

Characterization of aluminum titanate-mullite ceramics synthesized by a semi sol-gel method

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Ceramic powders of aluminum titanate (Al_2TiO_5)-mullite composites with submicrometre sizes were synthesized 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 ethanol colloidal suspension. All particles produced by the sol-gel process were amorphous and mono-dispersed ones with a narrow size distributions. The reaction of $\alpha\text{-Al}_2\text{O}_3$ with amorphous- TiO_2 and - SiO_2 to form aluminum titanate and mullite starts in the temperature range of 1280-1300°C and 1450-1480°C, respectively. Al_2TiO_5 -mullite composites sintered at 1600°C showed a moderately high mechanical strength and a low thermal expansion coefficient obtained by inhibiting grain growth of the Al_2TiO_5 by the addition of mullite.

Key words: Aluminum titanate, Mullite, Synthesis, Sol-Gel, Formation.

Introduction

Aluminum titanate (Al_2TiO_5) is a potential thermal insulating material for engines in an high temperature environment because of its excellent thermal shock resistance from its very low thermal expansion, low thermal conductivity and low Young's modulus [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]. This material is conventionally synthesized by reaction sintering of Al_2O_3 and TiO_2 . The reaction and formation of Al_2TiO_5 occurs above 1280°C in an oxidizing atmosphere. By contrast, mullite is first synthesized at 1480°C as shown in Table 1. However, a pure Al_2TiO_5 tends to decompose into Al_2O_3 and TiO_2 at temperatures ranging from 800° to 1300°C during cooling below the equilibrium temperature of 1280°C [16]. 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 [17], MgTi_2O_5 [18, 19] or Ti_3O_5 (anosovite) [20]. This chemical stabilizing effect is related to a decrease in the decomposition temperature of the iso-structural compounds. Al_2TiO_5 can also be mechanical stabilized by limiting its grain growth [21]. Another source of stabilization is the limitation of microcracks by the addition of addi-

tives such as SiO_2 [22], ZrO_2 [23], ZrTiO_4 [24, 25] or mullite [26], most of which do not form a solid solution with Al_2TiO_5 but rather restrain the tendency of Al_2TiO_5 toward decomposition. Most studies on the mullite system involve the preparation of materials by a high temperature reaction from oxide powders. By this conventional process, reactions between oxides are insufficiently fast to lead to completion. Therefore, in general, a new process such as the sol-gel method has been preferred to produce uniform a reacted products consists of Al_2TiO_5 and mullite;

$\alpha\text{-Al}_2\text{O}_3 + \text{TiO}_2\text{-rutile} + \text{SiO}_2\text{-cristobalite}$
→ $\beta\text{-Al}_2\text{TiO}_5 + \text{Mullite} + \text{Glass phase}$ 1600/4 h [27, 28]
 $\text{Al}_2\text{O}_3\text{-amorphous} + \text{TiO}_2\text{-amorphous} + \text{SiO}_2\text{-amorphous}$
→ $\beta\text{-Al}_2\text{TiO}_5 + \text{Mullite} + \text{Glass phase}$, 1600°C/4 h [29]
 $\alpha\text{-Al}_2\text{O}_3 + \text{TiO}_2\text{-amorphous} + \text{SiO}_2\text{-amorphous}$
→ $\beta\text{-Al}_2\text{TiO}_5 + \text{Mullite} + \text{Glass phase}$ [30]

The above studies have aimed at a detailed investigation of the amorphous Al_2O_3 , TiO_2 , and SiO_2 system of the composition; $\text{Al}_2\text{TiO}_5 + \text{Mullite}$ made by a sol-gel process, using a semi-alkoxide route [29]. However, the control of the particle size and homogeneous mixing still remain problems when titanium, aluminium and silicon alkoxides are used as precursors.

Therefore, in the present study, new materials with low thermal expansion, based on $\text{Al}_2\text{TiO}_5\text{-}3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$ composites of various compositions, were fabricated by a stepwise alkoxide hydrolysis to reduce the particle size and adjust the compositions of $\text{Al}_2\text{O}_3\text{:TiO}_2\text{:SiO}_2$.

