

Solid-state reaction kinetics for the formation of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) from amorphous SiO_2 and $\alpha\text{-Al}_2\text{O}_3$

Ik Jin Kim, Hyo Sup Kwak* and Young Shin Ko**

Institute for Processing and Application of Inorganic Materials, PAIM, Department of Material Science and Engineering, Hanseo University, Seosan 356-820, Korea

**Institute for Engineering Research, Department of Chemical Engineering, Daebul University, YoungAm 526-890, Korea*

***Department of Science Education, Seoul National University of Education, Seoul 137-070, Korea*

비정질 SiO_2 와 $\alpha\text{-Al}_2\text{O}_3$ 부터 Mullite를 합성하기 위한 고체상태 반응속도

김익진, 곽효섭*, 고영신**

한서대학교 재료공학과, 무기재료 공정 및 응용 연구소, 서산, 356-820

*대불대학교 화학 환경공학부, 공업기술연구소, 영암, 526-890

**서울교육대학교 과학교육과, 서울, 137-070

Abstract Reaction kinetics for the solid-state reaction of $\alpha\text{-Al}_2\text{O}_3$ with amorphous SiO_2 to produce mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) was studied in the temperature range of 1450~1480°C. Rate of kinetic reaction were determined by using SiO_2 -coated Al_2O_3 compact containing 28.16 wt.% SiO_2 and heating the reactant mixtures in 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 mullite indicated that the reaction of $\alpha\text{-Al}_2\text{O}_3$ with SiO_2 to form $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ start between 1450 and 1480°C. The activation energy for solid-state reaction was determined by using the Arrhenius equation; The activation energy was 31.9 kJ/mol.

요 약 $\alpha\text{-Al}_2\text{O}_3$ 와 비정질 SiO_2 부터 Mullite를 합성하기 위한 고체상태반응의 반응속도를 $1450\sim 1480^\circ\text{C}$ 온도 범위에서 연구하였다. 반응속도는 Al_2O_3 분말을 코팅한 28.16 wt.%의 SiO_2 와 일정한 온도에서 여러 시간동안 가열하여 생성된 혼합물에 의하여 결정되었다. MgO 안의 반응물과 미반응물의 양은 X-선 회절분석에 의하여 결정되었다. Mullite의 부피율과 peak intensity비의 자료로부터 Al_2O_3 와 SiO_2 의 $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ 형태로의 반응은 1450°C 와 1480°C 사이에서 시작되었다. 고체상태반응 활성화 에너지는 Arrhenius식에 의하여 결정되었다. 활성화 에너지는 31.9 KJ/mol 이다.

1. Introduction

Aluminium and silicon oxides are components of many refractory products because of their refractoriness and chemical stability. In the $\text{Al}_2\text{O}_3\text{-SiO}_2$ binary system, an important refractory material; Mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) is also formed [1,2]. Most studies of mullite system involve preparation of material by high temperature reactions from oxide powder [3,4]. By this conventional process, reaction kinetics between oxides are often insufficiently fast to lead to complete reactions. Therefore, sol-gel technique has been used to prepare reactive aluminosilicate gel and ceramics at low temperature [5-8].

The present study aims at a detailed investigation of amorphous $\text{SiO}_2\text{-}\alpha\text{-Al}_2\text{O}_3$ system of the composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ made by sol-gel process, using an half-alkoxide.

The quantitative X-ray determination for Mullite, corundum and cristobalite 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 α is proportional to the phase's concentration in an aggregate ; The following equation is valid :

$$I = C / \mu m \quad (1)$$

where I is intensity of the X-ray interference, C is concentration of the crystalline phase α , μ^*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 [9]. 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 SiO_2 and $\alpha\text{-Al}_2\text{O}_3$ to form mullite. A stoichiometric mixture of the reactants in MgO was a high-purity alumina which is coated with a dilute solution of tetraethylorthosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$, and the samples heated between 1450 and 1480°C for various times. The amount of mullite, Al_2O_3 , and SiO_2 in the final samples were determined by X-ray diffractometry. The rates for the mullite formation reaction were determined from these results.

