Thermal and Mechanical Properties of Aluminumtitanate–Mullite Composites (Part 3)

—Effects of Aluminumtitanate Particle Size—

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チタン酸アルミニウム–ムライト複合焼成体の熱的及び機械的性質 (第3報)

—チタン酸アルミニウム粒径の影響—

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The effects of aluminumtitanate (AT) particle size on the sinterability, bending strength, thermal expansion, thermal stability and thermal shock resistance of aluminumtitanate–mullite composites with various mixing ratios were studied. The results were summarized as follows. (1) The sintered density slightly increased with decreasing AT particle size. (2) The grain size of AT in sintered bodies was nearly equal to the particle size in raw mixtures, except for $<1\mu\text{m}$ powder. (3) The bending strength of the composites was not influenced significantly by the particle size of AT. It was the highest at 26 wt%AT composites and decreased with increasing amount of AT. (4) The degree of thermal expansion hysteresis increased with increasing amount of AT regardless the particle size. (5) The thermal expansion coefficients in heating stage of the composites were highest at 48 wt%AT except the largest particle size composites, and decreased in higher AT content. These coefficients slightly increased with decrease in particle size of AT in raw mixtures. (6) The critical temperature difference of the composites raised with increase in particle size in the same AT composition.

Key-words: Aluminumtitanate, Mullite, Composite, Bending strength, Thermal expansion, Thermal stability, Thermal shock resistance, Critical temperature difference

1. Introduction

Ceramic substrates with low thermal expansion coefficient, high thermal shock resistance property have been sought for the application to severe thermal environment. Aluminumtitanate (AT), one of very low thermal expansion materials, has been applied for components such as manifolds of automotive engines.¹⁾ It is also a candidate compound for use in a catalyst carrier at higher temperature than that of cordierite carrier, since the melting point of

AT ($\sim 1850^\circ\text{C}$) is much higher than that of cordierite ($\sim 1400^\circ\text{C}$).

Whereas AT sintered body shows very low coefficient of linear thermal expansion (CTE), the mechanical strength is unbelievably low. The reason of low thermal expansion is basically depend on the microstructure of sintered body, which contain many microcracks induced by strong anisotropy of axial thermal expansion.^{2),3)} Then, the mechanical strength of the sintered body is inevitably low. Some studies were carried out concerning the effects of starting powders,^{4)–6)} additives^{7),8)} on properties of AT sintered body, there were a few attempts to synthesize composites.^{9),10)} To increase the mechanical strength without missing the low thermal expansiveness, we have been studied the composites between AT and mullite.^{11),12)} It was clarified that the bending strength of the composite greatly improved in all range of composition, and the CTE was maintained medium values between that of mullite and AT. Furthermore, the decomposition of AT in the temperature near 1200°C ,^{13),14)} which is an other disadvantage of AT, was restrained almost completely in the composites. The thermal shock resistance property of the 85 wt%AT composite was nearly the same as that of pure AT.

In the present study, the effects of particle size of AT in raw material on thermal and mechanical properties of the AT–mullite composites are investigated to further improve and control those properties, since the bulk properties of the composites in the system seem to be affected strongly by the microstructure of sintered body. It was suggested that there were the critical grain sizes to form microcracks in some pseudobrookite compounds.⁶⁾

2. Experimental procedures

2.1 Synthesis of aluminumtitanate–mullite composites from classified aluminumtitanate powders

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The synthesis of AT powder was carried out according to the previous report.¹¹⁾ Then, it was milled in a ball mill lined with alumina for 53 h using alumina balls and ethanol, and classified by a sedimentation method into grain size ranges 5–10 μm , 3–5 μm , 1–3 μm and <1 μm . The particle size distribution was checked by an Andreasen pipet method. The mean (50 wt%) particle sizes were 4.8, 2.8, 2 μm for former 3 powders, respectively. The particle size of the last powder was observed as less than 1 μm by a scanning electron microscope (SEM). These powders were indicated as AT4.8, AT2.8, AT2 and AT1 in following sections. Before the sedimentation, the average particle size was 3 μm .

