The Korean Journal of Ceramics, **1** [1] 1-6 (1995)

Synthesis and Characterization of Submicrometer Monodispersed Ceramic Powders of Aluminium Titanate-Mullite Composite by Sol-Gel Process

Ik-Jin Kim, Do Kyung Kim*, Hyung Bock Lee* and Young-Shin Ko**

Dept. of Mater. Science and Engineering, Hanseo University, Seosan 352-820, Korea
**Dept. of Inorganic Mater. Science and Engineering, Myong Ji Univ., Yongin 449-728, Korea*
***Institute of Carbon Chemistry, Seoul National Univ. of Education, Seoul 137-070, Korea*

(Received January 4, 1995)

Submicrometer, monosized ceramic powder of Al_2TiO_5, mullite and aluminium titanate mullite composition was prepared by stepwise alkoxide hydrolysis of tetraethylorthosilicate and titaniumtetraethoxide in Al_2O_3 ethanolic solutions. All particles produced by sol-gel-process were amorphous, monodispersed and with a narrow particle-size distribution. Compacts fired above 1300°C formed aluminium titanate. Mullite formed first at 1480°C. After decomposition test at 1100°C and cyclic thermal decomposition test at 750-1400-750°C for 100hrs., aluminium titanate was well stablized by composition with mullite.

Key words : Al_2TiO_5(aluminium titanate), Mullite, Uniform size, Shrinkage, Thermal expansion hysteresis, Microcracks, Thermal shock, Stabilization.

I. Introduction

Aluminium titanate (Al_2TiO_5) is well known as a low thermal expansion and exellent thermal shock resistant material[1] but has low mechanical strength due to the presence of microcracks developed by the large difference in thermal expansion coefficients along crystallographic axes.[2,3] Unstabilized aluminium titanate tends to decompose fully into Al_2O_3 and TiO_2 in the range 800-1300°C. The decomposition occurs, it has been theorized, when adjacent aluminium and titanium octahedra collapse because the lattice site occupied by the aluminium is too large. The available thermal energy permits the aluminium to migrate from its position, and results in a structural dissolution to rutile and corundum.[4,5] Following the decomposition, the material exhibits neither a low thermal expansion coefficient nor a favorable thermal shock behavior, that rendered it apparently useless for industrial applications.[6]

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 polycrystalline aluminium titanate can be existed as metastable or stable form at temperature below 1300°C.[7,8] Al_2TiO_5 can be also kinetic stabilized by limitation of grain growth and microcracks with additives as SiO_2, ZrO_2, α-Al_2O_3, or mullite, almost of which form not solid solution with aluminium titanate, so that it was restrained the tendency towards decomposition of Al_2TiO_5.[9,10]

Mullite is a well known refractory material with very good high temperature hot strength properties, a low dielectric constant and a high creep resistance but moderately low thermal shock resistance.

Attempt to improve the mechanical strength and thermal stability (800-1300°C) 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 the $Al_2O_3/SiO_2/TiO_2$-ratios.

II. Experiment

Tetraethylorthosilicate $Si(OC_2H_5)_4$ (Huls AG), titanium tetraethoxide $Ti(OC_2H_5)_4$ (Huls AG), α-Al_2O_3 (A 16 SG; mean particle diameter: 0.3-0.5 μm; Alcoa Chem.) and ethanol (Merck) were used as starting materials. Al_2TiO_5, mullite and aluminium titanate-mullite ceramic 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 Al_2O_3 ethanolic solutions (0.3-0.5 μm). Typical final solutions concentrations were 0.4 mol $Si(OC_2H_5)_4$, 0.3 mol $Ti(OC_2H_5)_4$, 1.91 mol NH_3 and 33.2 mol H_2O. The dispersion 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. Before firing, compacts were calcined in air at 650°C for 1hr., to remove organic material. The procedure followed for the manufacture of the gel is shown schematically in

