The Polymorphic Crystallization of Titanium(IV) Oxide under Hydrothermal Conditions. II.⁽¹⁾ The Roles of Inorganic Anions in the Nucleation of Rutile and Anatase from Acid Solutions

Fujio Izumi

National Institute for Research in Inorganic Materials, Sakura-mura, Niihari-gun, Ibaraki 300-31

(Received December 7, 1977)

Titanic acid was treated with hydrochloric, nitric, sulfuric, and hydrofluoric acids at 350 °C and 49 MPa to give titanium(IV) oxide. With increasing acid concentration, its polymorphic forms changed from anatase to rutile in hydrochloric and nitric acids, but from anatase to rutile, then back to anatase in sulfuric and hydrofluoric acids. Rutile and anatase crystals were grown from 1.7—9.5 mol dm^{-3} hydrofluoric acid at 360—560 °C by the temperature-drop method. Lower temperatures and higher concentrations of the acid favored anatase formation. The mechanisms for crystallization of the two forms are discussed by considering the chemical behavior of titanium(IV) complexes involved in their primary nucleation.

Titanium(IV) oxide occurs naturally in three minerals: rutile (tetragonal), brookite (orthorhombic), and anatase (tetragonal). Rutile and anatase can readily be prepared in a large variety of ways;[2] they are produced industrially for use as important white pigments. By contrast, brookite has rarely been synthesized by conventional methods.[3,4] On the basis of thermochemical data, Navrotsky and Kleppa[5] established that anatase is thermodynamically always unstable with respect to rutile. Anatase formation should, therefore, be regarded as metastable crystallization. Many reports have been published on the kinetics and mechanism of the irreversible anatase-rutile phase transition.[6]

There is some information in the literature regarding the crystallization and chemical reactivities of the two polymorphs under hydrothermal conditions. Osborn[7] was the first to find that, in pure water, anatase was converted into rutile above *ca.* 600 °C, which is a good deal lower than the temperatures of the anatase-rutile transformation in air. Hydrothermal treatment of hydrous titanium(IV) oxide (titanic acid) with pure water yielded rutile and/or anatase; lower temperatures, and to a lesser extent lower pressures, favored the unstable formation of anatase.[3,4,8,9] Single crystals of rutile have been grown from sulfuric acid[10] and from solutions of several fluorides.[11,12] The previous work in this series[1] has shown that anatase crystals can be successfully grown from potassium fluoride–dipotassium hydrogenphosphate solutions at less than 600 °C.

Few papers report the polymorphism of titanium(IV) oxide in acid solutions, apart from the formation of hydrated titanium(IV) oxide of poor crystallinity at temperatures below 100 °C and at atmospheric pressure.[2] The present investigation deals chiefly with the hydrothermal synthesis of rutile and anatase in four different mineral acids. Attention will be paid to the roles of dissolved anions in the nucleation of the oxide, as in the preceding paper.[1] Information of this type is indispensable for an understanding of the mechanisms by which rutile and anatase are crystallized under hydrothermal conditions.

Experimental

Materials. Titanium(IV) ethoxide obtained commercially was used without further purification. The single crystal of rutile-type titanium(IV) oxide produced by the Verneuil technique was a highly-purified product from Nakazumi Crystal, Ltd. Rutile powder of 99.99% purity was obtained from the Kojundo Kagaku Kenkyusho. All the other reagents used were of a GR grade.

Preparation of Amorphous Titanic Acid. Titanium(IV) ethoxide was poured into a large excess of pure water. The white precipitate which formed was washed several times with pure water by decantation, filtered off with suction, and then dried over phosphorus(V) oxide at ambient temperature under reduced pressure. Thermogravimetry showed that this sample contained *ca.* 23 wt% of water, which was released almost completely at 420 °C in static air.

Hydrothermal Treatment of Titanic Acid with Acid Solutions. Titanic acid (30 mg) and mineralizer solutions (0.1 cm^3) were sealed into welded gold capsules 4 mm in diameter and 30 mm in effective length. Four capsules were placed together in a cold-seal pressure vessel (Nikkiso NK-H25-III) with a capacity of 27 cm^3 and an i.d. of 12.7 mm. Most of the unoccupied space above the capsules was filled with a hastelloy rod to minimize the temperature differences both between the interior and exterior of the pressure vessel and between the capsule ends.[13] The vessel was then allowed to heat to 350 °C in a tubular furnace arranged vertically. The reaction temperature was measured with an external chromel-alumel thermocouple. The pressures generated within the capsules were balanced by water pumped into the pressure vessel and measured with a Bourdon gauge.

