Formation of Anatase Precipitates Containing Fe(III) by the Air Oxidation at 95 °C of Strongly Acidic Solutions

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Strongly acidic titanium(III) chloride solutions containing iron(II) sulfate were subjected to oxidation with air at 95 °C. The products consist of spheres, 0.5—1.0 μm in size, each composed of extremely fine particles, 100—150 Å in size. Fe(III) is incorporated up to about 6% of the total metal ions in the product, in spite of the strongly acidic solution. The products, containing H_2O and SO_4^{2-} besides Fe(III), are dehydrated in the temperature range 100—400 °C and the sulfate decomposition begins at about 750 °C in air. The SO_4^{2-} in the products can be easily removed by washing at room temperature with NaOH solution. No marked differences can be detected in color, magnetic properties, or in growth of the extremely fine particles before and after the dehydration by heat treatment at 500 °C; a change in such physical properties begins to occur at 550 °C. It is concluded that the Fe(III) in the product is interposed between the extremely fine particles, whereas the H_2O and SO_4^{2-} are adsorbed in the spherical polycrystalline particles formed with oxo and hydroxo combination of the extremely fine particles.

Titanium dioxide, TiO_2, can be formed in three kinds of crystalline modifications—brookite, rutile and anatase. Two of the three modifications—precipitates of anatase and rutile, can be prepared by selecting the conditions of hydrolysis of titanium(IV) salts—*i.e.*, kinds and concentrations of the acid anions present in acidic solutions and the hydrolysis temperature.[1-4] Precipitates consisting of any one of the three modifications can be prepared by selecting the conditions for allowing Ti(III) ions gradually to oxidize in an acidic solution at 65—90 °C.[5]

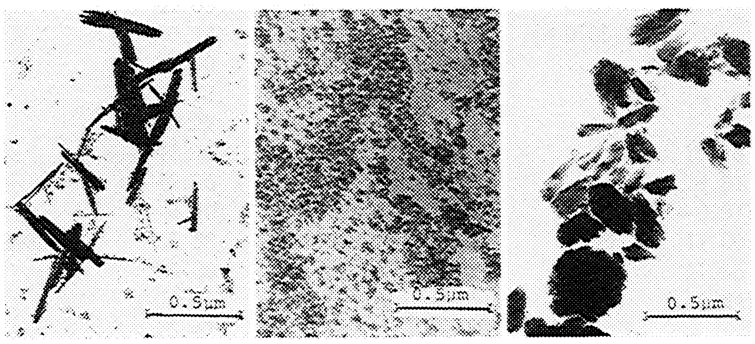
Ti(III) in HCl solution forms a precipitate of brookite or rutile according to the excess HCl concentration or oxidation temperature. Precipitates of brookite or rutile thus formed consist of fine needle-like(a) or extremely fine cubic(b) particles as shown in Fig. 1. The presence of SO_4^{2-} was found to promote the formation of a precipitate of anatase consisting of extremely fine particles, similar to the precipitates of brookite and rutile previously mentioned, as determined by X-ray diffraction examination.[5] Nevertheless, the BET surface area is much less than that of the precipitate of brookite or rutile, the anatase precipitate consisting of relatively large spherical or flat leaf polycrystalline particles as shown in Fig. 1(c). It has been found that in spite of a strongly acidic solution, Fe(III) is partly incorporated into the anatase precipitate in the presence of $FeSO_4$ in the starting solution. A clue to the elucidation of the mechanism of the formation of the polycrystalline particles of anatase would be obtained by clarifying the properties of the polycrystalline particles containing Fe(III).

This paper is an account of the formation of the anatase precipitates containing Fe(III) and the properties of such precipitates.

Experimental

The starting titanium(III) chloride solution (Wako Pure Chemical Industries Ltd.) contained 2.0 M (1 M=1 mol dm^{-3}) $TiCl_3$, 1.6 M $ZnCl_2$, and 1.2 M HCl. To this the required amount of either $FeSO_4\cdot 7H_2O$ or Na_2SO_4 (analytical grade) was added in various mole ratios of Fe(II) or SO_4^{2-} to Ti(III). Each mixed solution was diluted with water to 3 L (dm^3) in a 4 L flask. The oxidation of the mixed solutions was carried out at 95 °C by bubbling air into them at a constant rate of 200 L/h. The construction of the flask for the air-oxidation experiments has been previously described.[6] After a time lapse of 20 h, Ti(III) ions in the solutions changed completely to Ti(IV) and the solutions, originally colored bluish black, turned to yellowish white suspensions of various hues depending on the Fe(II) concentrations in the starting solutions.