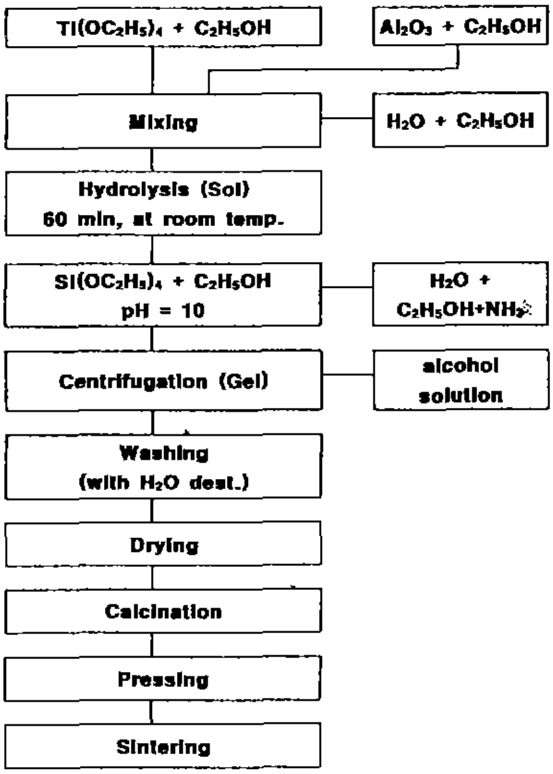


Fig. 1. Schematic diagram of the sol-gel-process for preparing AT-Mullite-gel

Fig. 1.

After adding KB 2010 as binder the powders were formed into bars ($7\times7\times50$ mm^3 and $5\times5\times25$ mm^3) and pellets (2×15 mm^2) at 200 N/mm^2. They were sintered at 1600°C for 2hrs in air in an electric furnace with Super Kanthal 33 heating elements. Temperatures were controlled using a Pt/Pt13Rh-thermocouple. Assesments of particle size and morphology, also the state of agglomeration were attained from SEM. The phase transformations from amorphous gel to various states of crystallinity have been studied by HT-XRD and DTA. Shrinkage and shrinkage rate were tested in air with heating and cooling rates of 10°C/min and cyclic thermal expansion hysteresis up to 1500°C was also measured using a dilatometer. 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°C/100 hrs.)

2) Cyclic thermal shock in a two-chamber furnace between 750-1400-750°C with a total number of 23 cycles in an interval of 100 hrs.

III. Result and Discussion

The SiO_2-, TiO_2-coated Al_2O_3 green compacts are shown in Fig. 2. The amorphous SiO_2-coated Al_2O_3 powders ($3Al_2O_3$ $2SiO_2$) consist of spheroidal particles having a narrow size distribution (0.5-0.6 μm) and a large surface area (76 m^2/g). This uniform size SiO_2-coated powder required the simultaneous satisfaction of several conditions[11] ; proper reagent concentration are necessary to promote nucleation and reagents must be mixed completely prior to particle nucleation, so that nucleation occurs uniformly throughout the solution. The amorphous TiO_2-coated Al_2O_3 powders (Al_2O_3 : TiO_2=1 mole ratio) gave multinuclei, partially agglomerated, and a large surface area (194 m^2/g). The agglomerations may be due to the rapid reaction of $Ti(OC_2H_5)_4$ with H_2O.

Table 1. Chemical Composition of Compacts(wt%, 1050°C/1hr).

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 2hrs.

Chemical compositions of the composite powders were determined by quantitative XRD, performed after calcination at 1050°C for 1hr. Table 1 lists the chemical composition of the compacts.

Fig. 3 shows the DTA-TGA curves of TiO_2-coated Al_2O_3 powder. Dehydration occurs in the temperature range 80-100°C. The exothermic peak located between 200 and 350°C is attributed to the oxidation of organic residues. In this temperature range, weight losses are greater than 8%. Low further weight losses are observed between 500°C and 1500°C. However the DTA curve shows endothermic peak located at 1300°C (ΔH=13.94 KJ/mol).[12] The molar free energy of formation is[13] :

