

## Solid-state reaction kinetics for the formation of aluminium titanate ( $\text{Al}_2\text{TiO}_5$ ) from amorphous $\text{TiO}_2$ and $\alpha\text{-Al}_2\text{O}_3$

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### 비정질 $\text{TiO}_2$ 와 $\alpha\text{-Al}_2\text{O}_3$ 부터 $\text{Al}_2\text{TiO}_5$ 를 합성하기 위한 고체상태 반응속도

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**Abstract** Reaction kinetics for the solid-state reaction of  $\alpha\text{-Al}_2\text{O}_3$  with amorphous  $\text{TiO}_2$  to produce  $\text{Al}_2\text{TiO}_5$  (Tialite) was studied in the temperature range of 1200~1300°C. Rate of kinetic reaction were determined by using  $\text{TiO}_2$ -coated  $\text{Al}_2\text{O}_3$  compact containing 50 mol%  $\text{TiO}_2$  and heating the reactant mixtures in  $\text{MgO}$  at definite temperature for various times. Amount of products and unreacted reactants were determined by X-ray diffractometry. Data from the volume fraction and ratio of peak intensities of  $\beta\text{-Al}_2\text{TiO}_5$  indicated that the reaction of  $\alpha\text{-Al}_2\text{O}_3$  with  $\text{TiO}_2$  to form pseudobrookite starts between 1280 and 1300°C. The activation energy for solid-state reaction was determined by using the Arrhenius equation ; The activation energy was 622.4 kJ/mol.

**요 약**  $\alpha\text{-Al}_2\text{O}_3$ 와 비정질  $\text{TiO}_2$ 부터  $\text{Al}_2\text{TiO}_5$ 를 합성하기 위한 고체상태반응의 반응속도를 1200~1300°C 온도 범위에서 연구하였다. 반응속도는  $\text{Al}_2\text{O}_3$ 분말을 코팅한 50 mol%의  $\text{TiO}_2$ 와

일정한 온도에서 여러 시간동안 가열하여 생성된 혼합물에 의하여 결정되었다. MgO안의 반응물과 미반응물의 양은 X-선 회절분석에 의하여 결정되었다.  $\text{Al}_2\text{TiO}_5$ 의 부피율과 peak intensity비의 자료로부터  $\text{Al}_2\text{O}_3$ 와  $\text{TiO}_2$ 의 pseudobrookite(Tialite)형태로의 반응은 1280°C와 1300°C 사이에서 시작되었다. 고체상태반응 활성화 에너지는 Arrhenius식에 의하여 결정되었다. 활성화 에너지는 622.4 kJ/mol이다.

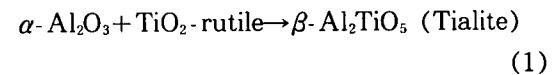
## 1. Introduction

Aluminium titanate ( $\text{Al}_2\text{TiO}_5$ ) is well known as a low thermal expansion, a good thermal insulation, and a low Young's modulus thereby has excellent thermal shock resistant material [1,2]. These properties allow for the insert-casting of ceramic portliners into the cylinder head (aluminium or cast iron), where they serve as a thermal insulation of the exhaust gas [3,4]. However, those composites have a low mechanical strength due to the presence of microcracks developed by the large difference in thermal expansion coefficients along crystallographic axes [5,6].  $\text{Al}_2\text{TiO}_5$  is a polycrystalline substance that exists in two forms,  $\alpha$  and  $\beta$  (Tialite), the first only being stable at temperature higher than 1820°C. Unstabilized aluminium titanate tends to decompose fully into  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  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 corun-

dum [7,8]. 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.

Successful application of the materials has depended on the ability to the control the sintering condition and decomposition behavior, together with an ability to understand the microcracking phenomena.

The crystal structure of the  $\beta$ - $\text{Al}_2\text{TiO}_5$  is of the pseudobrookite type with a theoretical density of 3.70 g/cm<sup>3</sup> [9]. The densities of the starting oxides  $\alpha$ - $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$ -rutile are 3.99 and 4.25 g/cm<sup>3</sup>, respectively. Therefore reaction (1) is accompanied by an 11 % molar volume increase.



