Preparation of Al_2TiO_5 from alkoxides and the effects of additives on its properties

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Al_2TiO_5 was prepared by the sol–gel method from alkoxides and its mechanical and thermal properties measured. The prepared Al_2TiO_5 powder was very fine and had a narrow particle-size distribution. The addition of mullite and Al_2O_3 to the prepared Al_2TiO_5 inhibited the grain growth during sintering, resulting in a decrease of microcracking and an increase of fracture strength. Al_2TiO_5/mullite composite exhibited a higher fracture strength than Al_2TiO_5/alumina composite. The thermal expansion coefficient of Al_2TiO_5 increased with the addition of mullite and alumina, and also increased with temperature up to 1000 °C; however, it decreased in the temperature range between 1000 and 1200 °C during heating, due to decomposition of Al_2TiO_5. The addition of mullite inhibited the decomposition of Al_2TiO_5, but the addition of Al_2O_3 accelerated it. Al_2TiO_5 prepared from metal alkoxides was also more stable than that prepared from the commercial alumina and titania powders.

1. Introduction

Recently there has been much interest in the applications of aluminium titanate (Al_2TiO_5) as a consequence of its low thermal expansion coefficient and high melting temperature [1, 2]. The low thermal expansion coefficient of Al_2TiO_5 is known to be the result of microcracking produced by anisotropy of thermal expansion coefficients [3, 4]. A large difference exists between average linear thermal expansion coefficients ($9.7 \times 10^{-6}\,K^{-1}$: $(\alpha_a + \alpha_b + \alpha_c)/3$) and the measured volumetric thermal expansion coefficients ($0.5 - 1.0 \times 10^{-6}\,K^{-1}$) [5].

Microcracking during the cooling step of sintering is known to be the origin of the low strength and the low thermal expansion coefficient of Al_2TiO_5 [5, 6]. There are many restrictions in the applications of Al_2TiO_5 because of its low strength and its decomposition to Al_2O_3 and TiO_2 at high temperatures of about 1000–1250 °C. Therefore, in order to improve its strength and prevent its decomposition, much work [7–12] has been directed towards trying to stabilize Al_2TiO_5 by the addition of mullite, MgO, or SiO_2.

Al_2TiO_5 has generally been prepared by mechanical mixing of alumina and titania powders before heating at temperatures higher than 1300 °C [13–15]. Recently, however, sol–gel processing has been adopted by many researchers [16–19] using alkoxides as the starting materials to obtain Al_2TiO_5 with better mechanical and thermal properties, by controlling the microcracking effectively during the cooling step of sintering.

In this study, sol–gel processing was carried out to produce Al_2TiO_5 with improved properties. Mullite and alumina were added to Al_2TiO_5 to produce Al_2TiO_5/mullite (alumina) composites which might be mechanically strong and thermally stable.

2. Experimental procedure

Aluminium sec-butoxide ($Al(OC_4H_9)_3$, ASB) and tetraethyl orthotitanate ($Ti(OC_2H_5)_4$ TEOT) were used as the starting alkoxides for Al_2O_3 and TiO_2 components, respectively, to prepare Al_2TiO_5 through the sol–gel technique. Two clear sols of alumina and titania which were prepared separately from the alkoxides ASB and TEOT, respectively, were mixed to obtain a mixed sol to prevent unbalanced hydrolysis due to their different hydrolysis rates.

Alumina clear sol was prepared by dropping the solution of 1 mol ASB per 100 mol isopropyl alcohol into 100 mol secondary distilled water containing 0.4 mol HNO_3 at 80 °C [20]. Titania clear sol was prepared by dropping 20 mol secondary distilled water into the solution of ethanol containing 0.2 mol HNO_3 per 1 mol TEOT [21]. The dropping was followed by vigorous stirring to achieve homogeneous mixing.

Two clear sols of alumina and titania were vigorously stirred for 15 min to allow gelling to occur. The obtained wet gel was partly dried at 80 °C and again dispersed in ethyl alcohol before drying at 80 °C to obtain an uncoagulated dried mixed gel of aluminium hydroxide and titanium hydroxide. The obtained dried mixed gel was heated at 1350 °C for 1 h to produce Al_2TiO_5. This Al_2TiO_5 was ball-milled using an alumina jar and high-purity balls using ethyl alcohol as the dispersoid to produce Al_2TiO_5 powder. Amounts of 0, 10 and 20 wt% mullite and alumina were separately added to Al_2TiO_5 powder to find the

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TABLE I Sample notation used in this research

Sample name	Starting material	Phase	Additive contents
AT	$Al_2O_3 + TiO_2$ mixed powder	Al_2TiO_5, $3Al_2O_3 \cdot 2SiO_2$ (mullite)	No mullite
ATM10			Mullite 10 wt %
ATM20			Mullite 20 wt %
SGATM0	Aluminium sec butoxide, tetra-ethyl ortho-titanate		No mullite
SGATM10			Mullite 10 wt %
SGATM20			Mullite 20 wt %
AT	$Al_2O_3 + TiO_2$ mixed powder	Al_2TiO_5, Al_2O_3	No alumina
ATA10			Alumina 10 wt %
ATA20			Alumina 20 wt %
SGAT	Aluminium sec butoxide, tetra-ethyl ortho-titanate		No alumina
SGATA10			Alumina 10 wt %
SGATA20			Alumina 20 wt %

effects of both additives, on Al_2TiO_5. The mixed powder was pressed into bars of 6 mm × 6 mm × 45 mm, which were isostatically pressed and sintered at 1500 and 1600 °C, respectively, for 2 h to obtain Al_2TiO_5/mullite and Al_2TiO_5/Al_2O_3 composite specimens. The specimen notations used in this study are given in Table I.

Al_2O_3 (AES11, Sumitomo Co., Japan) and TiO_2 (Junsei Chemical Co. Ltd) powders were mixed in 1 : 1 molar ratio and reaction-sintered at 1350 °C for 1 h to produce Al_2TiO_5, the properties of which were measured for comparison with those prepared from alkoxides after ball-milling, addition of mullite and alumina, and sintering by the same method as that used for alkoxides.

3. Results and discussion

3.1. Preparation of Al_2TiO_5 powder

X-ray diffraction (XRD) patterns of dried gels calcined over the temperature range 300–1350 °C for 1 h are given in Fig. 1. As can be seen, anatase appeared from 700 °C, corundum and rutile appeared at 800 °C; thus, these three phases coexisted up to 900 °C. At 1000 °C, corundum and rutile still existed but anatase disappeared. Al_2TiO_5 was observed from 1300 °C and Al_2TiO_5 was mostly produced with a negligible trace of alumina and titania at 1350 °C as shown in Fig. 1. The particles of Al_2TiO_5 produced from alkoxides were measured to be below 1.5 μm and more than 90% were below 1 μm as shown in Fig. 2a; however, those from commercial alumina and titania were over 0.5–7 μm, only 60% were below 1 μm and 90% were below 2.5 μm, as shown in Fig. 2b. Therefore, Al_2TiO_5 powder produced from alkoxides had the narrower size-distribution than that produced from the commercial alumina and titania powders.

