[논 문] 한국재료학회지
Korean Journal of Materials Research
Vol. 3, No. 6 (1993)

Aluminium Titanate-Mullite 복합체 : Part1, 열적 내구성

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Aluminium Titanate-Mullite Composites : Part1, Thermal Durability

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초 록 Aluminium titanate-mullite 복합체는 Al_2O_3 분말 아콜용액에서 $Si(OC_2H_5)_4$와 $Ti(OC_2H_5)_4$의 단계적인 가수분해로 합성하였다. Sol-Gel 방법으로 합성된 모든 분말은 비정질과 단분산이고 좁은 분말크기의 분포를 보였다. 소결체(1600℃/2h)는 임계분해온도인 1100℃에서 100시간 동안과 750와 1400℃ 100시간동안 반복적인 열적 내구성 및 열충격 시험을 수행하였다. 가장 좋은 열적 내구성은 aluminium titanate함유량이 70과 80vol%일때 얻어졌으며, 이들은 위 실험을 한후 아주 적은 미세구조와 열팽창 곡선의 변화를 나타내었다. 소결체 미세구조의 붕괴는 주사현미경, X-선회절분석과 Dilatometer로 연구하였다. 위 연구는 이와같은 과정에 의하여 합성된 aluminium titanate-mullite복합체의 서비스 수명을 예상하기 위하여 시도되었다.

ABSTRACT The composites in the system aluminium titanate-mullite were synthesized by stepwise alkoxide hydrolysis of tetraethylorthosilicate, $Si(OC_2H_5)_4$ and titaniumtetraethoxide, $Ti(OC_2H_5)_4$ in Al_2O_3 ethanolic colloidal solution. All particles produced by sol-gel-process were amorphous, monodispesed and had a narrow particle size distribution. Sintered bodies at 1600℃ for 2h were subjected to prolonged durability tests-on the one hand annealing at the critical decomposition temperature of 1100℃ for 100h and on the other cyclic thermal shock between 750 and 1400℃ for 100h. The best thermal durability was achieved by a composition containing 70 and 80 vol% aluminium titanate, which showed little change in microstructure and thermal expansion cycles during the tests. The microstructural degradation of samples studied using scanning electron microscopy, X-ray diffraction, and dilatometry, was presented here. The study was conducted in order to predict the service life of aluminium titanate-mullite ceramics formed by this processing route.

1. Introduction

Aluminium titanate (Al_2TiO_5) is known as excellent thermal shock resistant material because of its low thermal expansion, low thermal conductivity and low Young's modulus. These properties allow for the testing as an insulating material in engines for portliner, piston bottom and turbo charger [1]. However, these materials have low mechanical strength due to the presence of microcracks developed by a large difference in thermal expansion coefficients along crystallographic axes [2, 3]. Unstabilized aluminium titanate tends to decompose into Al_2O_3 and TiO_2 in the temperature range of 800-1300℃ [4, 5]. The decomposition occurs, it has been theorized, when adjacent aluminium and titanium octahedra collapse because the lattice site occupied by the aluminum is too large [6]. The available thermal energy permits the aluminium to migrate from its position, and results in a structural dissolution to rutitle and corundum [7]. Following the decomposition, the material

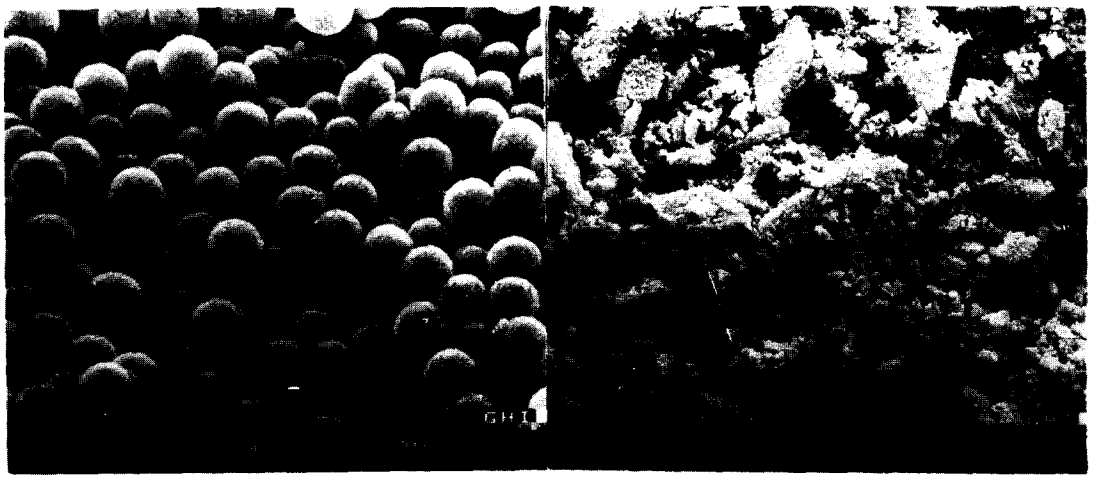
neither exhibits a low thermal expansion coefficient nor favorable thermal shock behavior, that rendered it apparently useless for industrial applications.

