

## GROWTH MECHANISM OF MONODISPERSED $\text{TiO}_2$ FINE PARTICLES BY THE HYDROLYSIS OF $\text{Ti}(\text{OC}_2\text{H}_5)_4$

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**Abstract**—In order to investigate the growth mechanism of  $\text{TiO}_2$ , the monodispersed  $\text{TiO}_2$  fine particles were prepared by hydrolysis of  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  using the seed preparation method. Although it was impossible to grow  $\text{TiO}_2$  particles to more than 1  $\mu\text{m}$  with conventional liquid phase reaction method, we obtained monodispersed  $\text{TiO}_2$  fine particles of up to 2.5  $\mu\text{m}$ . Nielsen's chronomal analysis and Overbeek's theory were applied to clarify the particle growth mechanism. The particle growth mechanism was found out as a first-order polynuclear layer growth mechanism and the growth rate constant,  $k_p$  was about  $6.45 \times 10^{-6}$  cm/s.

**Key words:** Growth Mechanism, Monodispersed Fine Particles, Nielsen's Chronomal Analysis

### INTRODUCTION

Titania powders are widely used in industrial applications as pigments, photocatalysts, sensors and ceramic's raw materials [Duonghong et al., 1981; Matijevic et al., 1977; Harris and Byers, 1988; Barringer and Bowen, 1985]. To fabricate high performance ceramics, nonagglomerated fine particles must be obtained. And they must have a narrow size distribution and high purity [Barringer et al., 1984]. Because polydispersed and agglomerated powders results in poor packing, incomplete densification and poor sintering [Okamura et al., 1986; Moller and Welsch, 1985; Edelson and Glaeser, 1988; Bailey and Mecartney, 1992; Yan, 1981; Sacks and Tseng, 1984].

In the early 60's to mid 70's, a group led by Mazdiasni at the Air Force Materials Lab was the first to systematically investigate the possibilities for synthesizing ceramic powders from metal alkoxides. One of their original goals was to prepare very high purity powders (>99.95% purity). Stöber, Fink and Bohn (SFB) synthesized spherical silica particles from the reaction of high purity  $\text{Si}(\text{OC}_2\text{H}_5)_4$  with ammoniated water in an alcoholic solution [Messing and Minehan, 1991]. After Stöber, Fink and Bohn's report, many investigations based on the SFB process have been reported [Hench and West, 1990]. Barringer and Bowen [1982] investigated a method for producing monodispersed spherical titania particles from  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  in a solution of anhydrous ethanol. Jean and Ring [1984] inhibited particle aggregation during growth by adding hydroxypropyl cellulose as a surfactant. The studies [Ogihara et al., 1989; Nakanishi and Takamiya, 1988] for growth mechanism of metal alkoxides have been performed steadily since Overbeek [1982] proposed a theory about controlled step of monodispersed colloidal particles. The growth mechanism of  $\text{SiO}_2$  and  $\text{TiO}_2$  has been found by many workers to be a diffusion-controlled mechanism [Jean and Ring, 1984, 1986; Yonemoto et al., 1992; Bogush and Zukoski, 1988]. However, the diffusion coefficient determined from the Jean and Ring's result was  $10^{-9}$   $\text{cm}^2/\text{s}$ , which is of the order of the Brownian diffusion coefficient for a particle with a diameter of 4  $\mu\text{m}$ , more than 10 times larger

than the particles they grew [Byers and Harris, 1988]. Bogush and Zukoski [1988] made a very thorough study of the growth kinetics of silica spheres according to the SFB process. The kinetics of growth were found to fit the theoretical curve for diffusion-controlled growth, but the diffusion coefficient was  $10^{-12}$   $\text{cm}^2/\text{s}$ , corresponding to Brownian diffusion of a particle with a diameter of one millimeter [Overbeek, 1977; Brinker et al., 1990]. This enormous discrepancy was tentatively attributed to the fact that the particles used in past studies have been almost polydispersed and agglomerated.

In this work, the monodispersed  $\text{TiO}_2$  fine particles were prepared by using the seed preparation method in order to find the growth mechanism. First, we prepared monodispersed  $\text{TiO}_2$  seed particles by controlled hydrolysis of titanium alkoxide solutions. And then seed particles were allowed to grow by further addition of titanium alkoxide and water under conditions in which new particles do not nucleate and grow. Particle size and size distribution were observed by SEM and TEM analysis during seed growth. Nielsen's Chronomal analysis [Mohanty et al., 1990] was used to establish the growth mechanism of systems in which titania particles have uniform size and shape and the number of particles in a unit volume remains nearly constant.

