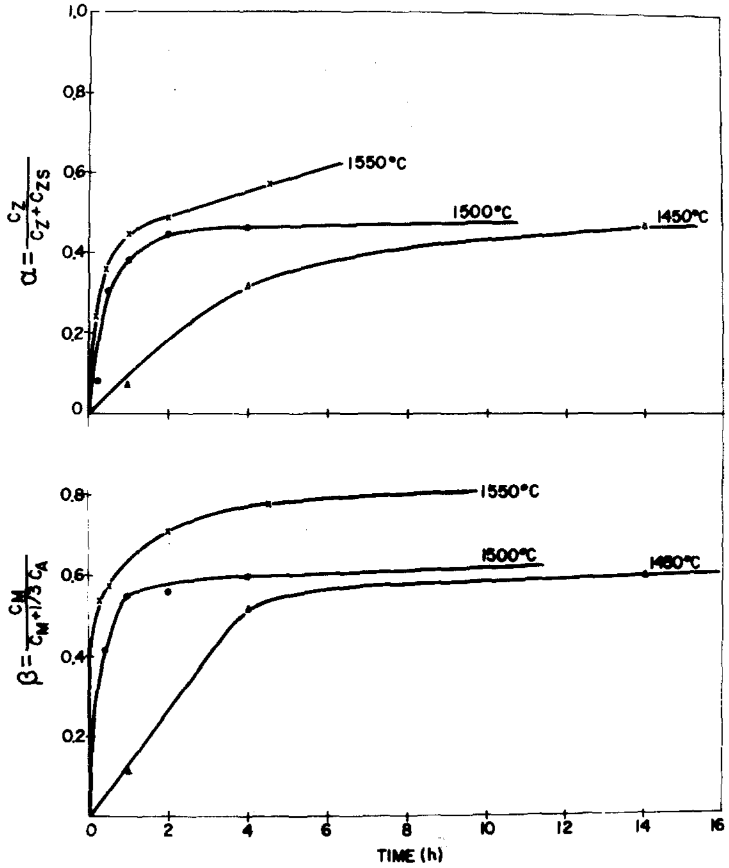
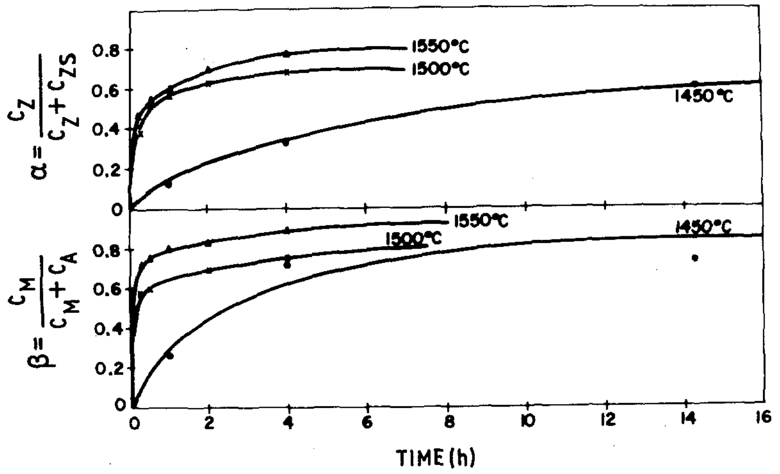


Figure 6 Reaction rate against time at different temperatures for $x = 0$.



present case the mullite grains are almost equiaxed with an average size of ~4 μm, and practically all zirconia grains located in intergranular positions. The aluminium titanate grains (Fig. 8) are intergranular with sizes ranging from 4 to 6 μm.

Table I gives the mechanical properties as well as the relative tetragonal content for $x = 1$ and $x = 0.25$ samples treated at different temperatures and times. From these data the following points can be deduced:

(a) TiO_2 additions over the solid solubility limit decrease the values of σ_f and K_{IC}. This fact can be explained by the appearance of a third phase of aluminium titanate (AT).

(b) No relationship is observed between the tetragonal zirconia content, K_{IC} and σ_f.

