

Thermal durability of aluminum titanate-mullite composites with high thermal shock resistance

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Aluminum titanate (Al_2TiO_5)-mullite composites with excellent thermal shock resistance were studied. Aluminum titanate with a moderately high mechanical strength and a low thermal expansion coefficient was obtained by inhibiting grain growth by the addition of mullite. The composites were fabricated from mono-dispersed powders, produced by the stepwise alkoxide hydrolysis of tetraethylorthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$ and titanium tetraethoxide, $\text{Ti}(\text{OC}_2\text{H}_5)_4$, in an Al_2O_3 ethanolic colloidal suspension. Several thermal durability tests were performed: annealing tests at the critical decomposition temperature, 1100°C , for 100 h; cyclic thermal shock between 750° and 1400°C for 100 h; and water quenching from 950° to room temperature (RT). Changes in the microstructure, thermal expansion coefficient, and strength were determined. The composites with 70-80 vol% Al_2TiO_5 showed the best thermal durability, exemplified by little change in their microstructure during the thermal durability tests. The role of microcracks in thermal shock resistance, strength, Young's modulus, sound velocity, and thermal expansion coefficient is discussed here.

Key words: Al_2TiO_5 , Mullite, Thermal durability, Thermal expansion coefficient, Thermal shock.

Introduction

Aluminum titanate (Al_2TiO_5) is well-known as an excellent thermal shock-resistant material, resulting from its unique combination of low thermal expansion and low Young's modulus, which, in turn, allows for applications as an insulating material in engine components such as portliners, piston bottoms, and turbochargers [1]. However, Al_2TiO_5 materials have a relatively low mechanical strength because of microcracks induced by the high anisotropy of the thermal expansion coefficients along the crystallographic axes [2, 3]. Unstabilized Al_2TiO_5 tends to decompose into Al_2O_3 and TiO_2 at temperatures ranging from 800° to 1300°C [4, 5]. The decomposition occurs when adjacent aluminum and titanium octahedra collapse because the lattice site occupied by the aluminum is too large [6]. The thermal energy available from this collapse permits the aluminum to migrate from its position and causes structural dissolution to rutile and corundum [7]. Following decomposition, the material no longer exhibits either a low thermal expansion coefficient or favorable thermal shock behavior, rendering it apparently useless for industrial applications.

The thermal stability of Al_2TiO_5 can be improved by the formation of solid solutions with MgO , Fe_2O_3 , or TiO_2 , which are isomorphous with the mineral pseudobrookite, such as Fe_2TiO_5 [8], MgTi_2O_5 [9, 10], or Ti_3O_5 (anosovite) [11]. This thermodynamic stabilizing effect is related to a decrease in the decomposition temperature of isostructural compounds. The compounds MgTi_2O_5 and Fe_2TiO_5 respectively decomposes to $\text{MgTiO}_3+\text{TiO}_2$ below 700°C and $\text{Fe}_2\text{O}_3+\text{TiO}_2$ at 565°C , whereas Al_2TiO_5 decompose into Al_2O_3 and TiO_2 below 1300°C [10-13]. Polycrystalline Al_2TiO_5 can also be stabilized by limiting its grain growth [12]. Another source of stabilization is the limitation of grain growth of Al_2TiO_5 by the addition of additives such as SiO_2 [14], ZrO_2 [15], ZrTiO_4 [16, 17], or mullite [18], most of which do not form a solid solution with Al_2TiO_5 but rather restrain the tendency of Al_2TiO_5 toward decomposition. However, the additives of SiO_2 and ZrO_2 do not have a significant effect on the thermal stability of Al_2TiO_5 , even after a long annealing test at 1100°C for 100h [13]. On the other hand, the addition of mullite or ZrTiO_4 not only restrains the decomposition but also increases the thermal stability at 1100°C [18, 19].

The largest increase in strength occurred with the synthesized Al_2TiO_5 powder, especially using Al_2O_3 , MgO or ZrO_2 additions. The increase of the mechanical strength reported for this material was linked microstructurally to the observation of fine particles of Al_2O_3 , MgAl_2O_4 , or ZrO_2 at the grain boundaries [16]. Such a

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distribution of fine particles at the grain boundaries would prevent grain growth and thus reduce micro-cracking, thereby increasing the strength [7, 13]. SiO_2 additions improve the strength of reaction-sintered material to a limiting amount of 3%. This is attributed to the formation of a grain boundary liquid phase during sintering [7]. Pena *et al.* [20] studied the properties of an aluminium titanate-mullite- ZrO_2 mixture and obtained a strength of 30 MPa, which represents a 10-fold improvement over their pure aluminium titanate material. Yano *et al.* [21] have reported a mechanical strength around 100 MPa for material containing 25 vol% mullite, which coincided with the point at which the decomposition was completely controlled. Morishima *et al.* [22] reported a strength of 70 MPa for an aluminum titanate-mullite composite material containing 91 vol% Al_2TiO_5 , but this material did not show strength retention.

Furthermore, thermal shock resistance is a property that is difficult to quantify, and as such is usually expressed in terms of a number of empirical resistance parameters. These are dependent on the conditions imposed, but one method that can be used is the examination of strength retention after quenching. For high temperature applications, long-annealing thermal durability, cycle thermal stability and residual mechanical properties are very important if these materials are to be used between 1000°C and 1300°C. Attempts to improve the thermal durability of Al_2TiO_5 at temperatures ranging from 750° to 1400°C are still under investigation.