2. Experimental Procedures

Tetraethylorthosilicate $\text{Si}(\text{OC}_2\text{H}_5)_4$ (Huels AG), $\alpha\text{-Al}_2\text{O}_3$ (A-16 SG; mean particle diameter: 0.3~0.5 μm ; Alcoa Chem.), and Ethanol (Merck) were used as starting materials. $\text{Al}_2\text{O}_3\text{-SiO}_2$ amorphous composite powder were prepared by stepwise alkoxide hydrolysis of a molar ratio $[\text{H}_2\text{O}/\text{Si}(\text{OC}_2\text{H}_5)_4]$ of 80 in $\alpha\text{-Al}_2\text{O}_3$ powder ethanolic colloid solutions. Typical final solution concentrations were 0.4 mol $\text{Si}(\text{OC}_2\text{H}_5)_4$, 32 mol H_2O , and 6.23 mol ethanol. The dispersion of coated powder was next centrifuged to remove the alcoholic solution, then washed with deionized water and redispersed in aqueous NH_4OH solution (pH=11). Powder compacts were

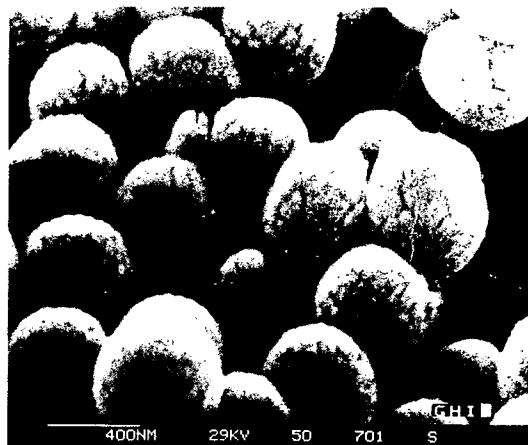


Fig. 1. Scanning electron micrograph of top surface of amorphous SiO_2 coated Al_2O_3 green compact (28.16 % SiO_2) made by centrifugal casting.

prepared by centrifugal casting, followed by drying at room temperature for one day. The unagglomerated $\text{Al}_2\text{O}_3\text{-SiO}_2$ amorphous composite powder (28.16 mol% SiO_2) is shown in Fig. 1. Before firing, compacts were calcined in air at 650°C for 1 hr to remove organic material.

After adding KB 2010 (Zschimmer & Schwarz, Lahnstein/Rh) as binder the powders were formed uniaxially into pellets (8 \times 15 mm²) at 400 N/mm². 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 5 min 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 $0.5^\circ 2\theta/\text{min}$. As an internal standard 50 wt% of MgO powder was added to the sample, which has chemical composition of $\text{Al}_2\text{O}_3 : \text{SiO}_2$ in rate of moles 1:4, 1:1, and 4:1, respectively. The mixture was during 5 min in a percussion mill. Such a time represents a compromise between particle size reduction which improves reproducibility and crystallite destruction which especially affected the SiO_2 peak intensity thus changing the peak height ratios. The following peaks were evaluated: MgO (220), Mullite (023), $\alpha\text{-Al}_2\text{O}_3$ (104), and SiO_2 -cristobalite (200). According to the internal standard method, the following equation is used for calculating the phase content of a phase mixture [10]:

$$X_a = I_{ax} / I_e \times \rho_a / \rho_e \times X_e / (1 - X_e) \quad (2)$$

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, ρ_a and ρ_e are density of a and e, respectively.

Table 1

Physical properties of amorphous SiO_2 -coated Al_2O_3 powders

Precursor	Corundum	$\text{Si}(\text{OC}_2\text{H}_5)_4$ + Corundum
Crystal form	α -corundum	Amorphous + Corundum
Average particle size range (μm)	0.2~0.3	0.4
Green density (g / m^3)	2.15	1.8
Density (g / m^3)	3.91	3.1
Surface area (m^2 / g)	10~15	76.3

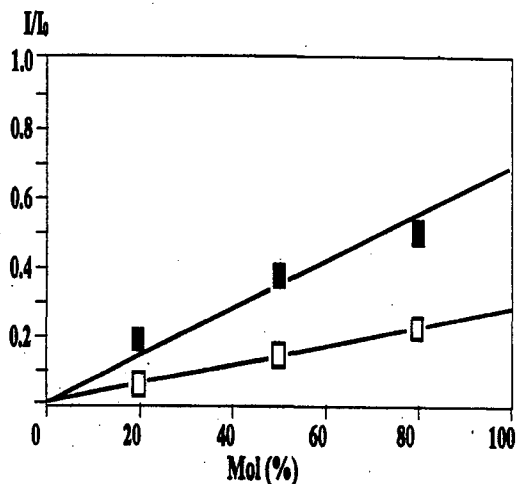


Fig. 2. The standard curve for the formation of mullite (■:Cristobalite, □:Corundum).

