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Polymorphic transformation of titanium dioxide by mechanical grinding

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The effect of mechanical grinding on the structural transformation of titanium dioxide was studied by using several anatase samples prepared from different starting materials and with various particle sizes. Three anatase samples were prepared by hydrolysis of $Ti(O \cdot i\text{-}C_3H_7)_4$, $TiCl_4$, and $TiOSO_4 \cdot 2H_2O$ and one is commercial reagent grade anatase. Each of the as-prepared or heat-treated samples (1.0 g) was ground in a mortar of sintered alumina for up to 96 h in air. The stability of brookite synthesized by grinding was examined by heating in air and under hydrothermal pressure. From the relative amount of the phases estimated by the measurement of the integrated intensity of X-ray line profile and of X-ray crystallite size, DTA and TG, IR spectra, and observation by electron microscope, it is concluded that: 1. the transformation proceeds by a consecutive process from anatase to rutile through brookite by grinding; 2. the smaller the initial particle size of anatase, the more stable the intermediate phase of brookite; 3. the very fine crystals of 5 ~ 20 nm of anatase can be grown to 50 ~ 150 nm of rutile by grinding for 96 h; 4. the rate process of the transformation depends on the initial particle size and is independent of the difference in starting materials or of surface adsorbants; 5. an appropriate lattice distortion introduced by grinding is considered to stabilize the brookite phase; and 6. the lattice constant and the density of brookite synthesized by grinding, $a_0 = 0.5447 \pm 0.005$ nm, $b_0 = 0.9150 \pm 0.0005$ nm, $c_0 = 0.5141 \pm 0.0005$ nm, and $D_x = 4.14\,\mathrm{g\,cm^{-3}}$ agree with those in natural brookite.

1. Introduction

Titanium dioxide exists in three polymorphic forms, anatase, brookite and rutile. Anatase and rutile have been studied from various viewpoints, especially of their structure, preparation technique and stability. The physico-chemical properties of these forms are well examined. However, the formation condition and stability of brookite have remained to be clarified.

Keesman reported the crystal growth of brookite from amorphous TiO_2 under hydrothermal condition in the presence of NaOH [1], and Kiyama *et al.* [2] prepared brookite by aerial oxidation of titaneous salts in the solution containing sodium ions. In these cases, sodium ion was supposed to stabilize the structure of brookite. Knoll reported the complete transformation of anatase to brookite by mechanical grinding. He obtained brookite from a mixture of titanium alkoxides [3–5]. On the other hand, it was also reported that anatase prepared from titanium tetrachloride or titanium sulphate was transformed directly to rutile by grinding, none or only a trace of brookite was detected during the transformation [6, 7].

In the present work, the polymorphic transformation of titanium dioxide by mechanical grinding was studied. The transformation was concluded to proceed by a consecutive process from anatase to rutile through brookite. The rate of transformation depends on the particle size of starting materials;

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TABLE I Starting materials, preparations and samples for grinding of each experimental series

Experimental series	Starting materials	Preparation	Samples for grinding
T-I	$Ti(O\cdot i\text{-}C_3H_7)_4$	Hydrolysed by water at 85° C	1. As-prepared anatase (~ 5 nm) 2. 300° C-heated anatase (6–12 nm)
T-II	$TiCl_4$	Hydrolysed by aqueous ammonium solution at room temperature	1. As-prepared amorphous TiO_2 (ca. 5 nm) 2. 300° C-heated anatase (6–12 nm) 3. 355° C-heated anatase (10–15 nm) with trace amount of rutile
T-III	$TiOSO_4\cdot 2H_2O$	Hydrolysed by aqueous ammonium solution at room temperature	1. As-prepared amorphous TiO_2 (~ 10 nm) 2. 300° C-heated anatase (10–15 nm) 3. 355° C-heated anatase (10–20 nm)
T-IV	Commercial TiO_2, Nakazumi Crystal Co. Ltd		As-received anatase with trace amount of rutile (50–200 nm)

the larger the particle size of anatase, the faster the transformation from brookite to rutile, so that the intermediate brookite could not be practically detected from the anatase with the particle size of more than a few hundreds nanometres. The crystallographic data on brookite are also presented.

2. Experimental

2.1. Preparation of samples

Starting materials used were $Ti(O\cdot i\text{-}C_3H_7)_4$, $TiCl_4$, $TiOSO_4\cdot 2H_2O$ and a commercial reagent grade anatase supplied by Nakazumi Crystal Company Ltd.