It is known that the thermal instability of Al_2TiO_5 can be controlled by solid solution with MgO, Fe_2O_3, or Cr_2O_3 in the aluminium titanate lattice, which are isomorphous with the mineral pseudobrookite (Fe_2TiO_5), $MgTi_2O_5$ or $(Al, Cr)_2TiO_5$ so that the polycrstalline aluminium titanate can be stabilized by limitation of grain growth and microcracks with additives such as SiO_2, ZrO_2, α-Al_2O_3, or mullite, most of which do not form solid solution with aluminium titanate, so that it was restrained the tendency towards decomposition of Al_2TiO_5 [8].

Attempt to improve the thermal durability (800-1300℃) of aluminium titanate, a new thermal shock resistant material consists of a two-phase material based on aluminium titanate -mullite in different proportions will be created by reducing the particle size or by adjusting composition of $Al_2O_3/TiO_2/SiO_2$-ratios.

2. Experimental procedure

Tetraethylorthosilicate $Si(OC_2H_5)_4$ (Huels AG), Ethyltitanate $Ti(OC_2H_5)_4$ (Huels AG), α -Al_2O_3 (A-16 SG; mean particle diameter; 0.3 -0.5μm; Alcoa Chem) and Ethanol (Merck) were used as starting materials. Al_2TiO_5 and aluminium titanate-mullite composites were prepared by stepwise alkoxide hydrolysis of a molar ratio $[H_2O/Si(OC_2H_5)_4]$ of 80 and $[H_2O/Ti(OC_2H_5)_4]$ of 4 in α-Al_2O_3 powder ethanolic solutions (0.3-0.5μm). Typical final solution concentrations were 0.4mol $Si(OC_2H_5)_4$, 0.3mol $Ti(OC_2H_5)_4$, 1.91mol NH_3 and 33.2mol H_2O. The solution of coated powder was next centrifugated to remove the alcoholic solution, then washed with deionized water and redispersed in aquous NH_4OH solution (pH=10). Powder compacts were prepared by centrifugal casting followed by drying at room temperature for one day. The SiO_2-and TiO_2-coated Al_2O_3 green compacts are shown in Fig. 1.



(a) (b)

Fig. 1. SEM micrographs of the top surface of (a) SiO_2-, (b) TiO_2-coated α-Al_2O_3 green compacts made by centrifugal casting.

Table 1 lists the chemical compositions of the composite powders which were determined by quantitative XRD, performed after the calcination at 1050℃ for 1h. Before firing, compacts were calcined in air at 650℃ for 1h to remove organic material. After adding KB

2010 (Zschimmer & Schwarz, Lahnstein/Rh) as a binder the powders were formed into bars ($7\times7\times50mm^3$ and $5\times5\times25mm^3$) and pellets ($10\times15mm^2$) at $300N/mm^2$. Specimens were sintered at 1600℃ for 2h in air in an electric chamber furance. The physical properties of the sintered specimens are given in Table 2.

Table 1. Chemical composition of the compacts(wt%, 1050℃/1h)

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℃ for 2h.

Table 2. Physical data of the sintered specimens

	AT	ATM1	ATM2	ATM3	ATM5
Green density/Theo. density[%]	47.5	55.3	55.2	50.9	52.2
Green density[g/cm^3]	1.8	2.1	2.1	1.9	1.9
Sintered density[g/cm^3]	2.9	3.3	3.5	3.3	3.4
Relative density[%]	76.0	88.2	93.3	88.0	92.2
Total porosity[%]	24.0	11.8	6.7	12.0	7.8
Shrinkage[%]	15.0	15.4	21.3	16.6	16.7

The mean grain sizes of β-Al_2TiO_5 were measured by the linear-intercept method with the Fullman's [9], on the surfaces coated with vapor-deposited Au and observed in the scanning electron microscope. In order to evaluate the thermal durability of the aluminium titanate-mullite composites, the following tests were carried out :

1) long-term thermal annealing at the critical decomposition temperature of Al_2TiO_5 (1100℃/100h).

