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The Crystallization of Anatase and the Conversion to Bronze-Type TiO_2 under Hydrothermal Conditions

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When the anatase form of TiO_2 was heated at a constant rate of 6°C/min to 450°C it crystallized from hydrated amorphous TiO_2 gel at 170°C in pure water or at <150°C in NaOH solutions. The uptake of Na^+ ions into crystallized anatase affected the reactions subsequent to this initial crystallization while only anatase crystals continued to grow with increasing temperature in pure water. Immediately after the nearly amorphous second stage at 325°C, conversion from colloidal anatase particles to square sheet-shaped bronze-type TiO_2 crystals began at 350°C and was complete at 425°C in 0.5 *M* NaOH. This conversion was considered to proceed via crystallographic shear rather than via dissolution and precipitation since this also happened with thermal treatment to 700°C in air.

I. Introduction

The kinetics and mechanism of the solid-state transformation anatase → rutile have been well studied (*1–4*). However, less attention has been paid to the relationships existing between the two polymorphs in hydrothermal aqueous conditions. The factors governing hydrothermal crystallization from amorphous reactant and subsequent transformation have been often discussed from the viewpoint of the crystallographic connection between reactant and products (*5, 6*) or the chemical properties of ionic species in aqueous solution (*7*). Matthews (*5*) investigated the hydrothermal crystallization of TiO_2 gel at 300 to 600°C at 1 kb pressure and showed that the transformation: amorphous reactant → anatase → rutile, is accelerated by increasing temperature and decreasing solution pH. It was presumed that anatase formation occurred through the gradual structural rearrangement of the Ti–O in the amorphous reactant, with accompanying dehydration and conversion to rutile through dissolution and precipitation. Danchille *et al.* (*6*) hydrothermally crystallized TiO_2 gel, obtaining metastable anatase at lower temperatures and rutile at higher temperatures. The crystallization of TiO_2 gel under hydrothermal conditions leads to brookite in the presence of Na^+ ions. As for natural minerals, rutile formation is facilitated by the presence of Fe, whereas its absence leads to anatase formation (*8*). Izumi (*7*) showed that lower temperatures and higher concentrations of acid favored anatase formation by considering the chemical behavior of Ti(IV) complexes involved in its primary nucleation. The crystallization process in such heterogeneous phases is very compli-

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cated and is not fully understood, but it is very important to know the interactions between the solid and the liquid phases during crystallization. Recently Nishizawa *et al.* (*9*) observed the crystallization process of ZrO_2 during constant-rate heating of hydrated amorphous ZrO_2 gel up to 350°C in NaOH aqueous solution. Metastable cubic ZrO_2 with very small crystallite size crystallized at about 120°C with the uptake of Na^+ ions. These fine cubic ZrO_2 particles abruptly changed into needle-like monoclinic ZrO_2 single crystals at 300°C with the exclusion of Na^+ ions from solid phase. This conversion of colloidal particles to single crystals was very similar to the formation of films of mica by gradually extracting water from bentonite sols of very small and uniform particle size (*10*). The characteristic of hydrothermal crystallization by constant-rate heating and rapid quenching is abrupt morphological changes and uptake (or liberation) of ions. In the present study, the hydrothermal crystallization of TiO_2 which seems to be easily affected by surface conditions and impurities was investigated by using constant-rate heating and rapid quenching.

II. Experimental

Hydrated amorphous TiO_2 gel (TiO_2 gel) was prepared by hydrolysis of $TiCl_4$ with 28% NH_3 aqueous solution at about pH 7. The resulting white gel was washed several times with pure water by decantation until Cl^- and NH_4^+ could not be detected. The TiO_2 gel was then dried at 40°C under vacuum.

Hydrothermal experiments were carried out according to previous work (*9*). The pulverized TiO_2 gel was placed in a microautoclave with 5 ml of pure water or NaOH aqueous solutions of various concentrations and heated up to 425°C at the autogeneous pressure of the autoclave (6 and 100 MPa at 250 and 425°C, respectively). The heating-rate was controlled at 6°C/min from 50 to 425°C. After the desired temperature was reached, the autoclave was quenched rapidly to room temperature by immersing it in ice water. The powder products and the solution in the reaction vessel were completely recovered. They were filtered, washed several times with distilled water, and oven-dried at 60°C. Crystalline phases were detected in the products by X-ray powder diffraction (XRD) using Ni-filtered Cu$K\alpha$ radiation. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out on a TG–DTA apparatus. Infrared absorption (ir) spectra were recorded using KBr pellets on a Shimazu IR-430 spectrophotometer. The crystallographic morphology was observed with a JEM-100U transmission electron microscope (TEM) with accelerating voltages of 80 and 100 kV. Small drops of very dilute suspensions were air-dried on a collodion film on a Cu-mesh screen for TEM examination. The composition ratios of Na to Ti in powder samples were determined semiquantitatively by scanning the X-ray fluorescence spectra JXA-5A in the $K\alpha$ region of Na and Ti with a Benth–Albee correction.