The quantitative X-ray determination for  $\text{Al}_2\text{TiO}_5$ , corundum and rutile contents is necessary in order to characterize the behavior and properties of such materials.

Quantitative X-ray diffractometric phase analysis assumes that the intensity, I, of the X-ray diffractometric reflection of a

crystalline phase  $\alpha$  is proportional to the phase's concentration in an aggregate ; The following equation is valid :

$$I = C/\mu^*m \quad (2)$$

where  $I$  is intensity of the X-ray interference,  $C$  is concentration of the crystalline phase  $\alpha$ ,  $\mu^*m$  is mass absorption coefficient of the bulk sample.

The intensity of one X-ray reflection of a crystalline phase is compared with a corresponding X-ray reflection of a reference material containing a known percentage of the phase to be determined. The X-ray reflection intensity is also dependent on the mean grain size and on the grain size distribution. The X-ray reflection intensity increase with decreasing grain size and displays a maximum between 20 and 1  $\mu\text{m}$ . Still smaller mean grain sizes are shown by line broadening and intensity decrease of the X-ray reflections. Crystal disordering and deformation of the crystal structure can also cause intensity decreases. Moreover, grain morphology also influences the reflection intensities: the more the crystallinity deviates from the globular state, the more certain lattice planes show preferred orientation under preparation of powder samples. The resultant higher intensity may simulate exaggerated phase contents.

In this study, the internal standard method is used for quantitative X-ray phase analysis and reaction kinetics between amorphous  $\text{TiO}_2$  and  $\alpha\text{-Al}_2\text{O}_3$  to

form  $\text{Al}_2\text{TiO}_5$ . A stoichiometric mixture of the reactants in MgO was a high-purity alumina which is coated with a dilute solutions of titanium tetraethoxide  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ , and the samples heated between 1250 and 1300°C for various times. The amount of  $\text{Al}_2\text{TiO}_5$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  in the final samples were determined by X-ray diffractometry. The rates for the  $\text{Al}_2\text{TiO}_5$  formation reaction were determined from these results.

## 2. Experimental procedures

Ethyltitanate  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  (Huels AG),  $\alpha\text{-Al}_2\text{O}_3$  (A-16 SG; mean particle diameter : 0.3~0.5  $\mu\text{m}$ ; Alcoa Chem.), and Ethanol (Merck) were used as starting materials.  $\text{Al}_2\text{O}_3\text{-TiO}_2$ -amorphous composite powder were prepared by stepwise alkoxide hydrolysis of a molar ratio  $[\text{H}_2\text{O}/\text{Ti}(\text{OC}_2\text{H}_5)_4]$  of 4 in  $\alpha\text{-Al}_2\text{O}_3$  powder ethanolic colloid solutions. Typical final solution concentrations were 0.05 mol  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ , 0.2 mol  $\text{H}_2\text{O}$ , and 16.9 mol ethanol. The dispersion of coated powder was next centrifuged to remove the alcoholic solution, then washed with deionized water and redispersed in aqueous  $\text{NH}_4\text{OH}$  solution (pH=10). Power compacts were prepared by centrifugal casting, followed by drying at room temperature for one day. The unagglomerated  $\text{Al}_2\text{O}_3\text{-TiO}_2$ -amorphous composite powder (50 mol%  $\text{TiO}_2$ ) is shown in Fig. 1. Before firing, compacts were calcined in air at 650°C for 1 h to remove organic material.

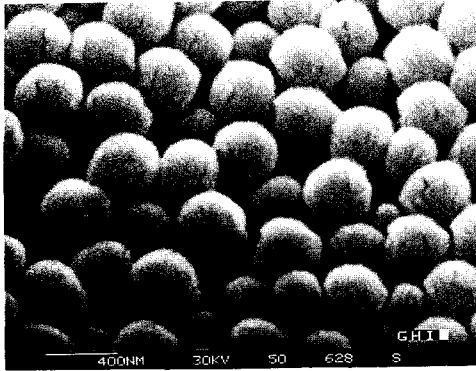


Fig. 1. Scanning electron micrograph of top surface of amorphous  $\text{TiO}_2$ -coated  $\text{Al}_2\text{O}_3$  green compact (50 mol%  $\text{TiO}_2$ ) made by centrifugal casting.