The following equations give the concentration of Al_2O_3 , SiO_2 , and mullite in mole percent as function of the peak height ratios:

$$\begin{aligned}
 C_{\text{Al}_2\text{O}_3} &= I_{\text{Al}_2\text{O}_3(104)} / I_{\text{MgO}(220)} \\
 C_{\text{SiO}_2} &= I_{\text{SiO}_2(200)} / I_{\text{MgO}(220)} \\
 C_{\text{Mullite}} &= I_{\text{Mullite}(023)} / I_{\text{MgO}(220)}
 \end{aligned} \quad (3)$$

If one knows the initial composition of the powder, these eq. (3) allow for the independent determination of the mole per-

cent of mullite. Figure 2 shows the standard sample of mullite obtained by XRD. The peak height relations have been established experimentally from powder mixtures of known compositions to serve as standards.

The final densities were measured for composite powders. The SiO_2 coated Al_2O_3 powders consist of spheroidal particles having a narrow size distribution and a large surface area ($76.03 \text{ m}^2/\text{g}$) in Table 1.

3. Chemical Kinetic Equation

After 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 [11].

$$r_0^2 [1 - (1-X)^{1/3-2}] = 2kt \quad (4)$$

Eq. (4) 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 equivalent to k/r_0^2 can be obtained, which is characteristic of the reaction conditions.

There are two oversimplifications in eq. (4) which limit its applicability and the range over which it adequately predicts reaction rates. First, eq. (4) is valid only for a small reaction thickness, Y ; and second, there was no consideration of a change in

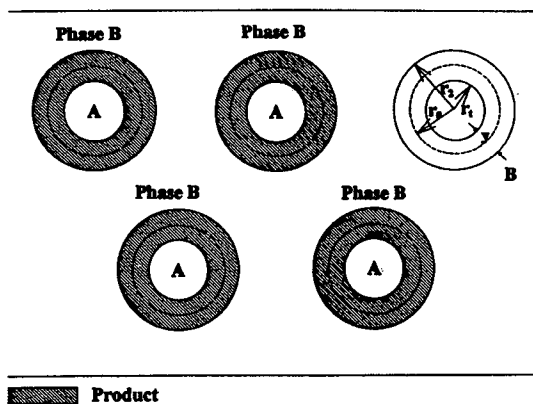


Fig. 3. Carter's solid-state reaction geometry (Phase A is completely and constantly covered with particles of component B) [9].

molar volume between the reactants and the product layer.

Carter's equation indicated that the time dependence of the fraction reacted corrected for these two constraints is given as [11]:

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

Eq. (5) 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.

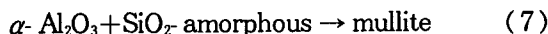
Figure 3 is a schematic representation of the Carter's mechanism.

Where r_0 is the initial radius, r_1 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.

$$\ln k - \ln k_0 = -E/RT \quad (6)$$

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 SiO_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.

$$X = \frac{V_{\text{Mullite}}}{V_{\text{Al}_2\text{O}_3} + V_{\text{SiO}_2} + V_{\text{Mullite}}} \quad (8)$$

The volume fraction X of the mullite can be calculated from Eq. (8). 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 SiO_2 , obtains one the ratio Z for SiO_2 -coated Al_2O_3 green compact (28.16 mol% SiO_2) of 1.58. Optical microscopic examination of equimolar sample of $\text{Al}_2\text{O}_3\text{-SiO}_2$ composite showed that the particle size was approximately 0.5 μm in diameter (0.25 μm in radius), substituted into Eq. (5).

4. Results and Discussion

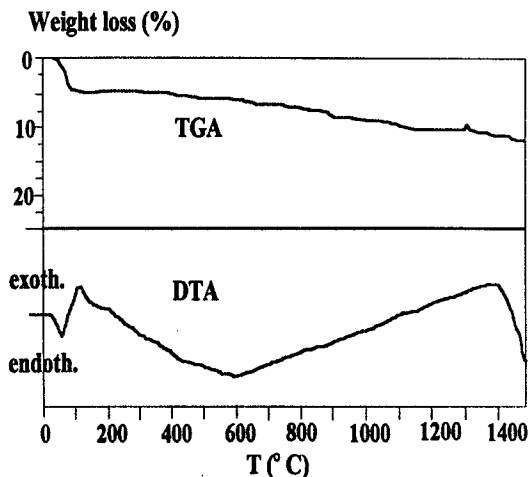


Fig. 4. DTA/TGA curves of the mullite gel.