### EXPERIMENTAL

#### 1. Materials

Technical-grade titanium(IV) tetraethoxide (TEOT) was obtained from Aldrich chemical company. Ethanol was obtained from Midwest Grain Product Co. All solutions were used as received without further purification. Water was distilled and then ion-exchanged (ELGASTAT B114, ELGACAN C114).

HPC (hydroxypropyl cellulose, wt100000), which was used to inhibit agglomeration during particle growth, was obtained from Aldrich chemical company.

Glassware was cleaned by soaking in 5% HF solution for 2 hr, followed by repeated rinsing with distilled water. After rinsing, glassware was dried in vacuum oven at 150°C overnight.

Before using as reaction vessels, the glassware was once again rinsed with ethanol, blown dry with dry nitrogen, and then cov-

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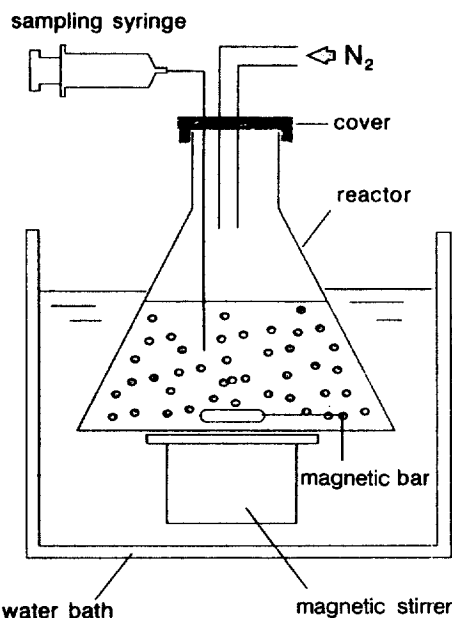


Fig. 1. Schematic diagram of the experimental apparatus.

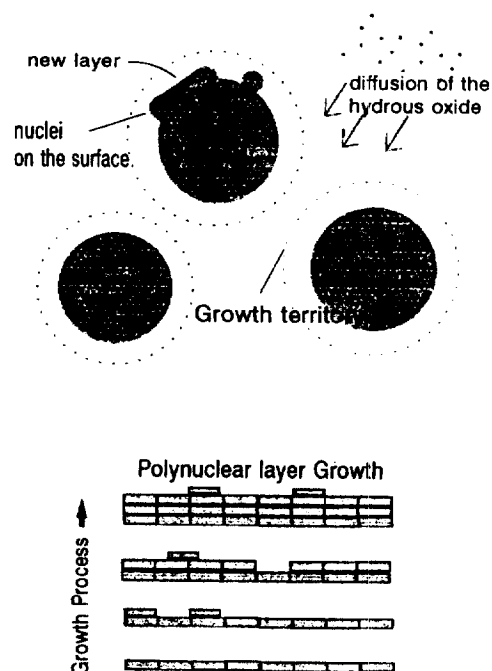


Fig. 2. Schematic diagram of growth mechanism.

ered to minimize contamination by moisture and dust particles.

## 2. Preparation of Monodispersed $\text{TiO}_2$ Seed Particles

Monodispersed  $\text{TiO}_2$  powders were prepared by controlled hydrolysis of titanium tetraethoxide in ethanol. Ethoxide and  $\text{H}_2\text{O}$  were mixed into separate portions of ethanol to concentration of 0.06 M and 0.15 M (based on total volume), respectively.

To inhibit agglomeration, 0.1 g/L (based on total volume) of the surfactant HPC was dissolved in the water containing ethanol portion.

The two ethanol portions were rapidly mixed with a magnetic stirrer for 10 sec. After mixing, the stirring rate was reduced to a minimal level (120 rpm) to minimize coagulation of the reaction and aged for 4 hr in a dry  $\text{N}_2$  atmosphere.

The  $\text{TiO}_2$  alcossols were transferred out of the reactor (Fig. 1) and the powders were washed with ethanol by repeated centrifugation (at 3000rpm for 5 min) and ultrasonic dispersion cycles, replacing the supernatant with ethanol prior to each dispersion step; two cycles were usually performed.

As-prepared particles were dried at  $70^\circ\text{C}$  for 12 hr. The particle size, shape and size distribution of prepared seed particles were observed by SEM and TEM.

## 3. Growth of Monodispersed $\text{TiO}_2$ Seed Particles

$\text{TiO}_2$  seed particles were first ultrasonically redispersed in ethanol (200 ml) and then 0.03 M double-distilled water in ethanol containing 0.1 g/L HPC was added and fully mixed for several minutes.