Different starting materials were chosen in order to examine the effect on the kinetics of the transformation process of titanium dioxide. Each of materials, except the commercial TiO_2, was hydrolysed by adding either water or aqueous ammonium solution. The precipitates obtained were washed repeatedly by water, and then dried under reduced pressure for 48 h and at 110° C in air for 48 h.

The precipitate prepared from titanium isopropoxide was necessary to be centrifuged at 3000 rpm for 10 min in order to obtain clear separation of hydrosol from the solution before drying. The samples were heat treated at 300 and 355° C for 24 h, as well as the as-prepared ones, were used for grinding. Starting materials, preparation methods and samples for grinding are summarized in Table I. By this selection of starting materials and heating condition we were able to examine the effect of starting materials and particle size on the process of transformation.

The powder of the sample (1.0 g) was ground in a mortar made of sintered alumina for various periods of up to 96 h at room temperature in air.

Brookite synthesized by grinding 300° C-heated anatase in T-I series for 6 h was heated in air at 500 and 600° C, and heated at 200 and 300° C under 300 kg cm^{-2} of hydrothermal condition.

2.2. Determination of relative amounts of phases

Relative amounts of phases, anatase, brookite and rutile, in the ground samples were determined from the change of X-ray diffraction intensities. The

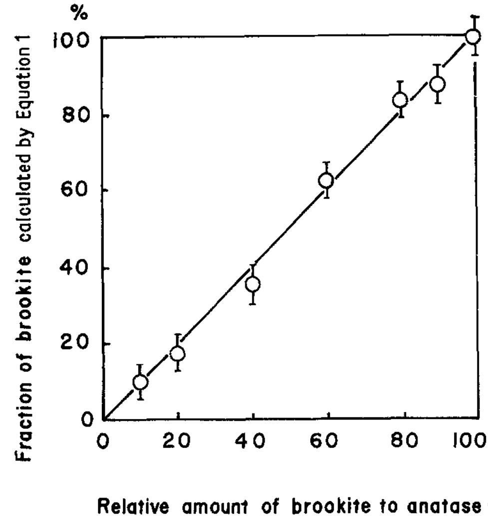


Figure 1 The change of the fraction of brookite calculated by using Equation 1 of the synthetic mixture of pure brookite and pure anatase against the relative amount of brookite to anatase in the mixture. Anatase used was obtained by heating T-I sample at 300° C, and brookite was obtained by grinding above anatase for 6 h.

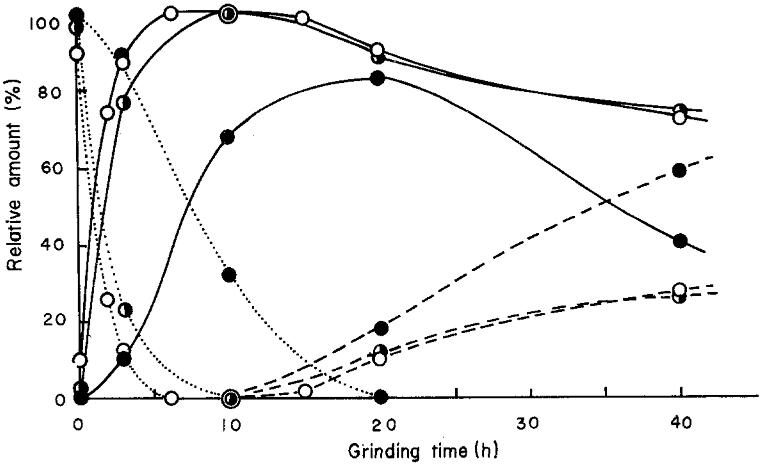


Figure 2 The change of relative amount of the phases on 300° C-heated T-I, -II and -III samples as a function of grinding time. The dotted line represents the fraction of anatase, solid line represents the fraction of brookite and broken line represents the fraction of rutile. ○: T-I, ◑: T-II and ●: T-III.

fraction of brookite relative to anatase, f_{brookite}, was evaluated from the following equation:

$$f_{\text{brookite}} = 1.55 \frac{I_{(2.90)}}{I_{(3.51)}} \tag{1}$$

where $I_{(3.51)}$ is the integrated intensity of the overlapped peaks of 101 line for anatase, and 110 and 120 lines for brookite at $d = 0.351$ nm, and $I_{(2.90)}$ is the integrated density at $d = 0.290$ nm for 121 line for brookite. The constant 1.55 in the equation comes from the value of the ratio $I_{(3.51)}/I_{(2.90)}$ for pure brookite.

The fraction of rutile to other phases, f_{rutile}, was evaluated from the ratio

$$f_{\text{rutile}} = \frac{I_{(3.24)}}{I_{(3.51)} + I_{(3.24)}} \tag{2}$$

where $I_{(3.24)}$ is the integrated intensity of 110 line for rutile at $d = 0.324$ nm.