Therefore, in the present study, new thermal shock-resistant materials, based on Al_2TiO_5 -mullite composites of various compositions, were fabricated by reducing the particle size and adjusting the composition of Al_2O_3 : TiO_2 : SiO_2 .

Experimental

Al_2TiO_5 -mullite composites were synthesized by the stepwise alkoxide hydrolysis of tetraethylorthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$ (98.9%), and titanium tetraethoxide, $\text{Ti}(\text{OC}_2\text{H}_5)_4$ (98%), in an Al_2O_3 ethanolic colloidal suspension. Dispersed powder was centrifuged to remove the alcoholic solution, washed with deionized water and redispersed in aqueous NH_4OH (NH_3 , 25%, Merck) solution (pH=10). Powder compacts were prepared by centrifugal casting followed by drying at 100°C. Before firing, the compacts were calcined in air at 600°C for 1h to remove organic materials. Bar specimens (7 mm × 7 mm × 50 mm or 5 mm × 5 mm × 25 mm) and pellet specimens (10 mm in diameter and 15 mm thick) were made by pressing at 300 MPa, and sintered at 1600°C for 2 h in air, in an electric furnace. The preparation route is shown schematically in Fig. 1. Compositions containing 10, 20, 30, and 50 vol% mullite were selected for the present study. The chemical composition of each of the compacts is shown in Table 1, where AT, ATM1, ATM2, ATM3, and ATM5 refer to as 0, 10, 20,

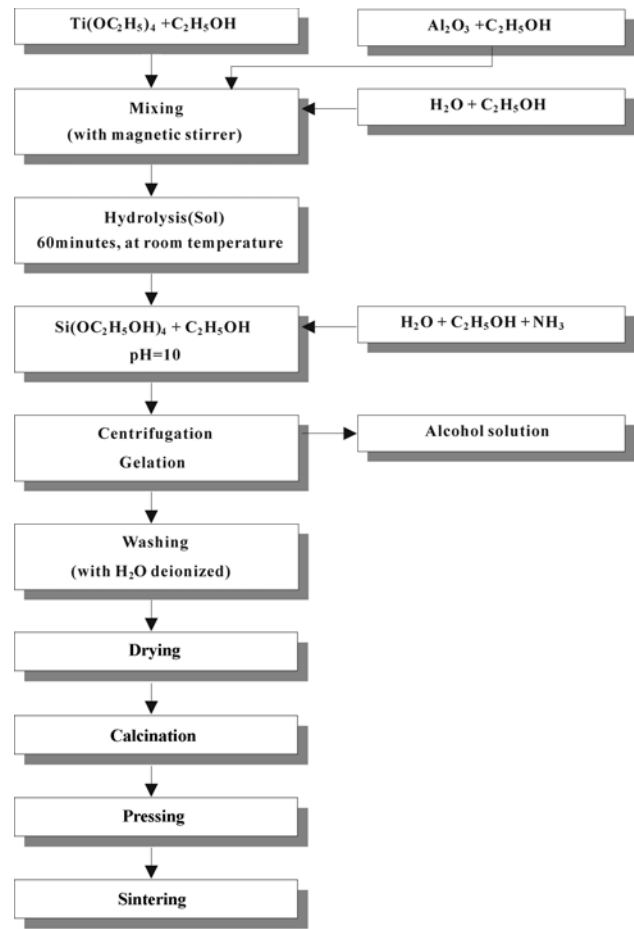


Fig. 1. Schematic diagram of the sol-gel process for preparing Al_2TiO_5 -Mullite composites.

Table 1. Chemical composition of the compacts (wt%, 1050°C for 1 hr)

Mullite vol%*	AT 0	ATM1 10	ATM2 20	ATM3 30	ATM5 50
Al_2O_3	56.92	53.44	57.67	65.19	63.39
TiO_2	42.72	42.81	35.50	25.53	24.39
SiO_2	0.02	3.44	6.67	8.56	11.81
Sum	99.66	99.69	99.84	99.26	99.59
Ignition loss [%]	8.37	7.83	6.67	5.88	6.48

*: Synthesized crystalline mullite vol% at 1600°C for 2h.

30, and 50 vol% addition of mullite, respectively. Samples were characterized by X-ray diffraction (Philips, PW1180/00, Ni-filtered $\text{CuK}\alpha$) and scanning electron microscopy (Cambridge, Steroscan 250 MK2) after the surface had been coated with vapor-deposited gold. Surface area and particle sizes are determined by N_2 adsorption (BET). The mean grain sizes of the sintered Al_2TiO_5 were measured by the linear-intercept method, with Fullman's method [23].

Some samples were pulled out of the furnace after sintering and water quenched. After that, the relative amounts of decomposed composition were calculated by quantitative X-ray measurements. As an internal standard

sample, 50 wt% of MgO was added to each mixed powder. Then the following peaks were evaluated; MgO(220), Al_2TiO_5 (023), $\alpha\text{-Al}_2\text{O}_3$ (104), and TiO_2 -rutile(101). According to the internal standard method, the following equation is used for calculating the content of each phase in the mixtures,

$$X_a = I_{ax} / I_e \times \rho_a / \rho_e \times X_e / (1 - X_e) \quad (1)$$

where X is content of each phase in the sample (wt %), I_{ax} the reflection intensity of each phase, ρ density of each phase, respectively. The following equations give the concentration of Al_2O_3 , TiO_2 and Al_2TiO_5 in mole percent:

$$\begin{aligned} C_{\text{Al}_2\text{O}_3} &= I_{\text{Al}_2\text{O}_3(104)} / I_{\text{MgO}(220)} \\ C_{\text{TiO}_2} &= I_{\text{TiO}_2(101)} / I_{\text{MgO}(220)} \\ C_{\text{Al}_2\text{TiO}_5} &= I_{\text{Al}_2\text{TiO}_5(023)} / I_{\text{MgO}(220)} \end{aligned} \quad (2)$$

The equations determine the amount of decomposition in Al_2TiO_5 -mullite composites.

