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Kinetics of the Transition of Titanium Dioxide Prepared by Sulfate Process and Chloride Process

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The kinetics of the phase transformation of anatase to rutile was studied by means of X-ray diffraction. Samples of anatase were prepared by sulfate and chloride processes. The kinetic data could well be expressed by the equation

$$\alpha = 1 - e^{-bt^n},$$

where α is the fraction of anatase transformed in time t, and b and n constants. The activation energy of the phase transformation is 105 kcal/mol for the sample prepared by the sulfate process, and 107 kcal/mol for the sample prepared by the chloride process. These values of activation energy are compared with those previously obtained.

The kinetics of the transition of polymorphic compounds such as silicon dioxide,$^{1)}$ titanium dioxide,$^{2-7)}$ germanium dioxide,$^{8)}$ zirconium dioxide,$^{9)}$ ferric oxide$^{10)}$ or calcium carbonate$^{11)}$ has been previously investigated. The rate of the transition of these compounds is complicated by the variable processes of the preparation of samples, the size of sample particles, the surrounding atmosphere and the presence of impurity, *etc.*

Titanium dioxide is prepared by the sulfate process or by the chloride process on an industrial scale. In the present study the rate of the transition of anatase to rutile has been measured using samples prepared by both processes. It might be interesting to compare the kinetic data of the two samples and to compare them with the data obtained by previous investigators.

Experimental

Samples. The samples of anatase were prepared by the two following processes.

(1) Sulfate Process. Sulfuric acid solution of titanium was prepared from purified titanium tetrachloride and extra pure grade sulfuric acid by the method previously reported.$^{5)}$ Concentrations of total sulfuric acid and titanium were 670 g/*l* and 100 g/*l* respectively. The sulfuric acid solution of titanium was poured into a beaker, which was set in an autoclave. The solution was hydrolyzed at 160—170°C for 2hr in the closed autoclave. The precipitated gel was washed several times with sulfurous acid and deioned water, and the product thus obtained was heated at 100°C for 12hr and then at 700°C for 2hr.

(2) Chloride Process. Pure titanium dioxide (anatase) can be prepared by the following reaction between pure titanium tetrachloride and oxygen at 650°C.

$$TiCl_4 + O_2 = TiO_2 + 2Cl_2$$

The method of preparing the sample was as follows. Pure titanium tetrachloride was brought into the silica tube, nitrogen being used as a carrier gas. Nitrogen was passed through the liquid of pur titanium tetrachloride in a reservoir and brought into the silica tube. Oxygen preheated at 500°C was added to titanium tetrachloride-nitrogen mixture at the entrance of the silica tube. The temperature of the reservoir was controlled to 100—120°C, and that of the silica tube at 650 ± 2°C. Titanium dioxide (anatase) formed was collected.

Properties of Sameples. Physical properties of anatase prepared by the two processes were examined by means of electron microscopy, the B.E.T. and picnometric method. The results are shown in Table 1 with those of rutile described below. A small number of crystals ($\sim 0.5\,\mu$) with tetragonal habit were observed among the particles prepared by the chloride process. X-ray diffraction lines of rutile were not observed in the

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1) R. W. Grimshaw, J. Hargreaues and A. L. Roberts, *Trans. Brit. Ceram. Soc.*, **55**, 36 (1956).

2) W. F. Sullivan and S. S. Cole, *J. Am. Ceram. Soc.*, **42**, 127 (1959).