Next, this prepared solution was poured into 0.06 M  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  solution. These solutions were rapidly mixed for 10 sec. After mixing, the stirring rate was reduced to a minimal level (120 rpm). The mixed solution was aged at room temperature for 6 hr. The particle growth process was observed by SEM and TEM.

Chronomal analysis is used to establish the growth mechanism of this system.

## 4. Characterization of $\text{TiO}_2$ Particles

### 4-1. SEM Analysis

Suspension was withdrawn into a disposable syringe which was rinsed with ethanol. A drop of the suspension was placed directly

onto a SEM holder and then rapidly dried in vacuum to minimize the particle growth on holder.

Another samples,  $\text{TiO}_2$  powder, obtained by drying was scattered onto a SEM holder.

Particle size distribution were estimated directly from SEM (JEOL JSM-35CF) images of gold-coated compact surfaces.

### 4-2. TEM Analysis

$\text{TiO}_2$  sample powders were redispersed in ethanol and then a drop of the suspension was placed directly onto a carbon-sputtered, Formvar-coated, TEM grid for particle size analysis.

Particle size distributions were estimated directly from TEM (JEOL JEM-2000 EX II) images of carbon-coated particles.

### 4-3. XRD Analysis

$\text{TiO}_2$  powders were calcined at 450, 500, 800 and  $1200^\circ\text{C}$  for 1 hr to observe XRD patterns.

XRD patterns were obtained with a diffractometer (Rigaku RAD-C) using Ni-filtered  $\text{CuK}\alpha$  radiation and a scanning rate of  $8^\circ/\text{min}$ .

### 4-4. DT-TGA Analysis

Differential thermal analysis (DTA) and thermal gravimetric analysis (TG) were carried out in a static air atmosphere at a heating rate of  $10^\circ\text{C}/\text{min}$  using Dupont 9900.

## RESULTS AND DISCUSSION

### 1. Preparation of Monodispersed $\text{TiO}_2$ Seed Particles

Fig. 3 shows the morphological difference of  $\text{TiO}_2$  particles obtained from the different water content for the titanium ethoxide in ethanol. In case of Fig. 3(a), particles were obtained after 1 hr aging from 2 molar ratio of water to  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ . The particles seem to be spherical and non-agglomerated but polydispersed. Because of a small amount of water, The particle size was smaller and the induction of hydrolysis was longer, 49 min, than other samples. These facts suggest that the hydrolysis and polymerization took place very slowly. Hence there were few nuclei and

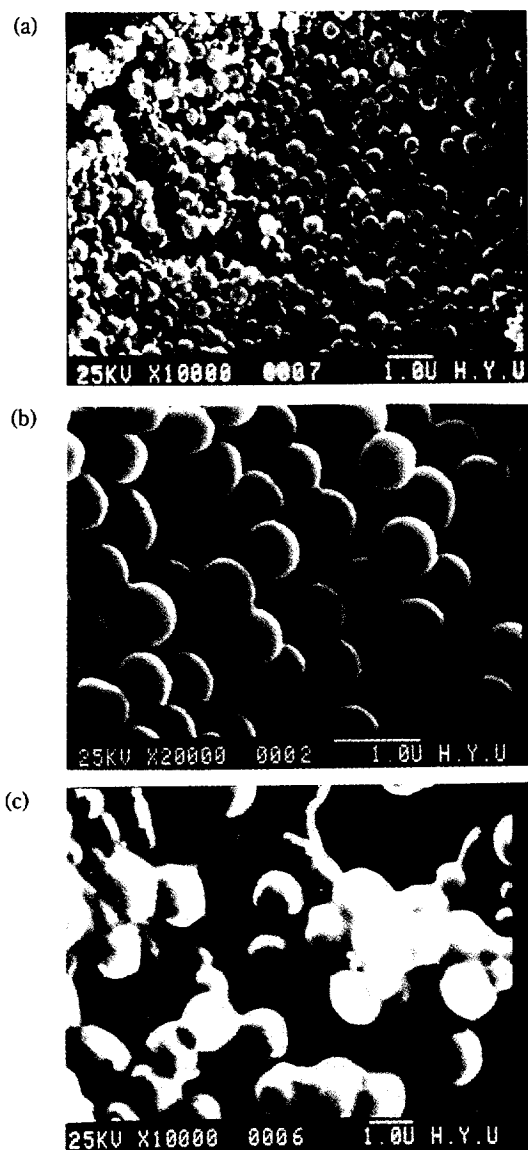


Fig. 3. SEM micrographs of the  $\text{TiO}_2$  particles.