The synthesis method of the AT–mullite composites was the same as reported,¹¹⁾ except for using classified AT powders. The crystalline phases detected by powder X-ray diffractometry (XRD) were AT and mullite in all composites.

2.2 Characterization methods

Thermal expansion was measured using a dilatometer from room temperature to 1415°C in air. The heating and cooling rates were fixed at 6°C/min except lower than 500°C in cooling cycle. A three-point bending strength was obtained using a universal testing machine under the crosshead speed of 0.5 mm/min, lower span of 10 mm for 4 × 4 × 16 mm specimens. The surface of the bending specimen was polished with a No. 1500 polishing cloth. The average strength of 6–9 pieces was obtained. The thermal shock resistance property was examined by a quenching into cool water method, i.e., the specimen was heated in a furnace at given temperature and kept at 30 min, then it was dropped quickly into cool water at nearly 0°C, subsequently bending strength of that specimen was obtained. The critical temperature difference (ΔT_c), the temperature corresponding to the sudden decrease in bending strength, was obtained from the temperature difference vs. bending strength relation. The number of the specimens tested in one temperature was 6–9.

3. Results and discussion

3.1 Density, microstructure and bending strength

Relative density and water absorption of the sintered body are shown in Fig. 1. Relative density was higher than 90% for all composites from different particle size except AT4.8–mullite. Within the AT1-, AT2- and AT2.8–mullite composites, slightly higher density in smaller AT particle size was observed. In the case of AT4.8–mullite composites, the highest density was achieved at 26 wt% AT composition, but it decreased markedly in higher AT compositions.

From SEM observation of fracture surface and composition analysis of polished surface of the composites, the following feature was clarified. (1) In the composites containing large amount of mullite,

Fig. 1. Relative density and water absorption of aluminumtitanate–mullite composites synthesized from different particle size of aluminumtitanate.

there was no microcracks between grains and fracture was mainly occurred trans-granularly. The range of this fracture mode expanded widely in low AT content and small particle size. (2) The grain size of AT in the composites was nearly equal to the particle size of AT in raw mixture, but in the AT1–mullite composites, growth of AT grains was observed in all composition, may be caused by agglomeration of AT powder. (3) Microcracks along grain boundaries were observed in the composites higher AT content than 67 wt% in all particle size of AT, and larger in crack width for larger AT grain size in the sintered bodies.

The bending strength of the composites is presented in Fig. 2. In the AT1–mullite composites, bending strength of 230–240 MPa was achieved in 26 wt% AT1 and 48 wt% AT1 composites, which were much higher than that of mullite. In the other particle size, the highest strength was obtained at 26 wt% AT and it decreased with increase in the amount of AT. At one composition, these had nearly the same values, slightly higher at smaller particle

Fig. 2. Bending strength of aluminumtitanate–mullite composites synthesized from different particle size of aluminumtitanate.

size of AT. The reason of high bending strength in lower AT content is attributable to the continuous microstructure in those specimens without grain boundary microcracks, therefore these composites showed trans-granular fracture mode. It is supposed that the sintering was assisted by a small amount of liquid phase at high mullite composition.¹⁵⁾ The high strength of 48 wt% AT1 composite was also attributable to increased sinterability due to liquid phase formation. At higher AT contents, the bending strength of all composites degraded markedly due to grain boundary microcracks in the bodies.

