

# Physical and thermal characteristics of aluminium titanate dispersed with $\beta$ -spodumene and zirconia

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The effects of  $\beta$ -spodumene ( $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$ ) and zirconia additives on the physical and thermal characteristics aluminium titanate (AT) ceramics have been investigated. XRD, DTA, SEM, TEM and dilatometry have been used to characterise the influence of these additives on phase relations, densification, microstructure, thermal expansion, thermal decomposition and thermal shock behaviour of AT. The results show that the presence of both  $\beta$ -spodumene and zirconia significantly reduces porosity, lowers thermal expansion, improves densification, hardness and thermal stability, without degradation of thermal shock resistance. Microstructural examinations have revealed the presence of glassy phase due to the phase separation of  $\beta$ -spodumene and spontaneous microcracks due to thermal expansion anisotropy of AT. © 2000 Kluwer Academic Publishers

## 1. Introduction

Aluminium titanate (AT) has a number of engineering applications due to its low thermal expansion, excellent thermal shock resistance, low thermal conductivity and nonwetting with many molten metals. Hence AT has been widely used as refractory crucibles for metal casting, flow regulators, and risers [1]. Other important applications include thermocouple sleeves, burner nozzles, and thermal insulators in heat engines [2]. However, its full exploitation has been limited by low the mechanical strength and poor thermal stability below 1280°C. In view of these limitations, considerable effort has been directed towards improving the mechanical properties and thermal stability of AT through (a) the addition of stabilisers (eg.  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{MgO}$ ) [3–5] (b) the incorporation of second phases [6–9] such as mullite and zirconia, (c) reaction sintering of [10]  $\text{Al}_2\text{O}_3/\text{TiO}_2/\text{ZrSiO}_4$  and  $\text{Al}_2\text{O}_3/\text{TiO}_2/\text{ZrSiO}_4/\text{MgO}$ , and (d) grain refinement [11]. The addition of  $\text{ZrO}_2$  (3–8 wt%) has been found to improve the mechanical strength of AT as a result of a grain-refinement effect [11].

AT is also difficult to sinter and density without the presence of additives. Although the use of sintering aid such as  $\text{Fe}_2\text{O}_3$  or  $\text{MgO}$  can significantly improve the densification of AT through liquid-phase sintering, its presence can raise the thermal expansion coefficient and thus has an undesirable affect on the thermal shock performance of AT. Hence it is desirable to use an additive which has a similar or lower thermal expansion coefficient. One such additive is spodumene ( $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2$ ).

Spodumene has been widely used in the glass and ceramic industry for decades as a lithia-bearing flux

and low-expansion filler in whiteware bodies [12–14]. The  $\alpha$ -polymorph of spodumene is a monoclinic pyroxene which is stable under ambient conditions. This phase undergoes an irreversible phase change at 1080°C, forming the more open tetragonal polymorph,  $\beta$ -spodumene, which melts at 1423°C. The transformation is accompanied by a 30% volume increase due to a density change from 3.2 to 2.4  $\text{g}\cdot\text{cm}^{-3}$ . It is also commonly used for making glasses and ceramics harder, smoother, and more chemical and thermal shock resistant. Recently, spodumene has been used as a liquid-phase sintering aid for the densification of alumina [15], mullite [16–18] and AT [19, 20] ceramics. The addition of spodumene has also been found to lower the thermal expansion coefficient of mullite [17, 18] and to improve the thermal shock resistance of alumina [21].

This paper describes the potential use of zirconia as a temporary stabiliser and  $\beta$ -spodumene as a sintering aid for the cost-effective processing and densification of AT ceramics. The effects of these additives on the sintering behaviour, phase relations, and physical and thermal characteristics are discussed.

## 2. Experimental procedure

### 2.1. Processing

Commercial titania (SCM Chemicals Ltd., median particle size ( $d_m$ ) 0.8  $\mu\text{m}$ ), alumina (A1000SG, Alcoa,  $d_m \approx 0.39 \mu\text{m}$ ), monoclinic zirconia (SF Ultra Z-Tech,  $d_m \approx 0.40 \mu\text{m}$ ), and calcined  $\beta$ -spodumene powders (Gwalia Consolidated Ltd.,  $d_m \approx 23 \mu\text{m}$ ) were used as the starting materials for the synthesis of zirconia-dispersed AT modified with spodumene. The chemical analyses of the titania, alumina and  $\beta$ -spodumene powders used are shown in Table I.

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TABLE I Chemical analyses (wt%) of starting raw materials

	Spodumene	Alumina	Titania
Al <sub>2</sub> O <sub>3</sub>	27.0	99.7	0.5
SiO <sub>2</sub>	64.0	<0.01	0.8
TiO <sub>2</sub>	0.02	<0.01	98.0
SO <sub>4</sub>			0.2
Li <sub>2</sub> O	8.10		
Fe <sub>2</sub> O <sub>3</sub>	0.16	0.03	
CaO	0.04	0.05	
MgO	0.02	<0.01	
Na <sub>2</sub> O	0.19	0.06	
K <sub>2</sub> O	0.05	0.06	
P <sub>2</sub> O <sub>5</sub>	0.11	<0.01	
LOI	0.3	0.46	0.5

TABLE II Formulations of various spodumene-modified AT/ZrO<sub>2</sub> ceramics

Sample	AT-ZrO <sub>2</sub> (wt%)	Spodumene (wt%)
ATZ0	100	0
ATZ2.5	97.5	2.5
ATZ5	95	5
ATZ10	90	10
ATZ15	85	15
ATZ30	70	30