III. Results and Discussion

1. X-Ray Powder Diffraction

The XRD patterns for the samples hydrothermally treated in pure water showed gradual crystallization of anatase from 170°C but the transformation to rutile did not occur up to 425°C. On the other hand, three successive stages of crystallization were recognized from differences in the XRD patterns during constant-rate heating TiO_2 gel in 0.5 *M* NaOH up to 425°C (Fig. 1). The first stage was crystallization of anatase which began at lower temperature with increasing concentration of NaOH and was complete below 150°C in 0.5 *M* NaOH.

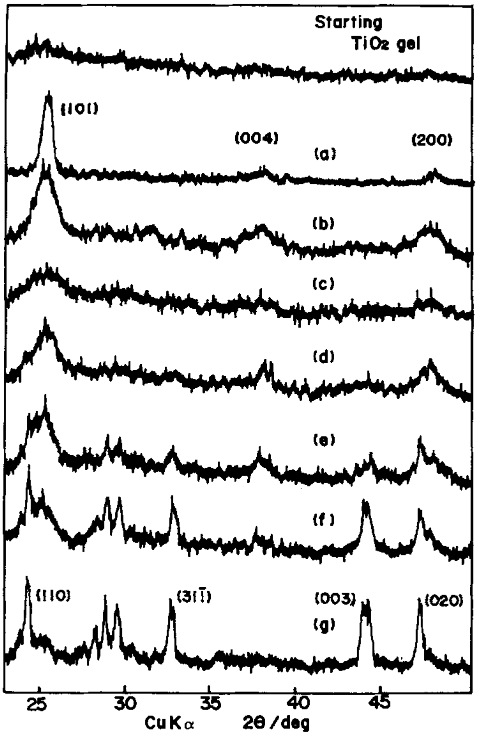

FIG. 1. X-Ray powder diffraction patterns (Cu$K\alpha$ radiation) of samples hydrothermally treated (a) in pure water up to 400°C (single phase of anatase) and in 0.5 *M* NaOH up to: (b) 300°C; (c) 325°C; (d) 350°C; (e) 375°C; (f) 400°C; (g) 425°C (single phase of $TiO_2(B)$).

The effective crystallite size of anatase, calculated from the broadening of the (101) diffraction line, decreased with increasing concentration of NaOH but remained almost unchanged between 150 and 300°C. Subsequent to the initial crystallization, the XRD pattern abruptly changed at 325°C and showed only a very broad (101) line which was comparable to that of the starting gel. In the third stage, the XRD intensity of anatase was restored at 350°C but became weaker at higher temperature. Additional sharp peaks gradually appeared, which were related to peaks of bronze-type compound. This bronze-type compound with blue–black color, obtained at 425°C as single phase, had lattice constants: a = 1.218 nm, b = 0.382 nm, c = 0.646 nm, β = 107°, which nearly agreed with that of a sodium titanium bronze prepared by the reduction in hydrogen of $Na_2Ti_3O_7$ at 950°C; a = 1.2146 nm, b = 0.3862 nm, c = 0.6451 nm, β = 106.85° (*11*). The concentration of NaOH apparently affected the progress of these three stages of crystallization. No trace of bronze-type TiO_2 ($TiO_2(B)$) appeared even at 425°C in 0.2 *M* NaOH. At higher concentrations such as 1 *M* NaOH, single phase of $TiO_2(B)$ was already obtained at 400°C. But above 2 *M* NaOH solutions neither crystallization of anatase nor conversion to $TiO_2(B)$ occurred and two-layered titanates could be detected by their characteristic X-ray spacing with reflections of 0.858 and 1.004 nm. Crystallization process in 2 *M* NaOH solution contained two successive stages. The first stage was crystallization of layered titanate with reflection of 0.858 nm at 325°C. The second stage was expansion of interlayer distance to 1.004 nm without change of the host layers which may be due to accommodation of H_3O^+ in the interlayer space. Actually the uptake of Na^+ ions was found to occur with increasing temperature or concentration of NaOH solution from the elemental analysis data of the bulk powder samples. The composition ratio of Na to Ti in these layered titanates always exceeded 0.4. On the other hand, Na/Ti ratio in anatase powders obtained at 300 and 325°C in 0.5 *M* NaOH were in the range of 0.18 to 0.186. The Na/Ti ratio in the third stage from 350 to 425°C were in the range of 0.23 to 0.27. The conversion of anatase to $TiO_2(B)$ was considered to depend on Na content since Na/Ti ratio in the powder samples containing $TiO_2(B)$ always exceeded 0.20. The schematic crystal structure of a sodium titanium bronze of composition Na_xTiO_2 (*11*) with that of anatase for comparison is shown in Fig. 2. The structure consists of an extended network of TiO_6 octahedra joined at edges or corners. Each sodium position is at the center of a group of four octahedra-