- (a)  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  0.06 M  $\text{H}_2\text{O}$  0.12 M
- (b)  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  0.06 M  $\text{H}_2\text{O}$  0.15 M
- (c)  $\text{Ti}(\text{OC}_2\text{H}_5)_4$  0.06 M  $\text{H}_2\text{O}$  0.36 M

it took a long time to grow to submicrometer size [Nakanishi and Takamiya, 1988; Lamer and Dinegar, 1950].

In case of Fig. 3(c), particles were obtained after 15 min aging from 6 molar ratio of water to  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ . Because of a large amount of water, the induction time of hydrolysis was less than 2 min, and the particles were polydispersed. This suggests that the hydrolysis and polymerization were rapid enough to generate a lot of nuclei and then the particles were agglomerated because of the high density of nuclei.

In case of Fig. 3(b), particles were obtained after 40 min aging from 2.5 molar ratio of water to  $\text{Ti}(\text{OC}_2\text{H}_5)_4$ . The induction time was 26 min. Also the particles were obtained as sphere, non-agglomerated and monodispersed because hydrolysis and polymerization were controlled. So the particles of Fig. 3(b) were used as seed powder to clarify the growth mechanism of  $\text{TiO}_2$  particles.

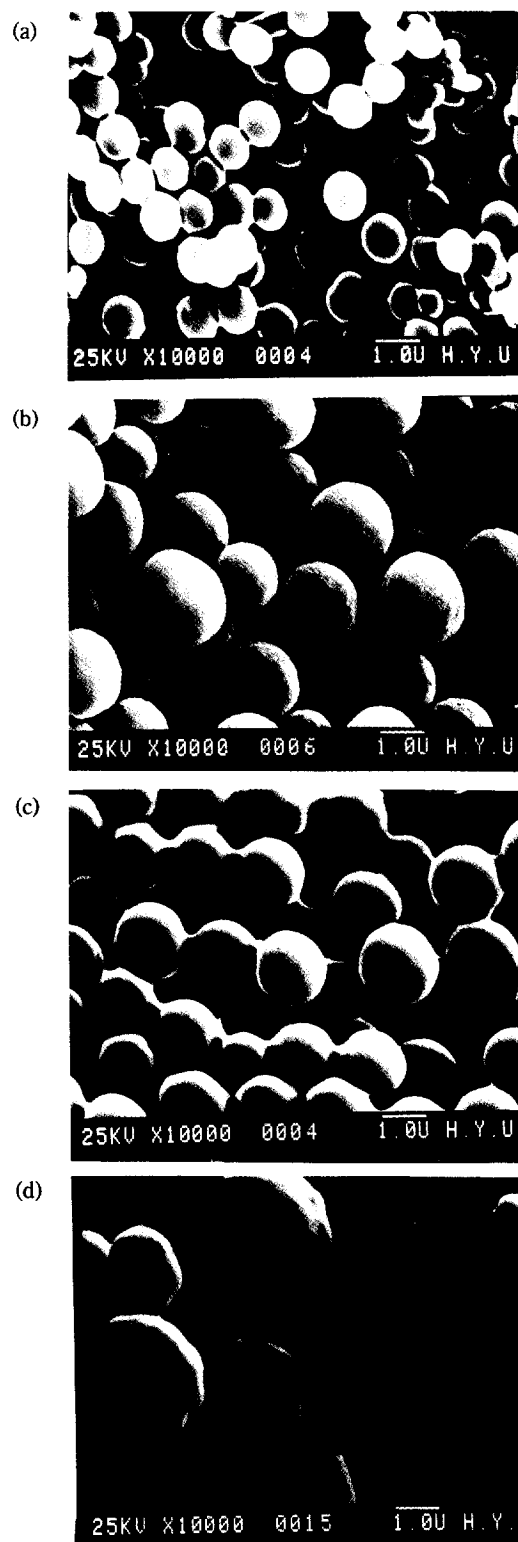
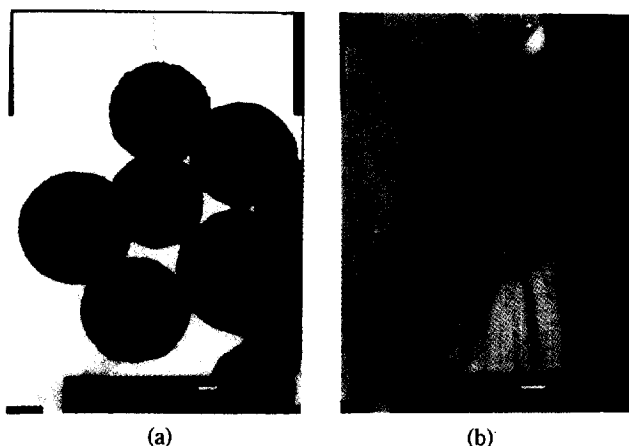


Fig. 4. SEM micrographs which represent growth process of  $\text{TiO}_2$  seed particles.