An initial powder mixture of alumina-zirconia was obtained by wet ball milling 95 wt%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and 5 wt% monoclinic ZrO<sub>2</sub>. The slurry was then dried and sieved until free-flowing (45  $\mu$ m grid-size). An equimolar powder mixture of alumina-zirconia and titania was then thoroughly mixed using mortar and pestle for 20 min, followed by 1 h in a Turbula mixer. The powder mixture was then calcined at 1400°C for 3 h to form AT. The synthesised AT/ZrO<sub>2</sub> powder was subsequently mixed with 0–30 wt%  $\beta$ -spodumene using the same mixing procedure. The final powder mixture was uniaxially pressed in metal dies at a pressure of 150 MPa to yield cylindrical pellets of diameter 12.5 mm and height 5 mm, and rectangular bars of 4 mm  $\times$  12 mm  $\times$  60 mm. These samples were pressureless-sintered to form spodumene-modified AT/ZrO<sub>2</sub> ceramics using a high-temperature furnace (Ceramic Engineering Model HT 04/17) at a rate of 3°C·min<sup>-1</sup> to 450°C for 30 min, followed by 5°C·min<sup>-1</sup> to 1600°C for 3 h, and then furnace-cooled at a rate of 10°C·min<sup>-1</sup>. The formulations for each of the samples are shown in Table II.

## 2.2. Characterisation

Analysis of the phases formed was performed with a Siemens D500 X-ray diffractometer. The operating conditions used were: CuK $\alpha$  radiation ( $\lambda$  = 0.15418 nm) produced at 40 kV and with 0.15° receiving slit, goniometer range = 15–60°, step size = 0.06, counting time 1 s/step, and post-diffraction graphite monochromator with NaI detector and PHA. An incident beam divergence of 0.3° was used.

DTA measurements on the powder mixture were carried out on a Stanton Redcroft STA-780 to monitor the

thermochemical reactions taking place in nitrogen atmosphere at a heating rate of 20 °C/min. The thermal expansion behaviour of sintered and diamond-blade cut samples (11 mm  $\times$  4 mm  $\times$  50 mm) was characterised using a Netzsch 402 EP dilatometer in air at a heating rate of 20°C/min. Alumina was used as a standard for both DTA and thermal expansion measurements. The effect of ZrO<sub>2</sub> and  $\beta$ -spodumene additions on the short-term thermal stability of AT phase at 1050°C was also investigated. XRD patterns were collected from sintered samples which had been annealed at 1050°C for up to 20 h in order to study the thermal decomposition of AT.

The porosity and bulk density of the sintered samples were measured using the water displacement method. The Vickers hardness of sintered and polished samples (down to 1  $\mu$  diamond paste) was measured using a Zwick microhardness tester at a load of 200 N. The lengths of both diagonals of the impression were measured. At least three indents were made for each hardness test.

The microstructure of polished and gold-coated samples was observed using a JEOL JSM 6400 scanning electron microscope. No thermal ageing was done on the samples prior to microstructural examination. In order to observe and confirm the presence of glassy phase in the microstructure due to the presence of  $\beta$ -spodumene, the transmission electron microscopy (Joel, 200 kV) coupled with the selected-area diffraction and energy dispersive spectroscopy were performed on powdered samples. Fine powders of the sample were sprinkled on a copper grid coated with carbon film.

The thermal shock resistance of sintered pure AT and ATZ5 samples was compared by water-quenching rectangular bar samples (4 mm  $\times$  10 mm  $\times$  45 mm) from temperatures in the range 20–820°C. A pulse-sonic equipment (Grindo-Sonic) was used to monitor the variations of flexural modulus ( $E_f$ ) of thermally-shocked samples to ascertain their resistance to the formation of microcracks. The absence of an abrupt change in  $E_f$  with increasing temperature would indicate good resistance to thermal shock by virtue of minimal change in microcracks density.

## 3. Results and discussion

### 3.1. Phase relations

Aluminium titanate, AT (Al<sub>2</sub>TiO<sub>5</sub>), tetragonal zirconia ( $t$ -ZrO<sub>2</sub>) and  $\beta$ -spodumene were the phases observed for all the sintered samples, except for sample ATZ0 where only AT and  $t$ -ZrO<sub>2</sub> were present. The x-ray diffractograms of AT/ZrO<sub>2</sub> samples containing 0, 2.5 and 15 wt%  $\beta$ -spodumene are shown in Fig. 1. The presence of both zirconia and  $\beta$ -spodumene has not caused any observable line-shift of AT peaks which may indicate the absence of incorporation of foreign ions (eg. Zr, Li, Si) into the AT lattice. The recrystallisation of excess  $\beta$ -spodumene is clearly evident for samples containing the  $\beta$ -spodumene addition. This suggests that only a small amount of  $\beta$ -spodumene was involved in the process of densification of AT via liquid-phase-sintering, with the excess remaining as glassy phase

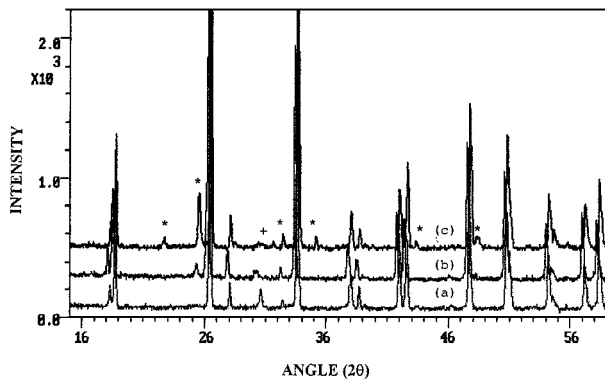


Figure 1 XRD plots of sintered AT/ZrO<sub>2</sub> samples containing various amounts of  $\beta$ -spodumene: (a) 0 wt%, (b) 2.5 wt%, and (c) 15 wt%. Note the recrystallisation of  $\beta$ -spodumene (\*) as a second phase. Tetragonal zirconia is denoted by (+).

and/or recrystallising during cooling. The glassy phase is believed to result from the melting and phase separation of  $\beta$ -spodumene at an elevated temperature. A similar behaviour was also observed for alumina ceramics containing 5–15 wt% spodumene [15].