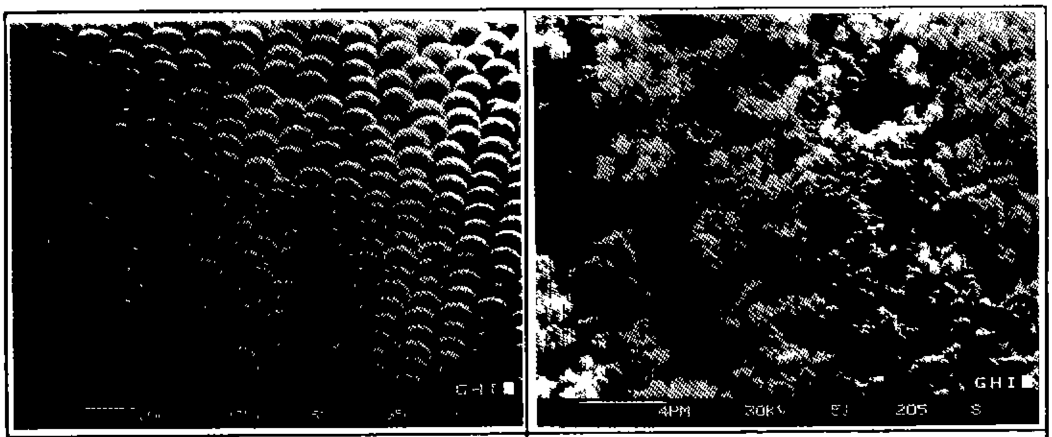
$$\alpha\text{-}Al_2O_3 + TiO_{2\text{-rutile}} \rightleftarrows \beta\text{-}Al_2TiO_5$$

$$\Delta G^0_{Al_2TiO_5} = \Delta H^0 - \Delta S^0 T = 1700 - 10.95\,T\ [J/mol]$$

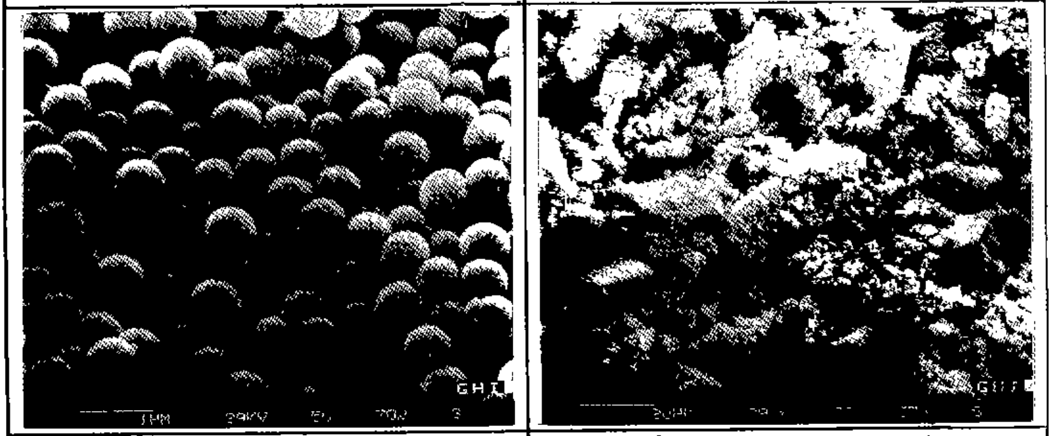
The endothermic reaction becomes feasible because of the positive entropy contribution ΔS^0. So Al_2TiO_5 is entropy-stabilized like other pseudobrookite phase[14] with a certain entropy contribution by cation disorder.[2] It is conceivable that positive entropy might be further enhanced by an additional entropy of mixing term, that is, by the formation of Al_2TiO_5, as confirmed by X-ray diffraction patterns.

The amorphous TiO_2-coating changed at 450°C into the anatase crystal phase, then at 600°C to rutile and at 1280°C finally to Al_2TiO_5(110), as shown by XRD in Fig. 4.

The dried mullite-gel exhibited a broad endothermic peak in the low-temperature range around 120°C due to the loss of water and organic solvents. With further heating the material showed a broad exothermic effect



(a) SiO_2 (b) TiO_2



(c) SiO_2-coated Al_2O_3 (d) TiO_2-coated Al_2O_3

Fig. 2. SEM micrographs of the top surface of green compacts made by centrifugal casting.