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Table 1. Synthesis conditions Al_2TiO_5 and Mullite by prior studies

Starting phases	Synthesized phase	Synthesized condition	Ref.
$\alpha\text{-Al}_2\text{O}_3$, TiO_2 - rutile	$\beta\text{-Al}_2\text{TiO}_5$	1500°C	[4,5,6]
$\gamma\text{-Al}_2\text{O}_3$, TiO_2 - rutile	$\beta\text{-Al}_2\text{TiO}_5$	1450°C for 4h	[7,8]
$\alpha\text{-Al}_2\text{O}_3$, TiO_2 - anatase	$\beta\text{-Al}_2\text{TiO}_5$		[9]
$\alpha\text{-Al}_2\text{O}_3$, TiO_2 - amorphous	$\beta\text{-Al}_2\text{TiO}_5$	1350°C for 30 min	[10,11]
Al_2O_3 - amorphous, TiO_2 - amorphous	$\beta\text{-Al}_2\text{TiO}_5$	1280°C	[12]
$3\text{Al}_2\text{O}_3$ -corundum, 2SiO_2 - cristobalite	Mullite	1600°C for 4h	[13]
$\alpha\text{-Al}_2\text{O}_3$, SiO_2 - rutile	Mullite	1450°C for 2h	[14]
$\alpha\text{-Al}_2\text{O}_3$, SiO_2 - rutile	Mullite	1450°C for 4h	[15]

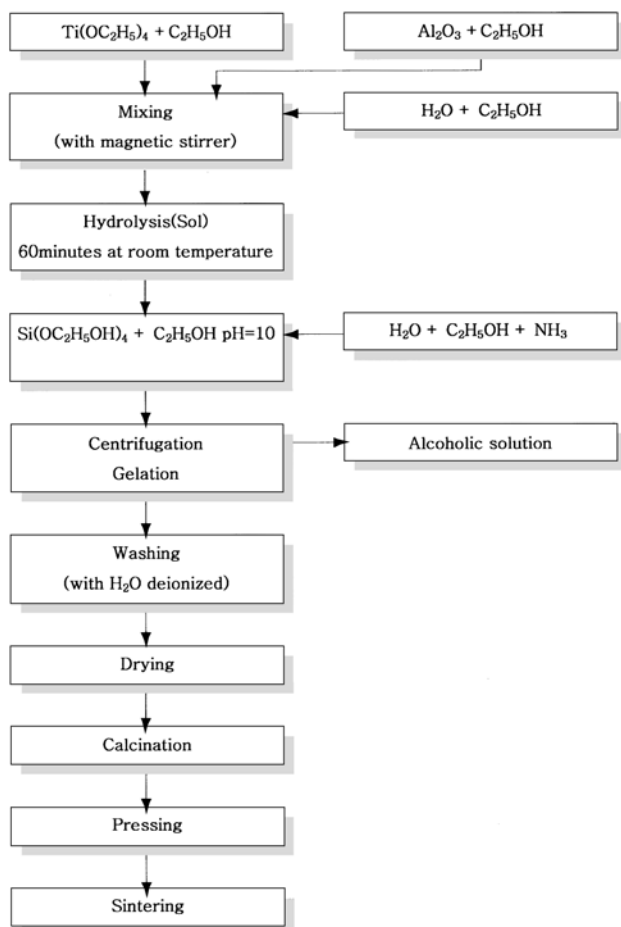
Experiments

We synthesized the Al_2TiO_5 -mullite composites by the stepwise alkoxide hydrolysis of tetraethylorthosilicate, $\text{Si}(\text{OC}_2\text{H}_5)_4$ (Huels AG, Troisdorf, 98.9%), and titanium tetraethoxide, $\text{Ti}(\text{OC}_2\text{H}_5)_4$ (Huels AG, Troisdorf, 98%), in an Al_2O_3 (A-16SG, Alcoa Chemie) ethanol colloidal suspension. Al_2O_3 coated - SiO_2 and - TiO_2 coated gel prepared from 0.4 mol $\text{Si}(\text{OC}_2\text{H}_5)_4/\text{l}$, $\text{H}_2\text{O}/\text{Si}(\text{OC}_2\text{H}_5)_4 = 80/\text{l}$, 6.23 mol $\text{C}_2\text{H}_5\text{OH}/\text{l}$ with 1.91 mol NH_3/l and 0.3 mol $\text{Ti}(\text{OC}_2\text{H}_5)_4/\text{l}$, $\text{H}_2\text{O}/\text{Ti}(\text{OC}_2\text{H}_5)_4 = 4/\text{l}$, 15.7 mol $\text{C}_2\text{H}_5\text{OH}/\text{l}$, respectively. Dispersed powder was centri-

Table 2. Chemical composition of the compacts (wt%, 1050°C for 1 h)

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 2 h.