The amorphous SiO_2 -coated Al_2O_3 powders ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) 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 [12]; 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 DTA-TGA heating curves of the sample dehydrated at 100°C is shown 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 around 200°C and another broad exotherm peak at 1300°C. This transformation can be assigned to cristobalite formation from amorphous SiO_2 as XRD in

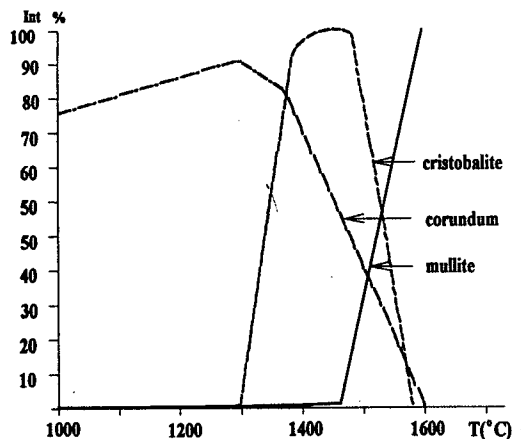


Fig. 5. Reaction between amorphous SiO_2 and Al_2O_3 to form mullite by Cater's equation.

Fig. 5 at this stage showed stable cristobalite phase and at 1480°C mullite formed ($\Delta H = 16.21 \text{ Kcal/mol}$) [13].

Powder X-ray diffraction intensities of amorphous SiO_2 -coated Al_2O_3 gel powder from 1000 to 1500°C without soaking time are shown in Fig. 5. These data were fitted by means of ratio of peak intensities of corundum(012), cristobalite(101) and mullite(210). The amorphous SiO_2 began to crystallize at 1300 to formation of cristobalite. Cristobalite peaks were detected between 1300 and 1550°C . Mullite was first detected at 1480°C .

Figure 6 showed shrinkage rate curves of green compact of SiO_2 -amorphous coated Al_2O_3 . When a green compact was heated at $5^\circ\text{C}/\text{min}$, shrinkage started at 900°C , reached a maximum rate of $3.73 \times 10^{-3} \text{ S}^{-1}$ at 1375°C . After mullite has initially formed at 1480°C ($1.69 \times 10^{-3} \text{ S}^{-1}$), the shrinkage rate was obtained between 1450 and 1500°C

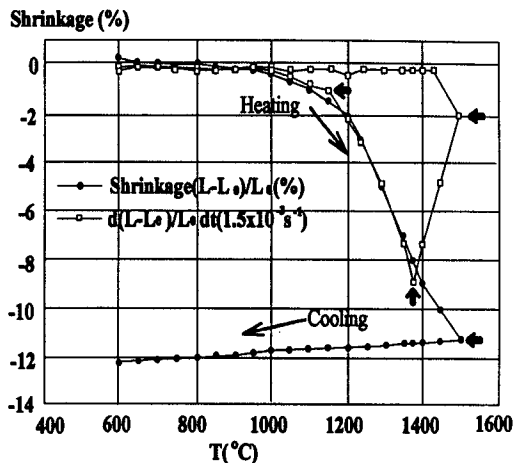


Fig. 6. Shrinkage and shrinkage rate of SiO_2 -coated Al_2O_3 powder.

from $2.53 \times 10^{-3} \text{ S}^{-1}$ to $0.85 \times 10^{-3} \text{ S}^{-1}$. However, the specimen shrinkage which occurs during mullite formation at about 1500°C decrease the shrinkage rate of $1.33 \times 10^{-4} \text{ S}^{-1}$. The coated powder has a density of 95.6 % theoretical density and consisted of 23 wt% mullite at 1500°C . Total shrinkage in this case was 11.7 %.

The crystalline phase of the amorphous SiO_2 -coated $\alpha\text{-Al}_2\text{O}_3$ gel powder as a function of temperature and soaking time is reported in Table 2. No mullite was detected in the heat-treated samples at 1400°C , even after soaking for 1 hr. This mullite-gel powder heat-treated at $1480^\circ\text{C} / 1 \text{ hrs}$ show cristobalite as the major phase with a small amount of $\alpha\text{-Al}_2\text{O}_3$ and mullite. The amorphous silica prepared from tetraethylorthosilicate (TEOS, $\text{Si}(\text{OC}_2\text{H}_5)_4$) has a simpler transformation [6].

Amorphous SiO_2 gel ----- Cristobalite

The reaction of various types of Al_2O_3 and SiO_2 to form the intermediate crystalline mullite phase is triggered by the formation of cristobalite. Others suggest that an amorphous aluminosilicate phase or a Al-Si spinel type forms before the formation of mullite phase [7]. But mullite forms by the reaction of Al_2O_3 and amorphous without the formation of the a precursor (either amorphous or spinel phase).