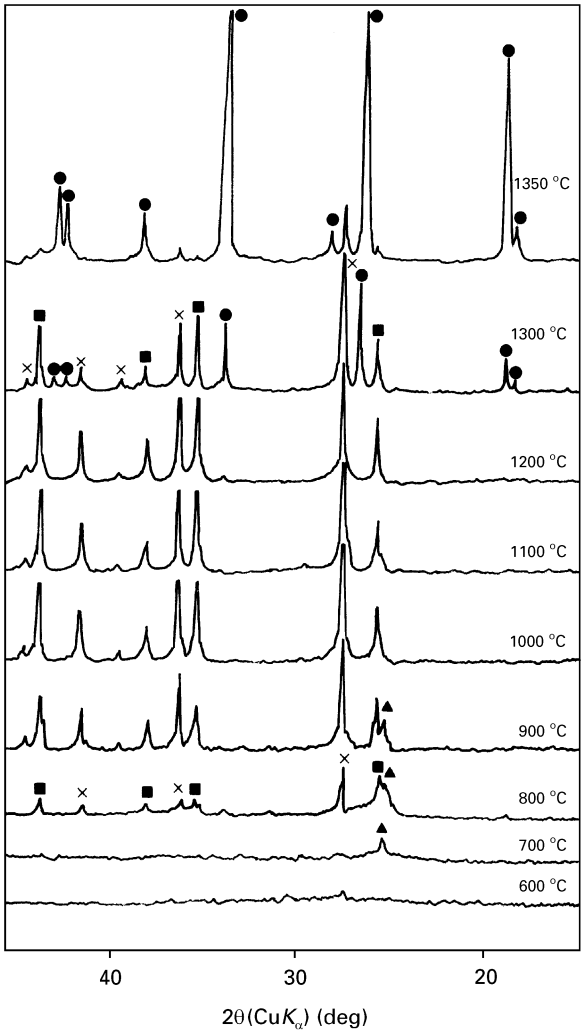

Figure 1 XRD patterns of the dried gel calcined at various temperatures for 1 h. (●) Al_2TiO_5, (■) Al_2O_3, (×) TiO_2 rutile, (▲) TiO_2 anatase.

3.2. Phases, microstructure and mechanical properties of Al_2TiO_5 and Al_2TiO_5/alumina (mullite) composites

Fig. 3 presents XRD patterns of Al_2TiO_5 and Al_2TiO_5/alumina composites sintered at 1500 °C for 2 h. All specimens, except ATA0, show alumina phase besides the main phase Al_2TiO_5. Fig. 4 shows XRD patterns of Al_2TiO_5 and Al_2TiO_5/mullite composites sintered at 1500 °C for 2 h. All specimens, except AT, show mullite phase besides the main phase Al_2TiO_5. Specimen AT represents Al_2TiO_5, and small peaks of alumina and titania which existed in the powder, as shown in Fig. 1, were no longer observed in sintered

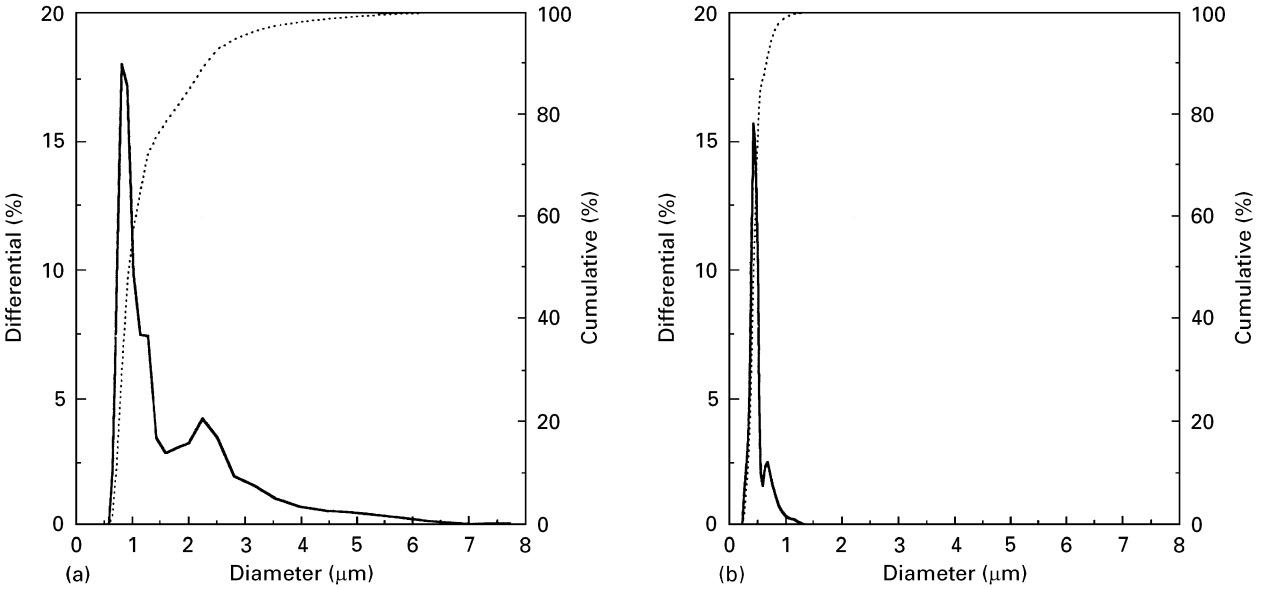

Figure 2 Particle-size distributions of Al_2TiO_5 powder prepared from (a) the commercial Al_2O_3 and TiO_2 mixed powder, and (b) from metal alkoxides.