Several tests were conducted to evaluate the thermal durability of the Al_2TiO_5 -mullite composites. First, the specimens were subjected to long-term thermal annealing, at the critical decomposition temperature of Al_2TiO_5 , 1100°C, for 100 h. Secondly, a cyclic thermal shock test, consisting of 23 cycles of 750°C-1400°C-750°C, was conducted in a two-chamber furnace over an

interval of 100 h. Thirdly, the thermal shock resistance of the material was determined by a water-quenching process analogous to the German industrial standard [24], by which three specimens of each composition were heated to 950°C for 15 min. in a muffle furnace and quenched with flowing water at 20°C for 15 min.; all of the specimens then were dried at 110°C for 30 min., and those that withstood the thermal shock without spontaneously developing major cracks were subjected to the following tests, in the cold condition:

(1) The residual three-point flexural strength of bar specimens (7 mm × 7 mm × 50 mm) was measured using a universal testing machine (Instron, 1186), with a span length of 40 mm and a crosshead speed of 0.2 mm minute⁻¹.

(2) The Young's modulus was measured by the resonance-frequency method, as a function of the number of quenching cycles, using the bending-test specimens.

(3) The microstructural degradation of cylindrical specimens (25 mm in diameter and 35 mm high) was measured by sound velocity, using a "Pundit" apparatus (C.N.S. Instruments, Ltd., Germany).

(4) The thermal expansion coefficient from room temperature (RT) to 1200°C was determined for a 5 mm × 5 mm × 25 mm specimen, in air, using a dilato-

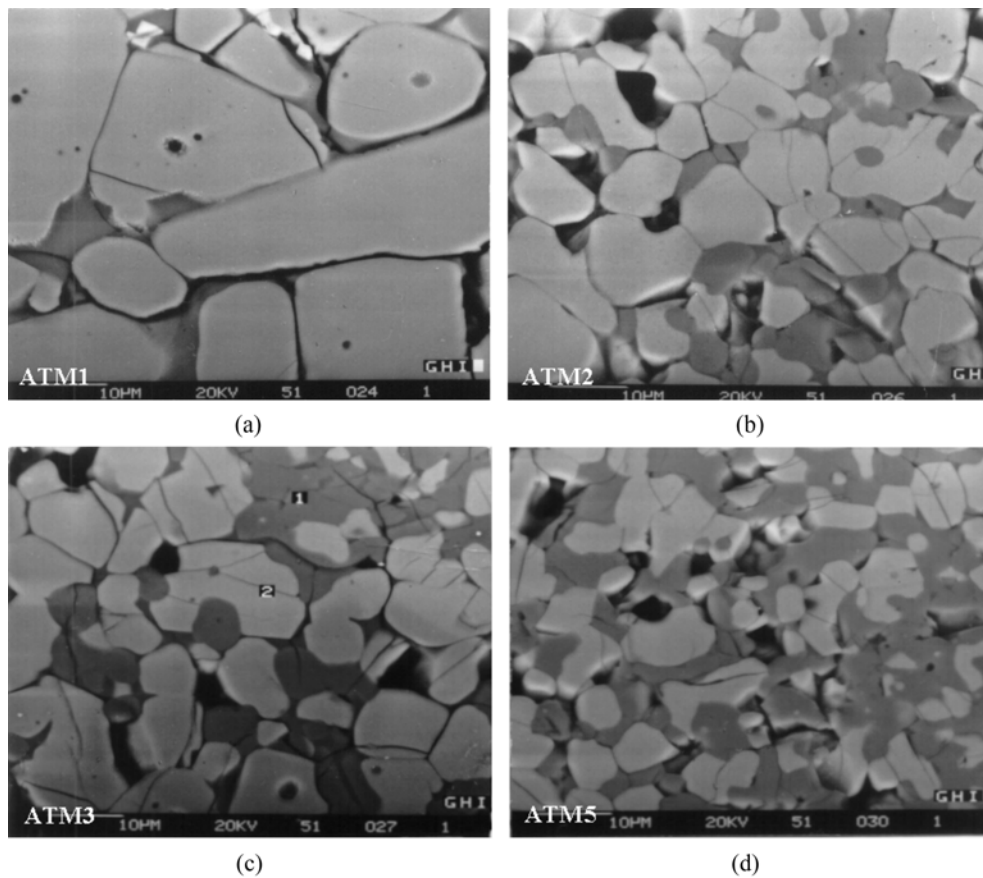


Fig. 2. Microstructure of sintered ATM-materials (a) ATM1, (b) ATM3, (c) ATM3 and (d) ATM5 at 1600°C for 2 hrs (gray or 2: AT, dim or 1: mullite, bright: rutile, black: porosity).

meter, at a heating rate of 5 Kmin⁻¹ and a cooling rate of 10 Kmin⁻¹. Cyclic thermal expansion coefficients were also measured, using a dilatometer at up to 1500°C, before and after the decomposition tests.