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 nomi-

nal 1450°C . Mixtures of Al_2O_3 and amorphous SiO_2 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 mullite. These data are presented in Table 3.

The subsequent nearly proportional lines for $T=1450$ and 1480°C correspond to initial formation temperature of mullite any significant overall volume fraction variation. A increased sample volume while the fraction is in progress means that the porosity reduction or densification closely matches

Tabel 2

Phase composition of the amorphous SiO_2 coated $\alpha\text{-Al}_2\text{O}_3$ (high temperature X-ray diffraction)

Temp/Soaking time ($^\circ\text{C}$ / hr)	Phase composition of the amorphous $\text{SiO}_2 + \alpha\text{-Al}_2\text{O}_3$ (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	vvw	vvw
1500 / 1	vw	vs	m	vw
1550 / 1	vw	vw	vs	m
1600 / 2	vvw		vvs	vvw

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

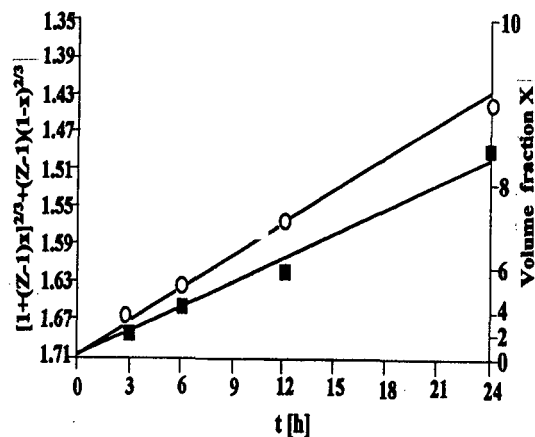


Fig. 7. Ratio of peak intensities of cristobalite, corundum and mullite vs heat-treatment.

the volume expansion due to mullite formation. A demonstration that eq(5) is to 3.0 % for 1450°C and 4.2 % for 1480°C for 3 hrs mullite volume fraction in Fig. 7 for the reaction $\text{Al}_2\text{O}_3 + \text{amorphous SiO}_2$. The vol-

ume fraction of mullite at 1450 and 1480°C increased with the soaking time. The reacted mullite volume fraction of 4.0 and 5.1 % were obtained only at 1450 and 1480°C with 6 hrs of heat treatment, respectively. An average growth velocity for product layer was estimated $k=7.97 \times 10^{-20} \text{ m}^2/\text{s}$ at 1450°C and $k=1.81 \times 10^{-19} \text{ m}^2/\text{s}$ at 1480°C. An Arrhenius plot of the powder rate constant yields an apparent activation energy of 31.9 kJ/mol. 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 mullite has been studied

Table 3

The data of quantitative X-ray measurements

1450°C							
Soaking time	Mol %			Mol- Vol.(cm ³ / mol)			M
	C	K	M	C	K	M	Vol- fraction X
1 hr.							
3 hrs.	39	53	8	11.0	15.6	11.3	3.0
6 hrs.	37	50	12	10.7	14.8	16.9	4.0
12 hrs.	32	46	22	9.0	13.6	30.9	5.8
24 hrs.	17	26	57	4.8	7.7	80.1	8.6
1480°C							
1 hr.*							
3 hrs.	37	50	30	10.4	14.8	18.3	4.2
6 hrs.	35	45	18	9.8	13.3	25.3	5.1
12 hrs.	27	38	22	7.6	11.2	49.0	7.2
24 hrs.	12	19	69	3.2	5.4	96.2	9.2

* see Fig. 5. and Table 2.

in an unagglomerated, monosized, SiO_2 -coated Al_2O_3 powder mixture of $0.4 \mu\text{m}$ small particle sizes and moderate purity (99.8 wt%) at temperature around 1450°C , where the volume fraction for the formation of mullite is very small. Crystallizations lead to SiO_2 (1200°C/1 h) which must be then lost the potential advantages of coating process. The transformation of Al_2O_3 and SiO_2 into mullite appears between 1450 and 1480°C with an average growth velocity of $k=7.97 \times 10^{-20} \text{ m}^2/\text{s}$ and $k=1.81 \times 10^{-19} \text{ m}^2/\text{s}$, respectively. The activation energy for the chemical kinetics for the solid-state reaction of amorphous SiO_2 with $\alpha\text{-Al}_2\text{O}_3$ to produce mullite was 31.9 kJ/mol.

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