2) cyclic thermal shock in a two-chamber furance between 750-1400-750℃ with a total number of 23 cycles in an interval of 100h.

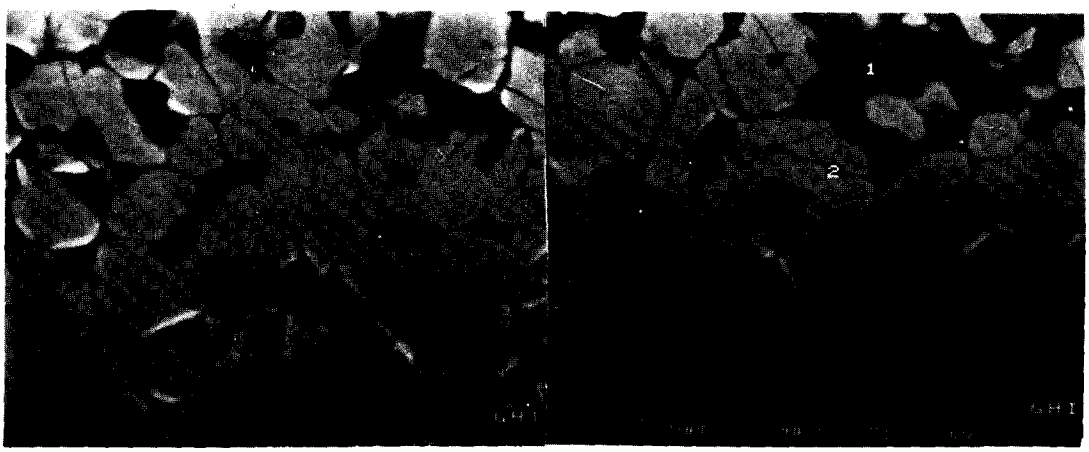
3) cyclic thermal expansion coefficients up to 1500℃ before and after decomposition tests was also measured using a dilatometer. The thermal expansion was determined on bar specimen ($5\times5\times25mm^3$) with a heating rate of 5℃/min and a cooling rate of 10℃/min in air.

These tests were complemented by analytical investigations (scanning electron microscopy combined with X-ray diffraction).

3. Results and Discussion

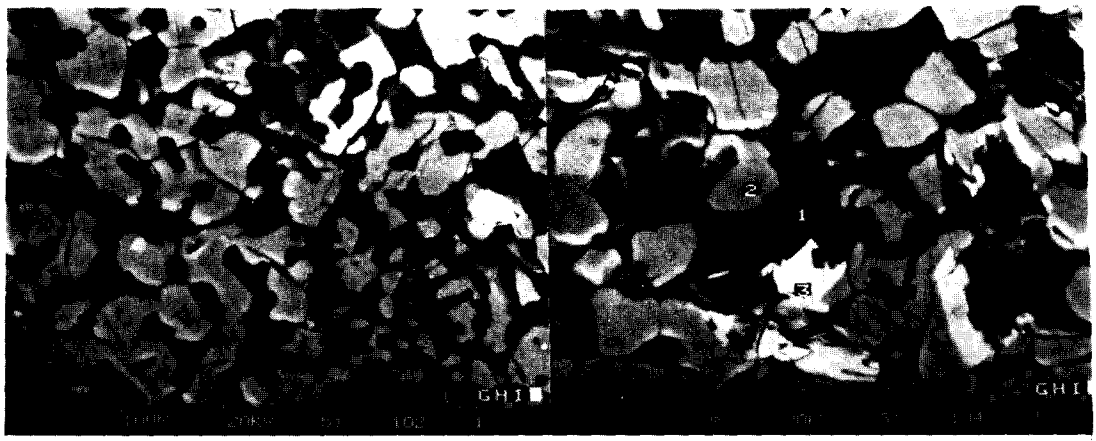
The amorphous SiO_2-coated Al_2O_3 powders ($3Al_2O_3\cdot2SiO_2$) consist of spheroidal particles having a narrow particle size distribution (0.5 $-0.6\mu m$) and a large surface are a ($76m^2/g$). The amorphous TiO_2-coated Al_2O_3 powders (Al_2O_3 : $TiO_2=1$) gave multinuclei, partially agglomerated, and a large surface area (194m $^2/g$). The agglomeration may be due to the rapid reaction of $Ti(OC_2H_5)_4$ with H_2O.