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

fuged to remove the alcoholic solution, washed with deionized water and dispersed again in aqueous NH_4OH (NH_3 , 25%, Merck Darmstadt) solution (pH=10) as shown in Fig. 1. The chemical composition of each of the compacts is shown in Table 2, where AT, ATM1, ATM2, ATM3, and ATM5 refer to 0, 10, 20, 30, and 50 vol% addition of mullite, respectively. Powder compacts were prepared by centrifugal casting followed by drying at 100°C. The powders were dry pressed at 200 N/mm² to produce pellets (10 mm in diameter and 15 mm thick) and bar specimens. They were sintered at 1400, 1500 and 1600°C for 2 h in air after the calcination in air 600°C for 1h, to remove organic materials. At this stage the heating rate was 10 K minute⁻¹ and the cooling rate was about 20 K minute⁻¹. The sintered densities were measured by the water-immersion method. Analyses of particle size, particle morphology, and the state of agglomeration were observed from SEM (Cambridge, Stereoscan 250 MK2). Surface area and particle sizes were determined by N_2 adsorption (BET). The phase transformation from amorphous gel to various state of crystallinity was studied by high-temperature X-ray diffraction (Philips, PW1180/00, Ni-filtered $\text{CuK}\alpha$) and DTA (Netzsch). The shrinkages were tested up to 1500°C in air with heating and cooling rates of 10 K minute⁻¹ and the thermal expansion coefficient from room temperature (RT) to 1500°C was determined for a 5 mm × 5 mm × 25 mm specimen, in air, using a dilatometer, at a heating rate of 5 K minute⁻¹ and a cooling rate of 10 K minute⁻¹. The 3-point bending strength of three bar specimens (7 mm × 7 mm × 70 mm) of each composition at room temperature was measured using a universal testing machine (Instron

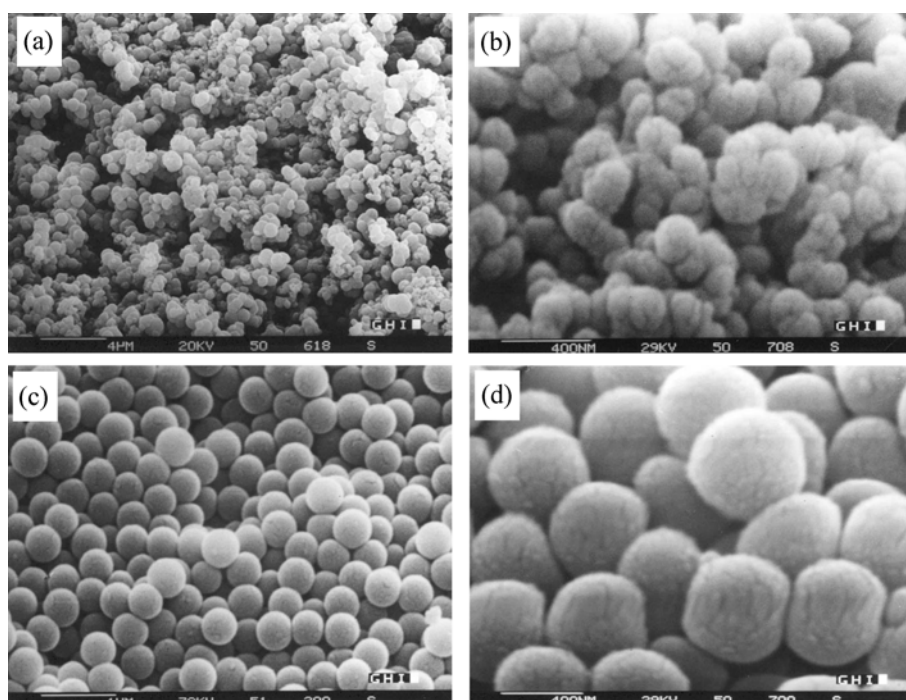


Fig. 2. Micrographs of the top surface of green compacts by centrifugal casting. (a) TiO_2 (b) TiO_2 -coated- Al_2O_3 (c) SiO_2 (d) SiO_2 -coated- Al_2O_3 .

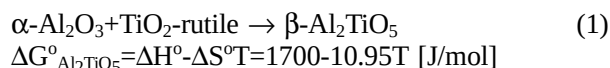
1186), with a span length of 40 mm and a cross head speed of 0.2 mm/minute. The Young's modulus was measured by a resonance-frequency method, as a function of sintering temperature using the bending-test specimens.

Results and Discussion

The TiO_2 -coated Al_2O_3 for Al_2TiO_5

The synthesized amorphous TiO_2 -coated Al_2O_3 powders ($\text{Al}_2\text{O}_3:\text{TiO}_2=1:1$) in this study exhibited an average narrow size distribution (0.2-0.4 μm) and partially agglomerated characteristics, with a high surface area of 194 m^2/g (Fig. 2). Agglomeration may have been a result of the rapid reaction of $\text{Ti}(\text{OC}_2\text{H}_5)_4$ with H_2O . Figure 3 shows the DTA-TGA curves of TiO_2 -coated

Al_2O_3 powder. Dehydration occurred in the temperature range of 80-100°C. The exothermic peak located between 200 and 350°C was attributed to the oxidation of organic residues. In this temperature range, weight losses were observed between 500 and 1500°C. On the other hand, the DTA curve showed an endothermic peak located at 1300°C ($\Delta H=13.94$ KJ/mol) [12]. The molar free energy of formation is [13].