The presence and intensity of the various crystalline phases in the samples are shown in Table III. As would be expected, the intensity of recrystallised  $\beta$ -spodumene increased as more  $\beta$ -spodumene was added. The presence of  $\beta$ -spodumene has clearly not reacted with AT and affected its stability. This is in contrast to a previous study on functionally-graded AT-ZTA composites [22] where presence of excess  $\beta$ -spodumene ( $\geq 9$  wt%) prevented the solid-state diffusion between Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> to form AT. In another study on alumina/calcium-hexaluminate (CaAl<sub>12</sub>O<sub>19</sub>) composites [23], the presence of excess  $\beta$ -spodumene ( $\geq 10$  wt%) reacted with CaAl<sub>12</sub>O<sub>19</sub> to form anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>). It remains unknown why the excess  $\beta$ -spodumene in this study had not reacted with AT to form another phase.

The presence of excess  $\beta$ -spodumene in this study is not expected to have undesirable effects on the thermo-mechanical properties of AT because it is widely known to possess a low coefficient of thermal expansion, relatively good strength and good thermal shock properties [14, 24].

TABLE III Petrographic phase analysis of various spodumene-modified AT/ZrO<sub>2</sub> ceramics

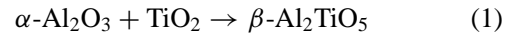
Samples	Intensity of Phases Detected		
	AT	$\beta$ -spodumene	<i>t</i> -ZrO <sub>2</sub>
ATZ0	vs	—	w
ATZ2.5	vs	w	w
ATZ5	vs	w-m	w
ATZ10	vs	m	w
ATZ15	vs	m	vw
ATZ30	vs	m-s	vw

Legends:

vs = very strong, s = strong, m-s = medium to strong, m = medium, m-w = medium to weak, vw = very weak

### 3.2. Thermal characteristics

The formation of AT in the samples is believed to occur via an endothermic reaction between Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> at approximately 1385°C [25, 26]:



The thermogram of sample ATZ15, recorded in the temperature range 20–1500°C is shown in Fig. 2. There was no evidence of AT endotherm at 1385°C because the sample contained previously synthesised AT powder. The endotherm at 1345°C was due to the melting of  $\beta$ -spodumene. This represents a shift of 78°C from the melting point of pure  $\beta$ -spodumene (1423°C), suggesting that there is an eutectic formed between  $\beta$ -spodumene and AT.

The effect of both zirconia and spodumene on the thermal expansion behaviour of AT for samples ATZ15 and pure AT is shown in Fig. 3. When compared to pure AT which experienced a positive thermal expansion, the presence of spodumene in ATZ15 caused an overall negative thermal expansion during heating between 20–1000°C. It is interesting to note that during cooling, the former showed a gradual contraction whereas the latter showed an initial *expansion* prior to contraction which may be attributed to the presence of the glassy phase. Such an initial expansion behaviour during cooling has also previously been observed for mullite containing 20 wt%  $\beta$ -spodumene [17, 18]. This suggests that the addition of  $\beta$ -spodumene to AT may result in improved thermal shock resistance by virtue of a lower thermal expansion coefficient (TEC). A similar reduction in TEC has also been observed for spodumene-modified mullite ceramics [17, 18].

The effect of zirconia and  $\beta$ -spodumene on the stability of AT against thermal decomposition during annealing at 1050°C for 20 h is shown in Fig. 4. When compared to pure AT, the presence of both zirconia and  $\beta$ -spodumene appears to have a significant effect in preventing the gradual decomposition of AT to TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, especially for the longer term thermal stability. However, the presence of  $\beta$ -spodumene alone (ie. without zirconia) does not appear to have any apparent thermal stabilisation effect for AT. This suggests that zirconia alone is responsible for the stabilisation effect. A similar phenomenon has also been observed for the graded AT/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> composites [27, 28] where the presence of zirconia (10 wt%) imparted a significant

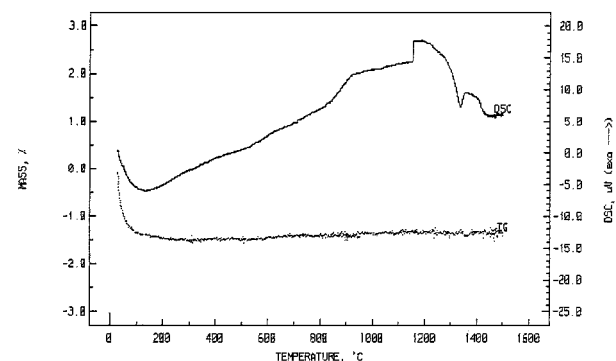


Figure 2 Thermogram of sample ATZ15.