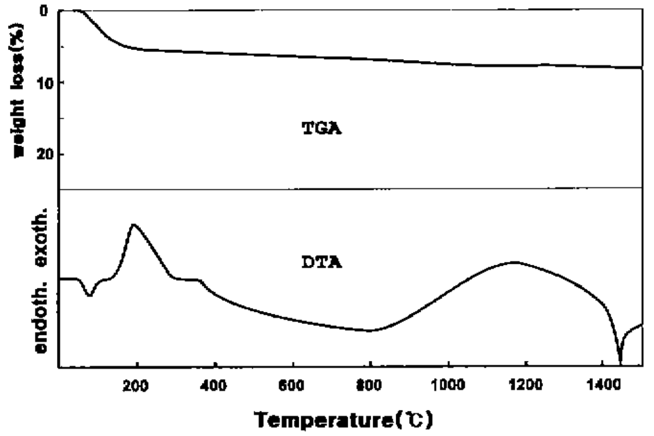


Fig. 3. DTA/TGA curves of the Al_2TiO_5-gel.

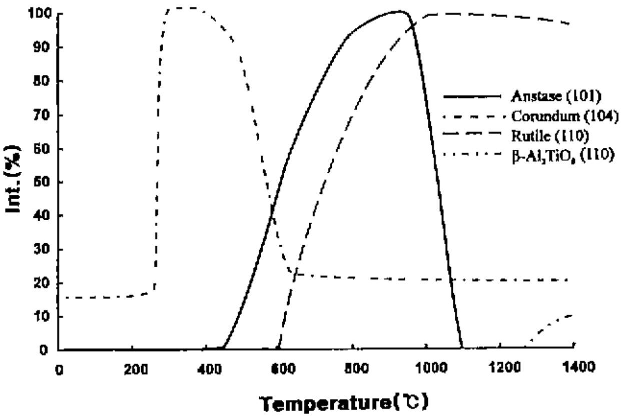


Fig. 4. The ratios of peak intensities of Al_2TiO_5, rutile, anatase and corundum vs. heat-treatment (without soaking time).

around 200°C and another broad exotherm peak at 1300°C. This transformation can be assigned to cristobalite formation from amorphous SiO_2 and at 1480°C mullite formed ($\Delta H=16.21$ Kcal/mol).[12]

The DTA/TGA heating curve of the mullite-gel is shown in Fig. 5 as XRD at this stage showed mullite phase. From Fig. 6 it is clear that major conversion of the material to mullite structure occured at 1470°C. Tak-

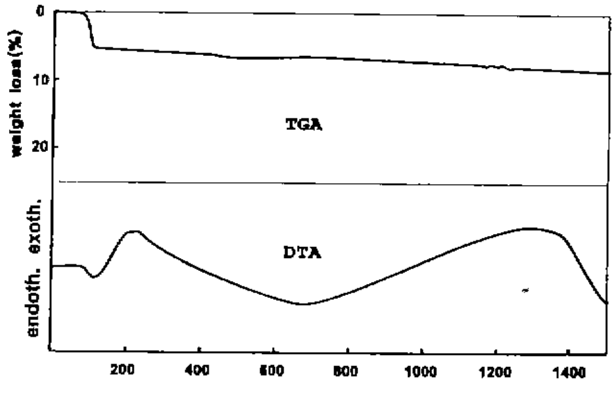


Fig. 5. DTA/TGA curves of the mullite-gel.

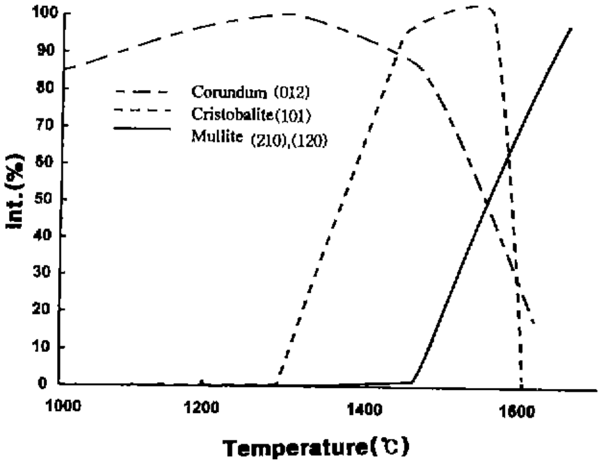


Fig. 6. The ratios of peak intensities of mullite, cristobalite and corundum vs. heat-treatment.

ing the (120) and (210) X-ray peak intensity of this sample as 100, the percentage of mullite present in other samples were calculated.