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

The crystalline phase of the amorphous TiO_2 -coated $\alpha\text{-Al}_2\text{O}_3$ gel powder as a function of temperature and soaking time is reported in Table 3. No $\beta\text{-Al}_2\text{TiO}_5$ was detected in the heat-treated samples at 1200°C, even after soaking for 2 hrs. However, AT-gel powder heat-treated at 1300°C/3 h showed $\beta\text{-Al}_2\text{TiO}_5$ as the major phase with a small amount of $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 . The presence of these starting materials could be due to a slow reaction rate because of the generation of large diffusion paths with the progressive formation of aluminium titanate. These results indicate that the formation of aluminium titanate occurs above 1300°C [5].

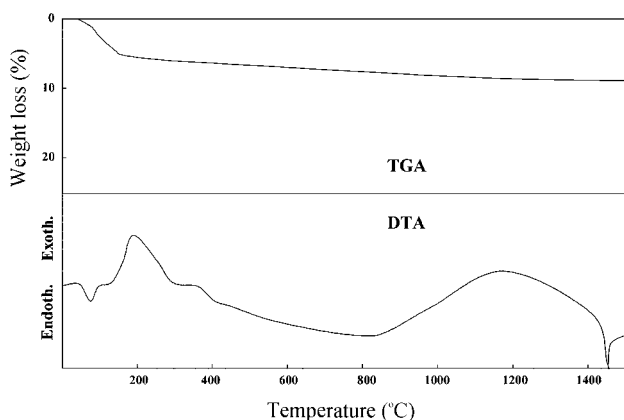


Fig. 3. DTA/TGA curves of the amorphous TiO_2 -coated Al_2O_3 powder.

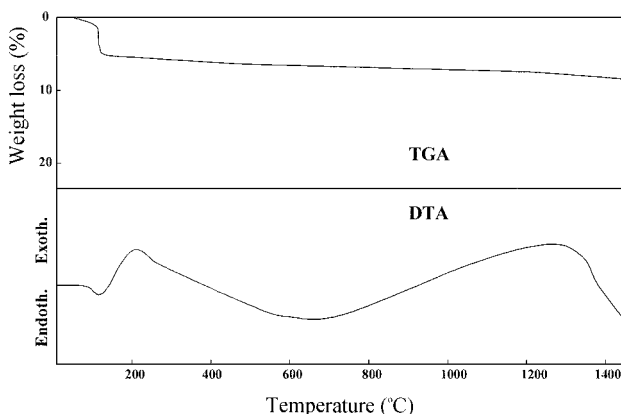
Table 3. Phase composition of the amorphous TiO_2 -coated $\alpha\text{-Al}_2\text{O}_3$ (high temperature X-ray diffraction)

Temp./Soaking Time (°C/h)	Phase composition of the amorphous TiO ₂ +α-Al ₂ O ₃								
	C(104)	C(012)	A(101)	C(110)	(hkl) A(004)	R(110)	R(110)	AT(110)	AT(023)
100	w	w							
200	s	m							
300	vs	s		w					
400	vs	s		m					
500	s	s	s	m	m				
600	w	vs	s	m	m	w	w		
900	w	vs	vs	w	w	m	s		
900/1	w	m	m	w		m	vs		
1000	w	m	m	w		s	vs		
1000/1	w	w		vw		s	vs		
1200	w	w		vw		s	vs		
1200/2	w	vw		vw		s	vs		
1300	w	vw				s	vs	w	vw
1300/2	vvw	vvw				m	s	m	m
1300/3	vvw	vvw				vm	m	s	s
1400	vw	vvw				w	m	vs	s

Phase: A=Anatase, R=Rutile, C=Corundum, AT= $\beta\text{-Al}_2\text{TiO}_5$

Intensity: vs=very strong, s=strong, m=middle, w=weak, vw=very weak, vvw=very very weak

When the green compact of TiO_2 -gel coated Al_2O_3 was heated at 10 K min^{-1} , the shrinkage started at 1050 and reached a maximum rate of $1.067 \times 10^{-3}\text{ S}^{-1}$ in the temperature range of 1300 and 1350°C . The lowest shrinkage rate was measured as $0.267 \times 10^{-3}\text{ S}^{-1}$ at 1400°C as shown in Fig. 4. Furthermore, the volume expansion occurred during the formation of aluminium titanate in the temperature range of 1400 and 1500°C . This showed a zero level of shrinkage rate. The crystal structure of the $\beta\text{-Al}_2\text{TiO}_5$ was the pseudobrookite type with a theoretical density of 3.70 g/cm^3 . The densities of the starting oxides $\alpha\text{-Al}_2\text{O}_3$ and TiO_2 -rutile were 3.995 and 4.25 g/cm^3 , respectively. Therefore, the reaction of Al_2TiO_5 such as (1) was accompanied by an 11% increase of molar volume [30]. After the Al_2TiO_5 had been formed, the total shrinkage was measured as 15.6% at 1500°C .