After adding KB 2010 (Zschimmer & Schwarz, Lahnstein/Rh) as binder the powders were formed uniaxially into pellets ( $8 \times 15 \text{ mm}^2$ ) at  $400 \text{ N/mm}^2$ . The firing was carried out in air in an electric furnace with molybdenum silicide heating elements. The sample were introduced at a constant rate so that they were exposed within 5min to the indicated temperature. The temperature of the furnace was controlled a Pt-13Rh/Pt thermocouple and at the end of each temperature, they were water quenched.

In this paper, quantitative X-ray measurements (XRD) were performed using Ni-filtered  $\text{CuK}\alpha$  radiation. The scanning speed was  $0.5 \text{ } 2\theta/\text{min}$ . As an internal standard 50 wt% of MgO powder was added to the sample, which has chemical composition of  $\text{Al}_2\text{O}_3 : \text{TiO}_2$  in rate of moles 1 : 4, 1 : 1, and 4 : 1, respectively. The mixture was during 5min in a percus-

sion mill. Such a time represents a compromise between particle size reduction which improves reproducibility and crystallite destruction which especially affected the  $\text{TiO}_2$  peak intensity thus changing the peak height ratios. The following peaks were evaluated : MgO(220),  $\text{Al}_2\text{TiO}_5(023)$ ,  $\alpha\text{-Al}_2\text{O}_3(104)$ , and  $\text{TiO}_2\text{-rutile}(101)$ . According to the internal standard method, the following equation is used for calculating the phase content of a phase mixture :

$$X_a = I_{ax}/I_e \times \rho_a/\rho_e \times X_e/(1-X_e) \quad (3)$$

Where  $X_a$  is content of the phase of a in the sample in weight %,  $X_e$  is content of the phase of e in the reference material in weight %,  $I_{ax}$  is reflection intensity of the phase of a,  $I_e$  is reflection intensity of the reference material,  $\rho_a$  and  $\rho_e$  are density of a and e, respectively.

The following equations give the concentration of  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{Al}_2\text{TiO}_5$  in mole percent as function of the peak height ratios :

$$\begin{aligned} C_{\text{Al}_2\text{O}_3} &= I_{\text{Al}_2\text{O}_3(104)}/I_{\text{MgO}(220)} \\ C_{\text{TiO}_2} &= I_{\text{TiO}_2(101)}/I_{\text{MgO}(220)} \\ C_{\text{Al}_2\text{TiO}_5} &= I_{\text{Al}_2\text{TiO}_5(023)}/I_{\text{MgO}(220)} \end{aligned} \quad (4)$$

If one knows the initial composition of the powder, these eq. (4) allow for the independent determination of the mole percent of  $\text{Al}_2\text{TiO}_5$ . Figure 2 shows the standard sample of  $\text{Al}_2\text{TiO}_5$  obtained by XRD. The peak height relations have been established experimentally from powder mix-

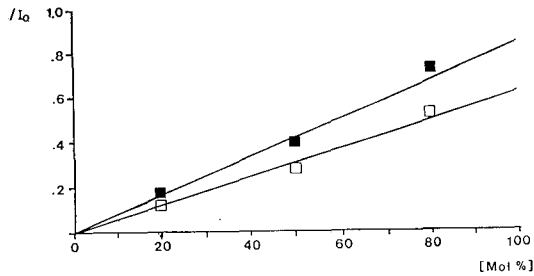


Fig. 2. The standard curve for the formation of  $\text{Al}_2\text{TiO}_5$  (■ :  $\alpha\text{-Al}_2\text{O}_3$ , □ :  $\text{TiO}_2\text{-rutile}$  ).

tures of known compositions to serve as standards.