- (a) 0 min (seed particles), (b) 60 min, (c) 75 min, (d) 360 min

This relationship between the shape of particle and water concentration for titanium ethoxide is similar to that for other alkoxides.

## 2. Growth of Monodispersed $\text{TiO}_2$ Seed Particles

Fig. 5. TEM micrographs of TiO<sub>2</sub> particles.

- (a) 0 min (seed particles)  
(b) 360 min (final particles)

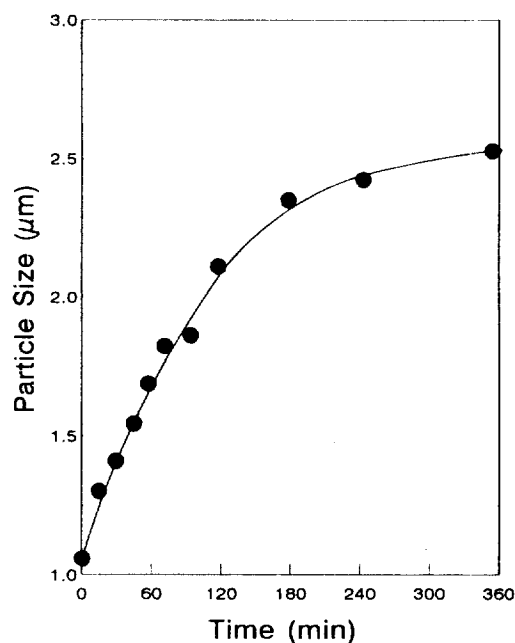


Fig. 6. Growth of seeded titania.

In Fig. 4(a) SEM picture of TiO<sub>2</sub> seed particles was obtained after washing with ethanol and drying. The standard deviation is 0.178 and average diameter is 1.05 μm. Three kinds of TiO<sub>2</sub> particles, Fig. 4(b), (c) and (d), were grown for 60 min, 75 min and 6 hr respectively. During the growth, agglomeration between particles was not observed. The changes in size standard deviation and average diameter with growth were evaluated by SEM image analysis. The number of particles determined from SEM image analysis was more than 100.

Fig. 5(a) and (b) are TEM images of seed particles and final particles after aging. Average size and size distribution are consistent with the result of SEM analysis.

No more nucleation was occurred and precipitated material was deposited on the surface of seed particles. This suggests that the concentration of hydroxide in the bulk could not reach  $C^*_{min}$  (Fig. 4) by adding the low molar ratio of water to Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>. Fig. 6

Table 1. Mean size, std., %std., degree of reaction, chronomal for polynuclear-layer growth

t(min)	Size (μm)	Std.	%Std.	$\alpha$	$I_{p-1}$
0	1.0532	0.1781	16.911	0.072371	1.27383
15	1.2956	0.2178	16.814	0.134723	1.59413
30	1.4036	0.2133	15.198	0.171301	1.74543
45	1.5373	0.2032	13.220	0.225050	1.94319
60	1.6801	0.2145	12.770	0.293796	2.17200
75	1.8168	0.2054	11.300	0.371510	2.41508
90	1.8652	0.2274	12.010	0.401988	2.50873
120	2.0976	0.2421	11.540	0.571739	3.04780
180	2.3330	0.2202	9.440	0.786636	3.94281
240	2.4306	0.2306	9.490	0.889501	4.68027
360	2.5273	0.2301	9.100		

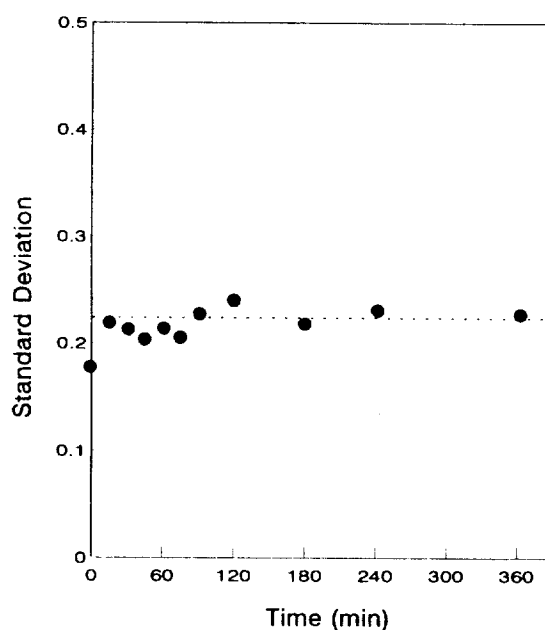


Fig. 7. Change of absolute standard deviation during growth.

shows that the particle size increases linearly until 180 min. No more growth was observed after 180 min.