**Fig. 4.** DTA/TGA curves of the amorphous SiO_2 -coated Al_2O_3 powder.

The SiO_2 -coated Al_2O_3 for Mullite

The amorphous SiO_2 -coated Al_2O_3 powders ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) synthesized in this study consisted of spherical particles with a narrow particle-size distribution ($0.5\text{--}0.6\text{ }\mu\text{m}$) and a high surface area ($76.3\text{ m}^2/\text{g}$) as shown by SEM in Fig. 2. This uniform size of the SiO_2 -coated powder required the simultaneous satisfaction of several conditions [10]; a proper reagent concentration was necessary to promote nucleation and the reagents must be mixed completely prior to particle nucleation, so that nucleation occurred uniformly throughout the solution. The DTA-TGA heating curves of the sample

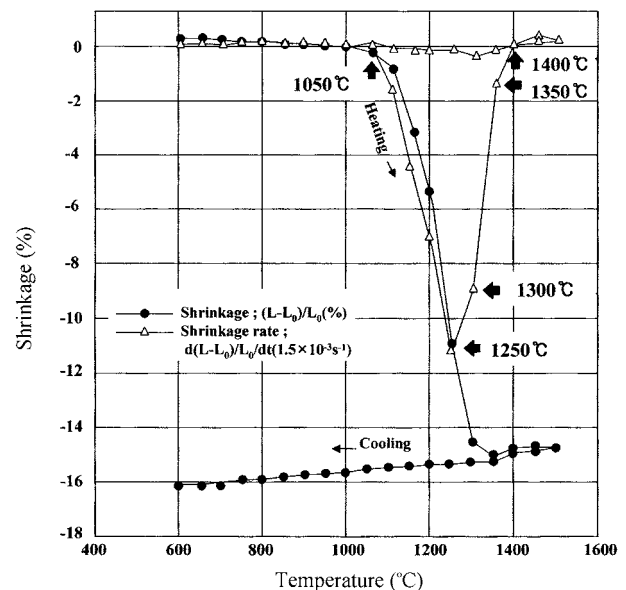
**Fig. 5.** Shrinkage and shrinkage rate of TiO_2 -coated Al_2O_3 powder.

Table 4. Phase composition of the amorphous SiO₂-coated α -Al₂O₃ (high temperature X-ray diffraction)

Temp./Soaking Time (h)	Phase composition of the amorphous SiO ₂ + α -Al ₂ O ₃ (hkl)			
	K(012)	C(101)	M(210)	M(120)
110	m			
1100	vs			
1100/2	vvs			
1200/2	vvs			
1300	vs	vw		
1300/2	vs	vvs		
1400	m	vvs		
1400/2	m	vvs		
1450/2	m	vvs		
1480/2	vw	vs	vw	vw
1500/1	vw	vs	m	vw
1550/1	vw	vw	vs	m
1600/2	vw		vvs	vw

Phase: K=Corundum, C=Cristobalite, M=Mullite

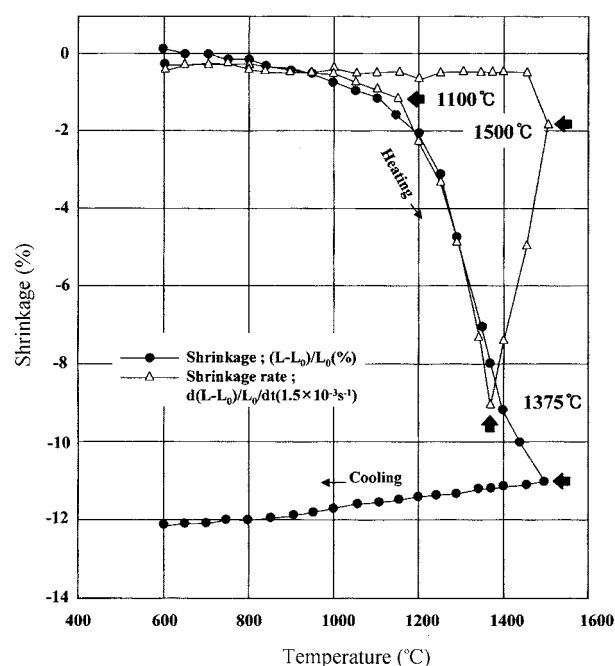
Intensity: vvs=very very strong, vs= very strong, s=strong, m=middle, w=weak, vw=very weak, vvw=very very weak

dehydrated at 100°C are shown in Fig. 5. 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 around 200°C and an other broad exothermic peak at 1300°C. This transformation can be assigned to cristobalite formation from amorphous SiO₂ on the basis of the XRD results in Table 4. These showed a stable cristobalite phase and mullite were formed at 1480°C ($\Delta H=16.21$ Kcal/mol) [11].