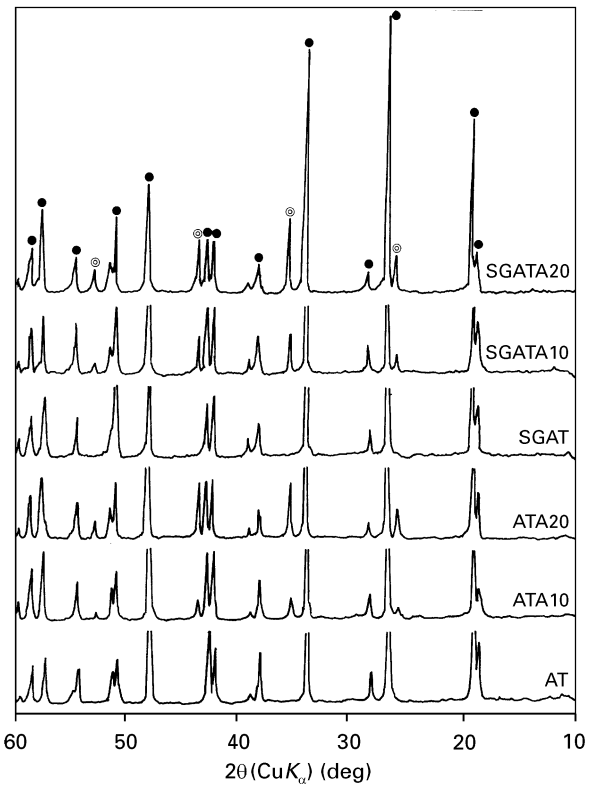

Figure 3 XRD patterns of ATA series and SGATA series sintered at 1500 °C for 2 h. (●) Al_2TiO_5, (●) Al_2O_3.

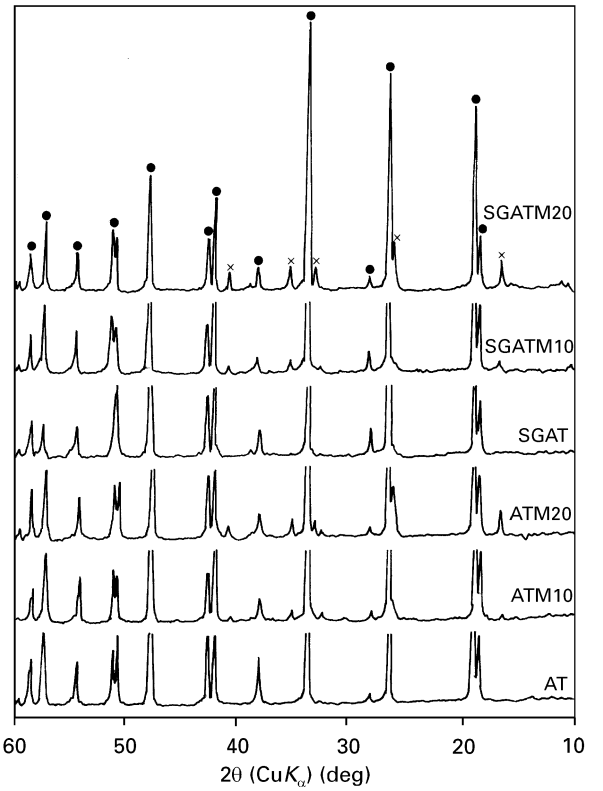

Figure 4 XRD patterns of ATM series and SGATA series sintered at 1600 °C for 2 h. (●) Al_2TiO_5, (×) mullite.

specimens, because the unreacted alumina and titania phases reacted completely at a sintering temperature of 1500 °C to produce single-phase Al_2TiO_5.

The relative density of the specimens is given in Fig. 5. It increased with the contents of alumina and mullite, probably by the grain-growth controlling effect of the second phases, mullite and alumina, and the subsequent densification effect. The density of Al_2TiO_5/mullite composite was higher than that of Al_2TiO_5/alumina composite because the thermal expansion coefficient of mullite and also the thermal mismatch with Al_2TiO_5 was smaller than that of alumina.

Fig. 6 shows scanning electron micrographs of the as-sintered surface of Al_2TiO_5 prepared from alkoxides and the commercial Al_2O_3–TiO_2 mixed powder, sintered at 1500 and 1600 °C. Microcracks were more severe in the specimen prepared from the commercial powder than that from alkoxides, and the grain growth was more remarkable at higher temperature, 1600 °C, than the lower temperature, 1500 °C, as can be seen in Fig. 6.

Fig. 7 shows scanning electron micrographs of surfaces of Al_2TiO_5/alumina (mullite) composite specimens prepared from alkoxides and sintered at 1500 and 1600 °C for 2 h. It can be understood that the grain growth was more effectively prevented and the specimen was more densified in Al_2TiO_5/20 wt% alumina (or mullite) composite specimen than in Al_2TiO_5/10 wt% alumina (mullite) composite specimen. Unfortunately, it is difficult to compare the effect of the second phase between alumina and mullite in the composites, because one was sintered at 1500 °C and the other at 1600 °C.

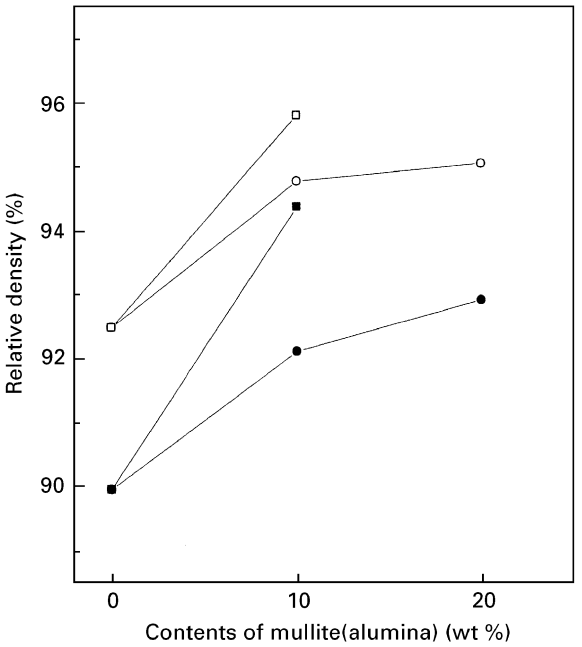

Figure 5 Relative density of Al_2TiO_5 sintered at 1500 °C for 2 h. (□) SGATM series, (○) SGATA series, (■) ATM series, (●) ATA series.

The four-point bending strength of Al_2TiO_5 sintered at 1500 °C for 2 h is given in Fig. 8. It can be seen that the strength increased with the contents of second-phase alumina and mullite. The addition of mullite to Al_2TiO_5 enhanced the strength more than the addition of alumina. This may be attributed to the difference in the thermal mismatch between Al_2TiO_5 and the second phases, alumina and mullite. The thermal expansion coefficients of Al_2TiO_5, mullite and alumina are $0.2–1 \times 10^{-6}$, 5×10^{-6} and $8.5 \times 10^{-6} K^{-1}$, respectively. Thermal mismatch between Al_2TiO_5 and mullite is smaller than that between Al_2TiO_5 and alumina; therefore Al_2TiO_5/mullite composite can produce denser, stronger, ceramics than Al_2TiO_5/alumina composite. Al_2TiO_5 specimens prepared by sol–gel processing from alkoxides show a higher strength than those prepared from commercial powders, as shown in Fig. 8.