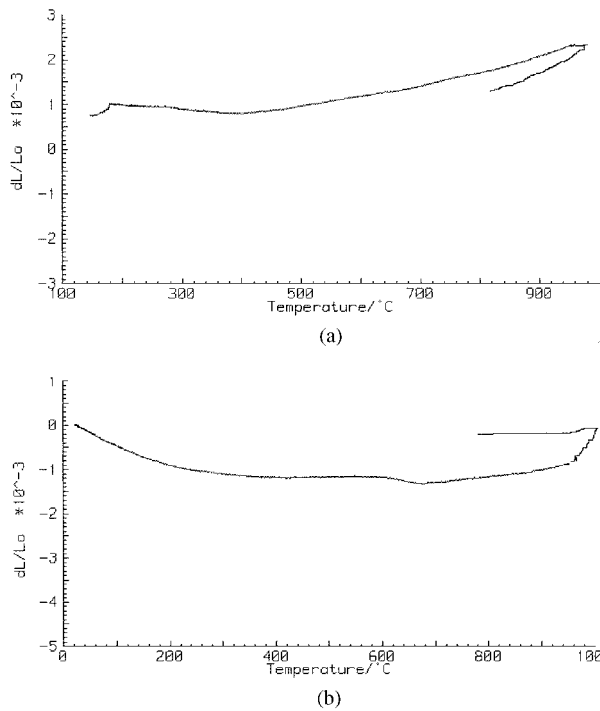


Figure 3 Thermal expansion behaviour of (b) ATZ15 and (a) pure AT samples.

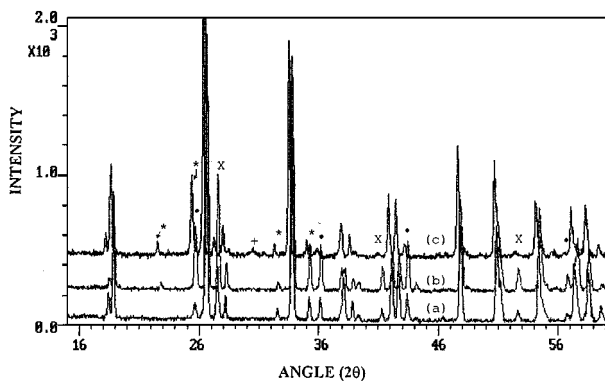


Figure 4 XRD plots of (a) pure AT, (b) AT + 10 wt% spodumene, and (c) ATZ10 samples which had been annealed at 1050°C for 20 h. Note the formation of  $\text{TiO}_2$  (denoted by  $\times$ ) and  $\alpha\text{-Al}_2\text{O}_3$  (denoted by  $\bullet$ ) as a result of thermal decomposition of AT.

temporary stabilisation to AT. Presence of more zirconia (> 10 wt%) has been found to have an even greater effect [29]. This stabilisation effect of  $\text{ZrO}_2$  is unexpected because it is known to be a poor stabiliser for AT [5] when compared with  $\text{MgO}$  and  $\text{Fe}_2\text{O}_3$ . As proposed by Wohlfromm *et al.* [9], the negligible effect of zirconia in the stabilisation of AT may be attributed to the inability of the relatively large  $\text{Zr}^{4+}$  (ionic radius = 0.79 Å) to substitute for the smaller  $\text{Ti}^{4+}$  (0.68 Å) or  $\text{Al}^{3+}$  (0.51 Å) in AT. This agrees with the absence of apparent line-shift for AT peaks as previously mentioned. Oxygen deficiency [7] in the AT structure may also reduce its ability to be stabilised by zirconia. In view of this, it is believed that the apparent “stabilisation” of AT observed is a temporary phenomenon which will eventually disappear following a long-term (200 h) annealing. Indeed further annealing of the ATZ15 sample for an additional 50 h showed evidence of continued phase decomposition of AT to  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$ . This

gradual disappearing of the “stabilisation” effect is consistent with the absence of line-shift for AT peaks and serves to indicate that both zirconia and  $\beta$ -spodumene do not form a solid-solution with AT and thus affect its lattice dimensions or  $d$ -spacing.

### 3.3. Physical characteristics

The shrinkage, apparent porosity and density results for the samples are shown in Figs 5–7. The shrinkage increased with  $\beta$ -spodumene addition as a result of an

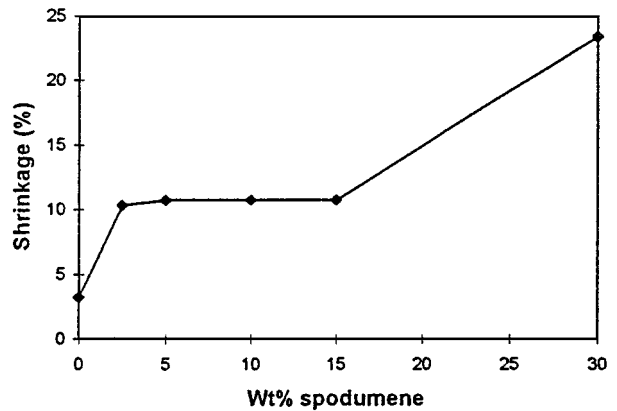


Figure 5 Shrinkage of sintered spodumene-modified AT/ $\text{ZrO}_2$  ceramics.

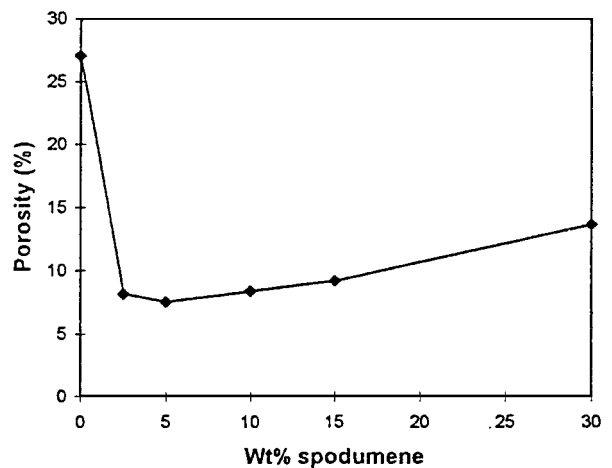


Figure 6 Porosity of sintered spodumene-modified AT/ $\text{ZrO}_2$  ceramics.