These data were analyzed by means of the ratio of peak intensities of corundum (012), cristobalite (101) and mullite (210). The amorphous SiO₂ began to crystallize at 1300°C and changed to the cristobalite phase. Cristobalite peaks were detected between 1300 and 1550°C. Mullite was first detected at 1480°C. The crystalline phases of the amorphous SiO₂-coated α -Al₂O₃ gel powder as a function of temperature and soaking time are summarized in Table 4. No mullite was detected in the heat-treated samples at 1400°C, even after soaking for 1h. This mullite-gel powder heat-treated at 1480°C/1h exhibits cristobalite as the major phase with a small amount of α -Al₂O₃ and mullite. The amorphous silica prepared from tetraethylorthosilicate (TEOS, Si(OC₂H₅)₄) has a simpler transformation [15].

Amorphous SiO₂ gel ----- Cristobalite (2)

The reaction of various types of Al₂O₃ and SiO₂ to form the intermediate crystalline mullite phase is triggered by the formation of cristobalite. The prior results suggest that an amorphous aluminium-silicate phase or

**Fig. 6.** Shrinkage and shrinkage rate of SiO₂-coated Al₂O₃ powder.

a Al-Si spinel forms before the formation of the mullite phase [15] even though some studies report mullite formation by the reaction of Al₂O₃ and amorphous without any formation of a precursor (either amorphous or a spinel phase). Fig. 6 shows the shrinkage rate curves of green compact of SiO₂-amorphous coated Al₂O₃. When a green compact was heated at 10 K minute⁻¹, shrinkage started at 900°C and reached a maximum rate of $3.73 \times 10^{-3} \text{ S}^{-1}$ at 1375°C. After mullite had been initially formed at 1480 ($1.69 \times 10^{-3} \text{ S}^{-1}$), the shrinkage rate obtained between 1450 and 1500°C were from $2.53 \times 10^{-3} \text{ S}^{-1}$ to $0.85 \times 10^{-3} \text{ S}^{-1}$. Additionally, shrinkage occurred during mullite formation at about 1500°C with a shrinkage rate of $1.33 \times 10^{-4} \text{ S}^{-1}$. The coated powder has a relative density of 95.6% and consisted of 23 wt% mullite at 1500°C. The total shrinkage in this case was 11.7%.

The SiO₂- and TiO₂-coated Al₂O₃ for Al₂TiO₅-Mullite

The relative linear shrinkage curves of green compacts of ATM1, ATM3, and ATM5 during the process are given Fig. 7. The shrinkage of ATM1 powder starts at about 600°C while, the ATM 3 and ATM5 have started their shrinkage already at approximately 500°C. This shrinkage at lower temperature is probably due to the crystallization process and the change of phase undergone by Al₂O₃-coated amorphous powders. Appreciable shrinkage occurs at 1000°C and increased steadily to 1350°C, when a change in the gradient is noticed and a minimum in the shrinkage is reached in the temperature range from 1350°C to 1400°C. Pure Al₂TiO₅ from the amorphous TiO₂-coated powder changed at 500°C into the anatase crystal phase, then at 600°C to rutile and at 1300°C finally 92% to Al₂TiO₅.

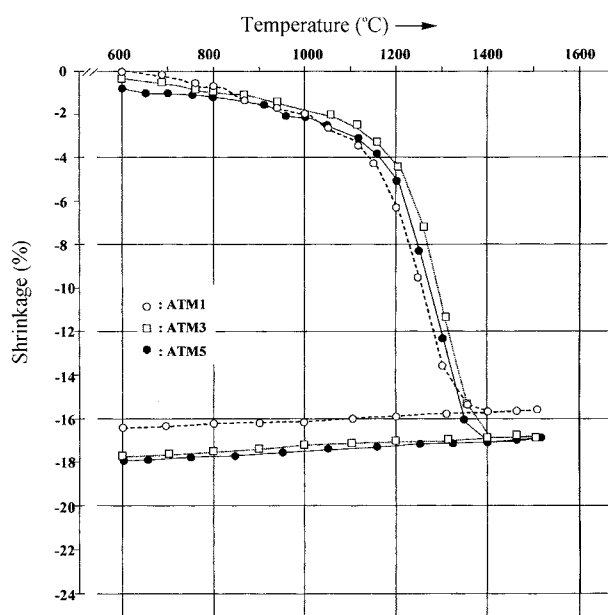


Fig. 7. Shrinkage curves of ATM1, ATM3 and ATM5 green compacts.