Recrystallization of Titanium(IV) Oxide in Fluoride Solutions by Means of a Double-capsule Technique. Small pieces (0.1—4 mm in size) of broken single crystals of rutile (Ru-I) and rutile powder (Ru-II) were used as starting materials. Either Ru-I (0.15 g) or Ru-II (0.1 g) was contained in a gold capsule 4 mm in diameter and 10 mm long, with a small hole. This nutrient capsule was fixed at one end of a larger gold capsule 5 mm in diameter and 60 mm in effective length. After 0.5 cm^3 of a mineralizer solution had been added, the larger capsule was sealed by crimping and welding the other end shut. This double capsule was placed in a conventional cold-seal pressure vessel (Nikkiso NK-H25-I: capacity, 5.5 cm^3; i.d., 6.4 mm), which was set horizontally in a tubular furnace. The temperature gradient between the capsule ends varied from 40 to 90 °C. The solid in the nutrient capsule was dissolved and then transported to the other end, where titanium(IV) oxide recrystallized spontaneously from supersaturated solutions.

The phases which formed were identified by X-ray powder diffraction using nickel-filtered Cu $K\alpha$ radiation. The relative amounts of rutile and anatase in their mixtures were calculated from the X-ray intensities of the strongest reflections for rutile (d=0.3245 nm) and anatase (d=0.351 nm).[14] Acid solutions were standardized against a sodium hydroxide solution.

Chemical Analysis of Fluoride Ions Coprecipitated with Titanium(IV) Oxide. A sample ground into a powder was fused with about 2.5 g of potassium sodium carbonate in a platinum crucible at 900 °C. After the resulting cake had been transferred quantitatively to a distillation flask together with a small amount of water, 15 cm^3 of concentrated sulfuric acid was slowly added into the flask, which was cooled in an ice bath. The mixture was steam-distilled at 130—150 °C until *ca.* 80 cm^3 of distillate was collected. The total volume of the solution was then adjusted to 100 cm^3 with pure water. About 90% of fluorine could be recovered as hexafluorosilicic acid by following the above procedure. The fluoride ion concentration of the distillate was determined colorimetrically with Dotite Alfusone (lanthanum–alizarin complexone).[15]

Results

Titanic acid was treated isothermally with dilute acids of various concentrations as well as pure water for *ca.* 70 h at 350 °C and 49 MPa. Rutile and/or anatase were crystallized by the action of hydrochloric, nitric, sulfuric, and hydrofluoric acids on the amorphous reactant. Anatase was formed exclusively in pure water. These products were fully crystalline powders, white or yellow-tinged white except for those obtained by using 0.1—1.0 mol dm^{-3} hydrofluoric acid, in which bluish-gray powders formed. This exceptional coloration will later be discussed in some detail. An attempt to prepare titanium(IV) oxide in about 7.5 mol dm^{-3} phosphoric acid failed; only a highly insoluble, poorly crystallized phosphate of titanium(IV) was formed.

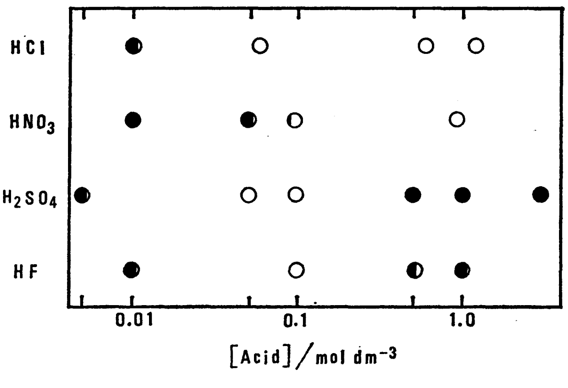


Fig. 1. Crystallization of rutile and anatase from titanic acid in four mineral acids at 350 °C and 49 MPa (t= 70 h). ○: Rutile, ●: anatase. Percentage of area of each circle shaded indicates percentage of anatase in the mixture.

Figure 1 shows the effects of the acid and its concentration on the relative amounts of rutile and anatase. With increasing acid concentration, the polymorphic forms of titanium(IV) oxide changed from anatase to rutile in hydrochloric acid and nitric acid, but from anatase to rutile, then to anatase again in sulfuric acid and hydrofluoric acid. The crystallization behavior of the oxide in the presence of hydrochloric acid is similar to that reported earlier by Matthews.[9] On the basis of experiments with only pure water, hydrochloric acid, and a sodium carbonate solution, he claimed that neutral, basic, and weakly acidic media were favorable for anatase formation, whereas more strongly acid environments resulted in the appearance of rutile. Judging from the conflicting results obtained by use of sulfuric acid and of hydrofluoric acid, his conclusion is highly questionable. The observations presented above support the idea that polymorphic crystallization of titanium(IV) oxide from aqueous solution is susceptible to the influence of not only the acid concentration but also the kind of acid.