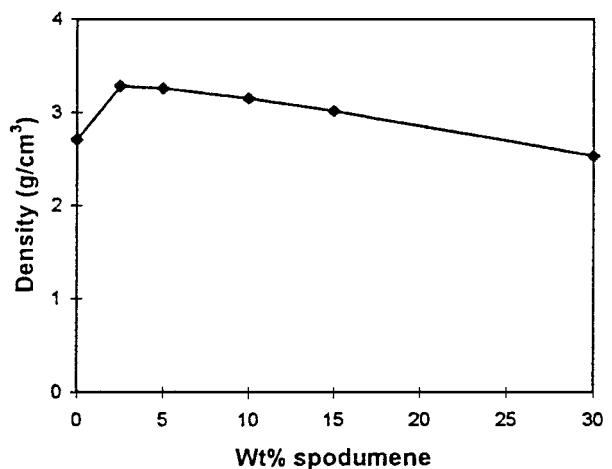


Figure 7 Density of sintered spodumene-modified AT/ $\text{ZrO}_2$  ceramics.

increased level of liquid phase formed. Similarly, the low porosity obtained (except for the 30% addition) for spodumene-modified AT/ZrO<sub>2</sub> samples can be attributed to the presence of a liquid phase at ~1345°C which served to enhance sintering and densification. The bulk density of the products increased to a maximum value of 3.29 g/cm<sup>3</sup> at 2.5 wt%  $\beta$ -spodumene and decreased thereafter for higher spodumene contents. This is consistent with the results of spodumene-modified mullites by Low *et al.* [16] and Kobayashi *et al.* [30] who found that additions of 20–90 wt%  $\beta$ -spodumene resulted in decreased density due to (a) the formation of 5–10  $\mu$ m pores caused by the excess liquid phase, and (b) the presence of less dense  $\beta$ -spodumene phase. The former reason is believed to be responsible for the presence of more than 10%

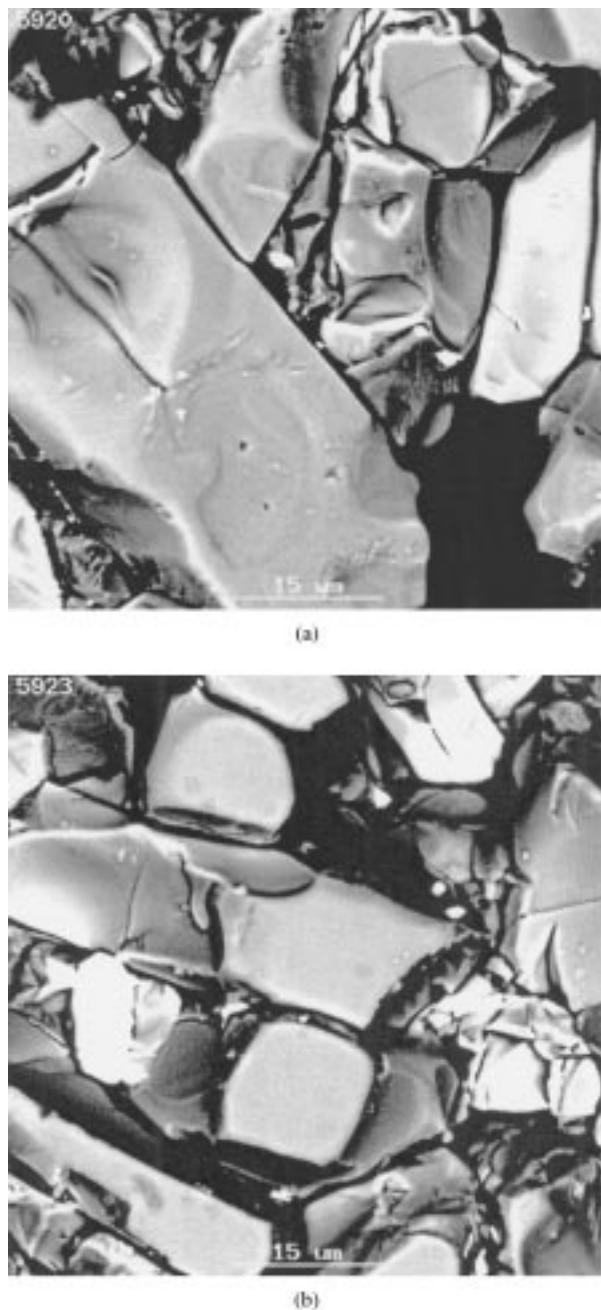


Figure 8 Back-scattered electron micrograph of (a) ATZ2.5 and (b) ATZ10. Large pockets of glassy phase can be seen at the triple junctions. Microcracks within certain AT grains can also be clearly seen.

porosity in the sample containing 30% spodumene addition (Fig. 6).

Typical microstructures of ATZ 2.5 and ATZ10 samples are shown by the back-scattered imaging micrographs in Fig. 8. A thin layer of glassy phase can be seen to be present between the AT grains, with large pockets of glassy phase situated at the triple junctions. The glassy phase is believed to originate from the phase separation of  $\beta$ -spodumene. Also evident is the presence of fine microcracks within certain AT grains. The formation of these microcracks can be attributed to the pronounced thermal expansion anisotropy of AT during cooling from an elevated temperature. The presence of the glassy phase,  $\beta$ -spodumene and AT has been confirmed by the energy-dispersive spectroscopy (EDS) and selected-area diffraction (SAD) during TEM analysis. Fig. 9 shows the EDS chart, SAD pattern and the corresponding bright-field image of a glassy phase. The  $\beta$ -spodumene can be seen to recrystallise within the glassy phase in Fig. 10. The morphology of an AT grain is revealed in Fig. 11.