When a green compact of TiO_2-gel coated Al_2O_3 was heated at 10°C/min, shrinkage started at 1050°C, reached a maximum rate at 1259°C and 1350°C, and showed a minimum rate at 1400°C (Fig. 7).

However, the volume expansion which occurs during the formation of aluminium titanate at about 1300°C decreases the shrinkage rate. The crystal structure of the β-Al_2TiO_5 is the pseudobrookite type with a theoretical density of 3.70 g/cm^3. The densities of the starting oxides α-Al_2O_3 and TiO_2-rutile are 3.995 and 4.25 g/cm^3, respectively. Therefore, reaction of tielite is accompanied by an 11% molar volume increase. After Al_2TiO_5 has formed, the total shrinkage is 14.8%.

Fig. 8 showed shrinkage rate curves of green compact of SiO_2-gel coated Al_2O_3. Shrinkage started at 900°C, reached a maximum rate at 1375°C. After mullite has formed at 1400°C, the shrinkage rate increases again. The coated powder has a density of 95.6% theoretical density and consist of 23 wt% mullite at 1500°C (see Fig. 6). Total shrinkage in this case is 11.7%.

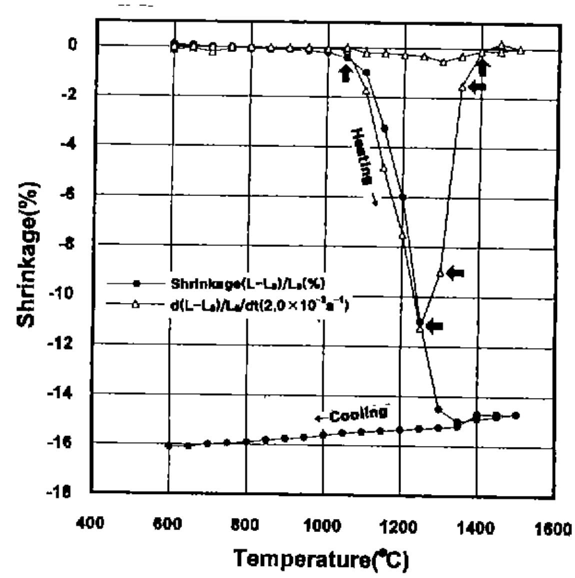


Fig. 7. Shrinkage and shrinkage rate of TiO_2-coated Al_2O_3 powder.

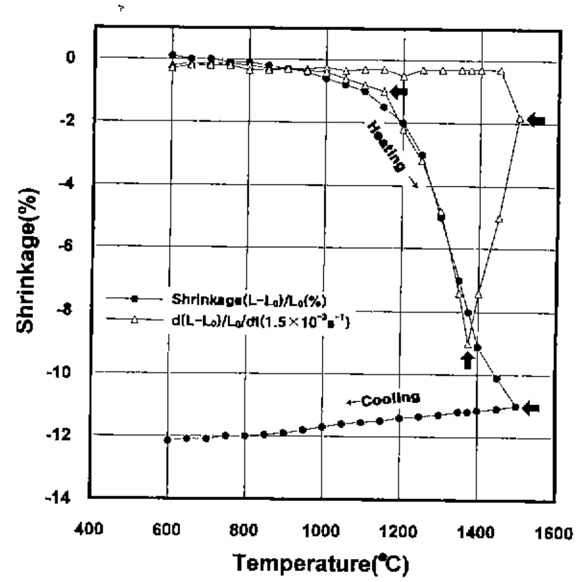


Fig. 8. Shrinkage and shrinkage rate of SiO_2-coated Al_2O_3 powder.