Several representative specimens prepared hydrothermally were observed by scanning electron microscopy

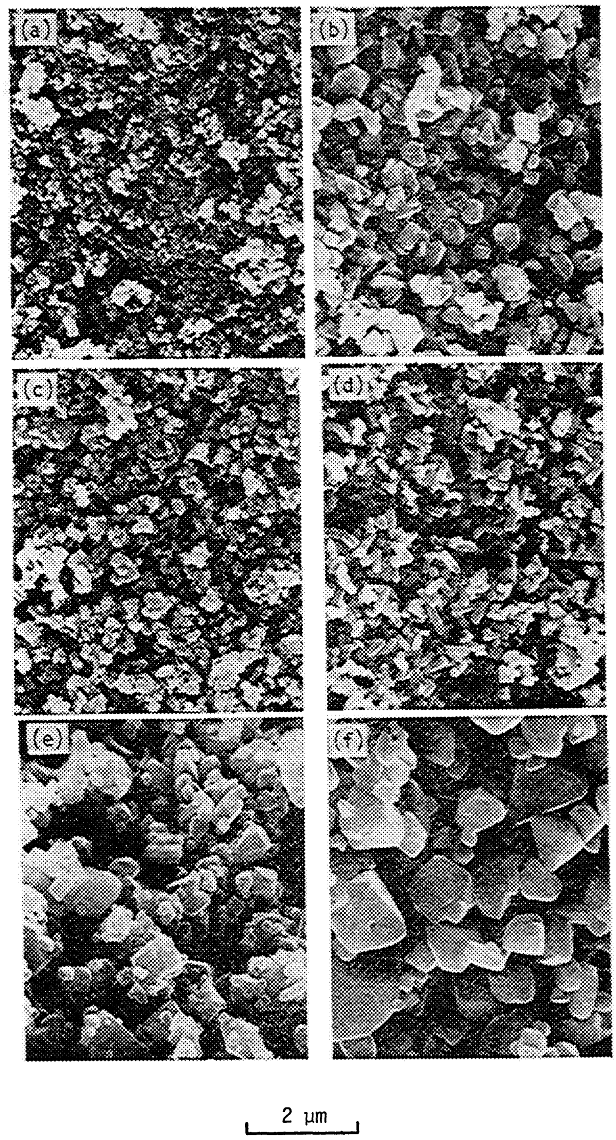


Fig. 2. Scanning electron micrographs of rutile and anatase prepared from titanic acid in dilute acids at 350 °C and 49 MPa.

(a) Anatase, pure water; (b) rutile, 0.058 mol dm^{-3} HCl; (c) rutile, 0.92 mol dm^{-3} HNO_3; (d) rutile, 0.049 mol dm^{-3} H_2SO_4; (e) anatase, 1.0 mol dm^{-3} H_2SO_4; (f) rutile, 0.10 mol dm^{-3} HF.

(Fig. 2). In pure water, anatase occurred as aggregates of reasonably equidimensional crystallites of the order of 0.1 μm in diameter [Fig. 2(a)]. The formation of the finely dispersed product is evidently due to the very low solubilities of titanic acid and the resulting anatase in pure water.

As pointed out by Matthews,⁹⁾ the anatase must be crystallized *via* the gradual structural rearrangement of the reactant with liberation of water. Dehydration probably precedes the structural rearrangement in the same way as in the crystallization of anatase by thermal dehydration of titanic acid in air. Titanic acid, which was amorphous to X rays, is assumed to have already a short-range order analogous in structure to anatase. Hence, anatase nucleation is readily induced in the reactive starting material and followed by a series of epitaxial growth processes. Practically the same reaction scheme as proposed above holds also for anatase formation in acids with concentrations lower than 50 mol m^{-3} (see Fig. 1).

By contrast, rutile and anatase grew into relatively large particles with characteristic crystal habits in acids of concentrations higher than 50 mol m^{-3} [Fig. 2 (b) to (f)]. The gross morphologies of their grains were quite different from those of the titanic acid grains from which they were obtained. Rutile crystallized in columns 0.07—0.2 μm in diameter from 49 mol m^{-3} sulfuric acid [Fig. 2(d)]. All the other products in acid solutions consisted of polygonal microcrystals with smooth faces. These observations are compatible with the dissolution and precipitation mechanism described below.