Results and Discussion

The amorphous SiO₂-coated Al₂O₃ powders (3Al₂O₃·2SiO₂) consisted of spherical particles with a narrow particle-size distribution (0.5~0.6 μm) and a high surface area (76 m²g⁻¹). The amorphous TiO₂-coated Al₂O₃ powders (Al₂O₃:TiO₂=1:1) were smaller in size composed of various sizes and partially agglomerated, with a high surface area (194 m²g⁻¹). Agglomeration may have been a result of the rapid reaction of Ti(OC₂H₅)₄ with H₂O. The sintered, ATM1 exhibited significant β-Al₂TiO₅ grain growth, with grain sizes of 10~70 μm, and a small amount of dispersed corundum and rutile. On the other hand, the specimens, ATM2 and ATM3, appeared to have a smaller mean grain size of β-Al₂TiO₅ (5~20 μm). Figure 2a clearly shows some of the large grains contained closed pores, created during densification. The mean grain diameter of the ATM5 was ~8 μm; such a distribution of interlinked fine-mullite particles at the grain boundaries would prevent β-Al₂TiO₅ grain growth. In all cases, the Al₂TiO₅ grain size decreased with increased mullite content and were surrounded by microcracks, as shown in Fig. 2.

Table 2 summarizes the phase compositions and physical properties of the materials sintered at 1600°C for 2 h. The final materials consisted mainly of two crystalline phases: Al₂TiO₅ and mullite. ATM1 consists of 90% Al₂TiO₅ and 10% mullite, and 10% of liquid where acts as a driving force for the grain growth of Al₂TiO₅. The density of the ATM materials increased as the mullite content increased, reaching a maximum at 20 vol% of mullite, and then decreased with further increased mullite contents, indicating increased microcracking with a porosity of 12% (Table 2). The low relative density of pure Al₂TiO₅ (76.0%) is related to the grain growth of Al₂TiO₅ and higher porosity because Al₂TiO₅ has a lower theoretical density of 3.70 gcm⁻³, in comparison with an equimolar Al₂O₃/TiO₂ mixture (4.19 gcm⁻³), accompanied by an about 11% molar volume increase [7]. As shown in Fig. 2, grain sizes of β-Al₂TiO₅ decreased with increased mullite content,

accounting for the observed increase in the thermal expansion coefficient, discussed later.

The changes caused in the phase compositions by the decomposition test are given in Table 3. The unstabilized material decomposed to corundum and rutile in both cases, and partial decomposition was observed in the ATM2, ATM3, and ATM5 composites after annealing at 1100°C. The amount of decomposition of Al₂TiO₅ decreased with increased mullite content, so that the composition with 20-50 vol% mullite still retained ~80% of Al₂TiO₅. Such a phenomenon is plausible within the critical temperature range, between ~800 and 1300°C. The changes caused in the phase compositions by cyclic thermal shock illustrate a similar trend. Mullite addition prevented AT materials from decomposing during the cyclic thermal shock test. The better results of the present cyclic test than those of the present annealing test indicate a possibility of the reversible formation of Al₂TiO₅ during testing at high temperature, 750°-1400°-750°C.

The thermal expansion hysteresis of the formation of β-Al₂TiO₅ from corundum and rutile, caused by the expansion anisotropy of the individual β-Al₂TiO₅ crystals, exhibited a strong microstructural dependency. In other words, the thermal expansion anisotropy was directly related to the degree of microcracking and the grain

Table 3. Phase composition of aluminum titanate-mullite composites after various thermal treatments

Phase composition	AT	ATM1	ATM2	ATM3	ATM5
Before decomposition test	β-AT C R	β-AT R	β-AT M	β-AT M	β-AT M
Decomposition test (annealing at 1100°C, for 100h)	R C β-AT	R C β-AT	β-AT R M C	β-AT M R C	β-AT M R C
Decomposition content [%]	95.0	95.0	22.6	12.3	7.2
Cyclic thermal shock test (750-1400-750°C, 23 cycles, for 100h)	R C β-AT	R C β-AT	β-AT M C	β-AT M R	β-AT M R
Decomposition content [%]	95.5	64.0	3.4	12.0	7.1

*Key: β-AT=β-Al₂TiO₅; M=Mullite; C=Corundum; R=Rutile

Table 2. The phase compositions and the physical properties of the materials (1600°C for 2 hrs)

Materials	Mullite content [vol%]	Phase composition	Bulk density [gcm ⁻³]	Relative density [%]	Porosity [%]	Average grain size of AT [μm]
AT	0	AT+R+C	2.9	76.0	24	20
ATM1	10	AT+Mullite+L	3.3	88.2	11.8	40
ATM2	20	AT+Mullite	3.5	93.3	6.87	18
ATM3	30	AT+Mullite	3.3	88.0	12.0	15
ATM5	50	AT+Mullite	3.4	92.2	7.8	8