The thermal expansion hysteresis of β-Al_2TiO_5 due to the expansion anisotropy of the individual 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 samples.[15]

The expansions of the AT- and ATM-materials at 1600°C for 2 hrs are shown in Fig. 9. The thermal expansion of samples lies between -0.75 and 0.37% in the temperature range of 200-1500°C. Maximum thermal expansion occurs between 1350 and 1500°C. The materials (AT, ATM1) show low thermal expansion to 800-900°C, but as the temperature is raised above this level, hysteresis increases markedly. This is ascribed to the onset of mechanical healing of microcrack above 800°C on heating *and their reopening or refracturing on cooling* being delayed until the temperature is below 900°C. It is pronounced that stresses on the microstructure of all composites build up only below about 900°C. The difference in the microcracking temperatures, which were 700, 600 and 550°C for the specimens ATM_2, ATM_3, ATM_5, respectively, is caused by the difference in mullite content. The thermal expansion coefficients lie 0.5 and $2.0\times10^{-6}K^{-1}$ (RT-1200°C). This can be compared with a theoretical expansion coefficient for dense Al_2TiO_5-ceramics of $9.7\times10^{-6}K^{-1}$ [I.e.,$(\alpha a+\alpha b+\alpha c)/3=\alpha_1$)].16) It is the pronounced thermal expansion anisotropy *of the individual* Al_2TiO_5 *grains that* gives rise to internal stress on a microscopic scale during cooling from the firing temperature. These localized internal stresses are the driving force for microcrack formation. During the reheating run the individual crystallite expands into the microcracks, which 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 1500°C the slope is far below the theoretical value, suggesting that a lot of fraction of the microcracks is still open.

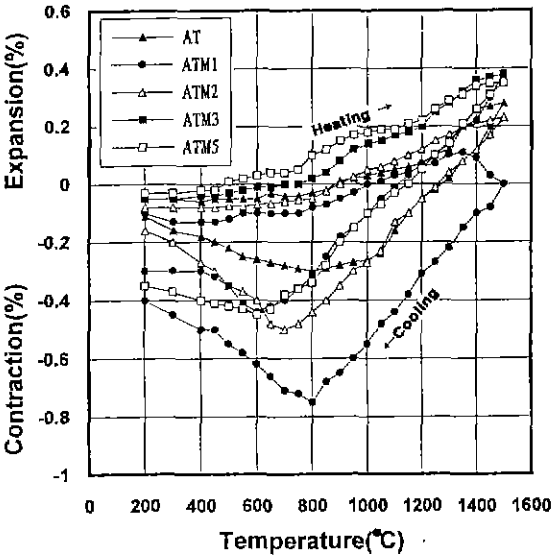


Fig. 9. Thermal expansion curves of the specimens AT, ATM1, ATM2, ATM3 and ATM5.

Table 2. Physical Data of Sintered Specimens.

	AT	ATM1	ATM2	ATM3	ATM5
Green 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)	2.8	3.3	3.5	3.3	3.4
Relative density (%)	75.3	88.2	93.3	88.0	92.2
Total porosity (%)	24.7	11.8	6.7	12.1	7.8
Shrinkage (%)	15.0	15.4	21.3	16.6	16.7

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%). Pure aluminium titanate the relative density was only 76% of theoretical one (see Table 2).

The change in the phase compositions due to decomposition tests are given in Table 3. Unstabilized material decompose to its corundum and rutile in both cases. With increasing mullite content, *the decomposition content* of Al_2TiO_5 decreased. Composites having 20-50 vol% mullite are still retained in approximately 80% undecomposed aluminium titanate. Such a phenomenon can be explained in terms of inhabited grain growth of Al_2TiO_5 by mullite grain.

IV. Conclusions

All particle produced by the sol-gel-process were amorphous (0.1-0.7 μm, monodispersed, narrow size distribution). XRD showed the amorphous TiO_2 changed via anatase to rutile form at 900°C and SiO_2-gel remained amorphous from RT to 1200°C. Compacts fired above 1300°C formed Al_2TiO_5 and at 1480°C mullite. The ther-

Table 3. Phase Compositions of Aluminium Titanate-Mullite Composite After Various Thermal Treatments.

Phase composition	AT	ATM1	ATM2	ATM3	ATM5
Sintering at 1600°C/2h	β-AT Corundum Rutile	β-AT Rutile	β-AT Mullite	β-AT Mullite	β-AT Mullite
Decomposition test (annealing at 1100°C, for 100h)	Rutile Corundum β-AT	Rutile Corundum β-AT	β-AT Rutile Mullite Corundum	β-AT Mullite Rutile Corundum	β-AT Mullite Rutile Corundum
Decomposition content (%)	95.0	95.0	22.6	12.3	7.2
Cyclic thermal shock test (750-1400-750°C, 23 cyclic, for *100h*)	Rutile Corundum β-AT	Rutile Corundum β-AT	β-AT Corundum Rutile	β-AT Mullite Rutile	β-AT Mullite Rutile
Decomposition content (%)	95.5	64.0	3.4	12.0	7.1

mal 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 expansion curves under thermal load. These phenomena are explained by the opening and closing of microcracks.