Table 1 shows data of SEM analysis results (mean size, standard deviation, % standard deviation, degree of reaction, chronomal). The change of absolute standard deviation is shown in Fig. 7. Although the particle size increased with the reaction time but the value of standard deviation was constant. Fig. 8 shows the change of relative standard deviation during growth. It was decreased with time. These results are consistent with polynuclear-layer growth mechanism (Fig. 2) proposed by Overbeek [1982].

If this growth phenomenon is diffusion-controlled growth, both absolute and relative standard deviation should be decreased. But if it is due to mononuclear-layer growth mechanism, both should be increased [Overbeek, 1977].

### 3. Chronomal Analysis

Chronomal analysis was applied to the SEM data to find the rate-limiting step during the growth of TiO<sub>2</sub> seed particles in the bulk. As mentioned before, constant particle number density, uniform particle shape and narrow size distribution are required for this analysis. The experimental results were found to exhibit sur-

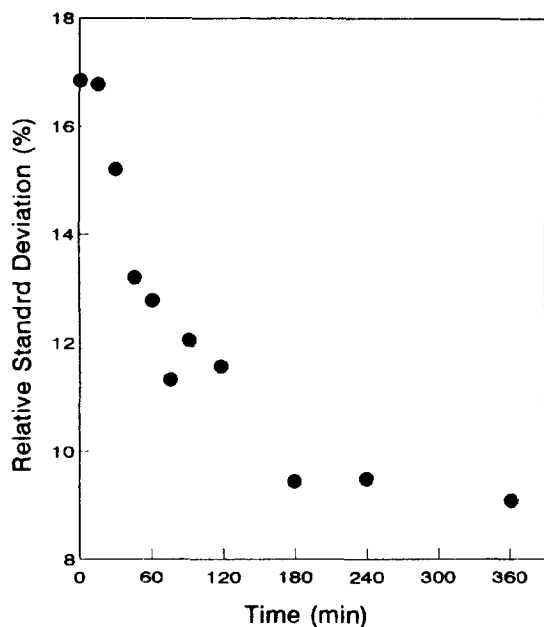


Fig. 8. Change of relative standard deviation during growth.

face reaction controlled growth. It can also be considered possible that surface reaction controlled growth is a mononuclear-layer mechanism. However, in case of mononuclear-layer growth the chronomal value did not agree with our experimental value.

In the present study, it was used to determine the chronomal value of the polynuclear-layer growth mechanism which was termed surface nucleation mechanism by Overbeek [1982].

The growth rate of kinetic order  $n$  is simply given by

$$\frac{dr}{dt} = V k_p C^n \quad (1)$$

where  $r$  is the particle radius,  $t$  is the time,  $V$  is the molar volume of precipitation and  $C$  is the concentration at precipitation [18]. The rate constant  $k_p$  is determined from the experimental data by using Eq. (1).

Alternatively, Eq. (1) can be expressed in terms of the degree of reaction,  $\alpha$  which is defined as

$$\alpha = 1 - C/C_0 \quad (2)$$

where  $C_0$  is the initial concentration and  $C$  is the concentration at time  $t$ . For the growth with seeds,  $\alpha$  can be written as

$$\alpha = \frac{r^3}{r_e^3} \quad (3)$$

Where  $r_e$  is the final particle radius.

Therefore, the following equations are obtained by integration of Eq. (1). For surface reaction controlled growth (i.e. polynuclear-layer growth), the chronomal is defined as

$$t = I_p K_p \quad (4)$$

where  $I_p$  is the polynuclear-layer growth chronomal at a defined value of  $\alpha$  for growth with seeds and  $K_p$  is a factor converting a chronomal to time. These variables  $I_p$  and  $K_p$  can be expressed as follows.