The amorphous SiO_2 -coated powder started crystallization at 700°C and formed cristobalite at 1300°C and then at 1470°C the formation of Mullite occurred, as shown by the DTA and XRD results in Fig. 3, 5 and Table 3, 4. The total shrinkage of ATM1 was about 15.8% at 1400°C , and for the ATM3 and ATM5 the total shrinkage at 1400°C was 17.7% and 17.9%, respectively, but up to 1500°C the shrinkage of all samples was slightly

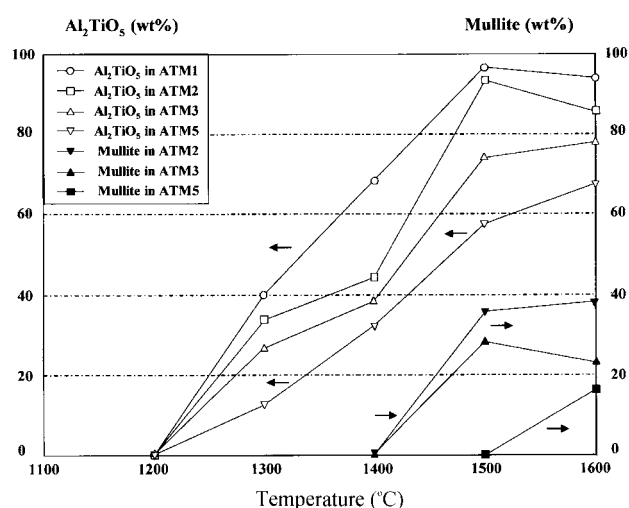


Fig. 8. The formation of Al_2TiO_5 and mullite from ATM composition as a function of temperature with 2h soaking time.

negative during Al_2TiO_5 phase formation because Al_2TiO_5 has a slightly lower density than does an equivalent mixture of alumina and rutile. These effects are illustrated better by the derivative of the curve, which represents the low shrinkage rate between 1350 and 1400°C and emphasises the change in gradient in Fig. 4. The formation of Al_2TiO_5 -mullite from the different values of composition as a function of sintering temperature with 2h soaking time is reported in Fig. 8. The conversion of Al_2TiO_5 in ATM compositions at the same temperature is strongly dependent on the amount of mullite gel. With an increasing amount of mullite gel,

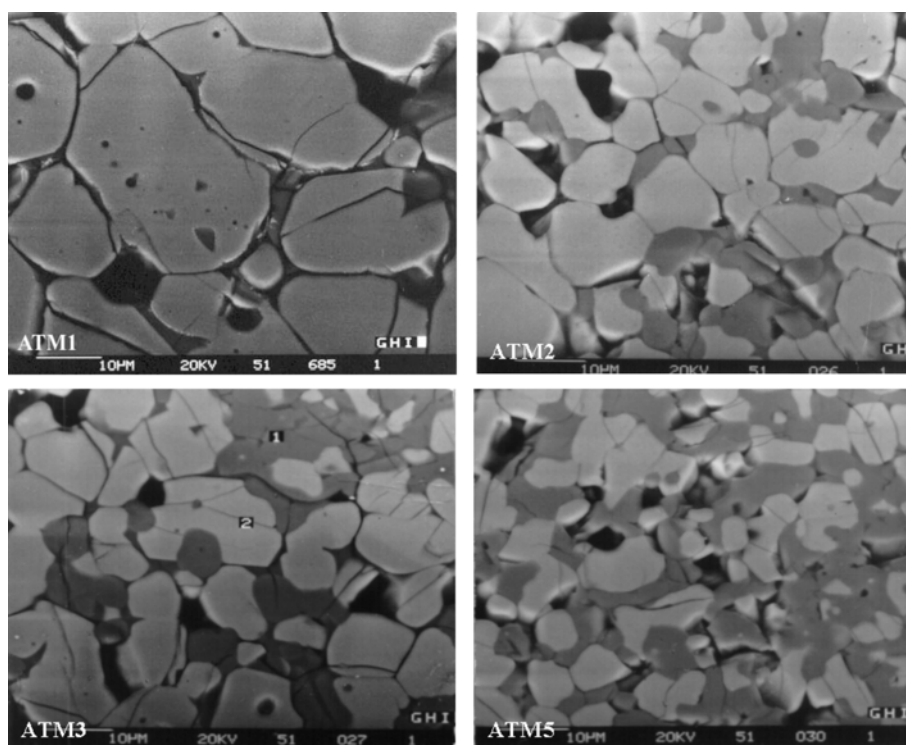


Fig. 9. Microstructure of sintered ATM-materials at 1600°C for 2 hrs (gray or 2: AT, dim or 1: mullite, bright: rutile, black: porosity).