When three phases coexisted, at first the fraction of rutile was determined from Equation 2 and then the remnant was divided into anatase and brookite by using Equation 1.

In order to confirm the validity of the equation, the fraction of brookite calculated by using Equation 1 was compared with the relative amount of brookite to anatase in the synthetic mixture of pure brookite and pure anatase, as shown in Fig. 1. This figure shows the linear relation with the accuracy of about 10%.

2.3. Characterization of samples

Particle size was measured from the transmission electron photomicrographs. Crystallite size was

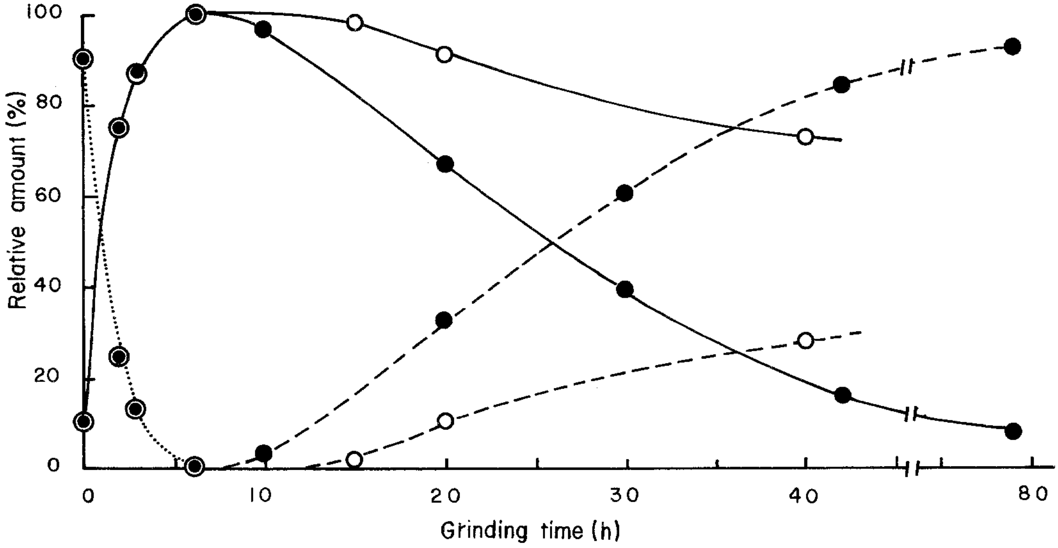


Figure 3 The change of relative amount of the phases on as-prepared and 300° C-heated T-I samples as a function of grinding time. ●: as-prepared, and ○: 300° C-heated. (The lines have the same meaning as those in Fig. 1).

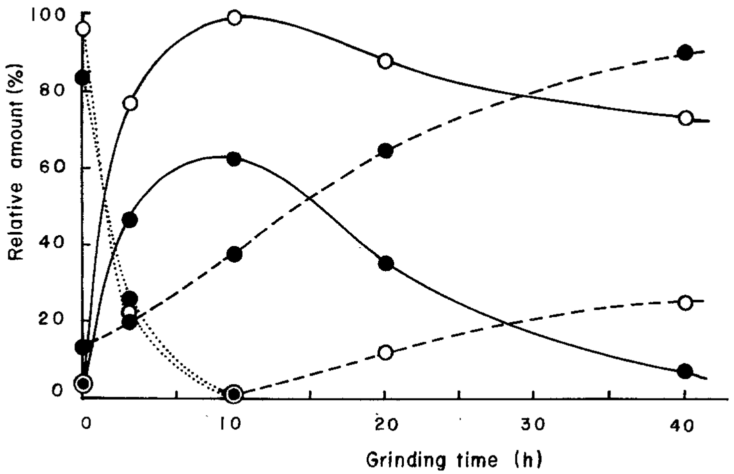


Figure 4 The change of relative amount of the phases on 300° C- and 355° C-heated T-II samples as a function of grinding time. ○: 300° C-heated and ●: 355° C-heated. (The lines have the same meaning as those in Fig. 1).

calculated from X-ray line broadening by application of Scherrer's equation, $L = K\lambda/\beta\cos\theta$, with $K = 0.9$ [8]. 101 line for anatase, 121 for brookite, and 110 for rutile were used. The breadth of the half maximum intensity of the pure diffraction profile, β, was evaluated after being separated from the α_2 component of copper radiation, and corrected for the instrumental line broadening using an internal standard of silicon powder.