$$I_p = \int_0^\alpha X^{-2/3} (1-X)^{-n} dX \quad (5)$$

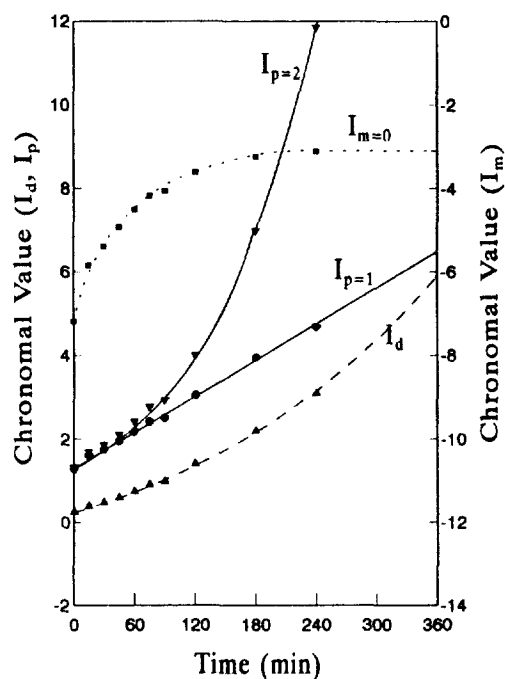


Fig. 9. Chronomal analysis for growth mechanism.

$$K_p = \frac{r_e}{3VC_0 k_p} \quad (6)$$

The first-order polynuclear-layer growth chronomal,  $I_{p=1}$  (at  $n=1$ ) is defined as

$$I_{p=1} = \int_0^\alpha X^{-2/3} (1-X)^{-1} dX \quad (7)$$

The second-order polynuclear-layer growth chronomal,  $I_{p=2}$  (at  $n=2$ ) is defined as

$$I_{p=2} = \int_0^\alpha X^{-2/3} (1-X)^{-2} dX \quad (8)$$

The value of  $I_{m=0}$  (at  $n=0$ ), mononuclear-layer growth chronomal, is defined as

$$I_{m=0} = \int_0^\alpha X^{-2/3} dX \quad (9)$$

If the diffusion is rate determining, the growth rate can be written as the follow.

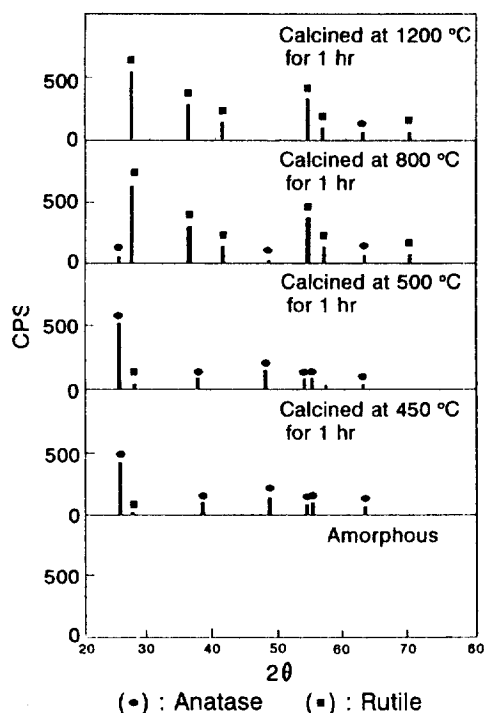
$$\frac{dr}{dt} = \frac{VD_s(C-C_s)}{r} \quad (10)$$

Therefore the following diffusion-controlled growth chronomal equation can be expressed by integration of Eq. (10).

$$I_d = \int_0^\alpha X^{-1/3} (1-X)^{-1} dX \quad (11)$$

Integration for  $I_{p=1}$ ,  $I_{p=2}$ ,  $I_{m=0}$  and  $I_d$  were performed numerically on a personal computer [Overbeek, 1982].

Fig. 9 shows various chronomal plots as a function of aging time. A straight line can be obtained only for  $I_{p=1}$ . Similar plot was also made for the diffusion-controlled growth mechanism, but the plot of the chronomal versus time shows higher correlation coefficient,  $r^2 = 0.9989336$ , for the polynuclear-layer model than that for the diffusion-controlled model.

Fig. 10. XRD analysis for TiO<sub>2</sub> powder.

Therefore, a more appropriate conclusion for this study must be that a first-order polynuclear-layer growth is the rate-limiting step, utilizing both the chronomal analysis and the correct form of the standard deviation information.