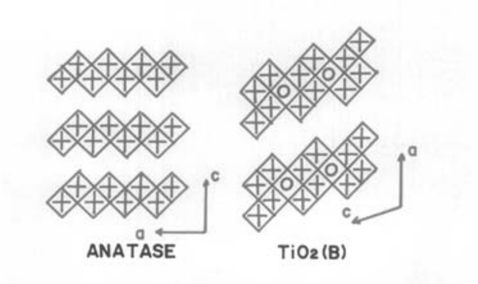

FIG. 2. Crystal structure of anatase and $TiO_2(B)$ seen from the direction of the *b*-axis. The squares are Ti–O octahedra and the open circles represent sodium ions.

sharing corners. The composition limits have not been established experimentally but on space-group requirements would be in the range $0 \leqq Na/Ti \leqq 0.25$. All of the sodium titanium bronze prepared in previous works (*11*, *12*) had the composition near $Na_{0.2}TiO_2$. The present results satisfactorily corresponded to this composition limit. $TiO_2(B)$ obtained is possibly stabilized by the presence of sodium ions.

2. *Electron Microscopy*

TEM observation showed that the hydrothermal treatment in pure water caused only grain growth of anatase and the grain size reached 50 to 100 nm at 425°C. In 0.5 *M* NaOH, the three stages recognized by the XRD patterns corresponded to the morphological changes as seen in Fig. 3. In the first stage, the structures were mostly composed of individual small crystals (Fig. 3a) but at 300°C the relatively well-defined conglomerate was detected (Fig. 3b). The SAD patterns showed sharp spots and faint rings, indicating that small crystals in the conglomerate may have strict crystallographic orientation with respect to each other. Both spots and rings were related to the diffraction spots of anatase. At the second stage, some flakes were observed (Fig. 3d) whose SAD patterns showed the same spots as in Fig. 3c and some extra spots. As the XRD pattern showed only amorphous lines near that of anatase (Fig. 1c), it is presumed that the flakes are not perfect single crystals of anatase but containing partial and short-range crystalline ordering. In the third stage, the square sheet-shaped crystals abruptly appeared at 350°C (Fig. 3f). The SAD pattern composed of the single-crystal diffraction spots typical of $TiO_2(B)$ showed that these crystals were oriented with the basal (001) planes. The residual anatase particles existed as adhering to the platy $TiO_2(B)$ crystals or as aggregates (Fig. 3h). The aggregates were converted to the platy crystals by increasing the temperature and simultaneously the platy crystals tended to tear along the *b*-axis and resulted in bundles of fibrous units at 425°C (Fig. 3i).

3. *Infrared Spectra*

The starting gel has intense bands at 3150 and 1400 cm^{-1} besides intense and broad bands at 3400 and 1635 cm^{-1} due to OH stretching and H_2O bending, respectively. These bands at 3150 and 1400 cm^{-1} are presumably related to NH_4^+ ions adsorbed on the surface of TiO_2 gel (*13*) and disappeared by heating in pure water up to 400°C (Fig. 4b). These bands disappeared also by heating in NaOH but a broad band at 1330 cm^{-1} and very broad shoulders at longer wavelength side appeared (Fig. 4). The intensities of the band and shoulders apparently were correspond to the formation of anatase containing Na^+ ions (Fig. 1) and gradually decreased with the conversion of anatase to $TiO_2(B)$. The shoulders may be due to OH vibration with hydrogen bonds by which the fine particles of anatase are gathered as seen in Fig. 3h. The lattice-deformation absorption bands between 350 and 1000 cm^{-1} were basically the same during the overall crystallization process except for the appearance of three distinct bands at 905, 525, and 460 cm^{-1} in the third stage. These three bands were characteristic of $TiO_2(B)$ and were presumed to be due to Ti–OH stretching, Ti–O stretching, and bending of TiO_6, respectively (*14–16*).