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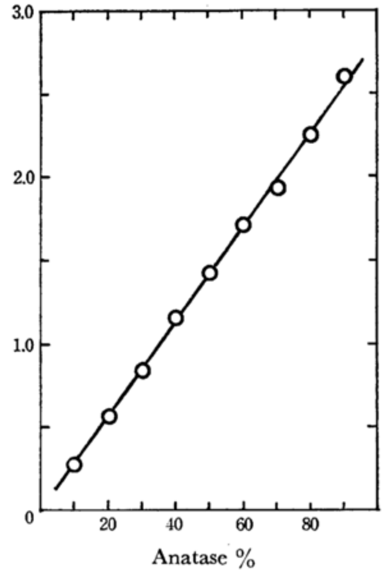

Fig. 1. Calibration curve for the determination of anatase content.
Internal standard: Magnesium oxide. I_A and I_{MgO} are integrated intensity of diffraction line of anatase (d=3.521 Å) and magnesium oxide (d=2.106 Å) respectively.

diffraction patterns of the samples. The relative intensities of all peaks of anatase agree well with those of an A.S.T.M. card.

Procedures of the Determination of the Kinetic Data. For the kinetic runs, samples were set in the sintered alumina boats and heated in a tube electric furnace. The heating procedure was the same as that already described.[5]

The composition of anatase-rutile mixtures was analyzed by the X-ray diffraction method using the Geiger Counter X-ray Diffractometer. Magnesium oxide was used as an internal standard. The weight ratio of magnesium oxide and the anatase-rutile mixture was 1 : 4. The d values of the peak used to compare the intensity were 3.521 Å and 2.106 Å, for anatase and magnesium oxide respectively. Figure 1 shows the calibration curve determined as follows: The I_A/I_{MgO} ratio was measured for a series of ten samples of anatase-rutile magnesium oxide mixture with a definite mixing ratio and the average value of this ratio was plotted against the anatase % in the anatase-rutile mixture. A series of five determinations of the I_A/I_{MgO} ratio for each sample-magnesium oxide mixture was made in the case of the determination of anatase content in the samples after partial transformation.

Results and Discussion

The two samples prepared by the sulfate process and by the chloride process were transformed to rutile after heating at 1050°C for 3 hr, and anatase was not detected in these samples. The properties of these two kinds of rutile are shown in Table 1, and their particle sizes, specific surface areas and specific gravities were almost the same. A small number of crystals with tetragonal habit were detected when the sample prepared by the chloride process was heated at 830°C for the longer time. It may indicate that transformation in these crystals begins later than that in other crystals.

TABLE 1. PHYSICAL PROPERTIES OF ANATASE AND RUTILE TYPES OF TITANIUM DIOXIDE

Process of the preparation of sample	Sulfate process		Chloride process	
	Anatase	Rutile	Anatase	Rutile
Particle form	round	round	angular, round, tetragonal habit	round
Particle size (μ)	0.2−0.3	0.5−0.7	0.05−0.3	0.5−0.7
Specific surface area (m²/g)	16	1.6	34	1.6
Specific gravity	3.77*	4.14	3.63*	4.10

Each rutile type sample was prepared from respective anatase type sample by heating at 1050°C for 3 hr.
* The difference in the specific gravities of the two kinds of anatase is difficult to explain, and seems to be attributed to the difference in the crystal growth during preparation.

The diffraction lines of anatase decreased and those of rutile increased monotonously in their intensities during the transformation and the relative intensities of all peaks of anatase or rutile agreed well with those of A.S.T.M. card.

The experimental results of the transformation rate studied over the temperature range between 800 and 880°C are shown in Figs. 2 and 3. From Figs. 2 and 3, it can be seen that in the early stage of the reaction carried out at the same temperature the transformed amount of the samples prepared by the sulfate process is lower than that of the samples prepared by the chloride process. These

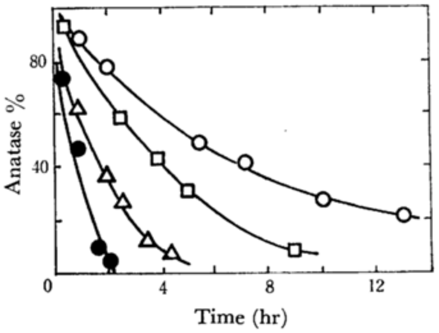

Fig. 2. Plots of anatase % as a function of time at different temperatures (Sulfate process).