The hardness results for the samples are shown in Fig. 12. In contrast to spodumene-modified mullites [16–18], the presence of up to 15 wt%  $\beta$ -spodumene caused a considerable improvement in hardness due to enhanced liquid-phase densification. The hardness increased rapidly and reached a maximum value of approximately 15 GPa at 2.5 wt%  $\beta$ -spodumene. The addition of 30 wt% softer  $\beta$ -spodumene resulted in a reduction of hardness. Because of the direct correlation between hardness and strength, it can be induced that the addition of up to 15 wt% spodumene would also impart a considerable improvement in fracture strength.

The improved thermal shock performance of ATZ5 samples when compared with pure AT is apparent from Fig. 13. There was a gradual but small degradation of flexural modulus in the former at temperatures greater than 400°C. In contrast, the degradation of flexural modulus in pure AT samples was more precipitous at temperatures above 400°C, which coincided with the visual appearance of substantial surface spalling and cracking. No such surface defects were apparent in the ATZ5 samples. The formation of these surface defects was probably caused by the coalescence microcracks induced during thermal cycling. A similar improvement in thermal shock resistance has recently been observed in alumina ceramics dispersed with 15 wt%  $\beta$ -spodumene [21]. A detailed microstructural examination of these surface and subsurface defects is currently being undertaken to ascertain the precise mechanism of material degradation.

The above results have clearly demonstrated the feasibility and cost-effectiveness of using  $\beta$ -spodumene as a liquid-phase-sintering additive for the processing of AT or ATZ materials which improved physical and mechanical performance. This approach has generic appeal and can be extended to other oxide or non-oxide systems which are difficult to sinter.

However, before the potential applications of these AT-based materials can be fully realised, it will be necessary to have a full understanding of the microstructure-property relationships, especially in

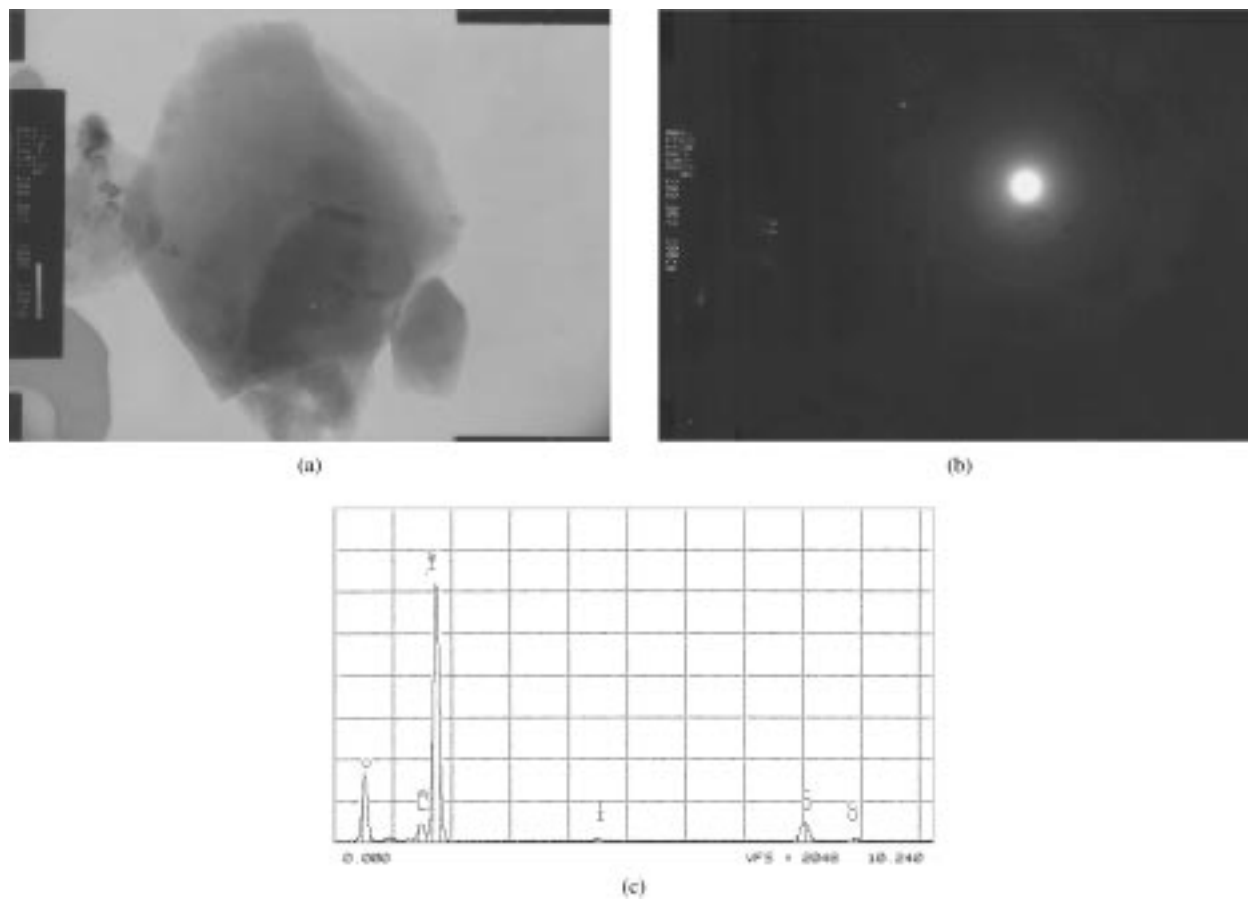


Figure 9 The presence of a glassy phase in the ATZ15 samples as revealed by (a) bright-field image, (b) SAD pattern, and (c) the corresponding EDS chart.