Cleveland et al. deduced that the critical grain size for inducing grain boundary microcracks in AT sintered body was about $1\text{--}2\text{ }\mu\text{m}$,⁶⁾ less than this value microcracking would be suppressed. From the SEM observation mentioned above and thermal expansion curves described below, it is believed that there are microcracks in the pure AT bodies synthesized from the powders with average particle size over $2.8\text{ }\mu\text{m}$. In the case of AT1 and AT2 sintered bodies, the abnormal grain growth with preferential orientation, so-called domain structure, was observed.^{4),16)}

3.2 Thermal expansion and thermal stability

The thermal expansion curves in heating and cooling stages of the AT1-mullite composites are shown in Fig. 3. It is known that the AT sintered body shows large thermal hysteresis between heating stage and cooling stage. The mechanism of hysteresis was given by Buessem et al.²⁾ Closing the grain boundary microcracks gives very low expansion during heating stage. At higher temperature the microcracks are closed almost completely and each grain connects together, showing relatively higher expansion. And then during the former step of cooling stage, it shrinks with high CTE corresponding to

the average of lattice expansion coefficients. During latter stage of cooling, the microcracking occurs again due to thermal expansion anisotropy, the body stops to shrink or expands slightly.

In the AT1-mullite composites, the degree of thermal hysteresis increased with increasing AT content over 64 wt%. It was supported by the SEM observation of microcracks. There are kink points in both heating and cooling curves which show typical thermal hysteresis, corresponding four stages mentioned above. The kink points of heating curves were observed at near 1000°C in 67 wt% AT1 and 85 wt% AT1 composites. That of cooling curve was influenced by the composition, 200°C in 85 wt% AT1 and below room temperature in 67 wt% AT1 composite. The thermal expansion curve of pure AT1 was somewhat complex. During heating stage, slight shrinkage at $1100\text{--}1200^\circ\text{C}$ due to decomposition was observed.¹⁶⁾ Furthermore, during cooling stage, the microcracking occurs at relatively higher temperature than 1000°C in some specimens and shows change in shrinkage rate. These two effects are overlapped on the formerly described four steps. In the case of AT1 and AT2 seen in Figs. 3 and 4 show the typical examples of these effects. The reason of latter behavior could be attributable to the domain structure in the pure AT body sintered from small particles.

In Fig. 4, the thermal expansion curves in heating and cooling stages of the AT2-mullite composites are shown. In general, the thermal expansion curves of AT2-mullite composites resemble those of AT1-mullite composites. The kink point during cooling stage was shifted to 400°C in 85 wt% AT2 composite and to 300°C in 67 wt% AT2 composite.

The thermal expansion curves in heating and cool-

Fig. 3. Thermal expansion curves in heating and cooling stages of aluminutitanate-mullite composites synthesized from $<1\text{ }\mu\text{m}$ aluminutitanate powder.

Fig. 4. Thermal expansion curves in heating and cooling stages of aluminutitanate-mullite composites synthesized from average particle size of $2\text{ }\mu\text{m}$ aluminutitanate powder.

Fig. 5. Thermal expansion curves in heating and cooling stages of aluminutitanate-mullite composites synthesized from average particle size of $2.8\ \mu\text{m}$ aluminutitanate powder.

Fig. 6. Thermal expansion curves in heating and cooling stages of aluminutitanate-mullite composites synthesized from average particle size of $4.8\ \mu\text{m}$ aluminutitanate powder.

ing stages of AT2.8-mullite and AT4.8-mullite composites are presented in Figs. 5 and 6, respectively. Most different feature from AT1-mullite and AT2-mullite composites, was the thermal expansion of 48 wt%AT composites. In AT2.8 composites, the curve of 48 wt%AT2.8 mostly overlapped with that of 26 wt%AT2.8 composite, whereas the curve of 48 wt% AT2 composite showed higher expansion rate than 26 wt%AT2 composite and that of 48 wt%AT4.8

composite showed lower expansion rate than 26 wt%AT4.8 composite.

The CTEs of the composites obtained from the observed curves shown above are plotted against content of AT. Because the curves were complex, the CTEs of three temperature ranges were calculated. In Fig. 7(a), those of room temperature to 1000°C (in AT4.8-mullite composites, room temperature to 1100°C) in heating stage of the various composites are presented. The CTE increased slightly with increase in AT content to 48 wt%AT and decreased greatly in further increase in AT content in AT1, AT2 and AT2.8 composites. In AT4.8 composites, it started to decrease at lower AT content. Comparing the data at 48 wt%AT composition, the higher CTE was obtained in smaller AT particle size. On the contrary, in pure AT, the higher coefficient was ob-

Fig. 7. Linear thermal expansion coefficients of aluminutitanate-mullite composites.