3.3. Thermal decomposition of Al_2TiO_5 and Al_2TiO_5/mullite (alumina) composites

Figs 9–12 show XRD patterns of Al_2TiO_5/mullite composites sintered at 1600 °C for 2 h and annealed at 1200 °C for 12, 24, 48 and 100 h, respectively. Because the peaks of Al_2O_3 (0 1 2), Al_2TiO_5 (1 1 0) and TiO_2 (rutile) (1 1 0) planes can be seen between 25° and 29° of 2θ (CuK_α), it is very easy to observe the decomposition of Al_2TiO_5 to Al_2O_3 and TiO_2 from Al_2TiO_5/mullite

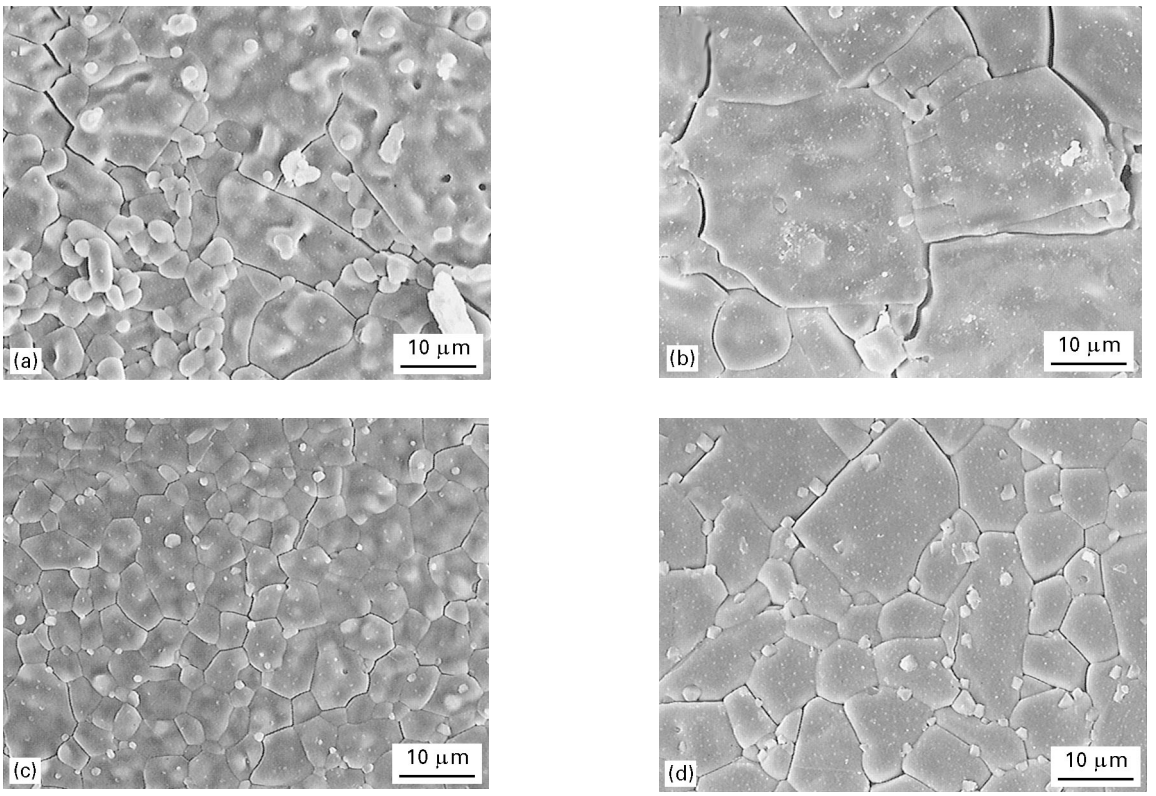

Figure 6 Scanning electron micrographs of as-sintered surfaces of Al_2TiO_5 specimens (a, b) prepared from Al_2O_3–TiO_2 mixed powder and sintered at (a) 1500 °C for 2 h, or (b) 1600 °C for 2 h, and (c, d) prepared by the sol–gel method and sintered at (c) 1500 °C for 2 h, or (d) 1600 °C for 2 h.

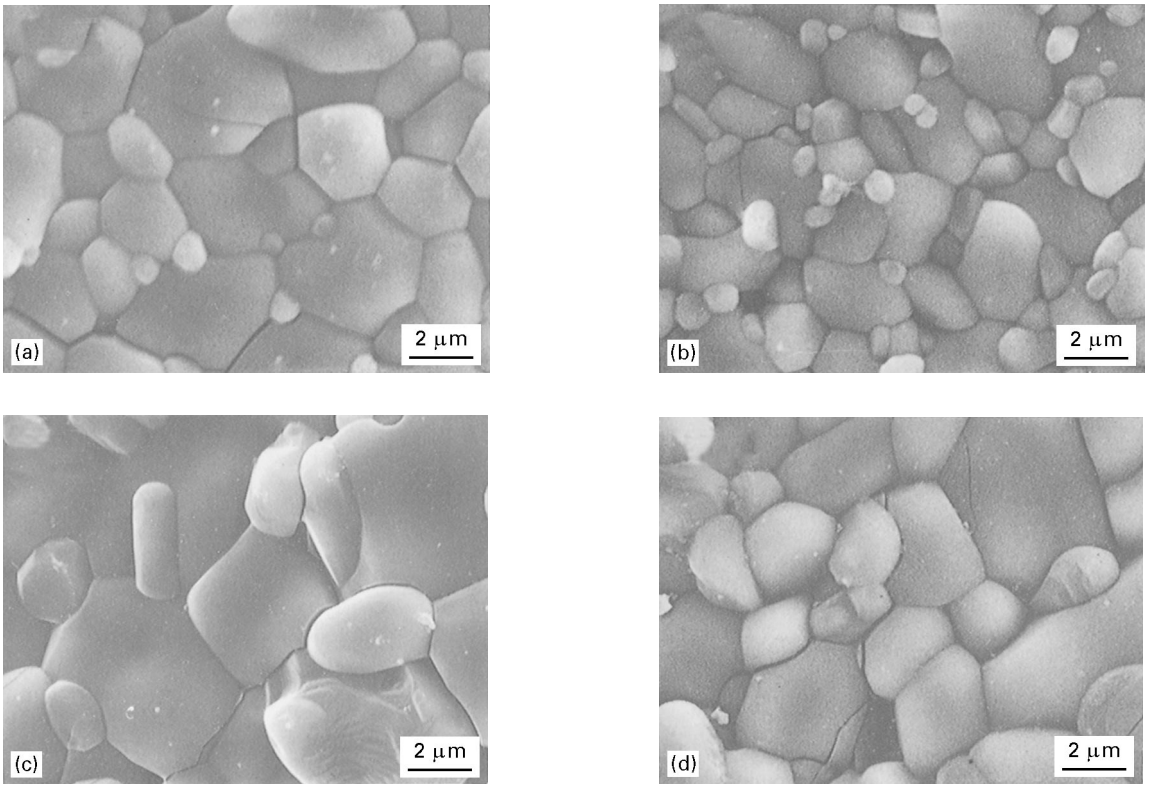

Figure 7 Scanning electron micrographs of surfaces of the specimens (a) SGATA10 and (b) SGATA20 sintered at 1500°C for 2 h; and (c) SGATM10 and (d) SGATM20 sintered at 1600°C for 2 h.