Amorphous titanic acid has much higher free energies of formation than has any polymorph of titanium(IV) oxide, with the result that mineralizer solutions equilibrated with titanic acid become supersaturated with respect to both rutile and anatase. Subsequently, rutile or anatase nucleates spontaneously and grows by transfer of material from titanic acid. Rutile growth at the expense of fully crystalline anatase seems to proceed to a very small extent, if at all, at a temperature as low as 350 °C.

Titanium(IV) oxide was more soluble in hydrofluoric acid than in any of the other mineral acids at relatively low temperatures, making it possible to grow crystals of rutile and anatase from the acid by the temperature-drop method.¹⁶⁾ It was transported from the cold to the hot zone (retrograde solubility) in 1.7—9.5 mol dm^{-3} hydrofluoric acid over the temperature range 320 to 600 °C under a constant pressure of 49 MPa. For this reason, its dissolution in hydrofluoric acid must be exothermic, at least under the above conditions.¹⁷⁾ Hydrofluoric acid enabled the oxide to be transported much more rapidly than did alkali fluoride solutions.¹,¹¹,¹²⁾ Unless otherwise stated, the reaction temperatures described below refer to those at the hot (crystallization) zone. Titanium(IV) compounds where fluorine is a dominant element were never formed, even in hydrofluoric acid at a concentration as high as 9.5 mol dm^{-3}, in disagreement with earlier work by Kuznetsov and Panteleev.¹⁸⁾

Figure 3 gives the results of mole fraction of anatase in titanium(IV) oxide formed in the temperature range 360—560 °C *versus* concentration of hydrofluoric acid.

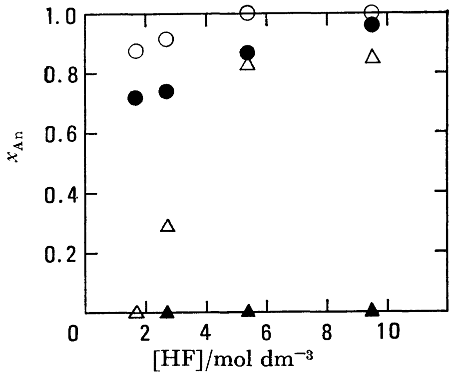


Fig. 3. Mole fraction of anatase in titanium(IV) oxide crystallized from hydrofluoric acid, x_{An}, *vs.* concentration of hydrofluoric acid. Nutrient, Ru-I; P=49 MPa; t=5—11 d. $x_{An}=w_{An}/(w_{Rn}+w_{An})$, where w_{Ru} and w_{An} are, respectively, the weights of rutile and anatase in the product. ○: 360 °C, ●: 400 °C, △: 480 °C, ▲: 560 °C.

As expected, higher concentrations of hydrofluoric acid and especially lower temperatures favored the precipitation of titanium(IV) oxide as anatase. Anatase was converted into rutile to a greater extent with rising reaction temperature; only rutile appeared at 560 °C or above. Anatase which was pure to X rays could be isolated at 360 °C from 5.4—9.5 mol dm^{-3} hydrofluoric acid.

Both rutile and anatase were obtained as almost opaque grains, blue or bluish black and less than 1 mm

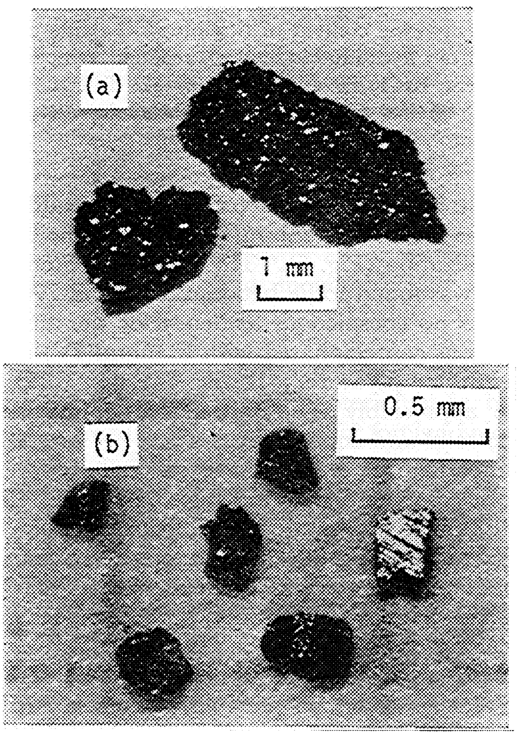


Fig. 4. Crystals of titanium(IV) oxide grown from hydrofluoric acid.

(a) Aggregates of rutile crystals. [HF]=1.7 mol dm^{-3}; θ=480 °C; t=258 h.