*Key: AT; β-Al₂TiO₅, R: Rutile, C: Corundum, L; Liquid phase

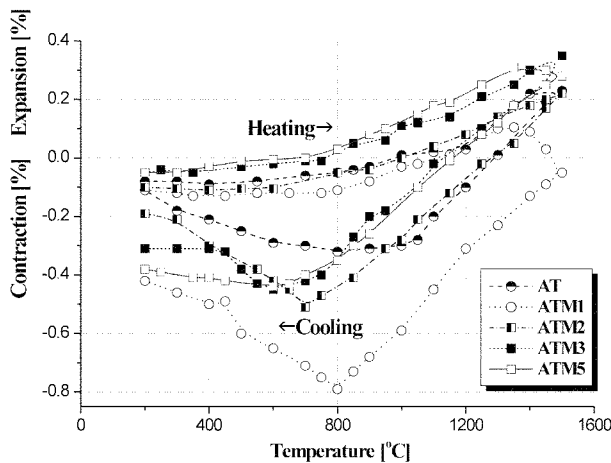


Fig. 3. Thermal expansion curves of the AT-and ATM-materials (1600°C for 2 hrs.).

size [25]. The thermal expansion and contraction behavior of the AT and ATM materials fabricated at 1600°C for 2 h is shown in Fig. 3. The thermal expansion of the specimens was between -0.75% and 0.37% in the temperature range 200°-1500°C. Maximum thermal expansion occurred between 1350 and 1500°C. The AT and ATM materials showed low thermal expansion up to 800°-900°C, but when the temperature was further increased, the thermal hysteresis increased relatively. This result is ascribed to the onset of mechanical closing of the microcracks with heating to >800°C and their reopening occurs when cooling below 900°C. This phenomenon of microcrack healing was reported previously using acoustic emission by Whight [5]. Furthermore the thermal contraction temperature difference, ΔT , as defined by Ohya Nagawa [3], between sintering and crack onset temperatures, increased with an increasing mullite content. The appreciably smaller expansion of ATM5 from onset temperature to room temperature is ascribed to the fact that the grain size of the specimen was relatively small, approximately 8 μm with density of 92.2% theoretical density. This low expansion below crack onset temperature suggests that the crack tip was possibly blunted by the large amount of mullite. Furthermore, this higher ΔT value can be understood in terms of the limitation of the onset of microcracks by the presence of mullite at the grain boundaries of Al_2TiO_5 . Consequently, the large grain size of Al_2TiO_5 have smaller ΔT values rather than dense specimens with a small grain size (see Table 2 and Fig. 3).

Table 4 summarizes the effect of mullite content on the thermal expansion coefficient, the area of hysteresis curves, the microcracking temperature, and the grain size after various heat treatments. The microcracking temperatures were defined as a saddle point in each thermal expansion curve during cooling in Fig. 3. Differences in the microcracking temperatures, which were 700, 650, and 550°C for specimens ATM2, ATM3, and ATM5, respectively, were caused by differences in

Table 4. Thermal expansion behavior and grain size of aluminum titanate-mullite composites, after sintered at 1600°C for 2 hrs and durability tests

Materials	Thermal expansion coefficient $\alpha_{200^\circ\text{C}-1500^\circ\text{C}}$ [10^{-6}K^{-1}]	Hysteresis Area [mm^2]	Microcracking temperature [°C]	Average grain size (AT) [μm]
1600°C/2h				
AT	1.8 (0.68)*	235	1000~800	20
ATM1	0.5 (0.50)*	580	800	40
ATM2	1.6 (0.90)*	305	700	15
ATM3	2.4 (1.80)*	345	650	15
ATM5	2.3 (2.00)*	210	550	5
1100°C/100h				
AT	7.2 (6.15)*	267		
ATM1	5.74 (3.40)*	133	850	
ATM2	3.20 (2.25)*	205	650	8
ATM3	3.54 (2.73)*	215	550	10
ATM5	0.60 (2.50)*	1037	450	7
750-1400-750°C/23				
AT	1.62 (0.58)*	236	800	
ATM1	1.72 (0.68)*	226	850	
ATM2	1.49 (0.82)*	291	800	20
ATM3	2.38 (1.91)*	300	650	30
ATM5	3.33 (3.00)*	240	400	15

(*) : Thermal expansion coefficient $\alpha_{200^\circ\text{C}-1200^\circ\text{C}}$

grain size and mullite content. The average thermal expansion coefficients of polycrystalline ATM materials were between $0.5 \times 10^{-6} \text{ K}^{-1}$ and $2.0 \times 10^{-6} \text{ K}^{-1}$ (RT-1200 °C) only, compared with the average theoretical thermal expansion coefficient of the Al_2TiO_5 unit cell, $9.7 \times 10^{-6} \text{ K}^{-1}$ [14]. The thermal expansion anisotropy of the individual Al_2TiO_5 grains apparently caused internal stresses on a microscopic scale during cooling from the firing temperature; those localized internal stresses were the driving force for microcrack formation. During the reheating run, the individual crystallites expanded at low temperature; thus, the solid volume of the specimen expanded into the microcracks, whereas the macroscopic dimensions remained almost unchanged. As a result, the material expanded very little. The microcracks closed at higher temperatures. This result is closely related to the relatively steeper thermal expansion curve in Fig. 3. However, with further higher temperature, the slope (i.e. expansion coefficient) was far below the crystalline average theoretical value, suggesting that a large proportion of the microcracks were still open. The hysteresis areas, which were integrated with a planimeter, showed a distinct maximum for ATM1 material, which an average grain size of 40 μm . These thermal expansion curves are in good agreement with the results of Buesen *et al.* [11] and with the tendency of grain size effect on the thermal expansion of MgTi_2O_5 reported by Kuzyk and Bradt [10]. On the other hand, fine-