Sintered-stabilized ATM2 and ATM3 (Fig. 2a) exhibits β-Al_2TiO_5 and mullite grain size between 5 and $20\mu m$ containing fine pores. In all cases the β-Al_2TiO_5 grains are surounded by microcracks. After decompsition test at 1100℃/100h, the specimens ATM2 and ATM3 (Fig. 2b) appear to have a smaller mean grain size of β-Al_2TiO_5 ($10\mu m$). In spite of good stabilization of tialite at critical temperature considerable amounts of decom posed corun-



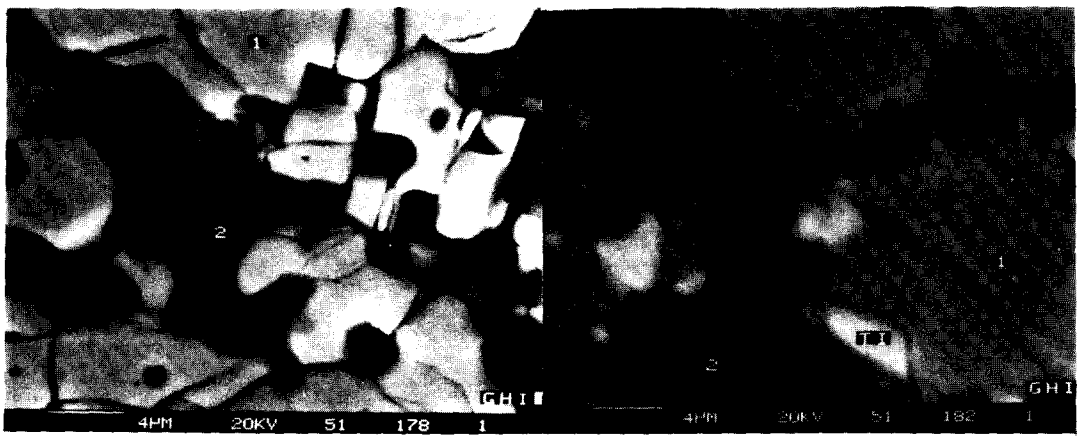
ATM2 ATM3

Fig. 2a. Microstructure of sinter-stabillized ATM2 (gray : AT, dim : mullite) and ATM3 (1 : mullite, 2 : AT) at 1600℃ for 2h.



ATM2 ATM3

Fig. 2b. Microstructure of ATM2(dim : mullite, gray : AT, bright : rutile) and ATM3 (1 : mullite, 2 : AT, 3 : rutile after decomposition test at 1100℃/100h.



ATM2 ATM3

Fig. 2c. Microstructure of ATM2 (1 : AT, 2 : mullite) and ATM3 (1 : AT, 2 : mullite, Ti : rutile) after cyclic thermal shock test, 750-1400-750℃/23.

dum and rutile were present. The thermal shock behavior under cyclic condition between 750 and 1400℃ shows little change in microstructure (Fig. 2c).

With increasing mullite content, relative density of ATM-composites increased up to 93.3% of theoretical density (20 vol% mullite) and decreased at still higher mullite contents (30, 50 vol%). At 100% aluminium titanate the relative density was only 76% of theoretical (see Table 2).

The thermal durability of aluminium titanate -mullite composites was investigated by subjecting them to cyclic thermal shock and thermal load at the critical decomposition temperature (1100℃) of aluminium titanate over a period of 100h [10]. The change in the phase compostions due to decomposition tests are given in Table 3. Unstabilized material decomposes to its corundum and rutile in both cases.

After annealing at the critical temperature of 1100℃ a partial decomposition is observed in ATM2-, ATM3- and ATM5-composites. With increasing mullite content, decreased the decomposition content of Al_2TiO_5. Composites having 20−50 vol% mullite are still retained in approximately 80% undecomposed aluminium titanate. Such a phenomenon can be explained in terms of inhibited grain growth of Al_2TiO_5 by mullite grain. In order to prevent decomposition of the aluminium titanate ceramics at the critical temperature range between about 800 and 1300℃ the grain sizes (5 −20μm) of aluminium titanate must be limited (see Figure 2a−2c).

The change in the phase compositions due to cyclic thermal shock gave different results. Materials having 10 vol% mullite have slightly better annealing test than cyclic thermal shock test. This investigation of cyclic test can be determined by the possibility of reversible formation of aluminium titanate during the testing to high temperature (750-1400℃).