-○- 820°C -□- 840°C
-△- 860°C -●- 880°C

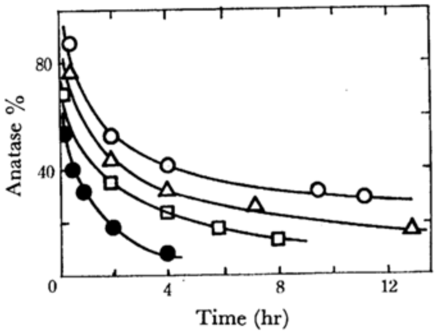

Fig. 3. Plots of anatase % as a function of time at different temperatures (Chloride process).

-○- 800°C -△- 820°C
-□- 840°C -●- 860°C

results would be explained by the fact that particles with small size are contained in the sample prepared by the chloride process. Experimental results in which the transformation rate of the sample with small particle size is larger than that of the sample with large particle size were published previously.[1,5)]

It is well known that the following kinetic equation describes the process of the reaction proceeding through nucleation and crystal growth.[12,13)]

$$\alpha = 1 - e^{-bt^n}, \tag{1}$$

where α is the fraction of material transformed in time t, and b and n constants. Differentiating Eq. (1), we get

$$\frac{d\alpha}{dt} = nbt^{(n-1)}(1-\alpha). \tag{2}$$

This is a first-order equation for $n=1$.
From Eq. (1), we get

$$\ln(1-\alpha) = -bt^n, \tag{3}$$

or

$$t = \left\{ \frac{-\ln(1-\alpha)}{b} \right\}^{1/n} . \tag{4}$$

From Eqs. (2) and (4), we have

$$\begin{aligned} \frac{d\alpha}{dt} &= nb^{1/n}\{-\ln(1-\alpha)\}^{(n-1)/n}(1-\alpha) \\ &= k\{-\ln(1-\alpha)\}^{(n-1)/n}(1-\alpha), \end{aligned} \tag{5}$$

where $k = nb^{1/n}$.
k is a constant, and may be defined as the rate constant of kinetic equation (5).
From Eq. (3) we have

$$\ln\{-\ln(1-\alpha)\} = \ln b + n \ln t. \tag{6}$$

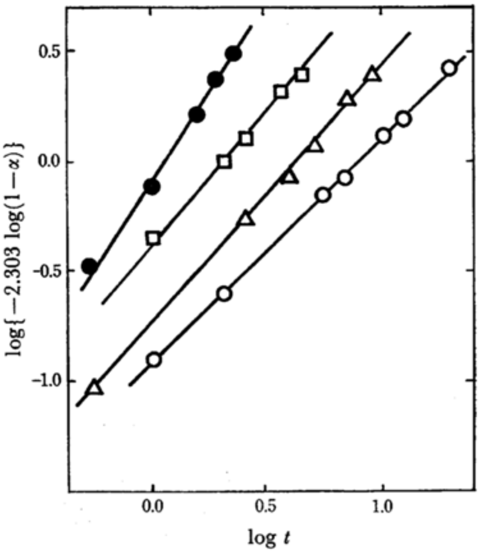

Fig. 4. Plots of log{−2.303 log(1−α)} as a function of log t at different temperatures (Sulfate process).

-○- 820°C -△- 840°C
-□- 860°C -●- 880°C

Thus, b and n can be obtained from the curves of the figure in which data are plotted with the coordinates $\ln\{-\ln(1-\alpha)\}$ and $\ln t$. As shown in Figs. 4 and 5, experimental data fit the relationship of Eq. (6) reasonably well except for the data of the early stage in the reaction for the sample prepared by the chloride process.