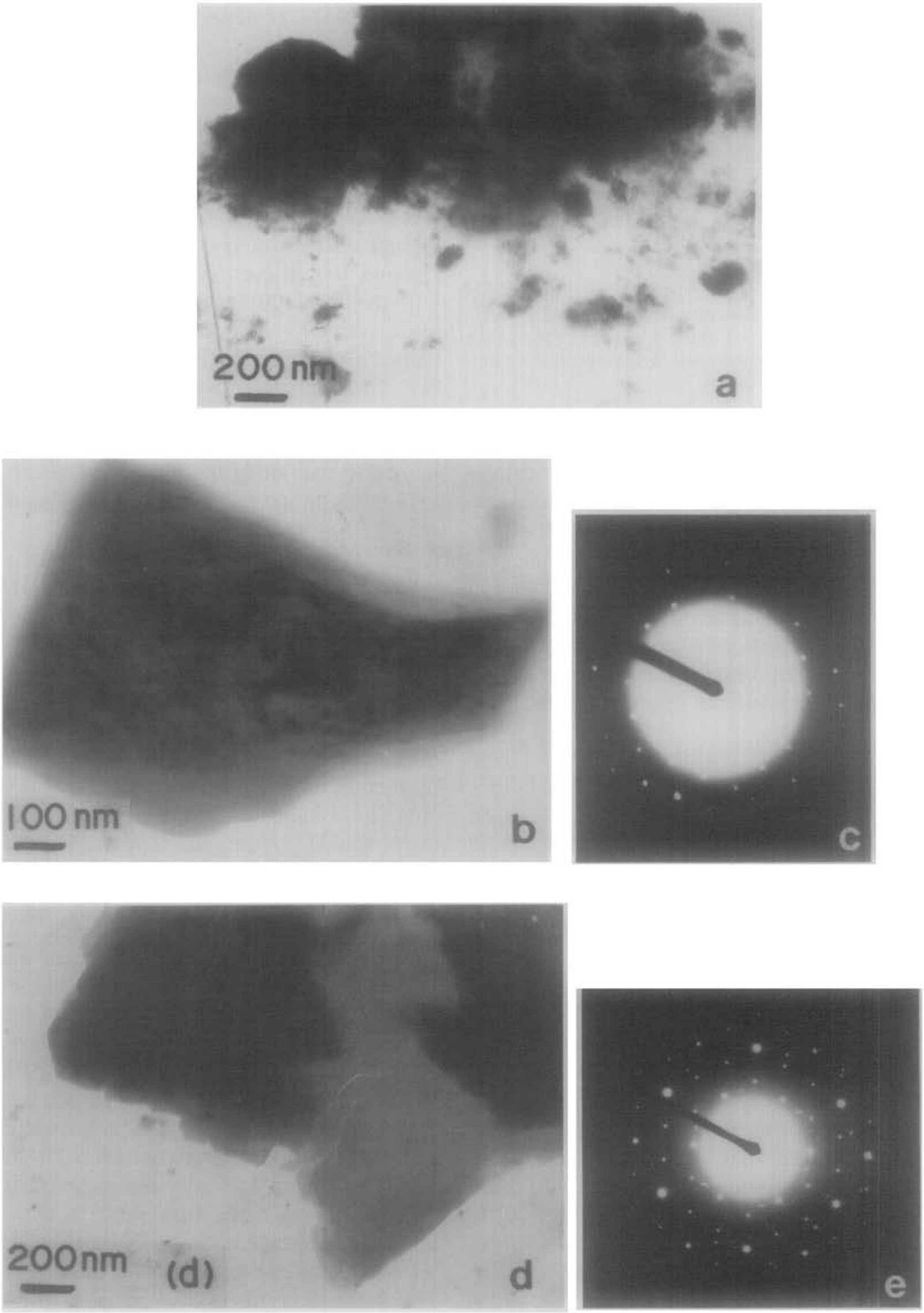

FIG. 3. TEM images and SAD patterns of samples hydrothermally treated in 0.5 *M* NaOH up to: (a)(b)(c) 300°C; (d)(e) 325°C; (f)(g) 350°C; (h) 400°C; (i) 425°C.