The thermal expansion hysteresis of β-Al_2TiO_5 due to the expansion anisotropy of the individural β-Al_2TiO_5 crystal has a very strong microstructural dependency. This directly related to the degree of microcracking and grain size present in the sample [11]. The expansion of the AT-and ATM-materials at 1600℃ for 2h are show in Figure 3. The thermal expansion of samples lies between -0.75 and 0.37% in the temperature range of 200-1500℃. Maximum thermal expansion occurs between 1350 and 1500℃.

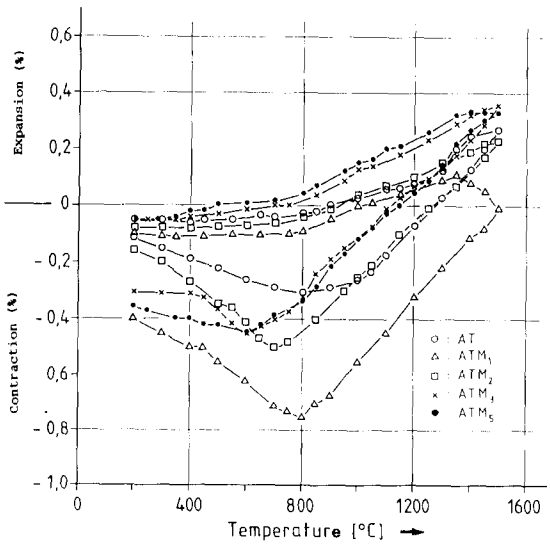


Fig. 3. Thermal expansion curves of the specimens AT, ATM1, ATM2, ATM3 and ATM5.

The materials (AT, ATM1) showed low thermal expansion to 800-900℃, but as the temperature is raised above this level, hysteresis increases markedly. This is ascribed to the onset of mechaincal healing of microcracks above 800℃ on heating and their reopening or refracturing on cooling being delayed until the temperature was below 900℃. It is pronounced that stresses on the microstructure of all composites build up only below about 900℃. The difference in the microcracking temperatures, which were 700, 700 and 550℃, for the specimens ATM2, ATM3 and ATM5, respectively, was caused by the difference in grain size and mullite con-

tent. The thermal expansion coefficients lies between 0.5 and $2.0*10^{-6}k^{-1}$ (RT-1200℃). This can be compared with a theoretical expansion coefficient for dense Al_2TiO_5-ceramic of $9.7*10^{-6}k^{-1}$ [1.e., $(\alpha_a+\alpha_b+\alpha_c)/3=\alpha_1$ [12]. It is the pronounced thermal expansion anisotropy of the individual Al_2TiO_5 grains that gives rise to internal stresses on a microscopic scale during cooling from the firing temperature. These localised internal stresses are the driving force for microcrack formation. During the the reheating run the individual crystallites expand at low temperature, thus the solid volume of sample expands into the microcracks, while the macroscopic dimensions remain almost constant. As a result, the material expands very little. The higher the temperature, the more cracks are closed, the steeper the thermal expansion curve. However, even at 1200℃ the slope is far below the theoretical value, suggesting that a lot of fraction of the microcracks is still open.

ATM-compositions has been studied to determine the thermal expansion characteristics after prolonged decomposition tests. Figure 4 demonstrates the thermal expansion hysteresis beavior of various materials after decomposition test at 1100℃ for 100h. This can be compared with a value of $2.5\text{-}6.15*10^{-6}k^{-1}$ (RT-1200℃) for ATM-compositions before and after thermal load tests at the critical decomposition temperature of aluminium titanate (comparable to Figure 3). Complete decomposition occurred on AT- and ATM1-materials (see Table 3), but giving a mean expansion coefficient of 6.15 and $3.4*10^{-6}k^{-1}$ (RT-1200℃), respectively.

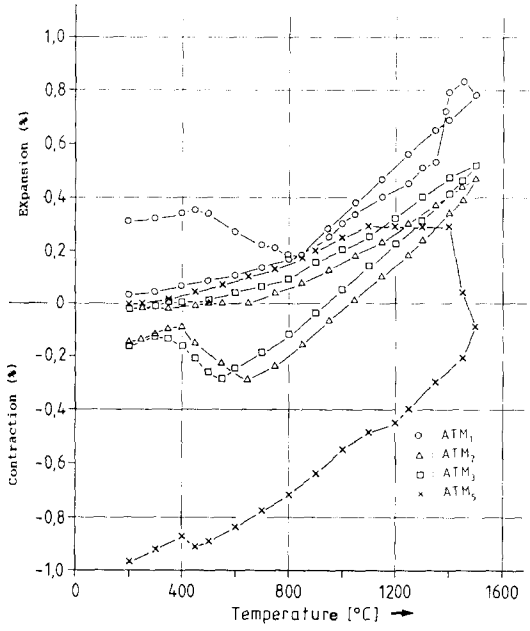


Fig. 4. Thermal expansion curves of ATM1, ATM2, ATM3 and ATM5 after decomposition test at 1100℃/10h.