3. Results and discussion

3.1. Transformation process by grinding

The change of the relative amount of the phase with grinding time are shown in Figs. 2 to 5. In Fig. 2, three samples prepared from different starting materials and then heated at 300° C for 24 h for dehydration are compared. In Figs. 3 and 4, the transformation rate on the samples with the same origin but with different heat-treated temperature are compared. Fig. 5 shows the result on the commercial sample.

All the experimental results show a general scheme for polymorphic transformation by mechanical grinding from anatase to rutile through brookite, suggesting the consecutive process of structure transformation:

$$\text{anatase} \xrightarrow{k_a} \text{brookite} \xrightarrow{k_b} \text{rutile}$$

where k_a and k_b are the rate constants of the transformation of anatase to the intermediate phase of brookite and of brookite to rutile, respectively. As-prepared precipitates in T-II and -III series were amorphous and also changed to rutile through anatase and brookite by grinding. However, it was difficult to estimate precisely the amount of anatase and brookite in the presence of amorphous phase. Therefore, only the results for anatase samples heated at 300 and 355° C are presented, as shown in Figs. 2 and 4.

On the 300° C heated samples in the T-I and T-II series, as shown in Fig. 2, anatase transforms rapidly to brookite, and the single phase of brookite

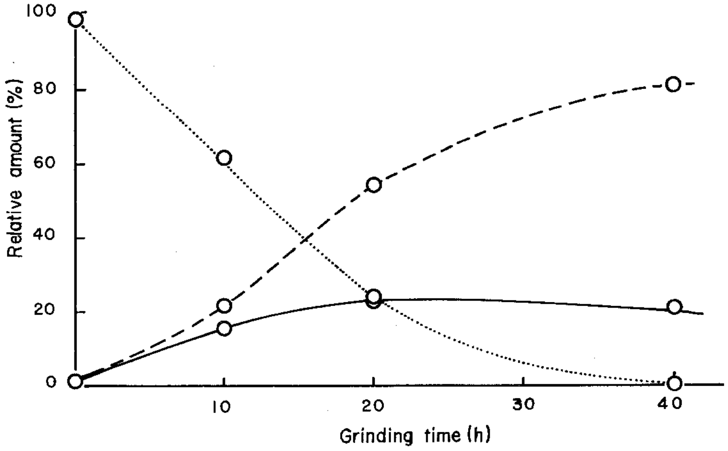


Figure 5 The change of relative amount of the phases on commercial sample as a function of grinding time. (The lines have the same meaning as those in Fig. 1.)

