DILATOMETRY OF $\beta$-SPODUMENE-MODIFIED ALUMINA/ALUMINIUM TITANATE COMPOSITES

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ABSTRACT

The use of $\beta$-spodumene has been investigated as a liquid phase-sintering aid for the densification of alumina/aluminium titanate (AAT) composites. The dilatomter was used to characterize the effect of $\beta$-spodumene on the thermal expansion of AAT. The average thermal expansion coefficient ($\alpha$) in the range temperature 20 - 1000°C increased from $7.55 \times 10^{-6}$°C - $8.57 \times 10^{-6}$°C. Generally, the presence of $\beta$-spodumene can cause a small increasing in the thermal expansion coefficient and the highest value of ($\alpha$) was found in the sample AATS2 ($\beta$-spodumene of 2 wt%).

Keywords: dilatometry, $\beta$-spodumene and alumina/aluminium titanate.

1. INTRODUCTION

Monoclinic $\alpha$-spodumene (Li$_2$O·Al$_2$O$_3$·4SiO$_2$) is stable under ambient conditions and transforms irreversibly at 1080°C to a tetragonal $\beta$ polymorph which melts at 1423°C. 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. It is also commonly used for making glasses and ceramics, which are harder, smoother, chemical and thermal shock resistant. The mean thermal expansion coefficient of $\beta$-spodumene is $9 \times 10^{-7}$°C in the temperature range 20-1000°C. Smoke$^2$ and Hummel$^2$ reported a negative thermal expansion coefficient for $\beta$-spodumene which may be due to anisotropy whereby the $c$-axis expands linearly whereas the $a$-axis contracts parabolically with increasing the temperature$^2$.

Spodumene has been used as a second phase for fabricating composites. Recently, Low and Shi$^5$ showed that by adding aluminium titanate (AT) with spodumene and zirconia significantly reduces porosity, lower thermal expansion, improves densification, hardness and thermal stability, without degradation of thermal shock resistance.

This paper describes the use of $\beta$-spodumene for liquid-phase-sintering of AAT composites. The composition examined in the study was the AAT30 system containing 0-15 wt% $\beta$-spodumene. AAT30 means alumina and aluminium titanate contents are 70 and 30 wt%, respectively. The physical characteristics and properties have been studied using dilatometry.

2. MATERIALS AND METHODS

Alumina powder (AES-11 SD-C, Mandoval Ltd., United Kingdom) was mixed with rutile powder (Rojan Co., Australia) and $\beta$-spodumene (Gwalia Consolidated Ltd., Greenbushes, Australia). The samples were designed in five compositions where AT content is 30 wt% plus $\beta$-spodumene of 0, 2, 5, 10 and 15 wt%, and called as AATS0, AATS2, AATS5, AATS10 and AATS15, respectively. The composition was mixed in ethanol used turbula mixer for 1 hour. The powder was pressed in bar (0.5 x 1.2 x 6) cm$^3$ at 150 MPa after powder was dried 100°C for 2 days. Bar sample was sintered at 1000°C for 2 hours and aimed for dilatometry. Theta 160 dilatometer was used to characterize the in-situ shrinkage or densification behaviour of the $\beta$-spodumene modified-AAT samples in air over the temperature range 20 - 1500°C. The measurement were conducted at the Materials Division of ANSTO at Lucas Height, Sydney. Sapphire was used as a reference in the equipment for examining the standard measurement.
3. RESULTS AND DISCUSSION

Dilatometry data were collected over the temperature range 20-1500°C. Figure 1 shows the in-situ thermal expansion and contraction results. The temperatures associated with the onset of densification and the maximum shrinkage are also shown in Figure 1.

The thermal expansion and contraction behaviour of all samples were similar up to 1100°C, with slight differences being noticeable beyond 1100°C. When compared to the control which had a maximum shrinkage of ~8.5%, samples AATS2 and AATS5 had greater shrinkage whereas samples AATS10 and AATS15 had lower shrinkage. In contrast to other samples which showed continuous shrinkage during heating, samples AATS10 and AATS15 displayed a discontinuity in shrinkage at ~1330 and 1320°C respectively and underwent thermal expansion thereafter. This distinct display of shrinkage to expansion transition at ~1330°C for sample AATS10 and ~1320°C for sample AATS15 can be attributed to the melting of spodumene. Besides the melting of spodumene, the concomitant formation of glassy phase which expanded during heating is also probable. This display of discontinuity during shrinkage was also reported by Thomas, Stevens and Gilbart for AT dispersed with 5 wt% ZrO₂.

Values of densification temperature ($T_D$), maximum shrinkage ($S_{max}$) and the average thermal expansion coefficient ($\bar{\alpha}$) for AATS samples in the range 20 -1000°C are shown respectively in Figures 2, 3 and 4.

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**Figure 1.** Dilatometric analyses of samples AATS0, AATS2, AATS5, AATS10 and AATS15. The temperatures associated with the start of densification ($T_D$) and maximum shrinkage ($S_{max}$) are highlighted.

**Figure 2.** Variation of densification temperature ($T_D$) for AATS0, AATS2, AATS5, AATS10 and AATS15 as a function of $\beta$-spodumene content.
Figure 3. Variation of shrinkage for AATS0, AATS2, AATS5, AATS10 and AATS15 as a function of β-spodumene content as measured by dilatometry (up to 1456°C) compared to sintered sample (up to 1600°C). Error bars indicate two estimated standard deviations (2σ).

Figure 3 shows that shrinkage values from dilatometry are lower than those of sintered samples. This is consistent with the values from dilatometry were dynamically measured only up to ~1450°C whereas the values for the sintered samples were obtained following 3 h sintering at 1600°C.

Figure 4. Average thermal expansion coefficient for AATS0, AATS2, AATS5, AATS10 and AATS15 in the range 20-1000°C as a function of β-spodumene content.

The densification temperature decreased from sample AATS0 to sample AATS2 (Figure 2) indicating that the presence of a small concentration of β-spodumene lowered the starting temperature for densification. However, the densification temperature increased with an increase of β-spodumene content (AATS2 to AATS15), indicating that the presence of excess β-spodumene would not assist the densification process.

If a solid material is heated to higher temperatures, the atom vibrates over a range centred on the equilibrium atomic spacing. The total atomic spacing accumulates over a macroscopic distance in the material and then produces a dimensional increase. In isotropic materials, this effect is the same in all directions but different in anisotropic materials. From Figure 4, the average thermal expansion coefficient (α) in the temperature range 20-1000°C increased from $7.55 \times 10^{-6} ^\circ \text{C}^{-1}$ to $8.48 \times 10^{-6} ^\circ \text{C}^{-1}$.
8.57 \times 10^{-6}/^\circ\text{C}. Generally the presence of \(\beta\)-spodumene can cause a small increase in the thermal expansion coefficient and the highest value of \(\alpha\) was found in sample AATS2.

4. CONCLUSIONS

When compared to the control, the presence of \(\leq 5\) wt\% \(\beta\)-spodumene gave rise to greater shrinkage, but lower shrinkage for samples containing \(\geq 10\) wt\% \(\beta\)-spodumene. The samples AATS0 and AATS2 also displayed a discontinuity in shrinkage at \(\sim 1330\) and \(1320^\circ\text{C}\) respectively and underwent thermal expansion thereafter. This unique display of shrinkage to expansion transition was attributed to the melting of spodumene and the concomitant formation of glassy phase which expanded readily during heating.

REFERENCES