- (a) Heating stage (room temperature- 1000°C , only AT4.8 room temperature- 1100°C),
- (b) Heating stage (1000°C - 1400°C , only AT4.8 1100°C - 1400°C and for pure AT, see text),
- (c) Cooling stage (1415°C -kink point in cooling curves).

Fig. 8. The relation between quenching temperature difference and bending strength of the composites synthesized from $<1\ \mu\text{m}$ aluminutitanate powder.

Fig. 9.

Fig. 10.

Fig. 11.

Fig. 9. The relation between quenching temperature difference and bending strength of the composites synthesized from average particle size of $2\ \mu\text{m}$ aluminutitanate powder.

Fig. 10. The relation between quenching temperature difference and bending strength of the composites synthesized from average particle size of $2.8\ \mu\text{m}$ aluminutitanate powder.

Fig. 11. The relation between quenching temperature difference and bending strength of the composites synthesized from average particle size of $4.8\ \mu\text{m}$ aluminutitanate powder.

tained in the larger AT particle size.

The increase in the coefficients of the specimens with lower AT contents is accepted as the simple rule of mixture of the mean CTE of mullite ($4.6 \times 10^{-6}/^\circ\text{C}$, $25^\circ\text{--}600^\circ\text{C}^{17}$), and that of AT ($9.7 \times 10^{-6}/^\circ\text{C}$, $25^\circ\text{--}600^\circ\text{C}^{31}$), calculated from lattice expansion. The deviation from the line between two values of mullite and AT indicates the microcrack formation in larger AT particle size composites. Those thermal expansion curves show small degree of thermal hysteresis observed in the figures. Large decrease in the CTEs of the composites containing large amount of AT indicates that extensive grain boundary microcracking occurred in those composites. The microcracking was clearly observed by SEM. The values of pure AT bodies from different particle sizes are related sensitively to each microstructure.¹⁶⁾

Secondary, the CTEs between $1000^\circ\text{--}1415^\circ\text{C}$ (in AT4.8–mullite composites, 1100°C to 1400°C) in heating stage are presented in Fig. 7(b), and those of 1400°C –kink point temperature in cooling stage are shown in Fig. 7(c). For pure AT, those coefficients were calculated from 1200°C (AT1 and AT2.8) or 1300°C (AT2 and AT4.8) to 1400°C to neglect the effects of thermal decomposition. The tendency that the coefficients increased with increase in AT contents was observed in all particle size composites both in heating stage and cooling stage except some specimen of pure AT. These two stages of thermal expansion and contraction are corresponding to the dense composites of mullite and AT without microcracks, thus the CTEs of composites reflect essential lattice expansion of mullite and that of AT. This is most clearly observed in the cooling stage's coefficients, whereas in heating stage's coefficients of high AT content may be slightly affect-

ed by the residual microcracks and sintering shrinkage. In these stages, no particle size effect is essentially occurred by the reason mentioned above. The large variation of pure AT bodies in heating and cooling stages influenced greatly by the microstructure, i. e., the domain structure formation and irregular crack formation, thus the calculated coefficient largely varied by the selection of temperature range.

Thermal decomposition behavior of all composites examined in this study was checked by heating at 1190°C for 5, 10 and 15 h. In all specimens, there is no decomposition products such as rutile and corundum. The reason of the suppression of the decomposition was mentioned before.¹¹⁾

3.3 Thermal shock resistance

The relations of quenching temperature difference and bending strength after quenching in various AT content composites synthesized from different AT particle size are shown in Figs. 8–11. The bending strength of a composite after quenching does not change or slightly increase until the critical temperature difference, then suddenly decrease to lower strength. In general, lower AT content composites show higher strength and smaller ΔT_c , and vice versa.