The final densities were measured for composite powders. The  $\text{TiO}_2$ -coated  $\text{Al}_2\text{O}_3$  powders consist of spheroidal particles having a narrow size distribution and a large surface area ( $118.2 \text{ m}^2/\text{g}$ )

### 3. Development of chemical kinetic equation

Most ceramic process is carried out by intimately mixing fine powders. In 1929, Jander applied the parabolic rate law, developed for planar interface reactions, to powdered compacts [10].

$$r_0^2[1-(1-X)^{1/3}]^2=2kt \quad (5)$$

Eq. (5) is the well-known Jander's equation relating  $X$  the fraction of reaction completed to time. Where  $k$  is the rate constant and  $r_0$  is the initial radius of the reacting particles. By plotting  $[1-(1-X)^{1/3}]^2$  versus time, reaction-rate constant equiva-

lent to  $k/r_0^2$  can be obtained, which is characteristic of the reaction conditions. A schematic representation of the geometry that Jander used in developing his solid-state kinetic model is given in Fig. 3.

There are two oversimplifications in eq. (6) which limit its applicability and the range over which it adequately predicts reaction rates. First, eq. (5) is valid only for a small reaction thickness,  $Y$ ; and second, there was no consideration of a change in molar volume between the reac-

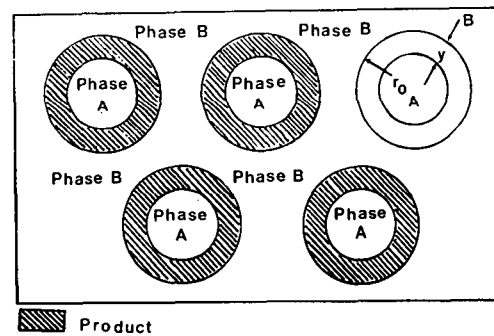


Fig. 3. Jander solid-state reaction geometry (Phase A is completely and constantly covered with particles of component B) [10].

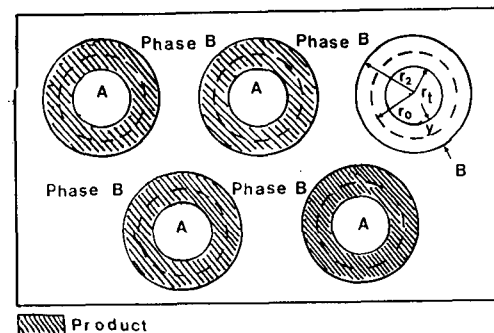


Fig. 4. Carter solid-state reaction geometry (Phase A is completely and constantly covered with particles of component B) [10].

tants and the product layer.

Carter's equation indicated that the time dependence of the fraction reacted corrected for these two constraints is given as :

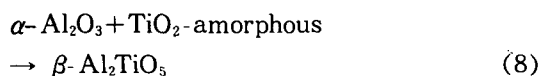
$$\begin{aligned} [1 + (Z-1)X]^{2/3} + (Z-1)(1-X)^{2/3} \\ = Z + 2(1-Z) kt/r_0 \end{aligned} \quad (6)$$

Eq. (6) to represent the rate of product forming and entered a Z term to account for the change in volume, where Z represent the volume of the reaction product formed per unit volume of reactants consumed. Figure 4 is a schematic representation of the Carter's mechanism.

Where  $r_0$  is the initial radius,  $r_t$  the radius of unreacted material at any time t and  $r_2$  the radius of the sphere which includes reacted and unreacted material at any time t. The values of the rate constant k, as a function of temperature, were analyzed by means of the Arrhenius equation.

$$\ln k - \ln k_0 = -E/RT \quad (7)$$

It is assumed that the intensities are proportional to the number of moles the species. The investigated test samples with 50 wt% of original standard by X-ray, was evaluated the rate of moles of unreacted mixture of  $Al_2O_3$  and  $TiO_2$ . Because of the stoichiometry of the chemical reaction, i.e.,



Through multiplication with the volumes of the moles was estimated the volume of solid species per mole on the layers on the spheres with following equation.

$$X = \frac{V_{Al_2TiO_5}}{V_{Al_2O_3} + V_{TiO_2} + V_{Al_2TiO_5}} \quad (9)$$

The volume fraction X of the  $Al_2TiO_5$  can be calculated from Eq. (9). Z can be obtained from the relation of the volume of moles. Because of  $Al_2O_3$  as the starting material was coated from amorphous  $TiO_2$ , obtains one the ratio Z for  $TiO_2$ -coated  $Al_2O_3$  green compact (50 mol%  $TiO_2$ ) of 1.69. Optical microscopic examination of equimolar sample of  $Al_2O_3$ - $TiO_2$  composite showed that the particle size was approximately 0.4  $\mu m$  in diameter (0.2  $\mu m$  in radius), substituted into Eq. (6).