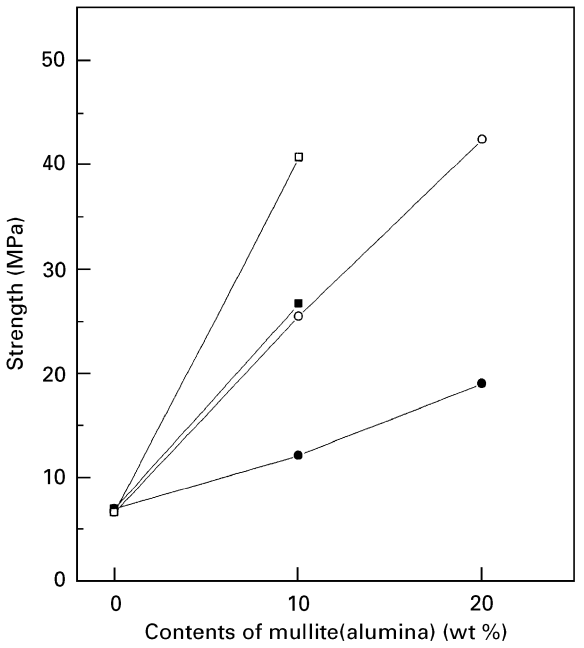

Figure 8 Four-point bending strength of Al_2TiO_5 sintered at 1500°C for 2 h. (□) SGATM series, (○) SGATA series, (■) ATM series, (●) ATA series.

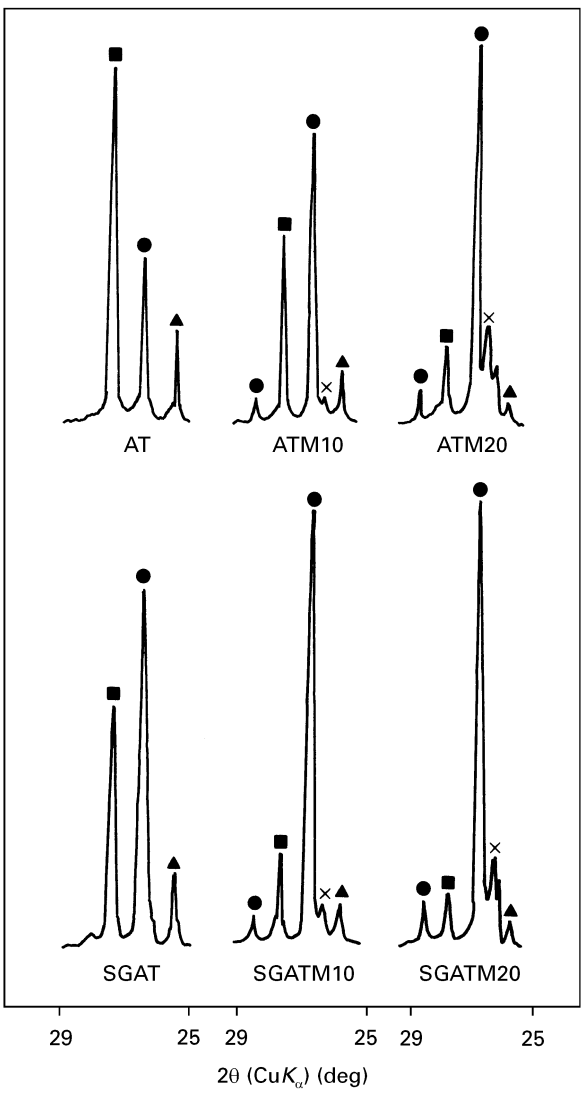

Figure 9 XRD patterns of Al_2TiO_5/mullite composites sintered at 1600°C for 2 h and annealed at 1200°C for 12 h. (●) Al_2TiO_5, (▲) Al_2O_3, (■) TiO_2, (×) mullite.

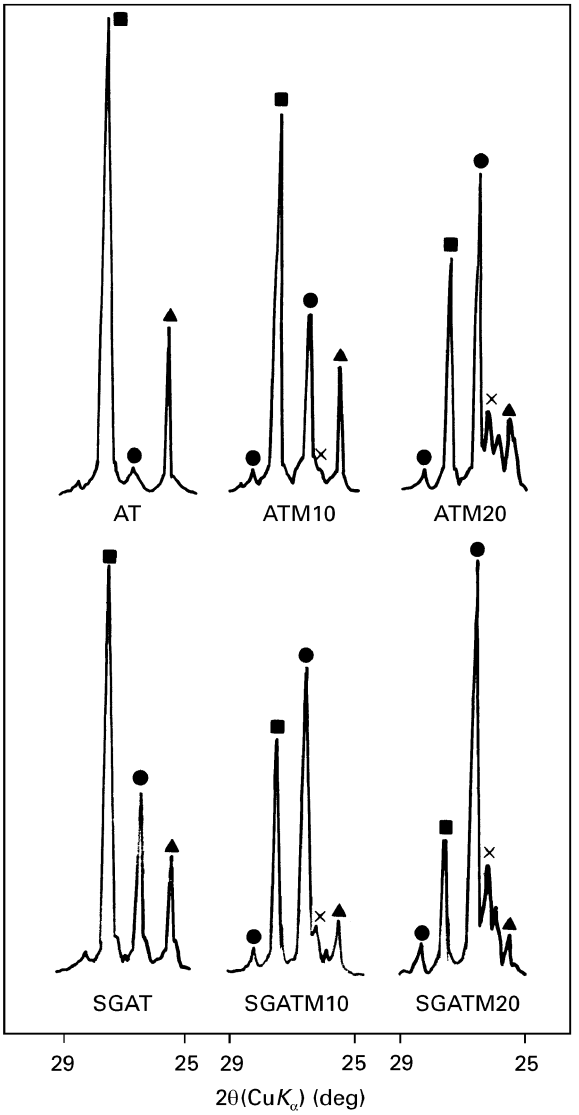

Figure 10 XRD patterns of Al_2TiO_5/mullite composites sintered at 1600 °C for 2 h and annealed at 1200 °C for 24 h. (●) Al_2TiO_5, (▲) Al_2O_3, (■) TiO_2, (×) mullite.