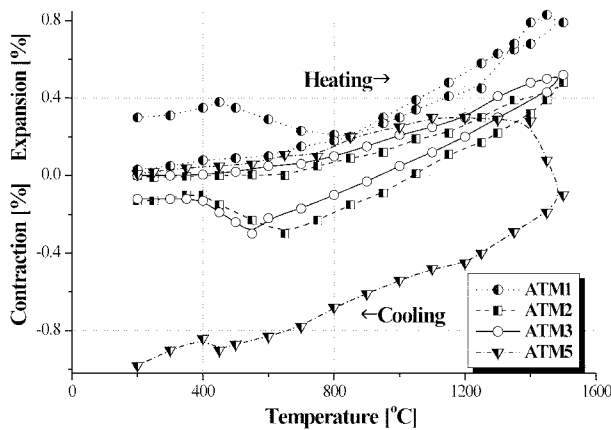


Fig. 4. Thermal expansion curves of the ATM-materials after decomposition test (1100°C for 100 hrs.).

grained materials exhibited small hysteresis areas.

Figure 4 illustrates the thermal expansion hysteresis behavior of the ATM composites after the decomposition test at 1100°C for 100 h. The hysteresis behavior of the AT composite could not be obtained because of fracture during cooling due to severe decomposition after the test. The thermal expansion coefficient of the ATM composites after durability tests were between $2.5 \times 10^{-6} \text{ K}^{-1}$ and $6.15 \times 10^{-6} \text{ K}^{-1}$ (RT-1200°C) for the ATM samples annealed at the critical decomposition temperature of 1100°C, which are much higher than that of the samples without annealing at 1100°C. The AT and ATM1 samples have much higher mean expansion coefficients of $6.15 \times 10^{-6} \text{ K}^{-1}$ and $3.4 \times 10^{-6} \text{ K}^{-1}$ (RT-1200°C), respectively, which are due to the decomposition of the AT phase.

Figure 5 shows the thermal expansion characteristics of the ATM composites after the cyclic thermal shock test, which show a mean thermal expansion coefficient between $0.68 \times 10^{-6} \text{ K}^{-1}$ and $3.01 \times 10^{-6} \text{ K}^{-1}$ at RT-1200°C. Moreover, little change in thermal hysteresis behavior during the heating and cooling cycles was found. These materials have slightly smaller hysteresis areas and a higher thermal expansion than those before the cyclic

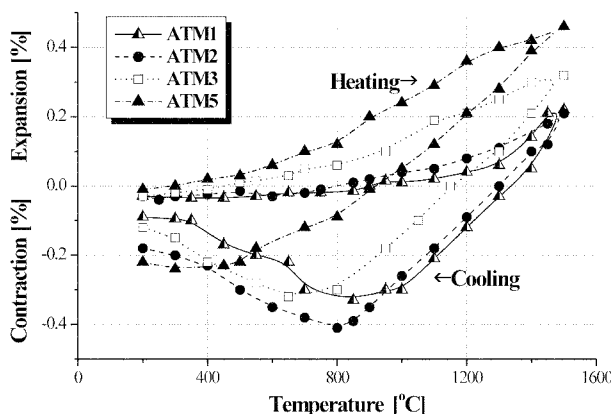
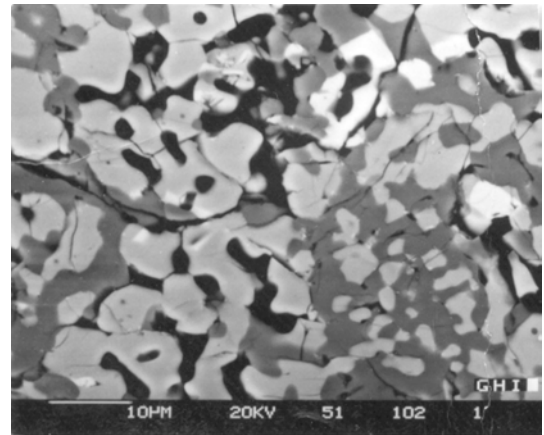
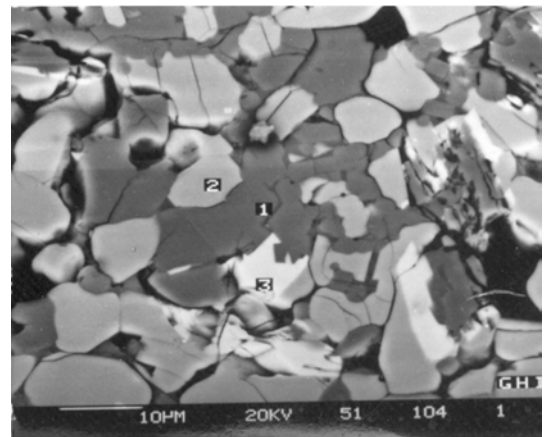


Fig. 5. Thermal expansion curves of the ATM-materials after cyclic thermal shock test (750-1400-750°C/23 cycles).



(a)



(b)

Fig. 6. Microstructure of (a) ATM2 (dim: mullite, gray: AT, bright: rutile) after a decomposition test at 1100°C for 100 hrs and (b) ATM2 (1: AT, 2: mullite) after a cyclic thermal shock test, 750-1400-750°C for 23 cycles.

test (Fig. 3), clearly indicating the influences of decomposition of the Al_2TiO_5 into its component oxides after the test. This result is in good agreement with the decomposition results in Table 3. On the other hand, severe decomposition occurred for AT materials.