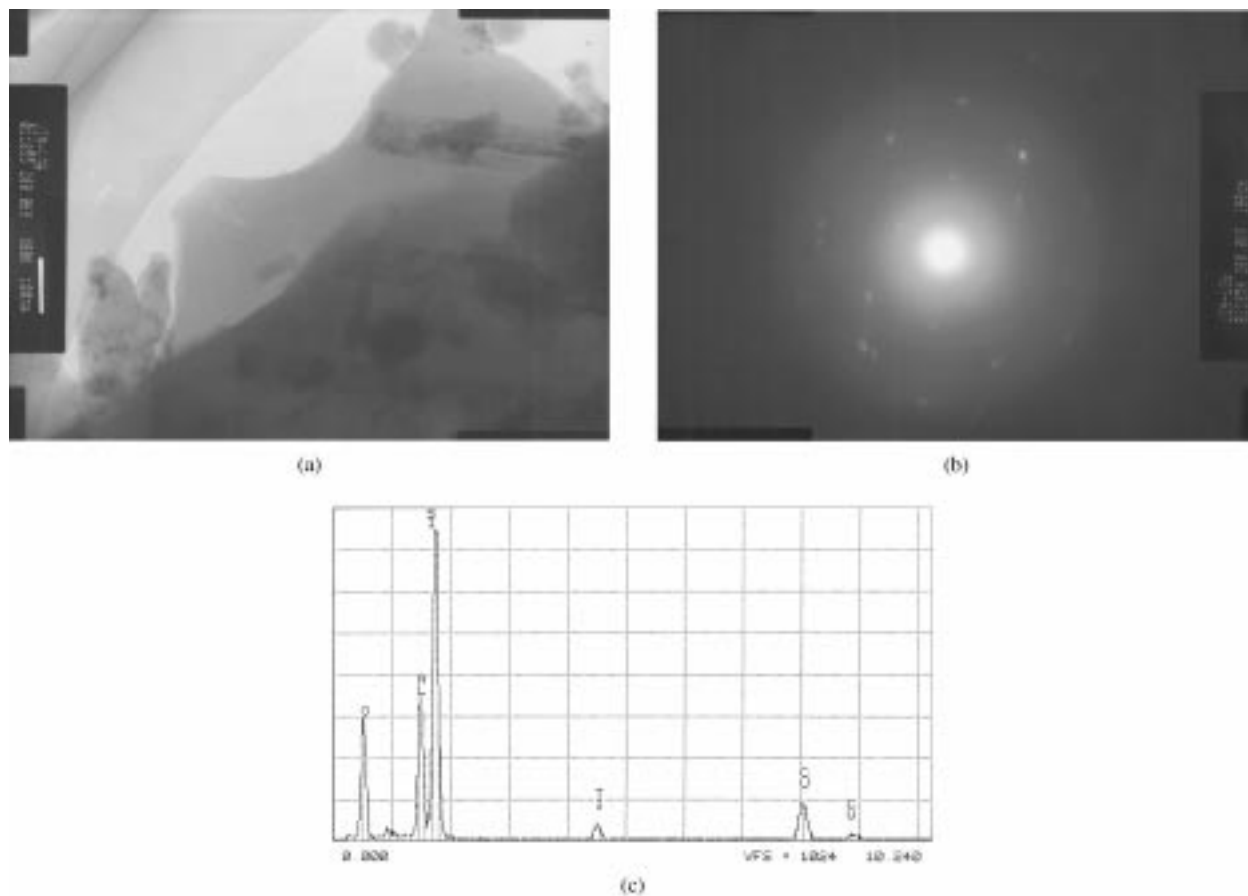


Figure 10 Recrystallisation of  $\beta$ -spodumene within a glassy phase as shown by (a) bright-field image, (b) SAD pattern, and (c) the corresponding EDS chart.