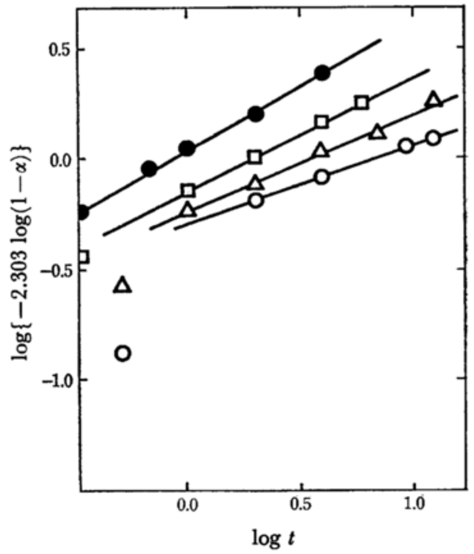

Fig. 5. Plots of log{−2.303 log(1−α)} as a function of log t at different temperatures (Chloride process).

-○- 800°C -△- 820°C
-□- 840°C -●- 860°C

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12) M. Avrami, *J. Chem. Phys.*, **7**, 1103 (1939); *ibid.*, **8**, 212 (1940).

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TABLE 2. VALUES OF n, b AND k AT DIFFERENT TEMPERATURES

Preparation process of anatase	Constant	Temperature (°C)				
		800	820	840	860	880
Sulfate process	n	—	0.961	1.16	1.21	1.61
	b	—	0.135	0.189	0.440	0.811
	k (t^{-1})	—	1.20×10^{-1}	2.75×10^{-1}	6.14×10^{-1}	1.41
Chloride process	n	0.344	0.432	0.492	0.621	—
	b	0.522	0.580	0.733	1.10	—
	k (t^{-1})	5.21×10^{-2}	1.20×10^{-1}	2.62×10^{-1}	7.40×10^{-1}	—

Values of n, b and k calculated from the curves of Figs. 4 and 5 are shown in Table 2. Table 2 indicates that there is not a large difference between k of the sample prepared by the sulfate process and that of the sample prepared by the chloride process at the same temperature. Attention should be paid to the fact that the data in the early stage of the transition for the sample prepared by the chloride process do not fit the relationship of Eq. (6). This fact may be related to a wide distribution of particle size in the sample prepared by the chloride process as shown in Table 1.

In the model presented by Avrami,[12] b depends on temperature, shape and growth rate of the new phase and nucleation frequency, and n has a value from 1 to 4 according to the variety of habit of the new phase.

In the present study the values of n varied in the vicinity of unity over the temperature range between 820 and 860°C among the samples prepared by the sulfate process as shown in Table 2. It is interesting to consider that the kinetic data followed the first-order law fairly well, when the sample prepared by the hydrolysis of sulfuric acid solution of titanium at 90—100°C was used.[5]

The values of n were all below unity for the samples prepared by the chloride process as shown in Table 2. Deviation from the values of n in the Avrami expression was observed.[9,14,15] Such a deviation might be related to the following facts.

1) The small number of nuclei occur and/or the samples with small particle size are used.[14]

2) The edgewise impingement of new phase occurs.[15]

Such situations may exist in the transition of anatase to rutile for the samples prepared by the chloride process.

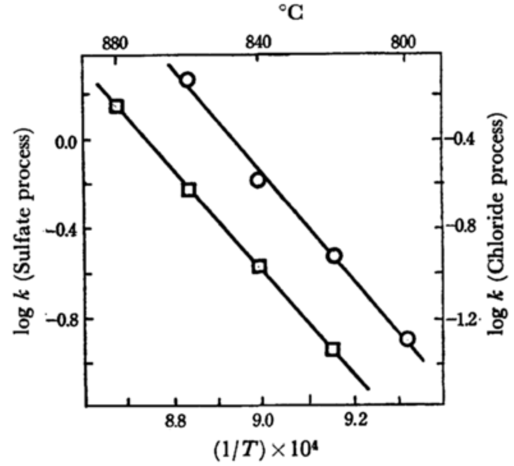

Fig. 6. Arrhenius plots of log k against $1/T$.
-□- Sulfate process
-○- Chloride process

Arrhenius plots of log k against $1/T$ are shown in Fig. 6. The activation energies estimated from Fig. 6 are 107 and 105 kcal/mol for the samples prepared by the sulfate process and by the chloride process respectively. Thus, both values of activation energies in this work are almost the same.