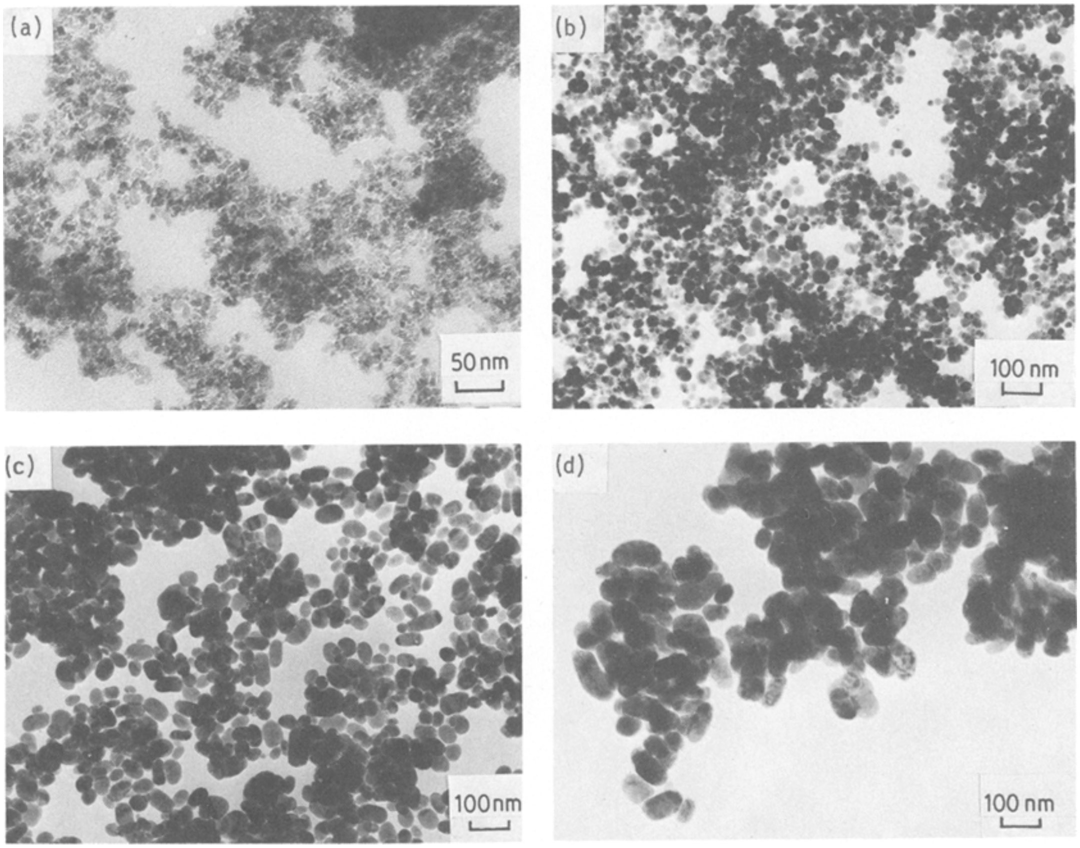


Figure 6 Electron photomicrographs of ground samples on T-1 samples. (a) as-prepared anatase, (b) brookite, after grinding for 7 h, (c) brookite and rutile, after grinding for 40 h, and (d) rutile, after grinding for 78 h.

is found after grinding for $6 \sim 10$ h and then changes to rutile slowly. From these changes of the relative amount of each phase with grinding time, the rate constant of the first step, k_a, is supposed to be much larger than that of the second step, k_b, and the rate-determining step appears to be the transformation of the intermediate phase of brookite to rutile. On the 300° C-heated T-III sample, however, the transformation of anatase to brookite is a little slower, but rutile appears in shorter time of grinding.

In the T-I series, there is no difference in the transformation rate of anatase to brookite between the as-prepared and 300° C heated samples (Fig. 3), but in the former sample the transformation from brookite to rutile is accelerated remarkably. About 8% of water adsorbed on the as-prepared sample may enhance the transformation rate from brookite to rutile. An induction period before the formation of rutile is observed on the as-prepared and on the 300° C-heated samples as shown in Figs. 2 and 3. On the 355° C-heated sample, however, there is no induction period and brookite transforms to rutile more rapidly than on the as-prepared or on the 300° C-heated samples (Fig. 4). A small amount of rutile present in the initial 355° C heated sample may provide the nucleation centre of rutile, and could reduce the induction period for the formation of rutile.

On the rate process of the transformation of anatase to brookite and of brookite to rutile, there is no large difference among T-I, -II and -III samples as to whether the induction period exists or not, that is, $k_a > k_b$, and the intermediate phase of brookite is rather stable. On the other hand, brookite phase is unstable at the commercial sample in which $k_a < k_b$ and most of anatase appears to transform to rutile directly (Fig. 5).

3.2. Growth of crystals by grinding

The particle size was found to increase for all samples in the T-I, -II, and -III series. The change

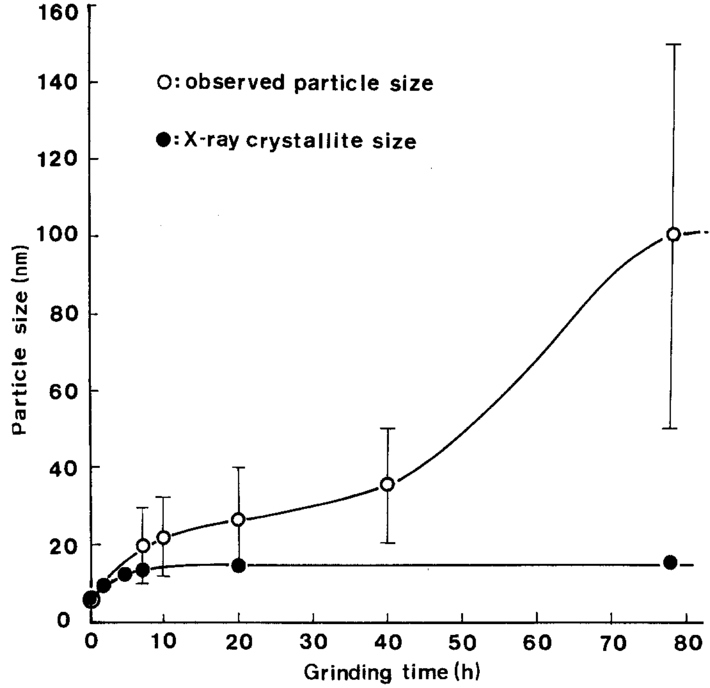


Figure 7 The change of the particle size determined by transmission electron microscopy, and of the crystallite size calculated from X-ray line broadening, as a function of grinding time.