The sedimentation velocities of most oxidation products consiting of anatase particles were extremely fast and they



(a) (b) (c)

Fig. 1. Electronmicrographs of rutile (a), brookite (b), and anatase (c) precipitates. Preparation conditions for samples (a), (b), and (c) correspond respectively to those for sample Nos. 4, 6, and 5 shown in Ref. 5.

could easily be separated from the solutions by filtration. After filtration, the products were washed with water, treated with acetone, and then dried in air at 100 °C. All powdery samples thus obtained were examined by X-ray diffraction using Ni filtered Cu $K\alpha$ radiation; some were further examined by electronmicroscopic observation, magnetic measurement using a magnetic torsion balance, BET surface area determination using nitrogen gas, and, thermal and chemical analyses.

The mean size of the extremely fine particles was estimated from the line broadening of the X-ray diffraction peak for the (101) plane of the anatase crystal structure. Thermogravimetry (TG) and differential thermal analysis (DTA) were carried out each with 40 mg samples at a heating rate of 5 °C/min in air using a Shimadzu Dt-TG simultaneous recording apparatus, Model DTG 30 M.

After the samples had been fused with Na_2CO_3 and then dissolved into water, the SO_4^{2-} content was gravimetrically determined as $BaSO_4$. The Cl^- content was determined by nephelometry for a mixture of $AgNO_3$ solution and the solution prepared by the dissolution of the samples in a HF solution by heating. The metal ion contents were determined by atomic absorption after the samples had been dissolved in a mixed solution of HF and HCl.

Results and Discussion

Four typical oxidation products of anatase are given in Table 1. These products were found to consist of spherical particles, 0.5—1.0 μm in size, each composed of a number of extremely fine anatase particles, 100—150 Å in size, as a result of electronmicroscopic and X-ray diffraction examination.

TABLE 1. ANATASE PRECIPITATES CONTAINING Fe(III)

Sample	Starting solution Concn/mol dm^{-3}		Oxidation product	
	Ti(III)	Fe(II)	Fe(III) content(At%)	S (m^{2}g^{-1})
A[a)]	0.166	0		1.34
B	0.166	0.166	1.8	2.17
C	0.166	0.333	4.2	3.49
D	0.083	0.333	5.9	4.34
E[b)]	0.166	0.333	1.3	

a) Sample prepared in the presence of 0.166 mol dm^{-3} Na_2SO_4. b) Rutile prepared by the use of $FeCl_2$ in place of $FeSO_4$.

As evident from the table, the mean size of the polycrystalline particles, as estimated from the BET surface area, slightly decreases with increasing Fe ion content; at the same time, the color changes from white to yellowish white. These samples contained 4—5 wt% SO_4^{2-}, about 10 wt% H_2O and less than 0.1 wt% Cl^-. It is noteworthy that in spite of being products from strongly acidic solutions, these samples contain Fe(III) to the extent of nearly 6% of the total metal ions. However they contained less than 0.02% Zn(II). Increasing the Fe(II) concentration in the starting solution yielded a whitish yellow product containing more than 6% Fe(III). In the whitish yellow products thus prepared, however, extremely fine particles of α-FeO(OH) were intermingled with the anatase particles.

Similar experiments were also conducted using iron(II) chloride in place of the sulfate. Whitish products consisting of rutile particles with or without brookite could be obtained int he absence of SO_4^{2-}. Their sedimentation velocities were extremely slow and the suspended particles could not easily be filtered off. The Fe(III) content was much smaller than would be obtained in the presence of SO_4^{2-} as will be evident from sample E in the table containing less than 0.02 wt% Zn(II).

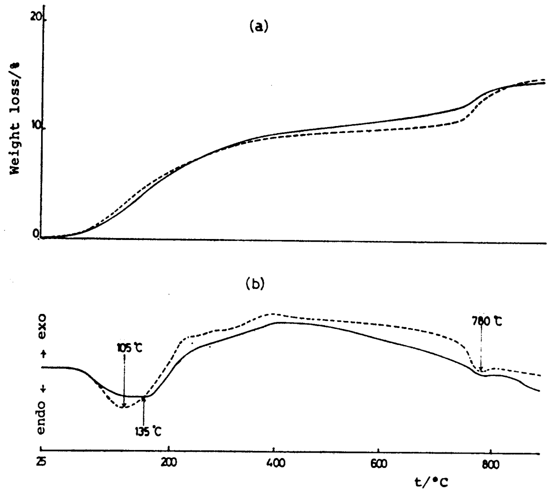


Fig. 2. TG (a) and DTA (b) curves for samples A (——) and D (------).