Several values of the activation energy for the anatase-rutile transformation were reported, and are listed in Table 3 with those in the present study. Sullivan and Cole[2] investigated the relation between the kinetics of the anatase-rutile transformation and the preparing conditions of anatase for the first time. They used four hydrated titanium dioxide samples obtained by the hydrolysis of industrial titanium sulfate. Though the details of preparing conditions, *e. g.* drying temperature, were not described, the values of activation energy obtained in their investigation are almost the same as those obtained in the present study. Yaganarasimhan and Rao pointed out that the activation energy of the transition of anatase prepared by sulphate hydrolysis (No. 5 in Table 3) is considerably higher than that of pure anatase (No. 2, 3, 6 in Table 3). It seems certain that the activation energy of the transition of anatase prepared by the sulfate process differs from that of pure anatase. However, attention should be paid to the effect of the drying temperature of the sample (anatase) on the activation energy of the transition. It is shown

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[14] W. G. Burgers and L. I. Groen, *Discussions Faraday Soc.*, **23**, 183 (1957).

[15] D. Turnbull, "Solid State Physics," Vol. 3, Academic Press, Inc., New York (1956), p. 225.

TABLE 3. ACTIVATION ENERGIES FOR ANATASE-RUTILE TRANSITION

No.	Investigator	Process of the preparation of anatase	E kcal/mol
1	W. F. Sullivan S. S. Cole	Hydrolysis from sulfuric acid solution of titanium by heating	100, 103 105, 111
2	A. W. Czanderna C. N. R. Rao J. M. Honig	Oxidation of titanium metal in ammoniacal solution of 90% H_2O_2 Drying at 160°C	110± 10 90± 10
3	C. N. R. Rao	Same as No. 2	80± 10
4	A. Suzuki Y. Kotera	Hydrolysis from sulfuric acid solution of titanium by heating at 90—100°C Drying at 700°C	110 116
5	S. R. Yaganarasimhan C. N. R. Rao	Hydrolysis from sulfuric acid solution of titanium with ag. ammonia Drying at 100°C	120± 10
6	S. R. Yaganarasimhan C. N. R. Rao	Same as No. 2 Drying at 400°C	102—114
7	R. Shannon J. A. Pask	Three commercial anatase samples	94—204
8	A. Suzuki R. Tukuda	Oxidation of titanium tetrachloride at 650°C	107
9	A. Suzuki R. Tukuda	Hydrolysis from sulfuric acid solution of titanium by heating at 160—170°C Drying at 700°C	105

by Suzuki and Kotera[5] that it is difficult to dehydrate completely the titania gel prepared by the hydrolysis of an aqueous solution of titanium salt and the crystal growth of anatase is incomplete, if titania gel is dried at a relatively low temperature. The precipitated titania gel prepared by hydrolysis of the sulfuric acid solution of titanium contains sulfate ion probably as sulfuric acid adsorbed on the surface of the gel. To remove the adsorbed sulfuric acid completely, it is necessary to heat the gel at considerably high temperature. The assumption that the adsorbed sulfuric acid could be removed with difficulty only by means of washing is partly supported by our preliminary experiments where pH of the suspensions prepared by mixing an equal amount of deioned water with two kinds of anatase dehydrated at 100°C and 700°C were 2.5 and 5.5 respectively. Meanwhile, it is interesting to note that the activation energies of the transition of anatase to rutile are not so different if the drying temperature of anatase is considerably high (No. 4, 6, 8, 9 in Table 3). These results suggest that the rate-determining reaction in transformation of anatase to rutile would be independent of the sample preparation. Shannon and Pask[7] also investigated the transition of the three commercial anatase powders to rutile and obtained various activation energies from 94 to 204 kcal/mol (Table 3). These results suggest that commercial anatase contains various impurities, thus causing variation in activation energies.

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