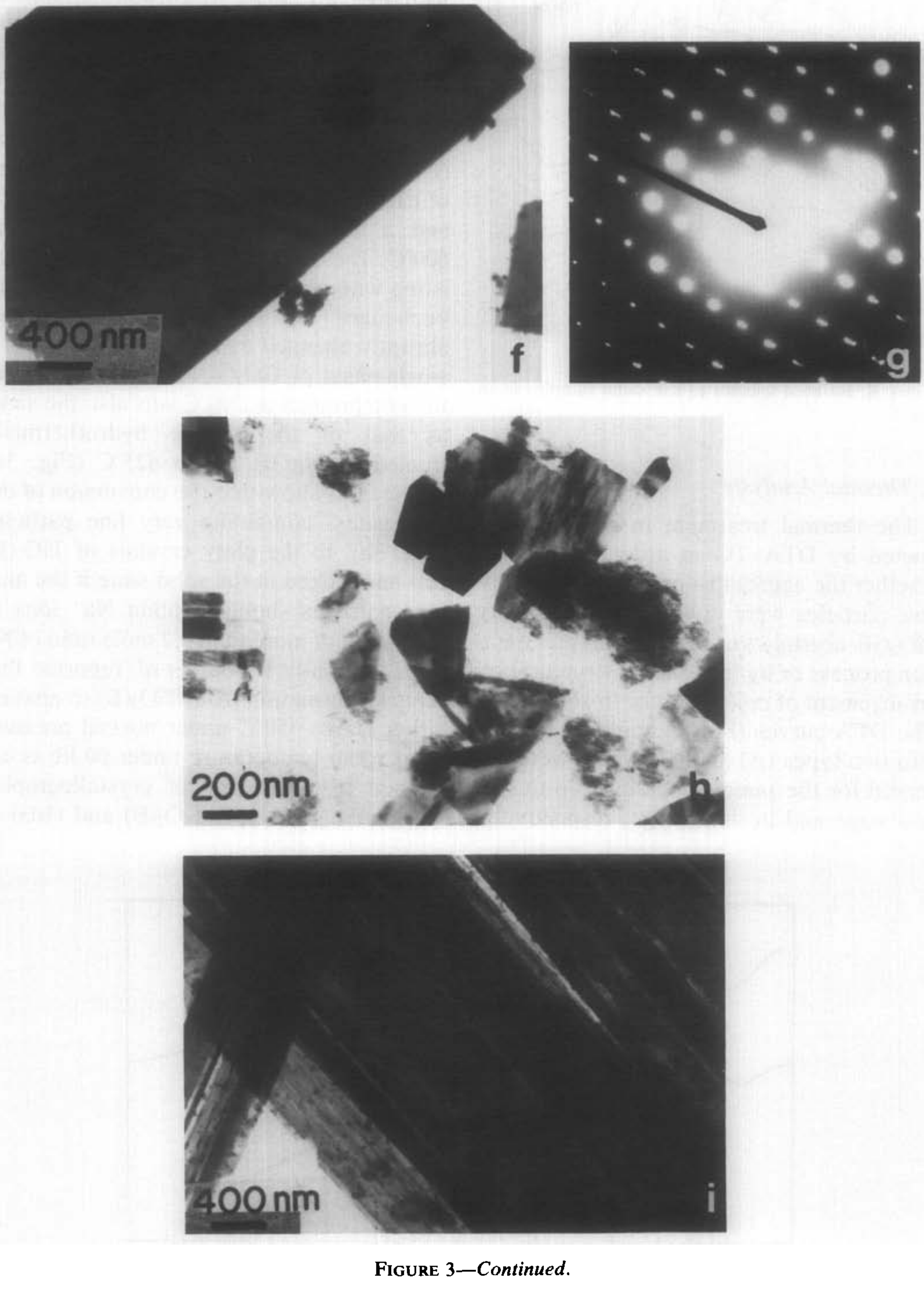

FIGURE 3—*Continued.*

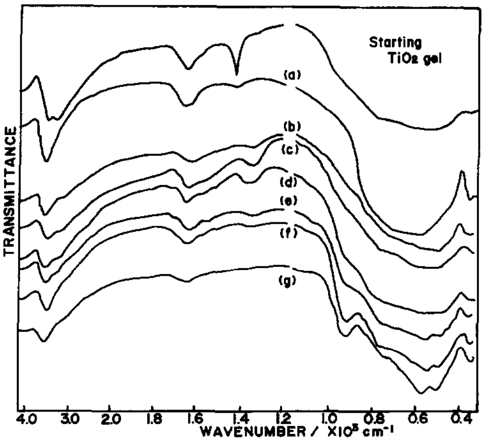

FIG. 4. Infrared spectra of the same samples as in Fig. 1.