(b) Plate crystals of anatase. [HF]=9.5 mol dm^{-3}; θ=400 °C; t=139 h.

in size, or as their irregular aggregates (Fig. 4). Anatase was hardly distinguishable from rutile without the aid of X-ray analysis. Anatase grew at such high supersaturations that most crystals were anhedral and had rather rough surfaces. It was also found as subhedral plate crystals [Fig. 4(b)]. The Laue in conjunction with the oscillation methods showed these single-domain crystals to be tabular on {001}. The anatase which was prepared in 9.5 mol dm^{-3} hydrofluoric acid at 400 °C was submitted to high-temperature X-ray diffraction. When heated in air at a temperature-scan rate of 6.5 °C min^{-1}, it began to change into rutile at 970 °C and disappeared by 1210 °C.

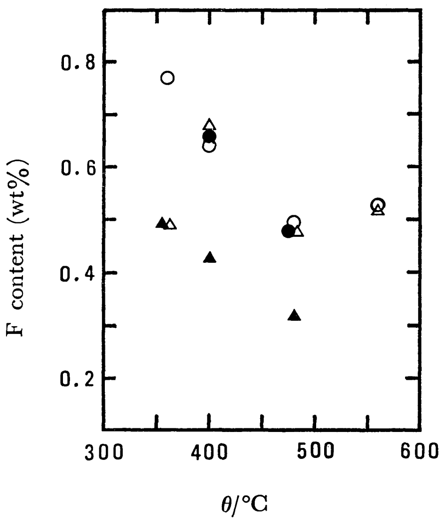


Fig. 5. Fluorine content of titanium(IV) oxide crystallized from hydrofluoric acid *vs.* reaction temperature. Nutrient, Ru-I; P=49 MPa; t=5—11 d. ○: 9.5 mol dm^{-3}, ●: 5.4 mol dm^{-3}, △: 2.7 mol dm^{-3}, ▲: 1.7 mol dm^{-3}.

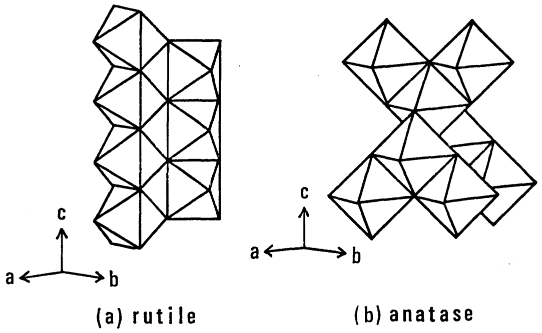
Fluoride ions in parent solutions were readily taken up into the lattice of titanium(IV) oxide in the course of its crystallization (Fig. 5). The fluorine content of the products was found to lie between 3200 and 7700 ppm. There was no conspicuous tendency for the amount of fluoride ions coprecipitated with titanium(IV) oxide to vary with temperature. Rutile did not differ from anatase appreciably in the partition of fluoride ions between solid and aqueous phases.

Chamberland *et al.*[19,20] have successfully prepared the black compound titanium fluoride oxide, TiFO, in which titanium is formally in a valence state of +3. It is isostructural with rutile and characterized by its n-type semiconducting properties. Furthermore, they have established that, for the titanium fluoride oxides system, nonstoichiometry can easily be achieved to form a series of solid solutions with the general formula TiF_xO_{2-x} ($0<x<1$). As described previously, anatase and rutile were crystallized as bluish-gray powders only by the action of dilute hydrofluoric acid on titanic acid. The almost colorless, transparent crystals of rutile used as a starting material turned blue during hydrothermal reactions in hydrofluoric acid. These blue crystals of rutile contained about 330 ppm of fluorine and showed an ESR spectrum characteristic of the presence of titanium(III) ions at liquid helium temperature.

All these facts provide convincing evidence that titanium(IV) oxide prepared in hydrofluoric acid owes its intense color not to the nonstoichiometry, which is expressed as TiO_{2-x} ($x<8\times10^{-3}$),[11,21] but to point defects arising from the non-equilibrium incorporation of fluoride ions into the growing crystals of rutile and anatase. In fact, crystals of titanium(IV) oxide prepared in various solutions containing fluoride ions (see Table 1) became darker with increasing fluorine content. Fluoride ions presumably substitute oxide ions with similar size in a random way to form $[Ti(O,F)_6]$ octahedra; this substitution causes equal numbers of titanium(IV) ions to be replaced by titanium(III) ions to maintain electrical neutrality. Reduction of quadrivalent titanium to trivalent titanium in the absence of any powerful reducing agent is not surprising because reducing atmospheres usually predominate under hydrothermal conditions.