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

Phase composition	AT	ATM1	ATM2	ATM3	ATM5
Sintered at 1600℃/2h	β-AT	β-AT	β-AT	β-AT	β-AT
	C	R	M	M	M
	R				
Decomposition test	R	R	β-AT	β-AT	β-AT
(annealed at 1100℃, for	C	C	R	M	M
100h)	β-AT	β-AT	M	R	R
			C	C	C
Decomposition content [%]	95.0	95.0	22.6	12.3	7.2
Cyclic thermal shock test	R	R	β-AT	β-AT	β-AT
(750-1400-750℃, 23 cycles,	C	C	M	M	M
for 100h)	β-AT	β-AT	C	R	R
Decomposition content [%]	95.5	64.0	3.4	12.0	7.1

*Key : β-AT=β-Al_2TiO_5 ; M=Mullite ; C=Corundum ; R=Rutile.

However, the microcracking temperature (850℃) of ATM1 during cooling can be explained that during the Dilatometer testing the decomposed content of aluminia and titania, which can be given a mean thermal expansion coefficient of $8.2*10^{-6}k^{-1}$ (RT-1200℃), can be reacted for the formation of aluminium titanate at high temperature of 1500℃.

Thermal expansion characteristics of ATM-materials after cyclic test in 23 cycles give a mean thermal expansion coefficient from RT to 1200℃ $0.68\text{-}3.0*10^{-6}k^{-1}$ (in Figure 5), which showed little change in thermal hysteresis behavior on heating and cooling. These materials have slight smaller hysteresis areas and higher thermal expansions than before durability test (see Figure 4). It can be clearly indicated the onset of decomposition of Al_2TiO_5 into its component oxides after testing (see Table 3).

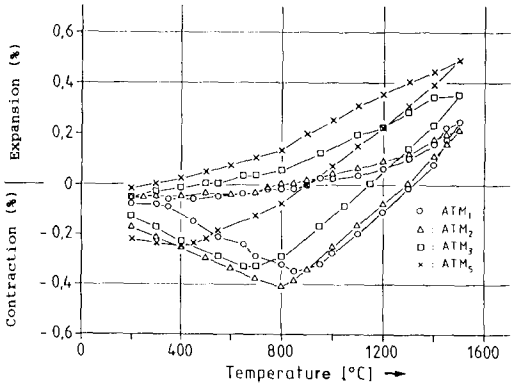


Fig. 5. Thermal expansion curves of ATM1, ATM2, ATM3 and ATM5 ater cyclic thermal shock test, 750-1400-750℃.

Table 4. Thermal expansion behavior and grain size of aluminium titanate-mullite composites, after sintered at 1600℃ for 2h and durability tests.

Materials	Thermal expansion coefficient $\alpha_{20℃-1500℃}[10^{-6}\cdot k^{-1}]$	Hyteresis area [mm^2]	Microcracking temperature [℃]	Average grain size (AT) [μm]
		-1600℃/2h-		
AT	1.8(0.68)*	235	800	20
ATM1	0.5(0.50)*	580	800	49
ATM2	1.6(0.9)*	305	700	15
ATM3	2.4(1.8)*	345	700	15
ATM5	2.3(2.0)*	210	550	5
		-1100℃/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	0.6 (2.50)*	1037	450	7
		-750-1400-750℃/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 $\alpha_{20℃-1200℃}$

4. Conclusions

All particles produced by the sol-gel-process were amorphous (0.2-0.7μm, narrow size distribution). Grain size of the aluminium titanate (5-20μm) fired at 1600℃ for 2h markedly re-

duced by mullite (20-50 vol%). The thermal expansion properties of the investigated aluminium titanate-mullite composites show several effects not encountered with dense ceramics, e.g. the hysteresis effects of thermal contraction and expanion curves under thermal load. These phenomena are explained by the opening and closing of microcracks. The most thermal durability was achieved by a composition containing 70 and 80 vol% aluminium titanate, which showed little change in microstructure and thermal expansion cycles during the tests.

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