As shown by the TG and DTA curves in Fig. 2 for samples A and D, these samples are dehydrated in the temperature range 100—400 °C and the sulfate decomposition begins at about 750 °C. The fact that dehydration for the samples takes place continuously from 100°C to temperatures as high as 400 °C indicates that part of the OH^- is interposed between the extremely fine particles. Sample D was divided into several parts and introduced into separate furnaces for heat treatment in air at temperatures between 400 and 750 °C for 20 h. Afterwards they were taken out from the furnaces and allowed to cool to room temperature.

For the sample heat-treated at 500 °C, a decrease in the BET surface area to 3.3 m^2 g^{-1} was observed, but no appreciable differences in color, half broadening of X-ray diffraction peaks and magnetic properties could be detected before and after the dehydration by heat treatment. The samples heat-treated at 550—700 °C became more yellowish and at the same time, their X-ray diffraction peaks became sharper with increasing heat treatment temperature as seen in Fig. 3.

As shown in Fig. 4, no particle growth due to sintering between the spherical polycrystalline particles at 700 °C could be detected, but the BET surface area decreased to 2.2 m^2 g^{-1} because of the decrease in fine projections. The SO_4^{2-} content of this sample still remained at 2.6 wt%. Part of the anatase changes to rutile on heat treatment at 750 °C (Fig. 3(d)).

Magnetic susceptibilities, χ, were measured with the original sample D and its heat treated samples in a

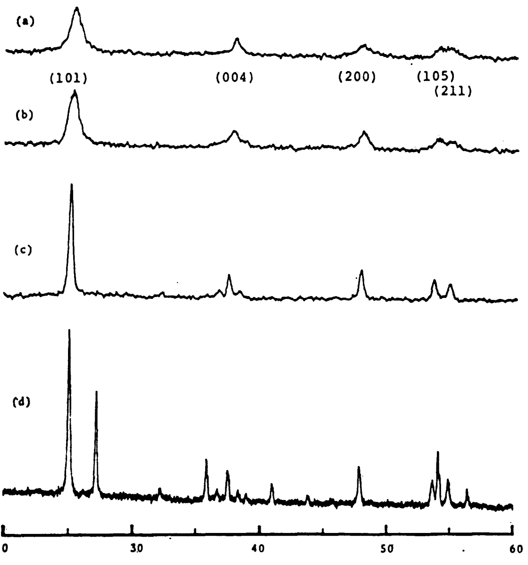


Fig. 3. X-Ray diffraction patterns of the original sample D (a) and its 500 (b), 700 (c), and 750°C (d) heat treated samples.

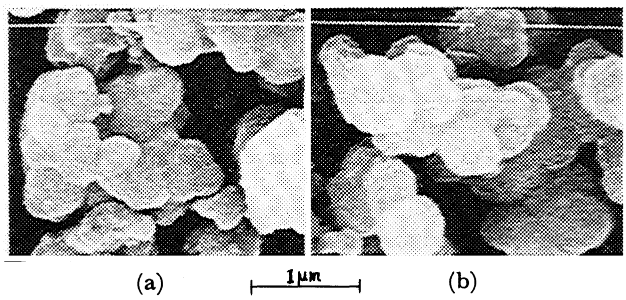


Fig. 4. Scanning electronmicrographs of sample D before (a) and after heat treatment at 700 °C in air.

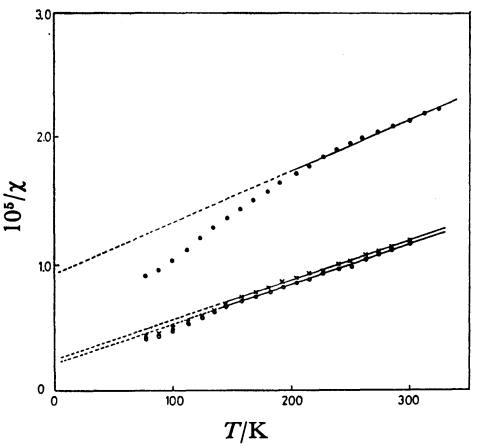


Fig. 5. A plot of reciprocal of magnetic susceptibility, χ emu/g ($4\pi 10^{-3}$ m^3 kg^{-1}), as a function of temperatures T for the original sample D (○) taken after heat treatment in air at 500 (×) and 700 °C (●).

magnetic field range 2—9 kOe (1 Oe=1000/4 π A m^{-1}) at temperatures between 77 and 300 K. No magnetic field dependency of χ could be detected with any of these samples.