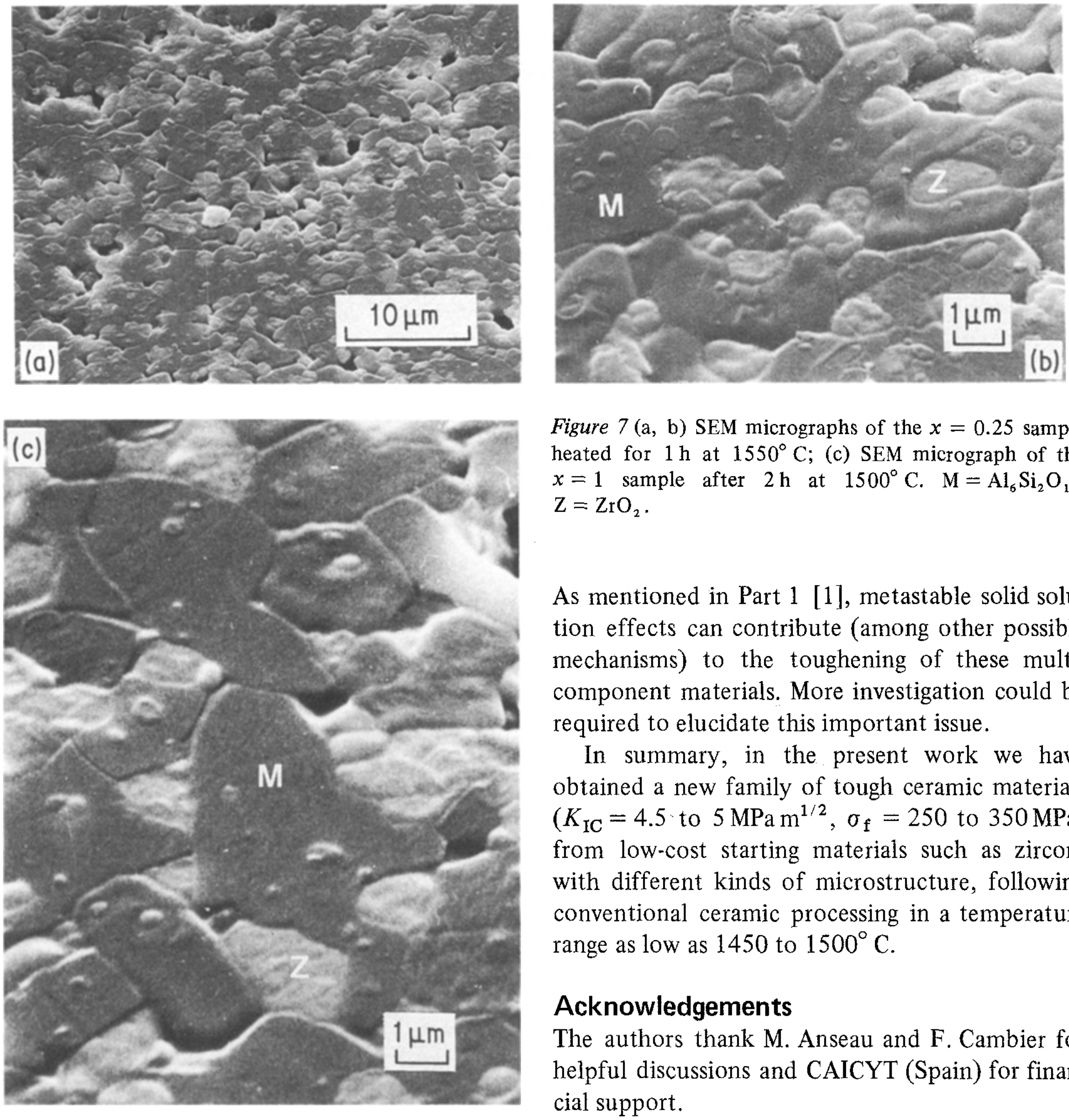


Figure 7 (a, b) SEM micrographs of the $x = 0.25$ sample heated for 1 h at 1550° C; (c) SEM micrograph of the $x = 1$ sample after 2 h at 1500° C. $M = Al_6Si_2O_{13}$; $Z = ZrO_2$.

As mentioned in Part 1 [1], metastable solid solution effects can contribute (among other possible mechanisms) to the toughening of these multicomponent materials. More investigation could be required to elucidate this important issue.

In summary, in the present work we have obtained a new family of tough ceramic materials ($K_{IC} = 4.5$ to $5\,\mathrm{MPa\,m^{1/2}}$, $\sigma_f = 250$ to $350\,\mathrm{MPa}$) from low-cost starting materials such as zircon, with different kinds of microstructure, following conventional ceramic processing in a temperature range as low as 1450 to 1500° C.

Acknowledgements

The authors thank M. Anseau and F. Cambier for helpful discussions and CAICYT (Spain) for financial support.

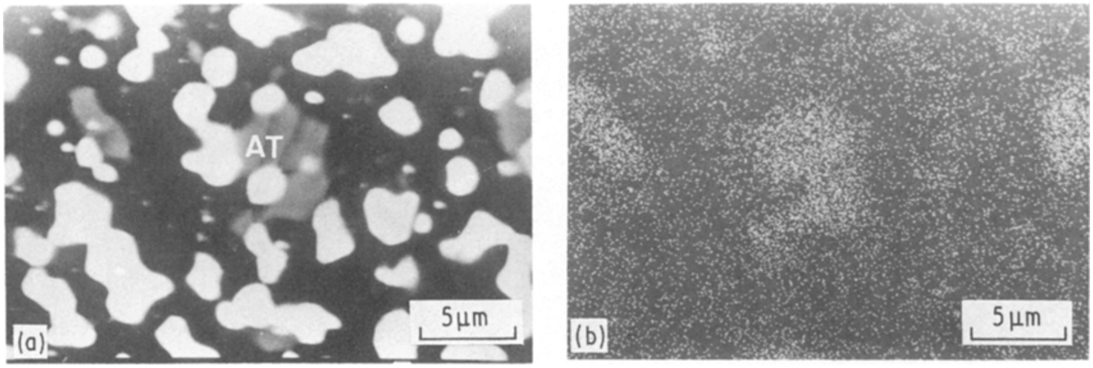


Figure 8 (a) Back-scattered electron image of $x = 1$ sample (2 h at 1500° C); AT = aluminium titanate. (b) TiK_α X-ray image of the same area.

References

1. P. PENA, P. MIRANZO, J. S. MOYA and S. de AZA, *J. Mater. Sci.* **20** (1985) 2011.
2. *Idem, ibid.* **20** (1985) 2702.
3. P. PENA and S. de AZA, *La Ceramica* **30** (1977) 1.
4. *Idem, Sci. Ceram.* **9** (1977) 247.
5. *Idem, ibid.* **12** (1983) 201.
6. P. MIRANZO and S. MOYA, Int. Ceramics (in press).
7. P. PENA and S. de AZA. *J. Mater. Sci.* **19** (1984) 135.

Received 25 June
and accepted 6 July 1984