#### 4. Results and discussion

Powder X-ray diffraction intensities of  $TiO_2$  gel without soaking time are shown in Fig. 5. These data were fitted by means of ratio of peak intensities of anatase (101), suboxide (104), (110), (111), and rutile (110). Anatase peaks were detected between 330°C and 920°C. The amorphous  $TiO_2$  began to crystallize at approximately 330°C, and suboxide ( $TiO_2$ ) peaks were detected between 480°C and 1200°C. Rutile was first detected at 400°C. The formation of extended defects in Titanium Oxides, with large deviation

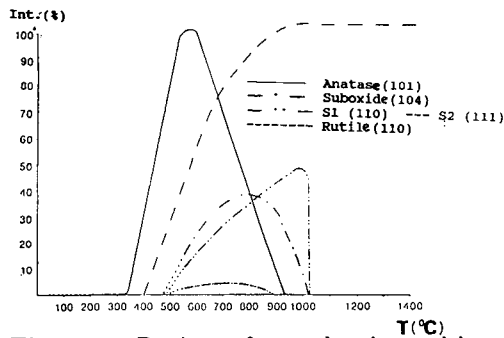


Fig. 5. Ratio of peak intensities of anatase, suboxide, and rutile vs heat-treatment.

from stoichiometry in the direction of a deficit of  $TiO_{2-x}$  (Suboxide,  $x=1.5\sim 2.0$ ), causes local reconstruction of the crystal lattice.

It has been known that deviation from stoichiometry are caused by the presence of defects in the cation sublattice, whereas the anion sublattice is almost perfectly ordered. The stoichiometric deviation of  $TiO_{2-x}$  increased with decreasing of the partial pressure of oxygen in eq. (10) [11].

$$X = \text{Const. } PO_2^{-1/6} \quad (10)$$

The octahedron of  $TiO_2$  are in general joined by their edges and form chains, connected by corners of the octahedra. In suboxide ( $TiO_2 \rightarrow Ti_2O_3$ ) are connected by common faces. The formation of extended defects of  $TiO_2$  by crystallographic shearing are shown schematically in Fig. 6.

The only difference between the crystal structures of higher and lower oxides is

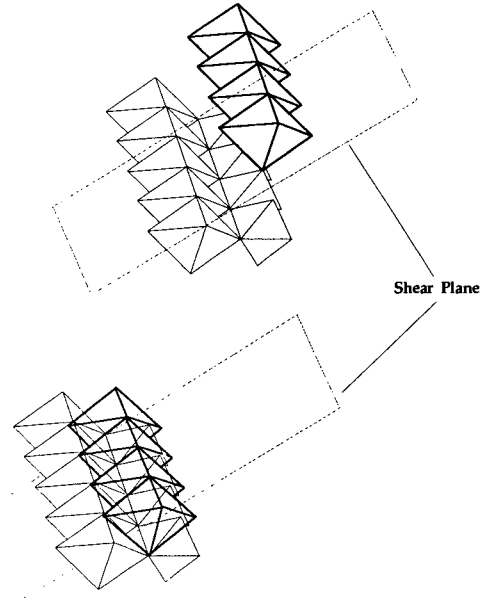


Fig. 6. Formation of  $Ti_2O_3$  (Suboxide) and  $Ti_3O_5$  (Anosovite).

the coordination number of anions, which changes from 3 to 4 on passing from oxides of the  $MeO_2$  type to  $Me_2O_3$ . The above consideration lead to the conclusion that the generation of shear plane in the crystal causes a deviation from stoichiometry in the direction of a deficit in oxygen (or excess of Metal), which is not related to the presence of point defects [12].

The crystalline phase of the amorphous  $TiO_2$  gel powder as function of temperature and soaking time in reported in Table 2. A very small peak of anatase are observed in the pattern of the  $TiO_2$  gel at 200°C, and crystallized at 300°C for 1 hr. Suboxides peaks were detected between 550°C and 900°C. Rutile was detected at 480°C for 1 hr.