The critical temperature difference, ΔT_c , of the AT–mullite composites are summarized in Table 1. The ΔT_c of mullite was 300°C , and those of AT–mullite composites fabricated from different particle size increased with an increase in AT content over 67 wt%AT in AT1– and AT2–mullite composites and over 48 wt%AT in AT2.8– and AT4.8–mullite composites. In 48 wt%AT composites, the ΔT_c of AT1– and AT2–mullite composites were the same as that of mullite, but in AT2.8– and AT4.8–mullite it increased $100^\circ\text{--}150^\circ\text{C}$. And 85 wt%AT composites, the same feature that greater ΔT_c in larger particle

Table 1. Observed critical temperature difference (ΔT_c , °C) of various AT–mullite composites.

composition (wt%AT)	AT1–mullite	AT2–mullite	AT2.8–mullite	AT4.8–mullite
26	300	300	300	300
48	300	300	400	450
67	600	550	650	**
85	900	950	1050	**
100	>1200	>1200	1100	1100

*: ΔT_c of mullite is 300°C. **: Not observed.

size was observed.

From the theory summarized by Hasselman,¹⁸⁾ one of the thermal shock resistance parameters (R) for relatively severe conditions such as quenching into water, it is expressed as the functions of S : fracture strength, ν : Poisson's ratio, E : Young's modulus, and α : linear thermal expansion coefficient;

$$R = S(1 - \nu) / E\alpha$$

Since Young's modulus of mullite is about 70 GPa,¹⁹⁾ and that of AT sintered body was reported as about 10 GPa,⁶⁾ and the CTE of AT–mullite composites decreased with increasing AT content, it is reasonable that higher AT content composites have much higher thermal shock resistance parameters in spite of low bending strength. In the same composition, R is the function of bending strength and CTE. In the 48 wt%AT composites, R was increased with increasing particle size of AT in the raw mixture. From Fig. 2, the bending strength of the 48 wt% AT1–mullite composite was twice of the other composites, and the CTEs of heating stages of those composites increased slightly with decreasing AT particle size as shown in Fig. 7. From this results, it is concluded that the effects of CTE on ΔT_c is greater than that of bending strength. This is confirmed by the results in 67 wt%AT and 85 wt%AT composites, that the bending strength of the composites were the same order, but the CTEs decreased with increasing particle size, gives higher ΔT_c .

4. Conclusions

The effects of aluminutitanate (AT) particle size in raw mixture on the sinterability, bending strength, thermal expansion, thermal stability and thermal shock behavior of aluminutitanate–mullite composites with various mixing ratios were observed. The results obtained were summarized as follows;

(1) The sintered density slightly increased with decreasing AT particle size.

(2) The grain size of AT in sintered bodies was nearly equal to the particle size in raw mixtures, except for $<1 \mu\text{m}$ powder. In the case of $<1 \mu\text{m}$ pow-

der, some agglomeration of the powder would occur in original AT powder and gives relatively large grains in sintered body. Then the most fine grain size in composites was obtained from AT2 powder.

(3) The bending strength of the composites was not influenced significantly by the particle size of AT. It was the highest at 26 wt% composites and decreased with increasing content of AT. In the case of AT1 composites, higher bending strength was obtained at both 26 and 48 wt%AT composites.

(4) The degree of thermal expansion hysteresis increased with increasing the AT content regardless the particle size.

(5) The thermal expansion coefficients in heating stage of the composites were highest at 48 wt% AT except the largest particle size composites, and decreased with an increase in content of AT. These coefficients slightly increased with decrease in particle size of AT in raw mixtures.

(6) The decomposition of AT was suppressed in all composites.

(7) The critical temperature difference of the composites raised with increase in particle size of AT in the same AT–mullite composition. The contribution of linear thermal expansion coefficient on ΔT_c was greater than that of bending strength.

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