4. *Thermal Analysis*

The thermal treatment in air was conducted by DTA–TG in order to examine whether the aggregates or the residual anatase particles were converted to the platy $TiO_2(B)$ crystals via dissolution–precipitation process or by the gradual structural rearrangement of crystal lattice in solid state. The DTA curves (Fig. 5) could be divided into two types (A) and (B) which were observed for the samples obtained up to second stage and in third stage, respectively.

The curve (A) showed endothermic peak with loss of 15 to 20 wt% water between 20 and 200°C, and exothermic peaks at 660 and 720°C. Then the original anatase phase which was almost unchanged up to 600°C was converted to the rutile phase with trace of $Na_2Ti_5O_{11}$. On the other hand, the curve (B) showed an endothermic peak with loss of ca. 8 wt% water between 20 and 150°C, and a broad endothermic peak around 600°C. The original anatase particles, coexisting with platy crystals of TiO_2 (B), were unchanged up to 600°C but hereafter abruptly changed to $TiO_2(B)$, resulting in a single phase of $TiO_2(B)$. The morphology of the end product at 700°C was also the same as that of the sample hydrothermally treated in NaOH up to 425°C (Fig. 3i). These facts show that the conversion of the aggregates, containing very fine particles (Fig. 3h), to the platy crystals of $TiO_2(B)$ can be realized in the solid state if the anatase particles should contain Na^+ ions to the extent of more than 0.2 mole ratio of Na to Ti. Recently Brohan *et al.* reported that the transformation from $TiO_2(B)$ to anatase either above 550°C under normal pressure or at room temperature under 60 kb is explained by a process of crystallographic shear, along (201) in $TiO_2(B)$ and (103) in

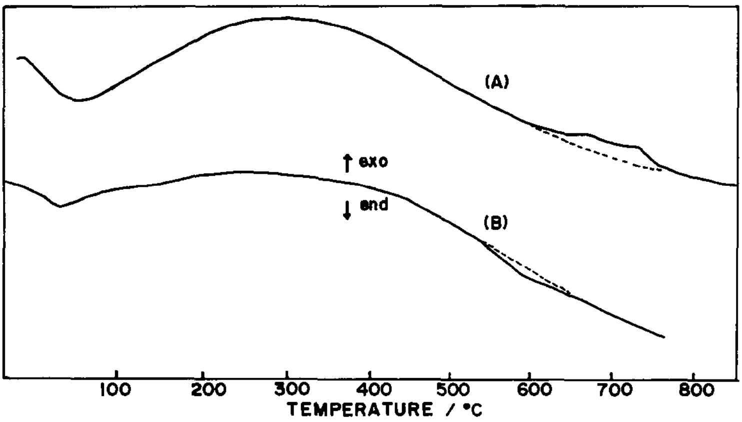

FIG. 5. DTA curves of samples hydrothermally treated in 0.5 *M* NaOH up to: (A) 325°C; (B) 350°C.

anatase shown in Fig. 2, with elimination of an equal number of anionic and cationic vacancies (*17*).

Summary

The hydrothermal crystallization of TiO_2 during constant-rate heating seems to be fully governed by (1) a series of epitaxial controls, in which products only form when sufficient surfaces of a structurally related precursor phase are available for nucleation, and (2) heterogeneous reaction containing the uptake of ions.

At first stage, crystallization of anatase occurred via collapse and structural rearrangement of the starting amorphous gel in pure water and in NaOH solutions $\leqq 1$ *M*. The uptake of Na^+ ions into anatase phase proceeded with increasing temperature in NaOH solutions. When Na/Ti ratio in anatase phase approached 0.2, complete destruction of crystal structure of anatase abruptly occurred and resulted in some flakes which contain partial and short-range crystalline ordering. These flakes were gradually changed into square sheet-shaped $TiO_2(B)$ crystals with increasing temperature from 350 to 425°C. This conversion was found to occur also in solid state because of the existence of the crystallographic connection between anatase and $TiO_2(B)$. The uptake of Na^+ ions into solid phase increased with increasing the concentration of NaOH solution. In NaOH solution $\leqq 2$ *M*, anatase and $TiO_2(B)$ were no longer detectable and only layered sodium titanates with Na/Ti ratio of above 0.4 crystallized.

Acknowledgments

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