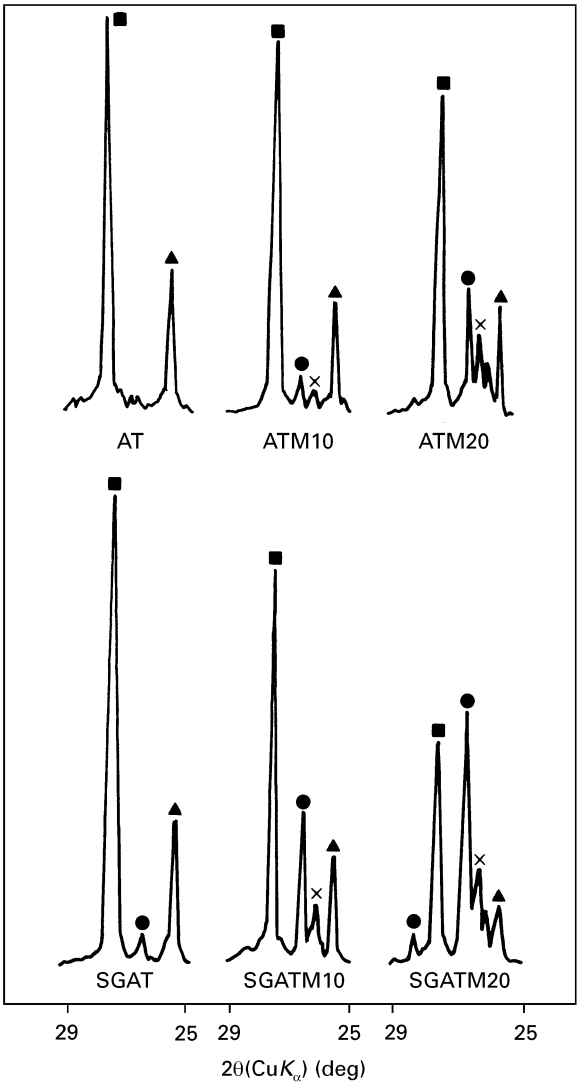

Figure 11 XRD patterns of Al_2TiO_5/mullite composites sintered at 1600 °C for 2 h and annealed at 1200 °C for 48 h. (●) Al_2TiO_5, (▲) Al_2O_3, (■) TiO_2, (×) mullite.

composites during annealing, by comparison of their XRD peak intensities. It can be seen in Figs 9–12 that Al_2TiO_5 was decomposed to Al_2O_3 and TiO_2. The degree of decomposition increased with annealing time and the specimens of single-phase Al_2TiO_5 (AT and SGAT) were completely decomposed to Al_2O_3 and TiO_2 at annealing times of 100 h, as shown in Fig. 12. However, decomposition was more effectively prevented in the SGAT series specimens prepared from alkoxides, than in the ATM series specimens prepared from the commercial powders, up to 100 h annealing time, as shown in Figs 9–12. The prevention of decomposition was effectively enhanced with the content of mullite because the XRD peak intensities of Al_2O_3 and TiO_2 of the specimens (ATM10 and SGATM10) containing 10 wt % mullite were higher than those of the specimens (ATM20 and SGATM20) containing 20 wt % mullite, and the reverse in the case of the Al_2TiO_5 phase, as shown in Figs 9–12.

The thermal expansion coefficient of mullite is very close to that of Al_2TiO_5 so that Al_2TiO_5/mullite composite can produce denser, stronger, ceramics. It is, therefore, considered that the addition of mullite may effectively prevent the decomposition of Al_2TiO_5.

Figs 13 and 14 show XRD patterns of Al_2TiO_5/alumina composites sintered at 1500 °C and 1600 °C for 2 h, respectively, and then both were annealed at 1200 °C for 12 h. As can be seen in Figs 13 and 14, Al_2TiO_5 in all specimens (ATA10, 20 and SGATA10, 20) containing 10 and 20 wt % alumina, were completely decomposed to Al_2O_3 and TiO_2; however, specimens (AT and SGAT) of single-phase Al_2TiO_5 were partly decomposed, that is, the XRD pattern of Al_2TiO_5 still existed. This means that the addition of alumina accelerated the decomposition reaction, probably by the seeding effect of the added alumina. The thermal expansion coefficient of alumina is larger than that of mullite. Therefore, it is considered that the addition of alumina may not effectively prevent the decomposition of Al_2TiO_5.

3.4. Thermal expansion and contraction behaviour of Al_2TiO_5 and Al_2TiO_5/mullite (alumina) composites

The thermal expansion behaviour of Al_2TiO_5 and Al_2TiO_5/mullite (alumina) composites during heating

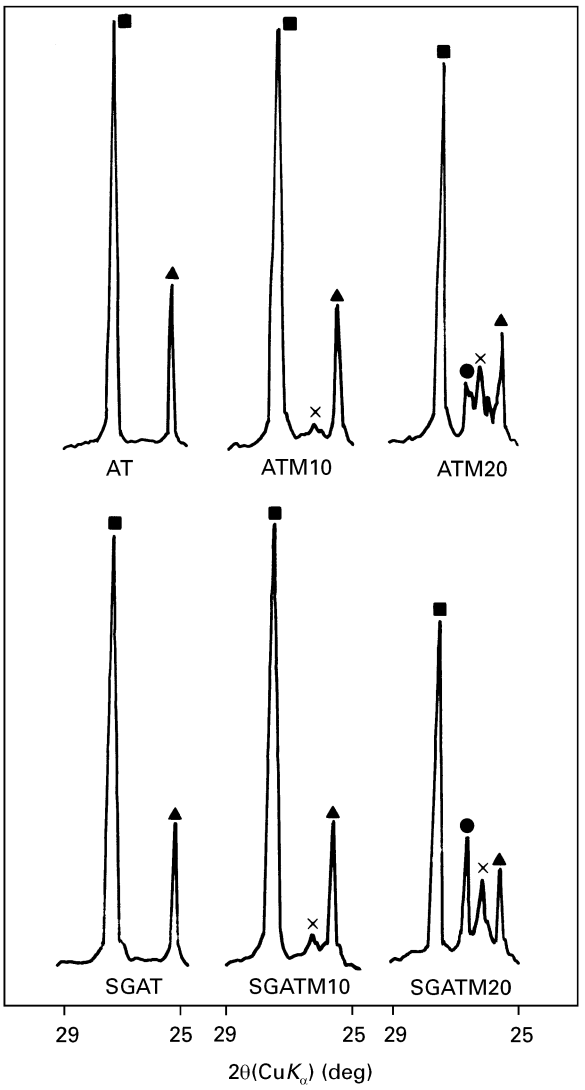

Figure 12 XRD patterns of Al_2TiO_5/mullite composites sintered at 1600 °C for 2 h and annealed at 1200 °C for 100 h. (●) Al_2TiO_5, (▲) Al_2O_3, (■) TiO_2, (×) mullite.