Discussion

The factors governing hydrothermal crystallization of rutile and anatase should be considered in the light of both the crystal structures of the two modifications and the chemical properties of titanium(IV) species in aqueous solution. Figure 6 illustrates the structures of rutile and anatase. In both crystal lattices, every titanium(IV) ion is surrounded by six oxide ions arranged octahedrally (slightly distorted), and each oxide ion by three titanium(IV) ions. Rutile consists of $[TiO_6]$ octahedra linked by sharing two opposite edges to form chains parallel to the c-axis. In less dense anatase, each $[TiO_6]$ octahedron shares edges with four adjacent $[TiO_6]$ octahedra, which form spiral chains round each fourfold axis. It follows from the above structural consideration that the formation of linear polynuclear species containing bidentate oxo or hydroxo bridges between titanium(IV) ions will give rise to rutile nucleation, while nonlinear ones must pass into anatase nuclei.



(a) rutile (b) anatase

Fig. 6. Structures of rutile and anatase drawn as arrays of regular octahedra joined by common corners and edges.

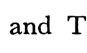
We shall, for the moment, confine ourselves to speculating about the nucleation process in solutions containing fluoride ions. Table 1 summarizes the results of a series of experiments on crystallization of titanium(IV) oxide from fluoride solutions by the temperature-drop

TABLE 1. HYDROTHERMAL CRYSTALLIZATION OF TITANIUM(IV) OXIDE FROM VARIOUS SOLUTIONS CONTAINING FLUORIDE IONS

Run No.	Nutrient[a]	Mineralizer solution	θ_1[b] / °C	θ_2[b] / °C	P / MPa	t / h	w[c] / mg	Products[d]	F content (wt%)
1[e]	Ru-II	1.42 mol/kg NH_4F	$\theta_1 \rightarrow$	480	49	95		Ru	
2[e]	Ru-II	1.45 mol/kg NH_4F 0.16 mol/kg $(NH_4)_2HPO_4$	$\theta_1 \rightarrow$	480	49	89		An>U.P.	
3	Ru-I	2.0 mol/dm^3 NH_4F	430→	480	49	162	136	Ru(52%) An(48%)	1.4
4	Ru-II	2.0 mol/dm^3 NH_4F	400→	480	49	190	89	Ru	
5	Ru-I	2.0 mol/dm^3 KF	454←	500	49	184	9	Ru	
6	Ru-I	2.0 mol/dm^3 KF	530←	600	78	163	59	Ru	0.21
7[e]	Ru-I	0.91 mol/kg KF	529←	600	98	353	61	Ru	0.14
8[e]	Ru-I	0.93 mol/kg KF 0.155 mol/kg K_2HPO_4	546←	600	98	329	52	An[f]	0.032

a) Ru-I, small pieces of broken single crystals of rutile; Ru-II, rutile powder. b) θ_1, temperature of the cold zone; θ_2, temperature of the hot zone. Arrows show the direction of transport of titanium(IV) oxide. c) Weight of transported titanium(IV) oxide. d) Ru, rutile; An, anatase; U.P., unknown phosphate. e) See Ref. 1. f) The phosphorus content of this product was determined to be 12 ppm.

method.[22] Strange to say, the polymorphic crystallization of the oxide from a 2 mol dm^{-3} solution of ammonium fluoride at 480 °C depended on the grain size of the original charge. A mixture of rutile and anatase separated out with Ru-I, whereas rutile alone was isolated by using Ru-II instead. The reasons for these reproducible phenomena have not been established. The crystallization behavior of titanium(IV) oxide in hydrofluoric acid was essentially uninfluenced by a change of the source material. Rutile was formed exclusively out of potassium fluoride solutions, regardless of the size of the starting rutile.[1]

The small, highly charged metals of Group IVA in the highest oxidation state of +4 are typical hard acids[23] and hence have strong affinities for hard bases such as fluoride,[24,25] sulfate (HSO_4^- and SO_4^{2-}),[26] and phosphate ($H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) ions. Since anatase was crystallizable from solutions containing fluoride ions with rutile as the nutrient in some instances, Ti–O–Ti and  $\mathrm{Ti}\langle\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}\rangle\mathrm{Ti}$ bonds in starting rutile are assumed to be thoroughly broken on dissolution in fluoride solutions. As a result, mononuclear titanium(IV) complexes are formed in which each titanium(IV) ion is octahedrally coordinated to hard bases including the fluoride ion, oxide ion, hydroxide ion, and water. The directions of transport of titanium(IV) oxide along temperature gradients show that it has negative partial molar enthalpies of solution in hydrofluoric acid and ammonium fluoride solutions, but positive ones in potassium fluoride solutions.[17] These experimental results indicate that the dissolved species in the above two types of fluoride solutions differ markedly from one another in composition and structure.