Powder X-ray diffraction intensities of

Table 1  
Physical properties of amorphous TiO<sub>2</sub>-coated Al<sub>2</sub>O<sub>3</sub> powders

Precursor	Corundum	Ti(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> +corundum
Crystal form	$\alpha$ -corundum	amorphous+corundum
Average particle size range ( $\mu$ m)	0.2~0.3	0.4
Green density (g/m <sup>3</sup> )	2.15	1.9
Density (g/m <sup>3</sup> )	3.91	3.1~3.4
Surface area (m <sup>2</sup> /g)	10~15	118.2

Table 2  
Phase composition of the amorphous TiO<sub>2</sub> gel (high temperature X-ray diffraction)

Temp./Soaking time (°C/hr.)	Phase composition of the amorphous TiO <sub>2</sub> -gel (hkl)				
	A(101)	S(104)	S(110)	S(012)	R(110)
200	vs				
300	vs				
300/1	m				
400/1	s				
480/1	s				vw
550	vs	w		vw	m
550/1	vs	w	w	vw	s
800	s	m	w	vw	s
800/2	m	s	m	vw	s
900	w	m	vw		vs
900/2	vw				vs
1000	vw				vs
1000/2					vs

Phase : A=Anatase, S=Suboxide, R=Rutile

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

the amorphous TiO<sub>2</sub>-coated  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> gel powder at 200 to 1400°C without soaking time are shown in Fig. 7. These data were fitted to Fig. 6 by means of ratio of peak intensities of  $\beta$ -Al<sub>2</sub>TiO<sub>5</sub>, anatase, rutile and corundum vs heat-treatment, which relative peak intensities with of  $\beta$ -

Al<sub>2</sub>TiO<sub>5</sub> (023), anatase (101), rutile (110) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (104) were measured on the X-ray powder diffraction. The crystallization of amorphous TiO<sub>2</sub> occurred and peaks were observed in the pattern of the samples heated at > 450°C, broad peaks of anatase between 450 and 1100°C and rutile



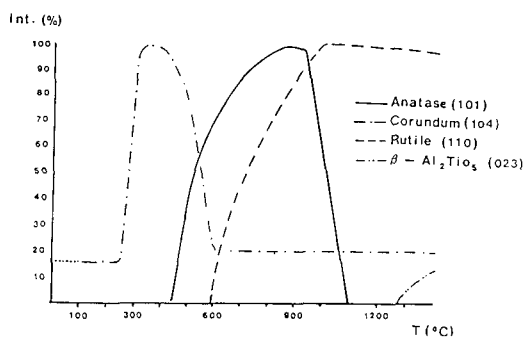


Fig. 7. Ratio of peak intensities of anatase, rutile, corundum, and  $\beta\text{-Al}_2\text{TiO}_5$  vs heat-treatment.

Table 3

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

Temp./Soaking time (°C/hr)	Phase composition of the amorphous $\text{TiO}_2 + \alpha\text{-Al}_2\text{O}_3$ (hkl)									
	C	C	A	C	A	R	R	AT	AT	
	(104)	(012)	(101)	(110)	(004)	(101)	(110)	(110)	(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				vw	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.

at  $> 600^\circ\text{C}$ .  $\beta\text{-Al}_2\text{TiO}_5$  was first detected in the heat-treated samples at  $1280^\circ\text{C}$ . No evidence of aluminium titanate formation can be found, which is consistent with the fact that the specimen had been heat-treated below the eutectoid temperature of  $1280^\circ\text{C}$  [13].

The crystalline phase of the amorphous  $\text{TiO}_2$ -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. This AT-gel powder heat-treated at 1300°C/3 hrs show  $\beta$ -Al<sub>2</sub>TiO<sub>5</sub> as the major phase with a small amount of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. The presence of this starting materials could arise either due to slow reaction rate because of the generation of large diffusion paths with the progressive formation of aluminium titanate. These results indicate that aluminium titanate formation occurs above 1300°C.