of particle size with grinding time on the as-prepared sample in the T-I series is shown in Fig. 6, as an example of a transmission electron photomicrograph. Very fine particles (about 5 nm) of the initial anatase grow to 10 ~ 30 nm of brookite after grinding for 7 h and to 20 ~ 50 nm after grinding for 40 h, of which about 80% are rutile and about 20% remain as brookite. After 78 h, most of the particles are composed of rutile and reach 50 ~ 150 nm in size, in which a little amount of amorphous TiO_2 may be contained. On further grinding the particle size remains unchanged and the amount of amorphous TiO_2 increases. The existence of the amorphous phase is evident by increasing the background in the X-ray powder patterns. A wide variation of particle size observed in the ground samples might result from a heterogeneous grinding in a mortar. From the dark field image under the electron microscope, it is clear that these particles are not aggregates of the small crystals, but the single domain of the crystals. The change of the particle size observed from X-ray line broadening against the grinding time is shown in Fig. 7. The particle size of TiO_2 increased by grinding stepwise. The initial rapid increase from 5 nm to 10 ~ 30 nm is accompanied by the trans-

TABLE II Heating results of brookite* in air and under hydrothermal condition

T (° C)	P (kg cm^{-2})	Time (h)	Crystallite size (nm)		f_{rutile}
			Brookite	Rutile	
500	in air	1	15.7	n.d.	0.03
500	in air	2	15.0	n.d.	0.07
500	in air	20	20.0	36.0	0.13
500	in air	50	28.0	43.0	0.22
600	in air	1	28.0	31.0	0.25
600	in air	2	26.0	55.0	0.30
600	in air	5	30.0	65.0	0.59
600	in air	20	n.d.	100.0	0.92
200	300	20	18.0	none	–
200	300	70	14.0	none	–
300	300	20	18.0	n.d.	0.05
300	300	70	20.0	100.0	0.37

*Brookite used was synthesized by grinding the 300° C-heated anatase in T-I series for 6 h and had the crystallite size of about 14.5 nm.

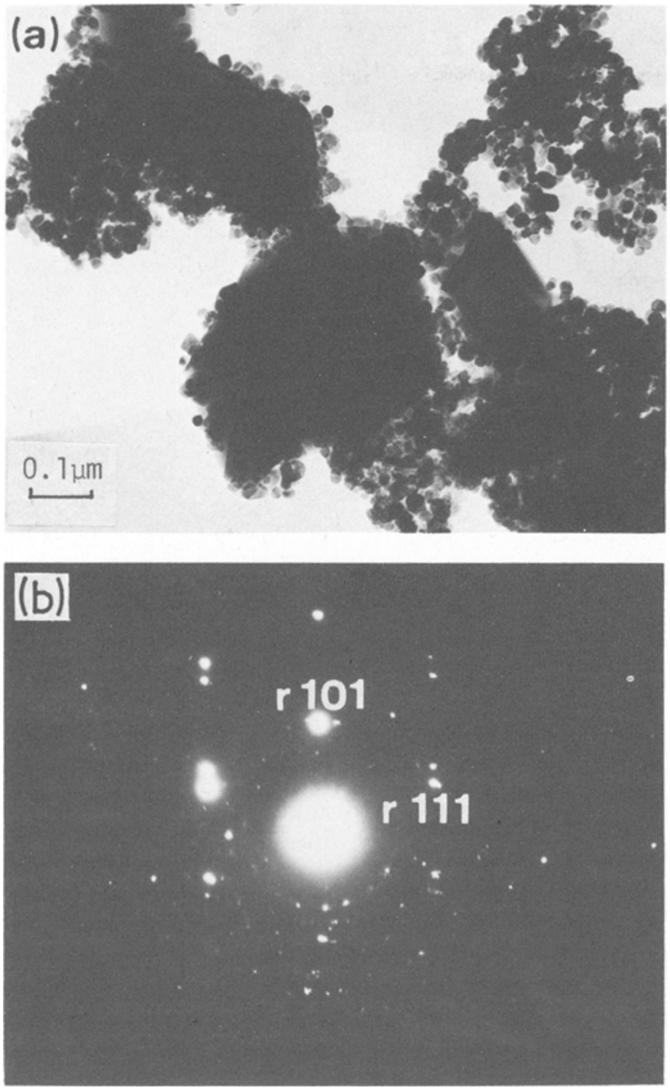
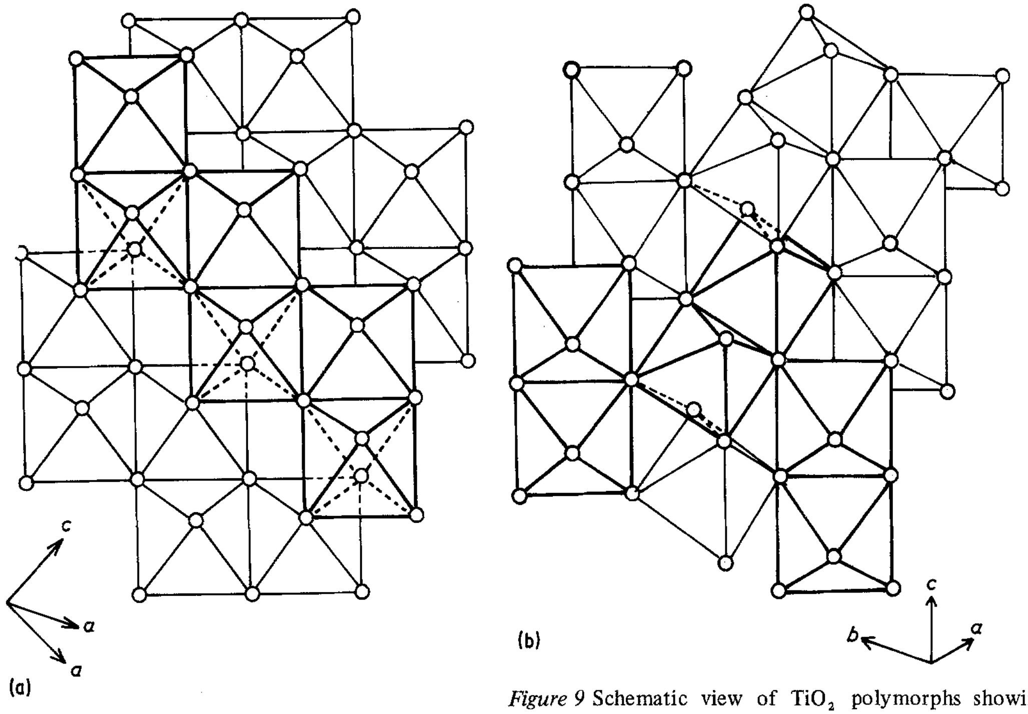