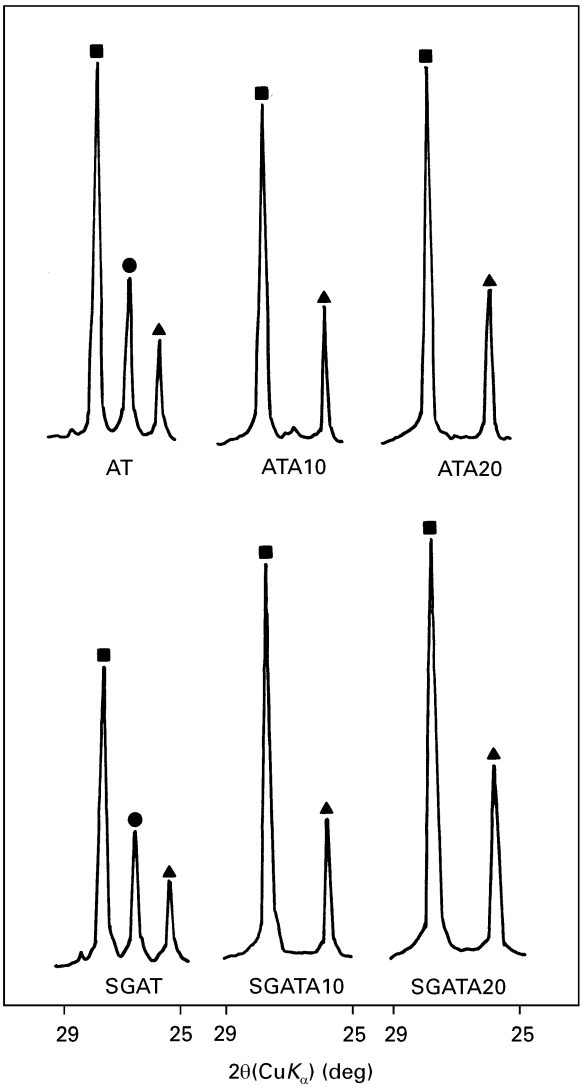

Figure 13 XRD patterns of Al_2TiO_5/alumina composites sintered at 1500 °C for 2 h and annealed at 1200 °C for 12 h. (●) Al_2TiO_5, (▲) Al_2O_3, (■) TiO_2.

is shown in Figs 15 and 16, and their contraction behaviour during cooling is given in Figs 17 and 18.

It can be seen in Figs 15 and 16 that the thermal expansion increased with the contents of mullite and alumina, because microcracks decreased with increasing contents of these second phases. However, the thermal expansion decreased between 1000 and 1250 °C, where Al_2TiO_5 is assumed to be decomposed to Al_2O_3 and TiO_2. Because the densities of Al_2TiO_5, Al_2O_3 and TiO_2 are 3.7, 3.99 and 4.25 g cm^{-3}, respectively, the decomposition of Al_2TiO_5 brings about 11% contraction of the Al_2TiO_5 specimen due to the density difference between the components before and after decomposition of Al_2TiO_5. The thermal expansion of the alumina-containing specimens (SGAT, SGATA10 and 20) decreased more rapidly compared with the mullite-containing specimens (SGAT, SGATM10 and 20) as shown in Figs 15 and 16, because the decomposition of the mullite-containing specimens was more effectively prevented by the mullite contents, as mentioned above, together with Figs 9–14.

The specimens contracted during cooling; however, at some point they again expanded to produce different minimum points according to the contents of the second phases, mullite and alumina, because microcracks initiated at these minimum points. The temperatures of the minimum points were lowered with increasing contents of the second phases, mullite and alumina, because the second phases prevented grain growth and thus enhanced the densification and strength of the Al_2TiO_5/mullite (alumina) composites.

4. Conclusions

Particles of Al_2TiO_5 powder prepared by the sol–gel method from alkoxides were below 1.5 μm in size and had a very narrow size distribution, more than 90% being below 1 μm; however, those from commercial alumina and titania powders were over 0.5–7 μm in size and only 60 % were below 1 μm and 90% were below 2.5 μm.

The mullite and alumina added as the second phases to Al_2TiO_5 limited the grain growth of

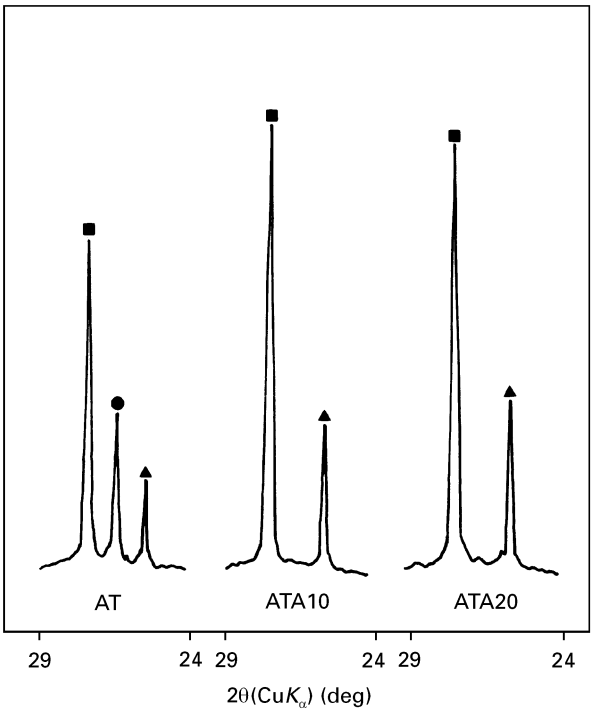

Figure 14 XRD patterns of Al_2TiO_5/alumina composites sintered at 1600 °C for 2 h and annealed at 1200 °C for 12 h. (●) Al_2TiO_5, (▲) Al_2O_3, (■) TiO_2.