As mentioned above a rather narrow temperature range could be investigated with the present powder mixture and most of results and discussion to follow will refer to heat treatments performed at nominal 1250°C. Equimolar mixtures of Al<sub>2</sub>O<sub>3</sub> and amorphous TiO<sub>2</sub> was heated at

a given temperature for a specified period of time. The experimental data are: (1) heating time, (2) temperature, (3) the mol % and volume of reacted and unreacted material at any time and (4) the volume fraction of Al<sub>2</sub>TiO<sub>5</sub>. These data are presented in Table 4.

The subsequent nearly horizontal lines for T=1250°C correspond to the lower temperature initial reaction stage operating without any significant overall volume fraction variation. A constant sample volume while the fraction is in progress means that the porosity reduction or densification closely matches the volume expansion due to aluminium titanate formation.

A demonstration that eq. (6) is to 8.6 % volume fraction in Fig. 8 for the reaction

Table 4  
The data of quantitative X-ray measurements

1250°C Soaking time	Mol%			Mol-Vol.(cm <sup>3</sup> /mol)			AT
	R	C	AT	R	C	AT	Vol.-fraction X
0 hr.	50	50	0	9.3	14.7	0.0	0.0
3 hrs.	49	49	2	9.2	14.5	1.0	0.4
6 hrs.	48	49	3	9.0	14.5	1.5	0.68
12 hrs.	48	48.5	3.5	9.0	14.3	1.75	0.7
24 hrs.	47	48.5	4.5	8.8	14.3	2.25	0.9
1300°C							
0 hr.*							
3 hrs.	40	41	19	7.5	12.1	9.5	3.3
6 hrs.	29.5	33	37.5	4.3	6.2	18.8	6.4
12 hrs.	18	19	63	2.6	3.5	31.5	8.4
24 hrs.	15.5	17.5	67	2.2	3.2	33.6	8.6

\* see Fig. 6 and Table 3.

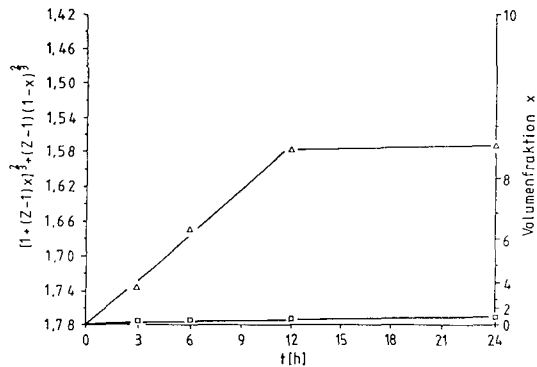


Fig. 8. Reaction between amorphous  $\text{TiO}_2$  and  $\text{Al}_2\text{O}_3$  to form  $\text{Al}_2\text{TiO}_5$  by Cater's equation.

$\text{Al}_2\text{O}_3 + \text{amorphous TiO}_2 \rightarrow \beta\text{-Al}_2\text{TiO}_5$ . The volume fraction of  $\text{Al}_2\text{TiO}_5$  at  $1300^\circ\text{C}$  increased with the soaking time. During the curve for  $T_1 = 1250^\circ\text{C}$  proceeded continuously with very low slope. The curve of  $T_2 = 1300^\circ\text{C}$  in the first stage to 12 hrs can be observed the higher gradient. This phenomena can be agreed the results of report [14].

Despite of longer soaking time, the  $\text{Al}_2\text{TiO}_5$  growth velocities in the second stage of the kinetic reaction turn out to be significantly smaller than those observed initially. Therefore an average growth velocity for product layer was estimated for comparison with fast growth regime;  $T = 1250^\circ\text{C}$  ( $k = 4.025 \times 10^{-21} \text{m}^2/\text{s}$ ),  $T = 1300^\circ\text{C}$  ( $k = 1.34 \times 10^{-19} \text{m}^2/\text{s}$ ), and after 12 hrs at  $1300^\circ\text{C}$  ( $k = 5.03 \times 10^{-21} \text{m}^2/\text{s}$ ). After consideration of differential product thickness, yielded the same results of literature [15] ( $k = 1.6 \times 10^{-18} \text{m}^2/\text{s}$  at  $1300^\circ\text{C}$ ).