After decomposition test at 1100°C for 100 hrs and cyclic thermal shock test between 750-1400-750°C, Al_2TiO_5 was stabilized 80% by kinetic effects with mullite phase. With increasing mullite content, thermal expansion coefficient and relative density increased.

References

1. H. A. J Thomas and R. Stevens, "Aluminium titanate; Part 1: Microcracking Phenomena; Part 2: Engineering Properties and Thermal Stability," *Br. Ceram. Trans. J.*, **88**, 144-151, 184-190 (1989).
2. B. Morosin and R. W. Lynch, "Structure Studies on Al_2TiO_5 at Room Temperature and at 600°C," *Acta Cryst. B.*, **28**, 1040 (1972).
3. Y. Ohya and Z. Nakagawa, "Grain Boundary Microcraking Due to Thermal Expansion Anisotropy in Aluminium Titanate Ceramics," *J. Am. Cer. Soc.*, **70**[8], C 184-186 (1987).
4. E. Kato, K. Daimon and I. Takahashi, "Decomposition Kinetics of Al_2TiO_5 in Powdered State," *J. Am. Cer. Soc.*, **63**, 355 (1980).
5. R. E. Wright, "Acoustic Emission of Aluminium Titanate," *J. Am. Cer. Soc.*, **55**[54], (1972).
6. I. J. Kim, "Anwendung des Sol-Gel-Verfahrens auf die Herstellung Keramischer Werkstoffe aus Aluminiumtitanat-Mullit, Dissertation, Institut fuer Gesteinshuettenkunde," Techn. University Aachen, Germany (1991).
7. Ch. Hahn and D. Selb, "Verbesserung von Aluminiumtitanat-keramik," *Sprechsaal*, **118**[12], 1157(1985).
8. S. A. Babayan, L. A. Kostanyan and J. A. Geodakyan, " Dilatometric Research of Solid Solutions on the Basis of Aluminium Titanate (Russ.)," *Arm. Khim. Zh.*, **26**, 549-554 (1973).
9. I. J. Kim, W. H. Kang and Y. S. Ko, "Aluminium Titanate-Mullite Composites : Part 1, Thermal Durability," *Korean Journal of Materials Research*, **3**[6], 624-631 (1993).
10. I. J. Kim, W. H. Kang and Y. S. Ko,"Aluminium Titanate-Mullite Composites : Part 2, Thermal Shock Resistance,"*Korean Journal of Materials Research*, **4**[2], 206-212 (1994).
11. E. A. Barringer and H. K. Bowen, "Formation, Packing, and Sintering of Monodisperse TiO_2 Powders," *Comm. Am. Ceram. Soc.*, **65**., C199-C201 (1982).
12. O. Knacke, O. Kubaschewski and K. Hasselmann, "Thermochemical Properties of Inorganic Substance," *Springer, Verlag, Verlag Stahleisen m.b.H. Duesseldorf*, **47**[70], 2097. (1991).
13. B. Freudenberg and A. Mocellin, "Aluminium Titanate Formation by Solid State Reaction of Fine Al_2O_3- and TiO_2-powders," *J. Am. Cerm. Soc.*, **70**, 33-38 (1987)
14. A. Navrotsky, "Thermodynamics of Formation of Some Compounds with the Pseudobrookite Structure of the $FeTi_2O_5$-Tia_3O_5 Solid Solution Series," *Am. Mineralogist* **60**, 249-256 (1975).
15. W. R. Buessem, N. R. Thielke and R. V. Sarakauskas, "Thermal Expansion Hysteresis of Al_2TiO_5 Ceramic Age 60," 39-40 (1952)
16. G. Bayer, "Thermal Expansion Characteristics and Stability of Pseudobrookite Type Compounds M_3O_5," *J. Less. Common. Met.*, **24**. **2**. 129 (1971).