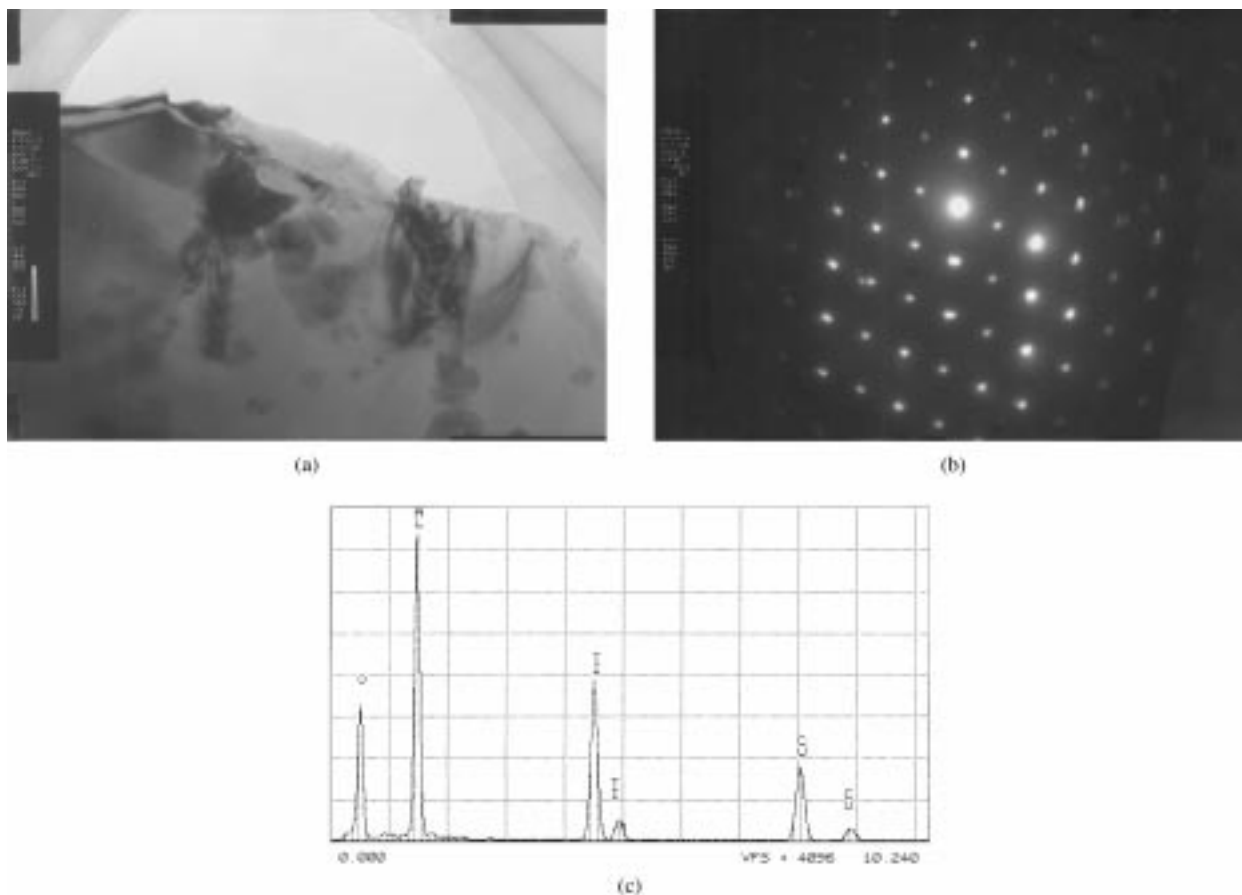


Figure 11 The morphology of an AT grain as revealed by (a) bright-field image, (b) SAD pattern, and (c) the corresponding EDS chart.

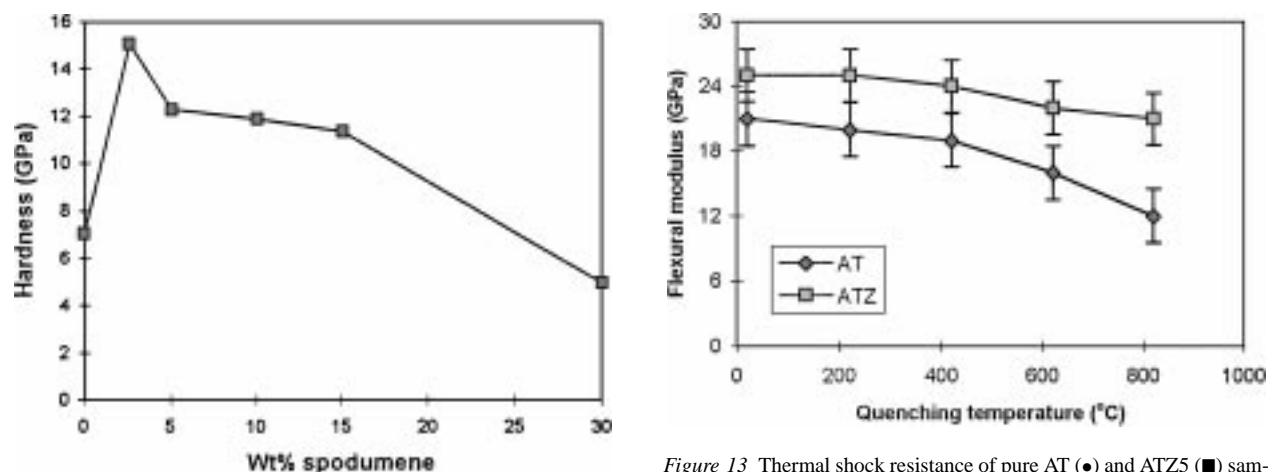


Figure 12 Vickers hardness of sintered spodumene-modified AT/ZrO<sub>2</sub> ceramics.

Figure 13 Thermal shock resistance of pure AT (●) and ATZ5 (■) samples at the various temperatures.

relation to the role of spodumene on thermal shock performance. These and other properties are currently being studied and will be reported in due course.

#### 4. Concluding remarks

$\beta$ -spodumene ( $\leq 15$  wt%) has been shown to be a suitable additive for the liquid-phase-sintering of AT ceramics, leading to significant improvements in densification, thermal characteristics, hardness and possibly strength. The presence of zirconia has a temporary thermal stabilisation effect on AT.

#### Acknowledgments

IML is grateful to Curtin University for research support under the Research Performance Index scheme and to the Australian Institute of Nuclear Science & Engineering (AINSE) for funding (Project No. 99/030). The authors thank Mr. G. Ferguson of SCM Chemicals Ltd. (Australia) for supplying the titania powder. We are very grateful to A/Prof. A. Yamamoto of Himeji Institute of Technology and Mr. S. Leong of ANSTO for taking respectively the TEM and SEM images. We thank Dr. B. Latella of ANSTO and Mr. R. Skala of SRCAMMP at UWA for technical assistance with measurements on flexural modulus and thermal expansion respectively.

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Received 24 October 1997  
and accepted 5 May 2000