Figure 8 Electron photomicrographs of the sample ground for 6 h T-I anatase and heated at 300° C for 20 h under a hydrothermal pressure of 300 kg cm^{-2}. Electron diffraction spots show that the fine crystal of brookite coexists with the large single crystals of rutile.

formation of anatase to brookite, and the second rather slow increase from 10 ~ 30 nm to 50 ~ 150 nm, being accompanied by the transformation of brookite to rutile. On the other hand, the crystallite size increases up to about 15 nm, then it was kept unchanged during the grinding. The discrepancy between the observed particle size and the X-ray crystallite size is found to increase with grinding.

Line broadening of X-ray diffraction profile of very small particles is composed of two components, i.e. effective crystallite size and effective lattice distortion. In order to separate them, many analytical methods have been proposed [8–10], in which appropriate multiple ordered diffraction lines have to be analysed. In the present case, however, most of the ground samples are a mixture of anatase and brookite, or brookite and rutile, and their X-ray peaks overlap and make it difficult to separate the respective peaks with good accuracy. Therefore the line broadening of the diffraction profiles is taken as an apparent crystallite size. The increasing discrepancy between observed particle size and X-ray crystallite size suggests that the lattice distortion increases with increasing the grinding time. The lattice distortion may be introduced by the misfit of the stacking layers of the growing particles, by the stress applied to the particles, and/or, by increasing the amount of amorphous phase with grinding.

Similar growth of the particles with grinding was observed on the 300° C-heated and 355° C-



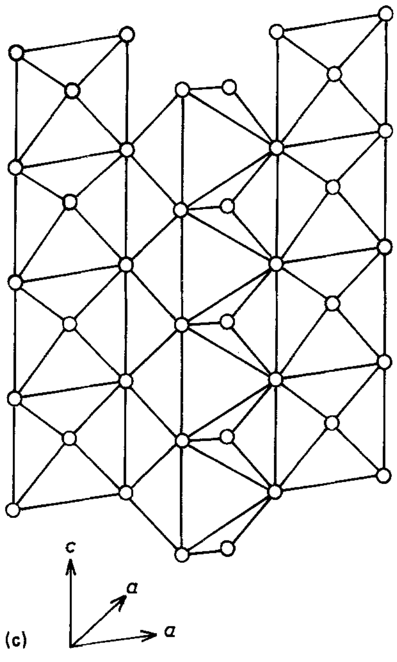


Figure 9 Schematic view of TiO_2 polymorphs showing with the array of TiO_6 octahedron for (a) anatase, (b) brookite, and (c) rutile.

heated samples in the T-I, -II and -III series. On the other hand, the anatase sample of T-IV (commercial sample), being 50 ~ 200 nm in size, showed a slight decrease to 50 ~ 100 nm after grinding for 40 h.