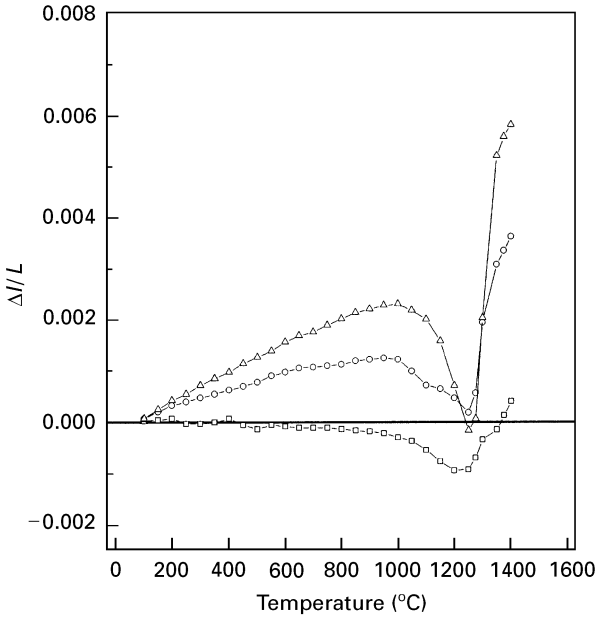

Figure 15 Thermal expansion behaviour during heating of Al_2TiO_5/Al_2O_3 composites sintered at 1500 °C for 2 h; (□) SGAT, (○) SGATA10, (△) SGATA20.

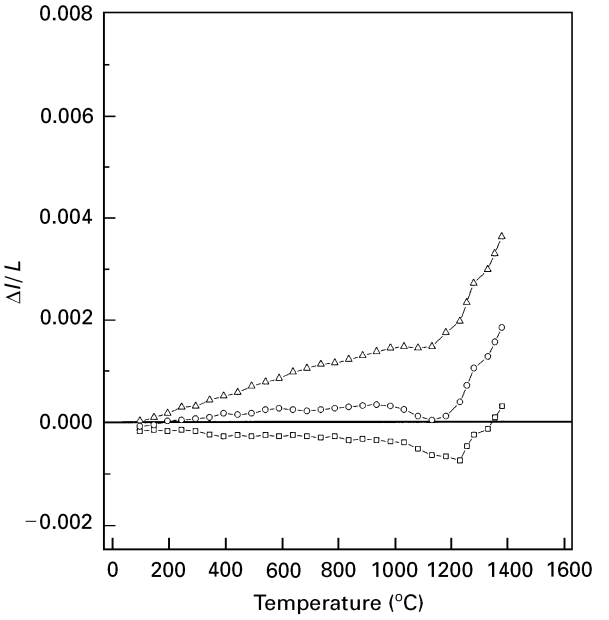

Figure 16 Thermal expansion behaviour during heating of Al_2TiO_5/mullite composites sintered at 1600 °C for 2 h; (□) SGAT, (○) SGATM10, (△) SGATM20.

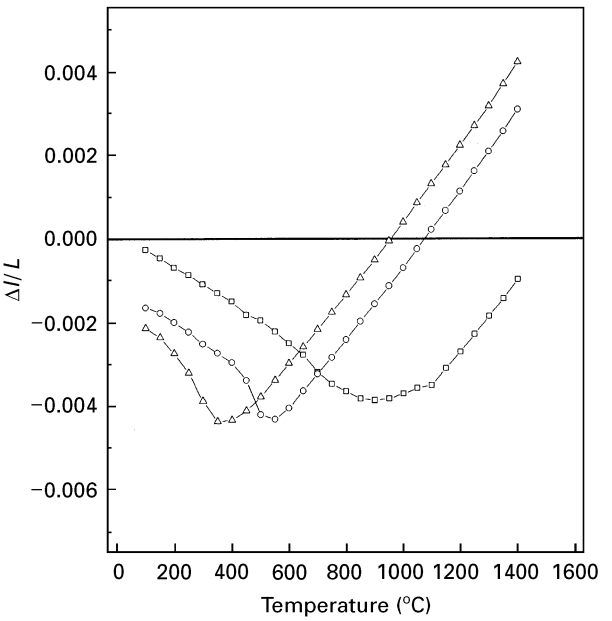

Figure 17 Thermal expansion behaviour during cooling of Al_2TiO_5/Al_2O_3 composites sintered at 1500 °C for 2 h; (□) SGAT, (○) SGATA10, (△) SGATA20.

Al_2TiO_5 and effectively prevented microcracking and increased the density, strength and thermal expansion coefficient.

Mullite prevented the decomposition of Al_2TiO_5; however, alumina accelerated the decomposition of Al_2TiO_5.

The thermal expansion coefficients of the alumina-containing specimens decreased with temperature more rapidly compared with the mullite-containing specimens, because the decomposition of the mullite-containing specimens was more effectively prevented by the mullite content.

Specimens contracted during cooling; however, at some point they again expanded to produce different minimum points, according to the contents of the second phases, mullite and alumina, because microcracks initiated at these minimum points. The temperatures of the minimum points were lowered by increasing the contents of the second phases, mullite and alumina, because the second phases prevented grain growth and thus enhanced the densification and strength of the Al_2TiO_5/mullite (alumina) composites.

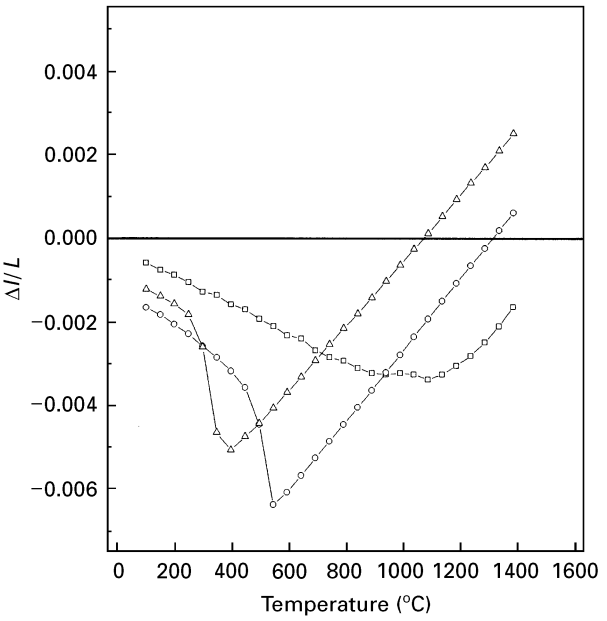

Figure 18 Thermal expansion behaviour during heating of Al_2TiO_5/mullite composites sintered at 1600 °C for 2 h; (□) SGAT, (○) SGATM10, (△) SGATM20.

Acknowledgement

Financial support from the Korean Ministry of Education Research Fund for Advanced Materials in 1995 is gratefully acknowledged.

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Received 30 September 1996
and accepted 4 April 1997