Mononuclear fluoro complexes of titanium(IV) are unstable toward hydrolysis at high supersaturations, where they are polymerized through fluctuation to afford polynuclear complexes (embryos) related structurally to either rutile or anatase. Further progress of polymerization leads to rutile or anatase nucleation, which is followed by the growth of the resulting crystal nuclei.

Phosphate ions dissolved in parent solutions were most effective in catalyzing anatase formation and/or retarding rutile formation (Runs No. 2 and No. 8).[1] On addition of an adequate amount of phosphate ions to fluoride solutions, titanium(IV) ions almost certainly form mixed-ligand complexes with fluoride and phosphate ions. In this case, phosphate ions bound coordinatively to titanium(IV) ions have a decisive influence on the selective nucleation of anatase. A crystalline phosphate of titanium(IV), together with anatase, precipitated from an ammonium fluoride–diammonium hydrogenphosphate solution (Run No. 2).[1] The concomitant formation of the phosphate undoubtedly reflects the strong complexation between titanium(IV) and phosphate ions. Duncan and Richards[27] have recently demonstrated that sulfate ions slow down the rate of hydrolysis of titanium(IV) ions by occupying a place in the first coordination sphere of each titanium(IV) ion.

Metal oxides in contact with air or water vapor are normally covered with a monomolecular hydroxide layer,[28,29] evidently because hydroxide ions can fit nearer to the centers of positive charge than half the quantity of oxide ions. Hydroxyl groups on the surface of titanium(IV) oxide are amphoteric; basic hydroxyl groups are readily exchangeable for foreign anions such as fluoride, sulfate, and phosphate ions in acidic or neutral media.[28,29] These facts suggest that the above anions are appreciably chemisorbed onto the surfaces of crystals (nuclei) of rutile and anatase under hydrothermal conditions as well.

The ease with which fluoride ions are incorporated into the lattice of titanium(IV) oxide is ascribable not only to the similarities in ionic radius and electronegativity between the fluoride and oxide ions, but also to the surface coverage by fluoride ions during crystal growth. As Table 1 and Fig. 5 show, the bulk uptakes of fluoride ions into titanium(IV) oxide crystallized from three different fluoride solutions (*ca.* 2 mol dm^{-3}) decreased in the order:

$$NH_4F > HF > KF$$

Anatase crystals grown from a potassium fluoride solution with addition of phosphate ions (Run No. 8) contained far fewer fluoride ions in solid solution than rutile crystals obtained in a potassium fluoride solution (Run No. 7). Very few phosphate ions were coprecipitated with anatase. These findings provide some indirect evidence for the adsorption (desorption) of phosphate ions on (from) the growing surface of anatase.

As the concentration of complexing anions is increased, their uptake at nucleus (crystal)/solution interfaces must also increase. When titanium(IV) oxide nucleates at high supersaturations through the hydrolytic polymerization of the dissolved species, anions initially bound to titanium(IV) ions are partly retained by the resulting polynuclear species on their surfaces and partly released into aqueous phases. Of course, the modes and extent of surface complexing by these ligands foreign to the titanium(IV) oxide lattice greatly affect the relative rates at which rutile and anatase nucleate, thus determining the structures of its crystal nuclei and macrocrystals.

In contrast with the three complexing anions already described, chloride and nitrate ions are known to be generally unattached to the surface of titanium(IV) oxide,[29] owing to their weak ability to complex the titanium(IV) ion. Those polymeric ions analogous in structure to rutile which contain as anions only oxide and hydroxide ions are formed selectively in hydrochloric and nitric acids.

The overall excess free energy, ΔG, between a crystal nucleus and the solute in solution is equal to the sum of the surface excess free energy, ΔG_S, and the volume excess free energy, ΔG_V:[30]

$$\Delta G = \Delta G_S + \Delta G_V$$

ΔG_S is the excess free energy between the surface of the nucleus and the bulk of the nucleus, and ΔG_V the excess free energy between a very large crystal and the solute in solution. Let us suppose that values of ΔG_S for anatase nuclei are smaller than those for rutile ones with comparable dimensions, as a result of the chemisorption of fluoride, sulfate, and phosphate ions. Then we find the possibility that the critical nucleus of anatase is more thermodynamically stable than that of rutile.[30,31] In other words, the relative stabilities for the two polymorphs of large particle size can be reversed in the nuclear state. The metastable formation of anatase in sulfuric and hydrofluoric acids with concentrations higher than 0.5 mol dm^{-3} (Fig. 1), as well as in fluoride solutions containing phosphate ions (Table 1), may be attributed to the pronounced stabilization of anatase nuclei by adsorption of sulfate, fluoride, or phosphate ions.