Figure 6 shows that the $\beta\text{-Al}_2\text{TiO}_5$ grain sizes of the ATM2 and ATM3 (Fig. 6a) appeared to be smaller (10 μm) after the decomposition test at 1100°C for 100 h. Although there were Al_2O_3 ; TiO_2 present as a decomposition product around the Al_2TiO_5 grains, the thermal shock behavior under cyclic conditions between 750° and 1400°C showed little change in the microstructure (Fig. 6b). The changes of grain size after various thermal durability tests are shown in Table 4.

Figure 7 shows the average residual flexural strengths of the ATM specimens after water quenching. A relatively high strength, 72 MPa, was found in the ATM1 composite, although this material was still at only 88.2% of relative density. This result may be attributed to the formation of a liquid phase in the grain-boundaries around Al_2TiO_5 grains (see Fig. 2). However, the strength decreased sharply after one quenching cycle.

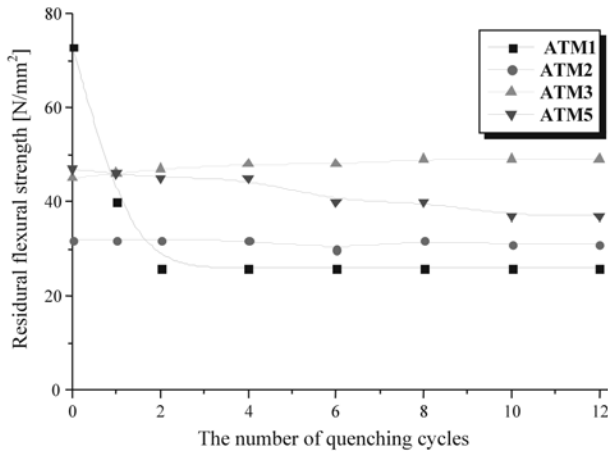


Fig. 7. Residual flexural strength of Al₂TiO₅-mullite composites with thermal shock in the water quench.

The average strengths of ATM2, ATM3, and ATM5 materials were ranged from 31 to 47 MPa at room temperature and from 30 to 47 MPa after 12 water-quenching cycles, indicating little change in strength. The strength values of ATM2 and ATM3 after quenching showed no distinct influence of temperature at 950°C, indicating that the composites had excellent thermal shock resistance. Perhaps the most significant aspect of the strength data is that, although the large grained materials have a dramatically lower strength of 26.0 MPa after one or two quenching cycles, the fine-grained materials exhibit respectable residual strengths and no crack extension.

As shown in Fig. 8, Young's modulus was measured, as a function of the number of quenches, by the resonance method. The ATM1 material had a higher Young's modulus, 50 GPa, than did the other specimens, which, although denser, contained appreciable amounts of cracks on their grain boundaries. The Young's modulus values of the ATM2, ATM3, and ATM5 composites containing grain-boundary microcracks were influenced

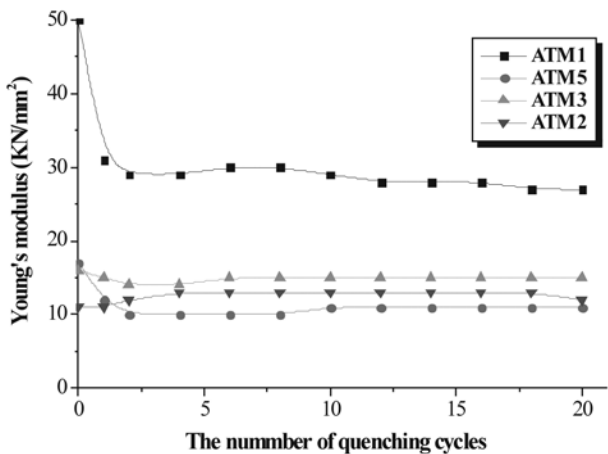


Fig. 8. Youngs modulus of Al₂TiO₅-mullite composites with thermal shock in the water quench.

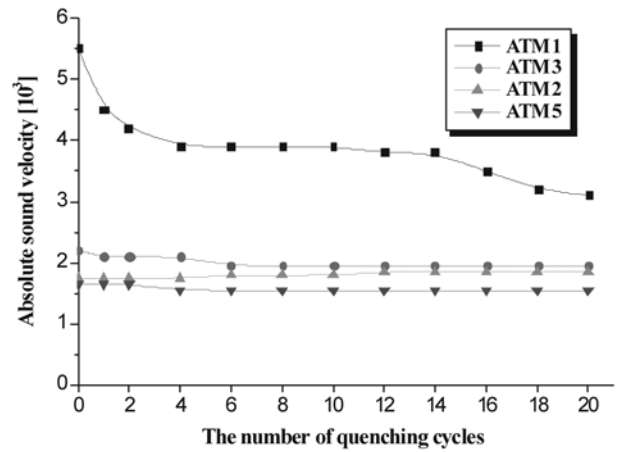


Fig. 9. Sound velocity of Al₂TiO₅-mullite composites with thermal shock in the water quench.

by the constant area of contact across the sintered grain boundaries.