Table 5. The phase compositions and the physical properties of the materials (1600°C for 2h)

		AT	ATM1	ATM2	ATM3	ATM5
Phase composition		AT+R+C	AT+Mullite+L	AT+Mullite	AT+Mullite	AT+Mullite
Bulk 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
Average grain size of AT [μm]		20	40	18	15	8
TEC	1400°C	0.8	2.0	1.70	3.6	4.20
$\alpha_{25-1500}$ [$\times 10^{-6}/\text{K}$]	1500°C	1.2	1.7	1.80	3.0	4.20
	1600°C	0.8	0.5	0.95	1.80	2.0
Bending	1400°C	40	60	75	95	125
Strength [Mpa]	1500°C	25	30	40	70	75
	1600°C	25	70(50)	35(12)	45(17)	40(15)

*Key: AT; β -Al₂TiO₅, R; Rutile, C; Corundum, L; Liquid phase, TEC; Thermal expansion coefficient, (); Young's modulus

we get a decrease in the formation of Al₂TiO₅ in ATM compositions at the same temperature. The formation of Al₂TiO₅ in ATM1 consisting of 90% Al₂TiO₅ and 10% mullite with increasing temperature showed 40%, 69%, 96% and 94%, respectively. The final phase of all ATM compositions sintered at 1600°C for 2 h consisted mainly of two crystalline phases: Al₂TiO₅ and mullite.

The microstructure of the sintered ATM composites at 1600°C/2h consists of a narrow size distribution of Al₂TiO₅ and mullite grains as shown in Fig. 9. However, ATM1 having 10% mullite exhibited significant β -Al₂TiO₅ grain growth, with grain sizes of about 10-50 μm, and a small amount of dispersed corundum and rutile at grain boundaries. It also clearly showed some of the large grains with closed pores, created during densification.

The mean grain diameter of the ATM5 was 5-8 μm; such a distribution of interlinked fine-mullite particles at the grain boundaries would prevent β -Al₂TiO₅ grain growth. In all cases, the Al₂TiO₅ grains decreased in size with increased mullite content and were surrounded by microcracks. The grain boundary microcracks observed at the Al₂TiO₅ grains are expected to be due to the highly anisotropic Al₂TiO₅ crystal structure.

Table 5 summarizes the phase compositions and physical properties of the materials sintered at 1400°C, 1500°C, and 1600°C for 2 h. The final phase consisted mainly of two crystalline phases: Al₂TiO₅ and mullite. 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 increase in mullite content, indicating increased microcracking with a porosity of 12%. However, irrespective of variations of the relative density, the densities were improved by the addition of mullite into Al₂TiO₅. 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 [30].

A relatively high bending strength of 72.0 Mpa and a moderately high Young's modulus of 50.0 KN/mm² were found in ATM1 (90 mol% of Al₂TiO₅) after sintering at 1600°C. This result can be attributed to the formation of a grain-boundary liquid phase during sintering, which aided densification and, thus, reduced microcracking, thereby increasing strength. However, the bending strength of AT and ATM materials sintered at 1400°C and 1500°C showed a higher strength than those at sintered at 1600°C. This result could be possibly explained by the microstructure developed having an increased amount of grain boundary microcracking in Al₂TiO₅ at the higher sintering temperature. The Young's modulus was measured as a function of quenching number by a resonance method. ATM1 having 10 mol% mullite has a relatively higher Young's modulus of 50 kN/mm² than the others. However, one gets a decrease of Young's modulus with increasing Al₂TiO₅ content. All ATM composites with increasing Al₂TiO₅ content and temperature exhibit reduced thermal expansion. Such a phenomenon can be explained also in terms of accumulated microcracking by the microstructure from thermal expansion anisotropy of the individual β -Al₂TiO₅ crystals that give rise to stresses on a microscopic scale during cooling; these localized internal stresses were the driving force for microcrack formation. During the reheating run, the individual crystallites expanded in the low temperature region; 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 [10]. The thermal expansion coefficients of ATM materials sintered at 1600°C were between 0.5×10^6 and $2.0 \times 10^6/\text{K}$ (RT-1200°C) only, compared with the theoretical thermal expansion coefficient for dense Al₂TiO₅ ceramics of $9.7 \times 10^6/\text{K}$. The ATM1 exhibited the lowest value, between 0.5×10^6 and $2.0 \times 10^6/\text{K}$, in the temperature range RT-1200°C.

Conclusions

The moderately good mechanical and thermal behavior of Al_2TiO_5 was improved by the addition of mullite and by using monodispersed amorphous ($0.2\text{--}0.7\ \mu\text{m}$, narrow size distribution) powders produced by a sol-gel process. The reaction of $\alpha\text{-Al}_2\text{O}_3$ with amorphous- TiO_2 and -SiO_2 to form Al_2TiO_5 and mullite starts in the temperature range of $1280\text{--}1300^\circ\text{C}$ and $1450\text{--}1480^\circ\text{C}$, respectively. Al_2TiO_5 -mullite composites sintered at 1600°C showed a moderately high mechanical strength and a low thermal expansion coefficient of $0.5\text{--}2.0 \times 10^{-6}/\text{K}$ obtained by inhibiting grain growth by the addition of mullite.

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.

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