The details of the mechanisms whereby rutile and anatase are crystallized remain unknown, since we are technically incapable of observing the hydrothermal crystallization process *in situ*.

The author is much indebted to Michiko Kobayashi and Yoshiyuki Yajima for their experimental assistance in the chemical analyses and to Masayuki Tsutsumi for his cooperation in the scanning electron microscopy The author also benefited from stimulating discussions with the members of Seventh Research Group of this institute.

References

1) Part I: F. Izumi and Y. Fujiki, *Bull. Chem. Soc. Jpn.*, **49**, 709 (1976).

2) "Gmelins Handbuch der Anorganischen Chemie," Titan, Verlag Chemie, Weinheim (1951) pp. 226—231.

3) I. Keesmann, *Z. Anorg. Allg. Chem.*, **346**, 30 (1966).

4) E. Schwarzmann and K. -H. Ognibeni, *Z. Naturforsch., Teil B*, **29**, 435 (1974).

5) A. Navrotsky and O. J. Kleppa, *J. Am. Ceram. Soc.*, **50**, 626 (1967).

6) K. J. D. MacKenzie, *Trans. J. Br. Ceram. Soc.*, **74**, 77 (1975) and references cited therein.

7) E. F. Osborn, *J. Am. Ceram. Soc.*, **36**, 147 (1953).

8) F. Dachille, P. Y. Simons, and R. Roy, *Am. Mineral.*, **53**, 1929 (1968).

9) A. Matthews, *Am. Mineral.*, **61**, 419 (1976).

10) M. L. Harvill and R. Roy, "Crystal Growth," ed by H. S. Peiser, Pergamon Press, Oxford (1967), p. 563.

11) V. A. Kuznetzov, *J. Cryst. Growth*, **3**,**4**, 405 (1968).

12) M. Passaret, Y. Toudic, A. Regreny, R. Aumont, and J. F. Bayon, *J. Cryst. Growth*, **13**, **14**, 524 (1972).

13) A. L. Boettcher and D. M. Kerrcik. "Research Techniques for High Pressure and High Temperature," ed by G. C. Ulmer, Springer-Verlag, New York (1971), p. 179.

14) R. A. Spurr and H. Myers, *Anal. Chem.*, **29**, 760 (1957).

15) H. Hashitani, H. Yoshida, and H. Muto, *Bunseki Kagaku*, **16**, 44 (1967).

16) A preliminary report on this subject has been published: F. Izumi, H. Kodama, and Y. Fujiki, *Inorg. Nucl. Chem. Lett.*, **13**, 157 (1977).

17) L. Pauling, "General Chemistry," 3rd ed, W. H. Freeman, San Francisco (1970), p. 450.

18) V. A. Kuznetsov and V. V. Panteleev, *Kristallografiya*, **10**, 445 (1965).

19) B. L. Chamberland and A. W. Sleight, *Solid State Commun.*, **5**, 765 (1967).

20) B. L. Chamberland, A. W. Sleight, and W. H. Cloud, *J. Solid State Chem.*, **2**, 49 (1970).

21) R. N. Blumenthal and D. H. Whitmore, *J. Electrochem. Soc.*, **110**, 92 (1963).

22) Some of these data have been reported in Ref. 1.

23) R. G. Pearson, *J. Chem. Educ.*, **45**, 581, 643 (1968).

24) V. Caglioti, L. Ciavatta, and A. Liberti, *J. Inorg. Nucl. Chem.*, **15**, 115 (1960).

25) Yu A. Buslaev, D. S. Dyer, and R. O. Ragsdale, *Inorg. Chem.*, **6**, 2208 (1967).

26) J. Beukenkamp and K. D. Herrington, *J. Am. Chem. Soc.*, **82**, 3025 (1960).

27) J. F. Duncan and R. G. Richards, *N. Z. J. Sci.*, **19**, 171, 179, and 185 (1976).

28) H. P. Boehm, *Angew. Chem.*, **78**, 617 (1966); *Angew. Chem., Int. Ed. Engl.*, **5**, 533 (1966).

29) H. P. Boehm, *Discuss. Faraday Soc.*, **52**, 264 (1971).

30) R. Kiriyama, Y. Bando, and T. Takada, *Kagaku Sosetsu*, **9**, 61 (1975).

31) A fuller discussion of this notion will be published in *Gendai Kagaku* (in press).