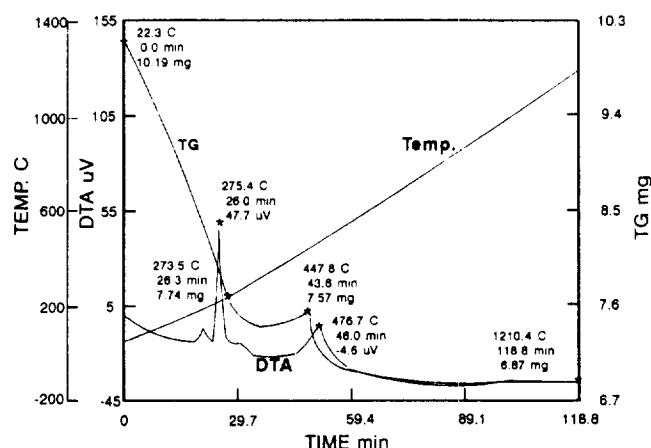
$K_p$  obtained from the slope of the plot is  $4.22 \times 10^3$  sec. Density of amorphous TiO<sub>2</sub> particles is 3.1 g/cm<sup>3</sup> and molecular weight is 79.9 g/mol [Barringer and Bowen, 1985]. And then the molar volume is 25.8 cm<sup>3</sup>/mol. The rate constant  $k_p$ , obtained from Eq. (6) is  $6.45 \times 10^{-6}$  cm/sec. This value means that theoretical growth rate is about 0.36  $\mu$ m/hr. And it is consistent with the result of Fig. 6.

In the conventional powder synthesis, although particles grow more than 1  $\mu$ m with increasing concentration of alkoxide and water, they are agglomerated and polydispersed [Harris and Byers, 1988]. But in our study, non-agglomerated and monodispersed particles of up to 2.5  $\mu$ m can be prepared with adding limited amount of water and alkoxide in solution which contain seed particles.

#### 4. TiO<sub>2</sub> Powder Properties

XRD for the as-prepared material showed it to be amorphous (Fig. 10). The anatase peaks of a powder calcined at 450°C for 1 hr are observed. After the powders were calcined at 500°C for 1 hr, XRD showed that most of TiO<sub>2</sub> powders were anatase and a little amount of powder were rutile. But after the powders were calcined at 800°C, 1200°C for 1hr, most of TiO<sub>2</sub> powders were transformed from anatase to rutile [Edelson and Glaeser, 1988; Ragai and Lotfi, 1991].

Thermal behavior of the particle was studied by DT-TGA techniques. This analysis gives a 32.5% weight loss. It indicates a loss of residual water and an ignition of unreacted alkoxide group and ethanol. DT-TGA studies for TiO<sub>2</sub> powder, Fig. 11, shows a broad endothermic peak near 200°C, corresponding to removing of the chemisorbed water and a sharp, intense exothermic peak, typical of an ignition process of unreacted organic compounds,

Fig. 11. DT-TGA analysis for TiO<sub>2</sub> powder.

at 275.4°C [Barringer and Bowen, 1982]. An exothermic peak at 476.7°C represents transformation of amorphous TiO<sub>2</sub> to anatase. The results of DT-TGA analysis are consistent with that of XRD analysis.

## CONCLUSIONS

Unagglomerated and monodispersed TiO<sub>2</sub> seed particles were prepared by hydrolysis of Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub>. And then seed particles were dispersed ultrasonically in ethanol and allowed to grow by further addition of Ti(OC<sub>2</sub>H<sub>5</sub>)<sub>4</sub> and H<sub>2</sub>O under conditions in which new particles do not nucleate and grow.

Nielsen's chronomal analysis and Overbeek's theory for growth mechanism were applied to clarify the particle growth mechanism. SEM & TEM observations indicated that absolute standard deviation was constant and particles were monodispersed during growth.

The particle growth mechanism is presumed to be a surface reaction in which the rate determining step is a first-order polynuclear layer growth mechanism. The growth rate constant,  $k_p$ , has a value corresponding to  $6.45 \times 10^{-6}$  cm/s.

Although it was impossible to grow TiO<sub>2</sub> particles to more than 1  $\mu$ m with conventional liquid phase reaction, we obtained TiO<sub>2</sub> particles of up to 2.5  $\mu$ m with seed preparation method.

## ACKNOWLEDGEMENT

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## NOMENCLATURE

- $\alpha$  : degree of reaction
- $C$  : concentration of disperse-phase material in bulk solution
- $C_0$  : initial concentration
- $C_s$  : solubility of disperse-phase material in bulk solution
- $C_{min}^*$  : minimum concentration for self nucleation
- $D_e$  : diffusivity
- $I_p$  : polynuclear-layer growth chronomal
- $I_m$  : mononuclear-layer growth chronomal
- $I_d$  : diffusion controlled growth chronomal
- $K_p$  : factor converting a chronomal to time
- $k_p$  : growth rate constant

n : kinetic order  
 r : particle radius  
 $r_f$  : final particle radius  
 Std. : geometric standard deviation  
 %Std. : % standard deviation  
 t : time  
 V : molar volume of precipitation

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