Figure 5 is a plot of χ^{-1} of typical samples as a function of T(K). An inspection of these curves readily reveals the following: χ values of sample D on the higher temperature side follow the Curie-Weiss equation

$$\chi = C(T-\theta)^{-1},$$

the paramagnetic Curie temperature θ is -60 K, and the Curie constant C is 31×10^{-4} emu. From the C value, sample D is estimated to contain 4.0 wt% Fe(III) with an effective magnetic moment of 5.9—that is, Fe(III) content is 6.6% in the total metal ions.

No marked differences in the values of C and θ can be observed before and after the heat treatment at 500 °C for sample D. The temperature range to follow the Curie-Weiss equation becomes narrow with the sample heat-treated at 700 °C, and its θ value is -230 K. A shift in θ to the lower temperature side is attributable to the greater magnetic interaction generated between the Fe (III) ions.

To clarify how SO_4^{2-} is intermingled within the polycrystalline particles, the following experiments were conducted. Samples A and D, each weighing 5 g, were immersed in separate 100 mL 1 M NaOH solutions and left at room temperature for 8 h. During this period, ultrasonic dispersion was applied several times, 5 min each time, to each of these suspensions. Precipitates were separated from alkaline solutions by filtration, thoroughly washed with water, treated with acetone, and dried at 100 °C to obtain white and yellowish white samples.

X-Ray diffraction and electron-microscopic examinations of these samples before and after the alkaline treatment, could detect no appreciable differences between the two samples. It was found, however, that the BET surface area increased to 4.0 (sample A) and to 7.9 m^2 g^{-1} (sample D), probably because of chipping of polycrystalline particles due to the ultrasonic dispersion,whereas the SO_4^{2-} content of the samples A and D decreased markedly to 0.38 and to 0.47 wt%, respectively, with the alkaline treatment. From these results, it can be concluded that the major portion of the SO_4^{2-} ions is adsorbed, similar to H_2O, in the polycrystalline particles, without being interposed between extremely fine anatase particles.

It is well known that since titanium(III) chloride solutions are powerful reducing agents, Ti(III) easily reduces Fe(III) in a strongly acidic solution. Accordingly, the oxidation with air of Ti(III) to Ti(IV) must take place before that of Fe(II) to Fe(III). The Ti(IV) in a HCl solution containing SO_4^{2-} will be present as sulfato complexes.[7] It is presumed, therefore, that the Ti(IV) in the strongly acidic solution formed by oxidation generates the polynuclear complexes, each consisting of the oxo, aqua, hydroxo, and sulfato groups where the Ti(IV) concentration is high. These complexes would form extremely fine particles of anatase with the oxo combining as a result of the dissociation by hydrolysis of the H_2O, OH^-, and SO_4^{2-}. The Ti(IV) ions present in the subsurfaces of extremely fine particles will be still combined with SO_4^{2-} besides OH^- and H_2O. With the desorption by further hydrolysis of these SO_4^{2-} and H_2O from the subsurfaces, the formation of polycrystalline particles will take place with oxo and hydroxo combinings of the extremely fine particles in the absence of Fe(III). The oxidation into Fe(III) would begin to take place after most of the Ti(III) ions have been changed to Ti(IV). The Fe(III) ions formed by oxidation exist as monomers[8)] and part of them must exist as hydroxo complexes.

Ramakrishna and Seneratyapa reported as a result of their spectrometric studies, that Fe(III) hydroxo complexes in strongly acidic solutions easily reacted with Ti(IV) hydroxo complexes to form mixed complexes, whose formation was governed by the nature of the dissolved acid anions.[9)] This reaction suggests that under the existence of the Fe(III) hydroxo complexes, part of the Ti(IV) combined with H_2O, OH^-, or SO_4^{2-} in the subsurface of each extremely fine particle would be combined with the Fe(III) hydroxo complexes. Each polycrystalline particle, in which the Fe(III) ions are relatively evenly interposed between the extremely fine particles, would be formed and become greater in size with the oxo and hydroxo combination caused during the progress of hydrolysis.

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