An Arrhenius plot of the powder rate constants yields an apparent activation en-

ergy of  $622.4 \text{ kJ/mol}$ . This high activation energy for nucleation was related to the grain boundary stresses interfering with the nucleation process. The same activation energy reported in the literature [11] is  $700 \text{ kJ/mol}$ . The only other activation energy for solid-state reaction for the formation of  $\text{Al}_2\text{TiO}_5$  from oxygen-deficient  $\text{TiO}_2$  and  $\alpha\text{-Al}_2\text{O}_3$  was  $299.45 \text{ kJ/mol}$  [16]. But it was measured at low unspecified oxygen pressure, i.e., under condition that many not be directly comparable to ours.

## 5. Conclusions

The formation of  $\text{Al}_2\text{TiO}_5$  has been studied in an unagglomerated, monosized, equimolar  $\text{TiO}_2$ -coated  $\text{Al}_2\text{O}_3$  powder mixture of  $0.4 \mu\text{m}$  small particle sizes and moderate purity (99.8 wt%) at temperature around  $1250^\circ\text{C}$ , where the volume fraction for the formation of  $\text{Al}_2\text{TiO}_5$  is very small. Crystallizations lead to  $\text{TiO}_2$  ( $1000^\circ\text{C}/1 \text{ h}$ ) which must be then lost the potential advantages of coating process. The transformation of  $\text{Al}_2\text{O}_3$  and  $\text{TiO}_2$  into  $\beta\text{-Al}_2\text{TiO}_5$  appears between  $1280$  and  $1300^\circ\text{C}$ . The activation energy for the chemical kinetics for the solid-state reaction of amorphous  $\text{TiO}_2$  with  $\alpha\text{-Al}_2\text{O}_3$  to produce  $\beta\text{-Al}_2\text{TiO}_5$  was  $622.4 \text{ kJ/mol}$ .

## References

- [ 1 ] H.A.J. Thomas and R. Stevens, Br. Ceram. Trans. J. 88 (1989) 144.
- [ 2 ] I.J. Kim, C. Zografou and W. Kroenert, Unified International Technical Conference on Refractories, Aachen, Germany, Sept. (1991) 135.
- [ 3 ] J. Heinrich, J. Huber and P. Stingl, Erste Duisburger Sonderkeramik-Tage, Moers, Federal Republic of Germany, Augst (1986) 135.
- [ 4 ] I.J. Kim, H.B. Lee and Y.S. Ko, Bul. Kor. Ceram. Soc. 10 (1995) 68.
- [ 5 ] B. Morosin and R.W. Lynch, Acta Cryst. B 28 1040 (1972) 135.
- [ 6 ] Y. Ohya and Z. Nakagawa, J. Am. Ceram. Soc. 63 (1980) 355.
- [ 7 ] M. Ishitsuka, T. Sato, T. Endo and M. Shimada, Ibid. 70 (1987) 69.
- [ 8 ] I.J. Kim, Dissertation, Anwendung des Sol-Gel-Verfahrens auf die Herstellung Keramischer Werkstoffe aus Aluminiumtitanat-Mullit, Institut für Gesteinshüttenkunde, Aachen, Germany (1991).
- [ 9 ] C.E. Holcombe and A.L. Coffey, J. Am. Ceram. Soc. 56 (1973) 220.
- [10] S.F. Hulbert, College of Engineering, Clemson University, South Carolina (1968) 11.
- [11] S. Mrowec, Defects and Diffusion in Solids, (Elsevier Scientific Publishing Co., 1980) p.140.
- [12] J.S. Anderson, The Thermodynamics and Theory of Nonstoichiometric Compounds in Problems of Nonstoichiometry, Collective Work, Ed. A. Rabenau, (North-Holland, Amsterdam, 1970) p.1.
- [13] E. Kato, K. Daimon and I. Takahashi, J. Am. Ceram. Soc. 63 (1980) 355.
- [14] B. Freudenberg and A. Mocellin, Ibid. 70 (1987) 33.
- [15] B. Freudenberg and A. Mocellin, Ibid. 71 (1988) 22.
- [16] S.C. Lee and P.G. Wahlberg, High Temperature Science 21 (1986) 27.