Figure 9 shows the dependence of absolute sound-velocity on the number of quenching cycles. It is postulated that the decreased velocity of sound in the ATM1 composites after one quenching cycle is related to microstructural degradation. The value of the velocity of sound is also dependent on the amount of micro-cracking and the microcrack density. Higher micro-crack densities also have a positive effect on resistance to damage by critical thermal shock [26]. The porosity dependence of the strength and Young's modulus are best described by Duckworth's exponential approach [26], where the open porosity has more effect on the modulus of elasticity than does the closed porosity (comparable to ATM1 and ATM2 or ATM3). The ATM2, ATM3, and ATM5 composites showed especially homogeneous microstructures, with a defined micro-crack system (Fig. 2). This result is grounds for the lower Young's modulus and lower flexural strength, but simultaneously provides excellent thermal shock resistance.

Table 5 shows the effect of mullite contents on Young's modulus, thermal expansion coefficient, flexural strength, and the thermal-stress-resistance factor (R_1 , R_2). Among the thermal expansion coefficients of the

Table 5. Characteristics of specimens of aluminum titanate-mullite composites, after heat treatment at 1600°C for 2 hrs

Materials	Flexural strength σ_{br} [MPa]	Young's modulus E [GPa]	Thermal expansion coefficient $\alpha_{20^\circ\text{C}-1200^\circ\text{C}}$ [10^{-6} K^{-1}]	R_1 [K]	R_2 [Wm ⁻¹]
AT	20	13	0.68	1670	2505
ATM1	72	50	0.50	2189	3283
ATM2	31	11	0.90	2379	3568
ATM3	45	16	1.80	1187	1780
ATM5	47	17	2.00	1050	1575

composites fabricated in the present study, the ATM materials exhibited the lowest value, between $0.5 \times 10^{-6} \text{ K}^{-1}$ and $2.0 \times 10^{-6} \text{ K}^{-1}$, in the temperature range RT–1200°C. SiO_2 additions (3.44 wt%) improved the strength, 72 MPa, with a low thermal expansion coefficient, $0.5 \times 10^{-6} \text{ K}^{-1}$. This increase in strength, attributed to the formation of a grain-boundary liquid phase during sintering, aided densification and, thus, reduced microcracking, thereby increasing strength. The result is shown in Table 5, with the higher calculated values. The theoretical thermal shock resistance is calculated from the thermal stress parameters, R_1 and R_2 (pertaining to severe and mild quenching, respectively). Thus,

$$R_1 = [\sigma_{br}(1-\nu)]/\alpha E \quad (3)$$

$$R_2 = R_1 \lambda \times \lambda \quad (4)$$

where R_1 and R_2 are the material constants, which can be described as a material resistance factor for thermal stresses; σ_{br} the flexural strength; E Young's modulus; the thermal expansion coefficient; ν Poisson's ratio; and λ the thermal conductivity, with the latter two values assumed to be constant ($\nu=0.24$, $\lambda=1.5 \text{ WmK}^{-1}$) in this study [25, 28]. Once the material's resistance to crack initiation has been exceeded, its resistance to damage (from crack propagation) becomes the decisive element of the thermal cycling behavior; that resistance is described by the thermal stress parameter, R_7 [29].

$$R_7 = \gamma_{eff} E / [\sigma_{br}^2 (1-\nu)] \quad (5)$$

Here, γ_{eff} is the specific fracture-surface energy [30]. The above discussion of the dependence of σ_{br} , E , and ν on the mineral-phase content indicates that the resistance to damage described by Eq. (5) is not uniquely dependent in the same sense. The fracture-surface energy (not investigated in the present study) should have been determined primarily on the basis of the microcracks, depending on the type and extent of second phase, as indicated by the temperature dependence of stress-induced transformation and other results [31]. The last remaining materials (ATM2, ATM3, and ATM5 in Figs. 3 and 4) suffered no measurable damage. Considering the material's 6.7–12.0 vol% porosity and microcracks, that result can be attributed to very high damage resistance. This conclusion was deduced from the low Young's modulus, low strength, and low thermal expansion coefficient ($0.9 \times 10^{-6} \text{ K}^{-1}$ to $2.0 \times 10^{-6} \text{ K}^{-1}$) of the Al_2TiO_5 -mullite composites, caused by the presence of microcracks.

Conclusions

The thermal durability of Al_2TiO_5 was improved by the addition of mullite and by using monodispersed amorphous (0.2–0.7 μm , narrow size distribution) powders produced by the sol-gel process. The grain size of Al_2TiO_5 (5–20 μm) fired at 1600°C for 2 h was markedly

decreased by mullite additions (20–50 vol%). The thermal expansion properties of the Al_2TiO_5 -mullite composites investigated showed several effects not encountered with dense ceramics-e.g., the hysteresis effects of the thermal contraction and expansion curves under thermal load. These phenomena were analyzed according to their relationship with the opening and closing of microcracks. The highest thermal durability in the present study was achieved for the compositions containing 70 and 80 vol% Al_2TiO_5 , which showed little change in microstructure and thermal expansion cycles during the tests. The Young's modulus and flexural strength were highest at a mullite content of 10 vol%, but those maximum values were accompanied by lower thermal shock resistance, a result attributed to fewer grain-boundary microcracks acting as stress absorbers. When the mullite content increased to >10 vol%, the Young's modulus, thermal expansion coefficient, and RT strength also increased. Specimens with 80, 70, and 50 vol% Al_2TiO_5 had excellent thermal shock resistance because of the presence of fine microcracks.

Acknowledgements

This work was supported by Frontier 21C, Carbon Dioxide Reduction & Sequestration R&D Center, Korea Institute of Energy Research

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