3.3. Mechanism of polymorphic transformation by grinding and stability of brookite

The results described above indicate that: 1. very fine particles of TiO_2 grow to larger particles by grinding, and 2. the intermediate phase of brookite seems to be stabilized when initial fine anatase crystals grow to a few tens nanometres and accumulate an appropriate lattice distortion, as shown in Fig. 7.

To examine the effect of particle size and lattice distortion on the stability of brookite, brookite synthesized by grinding was heated in air and under hydrothermal pressure. Heating results are shown in Table II. On heating, rutile was grown faster than brookite, and under hydrothermal conditions this tendency was quite significant. The crystallite size of the heat-treated samples was comparable with the observed particle size. A transmission electron photomicrograph of the sample heated at 300° C for 20 h under 300 kg cm^{-2} is shown in Fig. 8, with its electron diffraction pattern. Large single crystals of rutile are found to coexist with fine crystals of brookite. It is suggested that crystal growth by heat treatment allowed the lattice distortion to diminish and the metastable brookite to transform to a stable rutile phase.

TABLE III X-ray powder diffraction data of brookite (Cu$K\alpha_1$ radiation with nickel filter)

d_{obs} (nm)	d_{calc} (nm)	I/I_1	hkl
0.3505	0.3503	100	120
0.3470	0.3461	70	111
0.2895	0.2900	66	121
0.2728	0.2724	3	200
0.2475	0.2475	15	012
0.2407	0.2407	11	201
0.2372	0.2363	2	131
–	0.2340	–	220
0.2329	0.2328	1	211
0.2293	0.2287	< 1	040
0.2257	0.2253	9	112
0.2241	0.2241	7	022
0.2129	0.2130	15	221
0.1966	0.1965	10	032
0.1891	0.1889	21	231
0.1849	0.1849	11	132
0.1830	0.1832	< 1	212
0.1756	0.1752	2	240
0.1687	0.1688	17	320
0.1659	0.1658	26	241
0.1648	0.1644	2	151
0.1607	0.1609	10	113
0.1592	0.1594	2	232
0.1538	0.1539	5	123
0.1493	0.1491	7	052

In addition to adsorbed water, several kinds of adsorbants were detected from the IR spectra. Alcoholic species were adsorbed on the as-prepared sample and a trace of them remained even after heating at 300° C in the T-I series. In the T-II series, NH^{4+} was adsorbed on the as-prepared sample and desorbed after heating at 300° C, but in the T-III series, SO$_4^{2+}$ remained even after heating at 355° C. Therefore, the presence of adsorbants or the difference in starting materials did not seem to play a substantial role in the kinetics of the transformation from anatase to rutile through brookite, though a small amount of water may, enhance the nucleation and growth.

In Fig. 9, the structure of anatase, brookite and rutile are schematically illustrated by representing the TiO$_6$ octahedra. It is clearly visible in this figure that the transformation from anatase to brookite is accomplished by the rotation and the displacement of octahedra, but that from brookite to rutile it is accomplished only by the displacement of octahedra. The fact that only under the coexistence of foreign elements, such as sodium, brookite has been synthesized, suggests that brookite is stabilized by an appropriate lattice distortion. This distortion may be pinned up by a high surface energy and released by decreasing the surface energy, that is, with the crystal growth of brookite. The direct transformation of anatase to rutile by grinding [6, 7] probably is an apparent phenomenon due to the simultaneous occurrence of both the transformation of anatase to brookite and of brookite to rutile.

3.4. Crystallographic data of brookite

On the single phase of brookite, which was obtained by grinding the as-prepared anatase of the T-I series, and by subsequent heating at 400° C for 5 h, the lattice constants were determined from 012, 201 and 302 diffractions referred to the internal standard of silicon. The data obtained are as follows: $a_0 = 0.5447 \pm 0.0005$ nm, $b_0 = 0.9150 \pm 0.0005$ nm, $c_0 = 0.5141 \pm 0.0005$ nm, and $D_x = 4.14\,\text{g cm}^{-3}$.

The lattice constants presented are in agreement with the values reported for natural brookite ($a_0 = 0.5447 \sim 0.5456$ nm, $b_0 = 0.9154 \sim 0.9182$ nm, $c_0 = 0.5138 \sim 0.5163$ nm, and $D_x = 4.12 \sim 4.13\,\text{g cm}^{-3}$) [11]. X-ray powder data up to 052 diffraction are presented in Table III.

Acknowledgements

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