Manufacture of Pure Titanium(IV) Oxide by the Chloride Process. III. Precipitation of Hydrous Titanium(IV) Oxide in Hydrochloric Acid Solution at Elevated Temperatures

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Thermal hydrolysis of titanium(IV) in hydrochloric acid solutions (0.2 mol dm^{-3} in Ti(IV); 2 mol dm^{-3} in HCl) was carried out at temperatures up to 110 °C to investigate the effects of heating rate, heating temperature, aging time, and coexisting ions on the particle shape, size, crystal form, crystalline size, and content of water of the hydrous titanium(IV) oxide precipitated. The resulting polycrystalline particles having rutile structure were all distorted ellipsoids at the beginning of the hydrolysis, and gradually changed to spheres with rising temperature or with the duration of time. However, no effects of heating rate on the particle shape and size distribution were observed at the beginning of the hydrolysis. On the other hand, the precipitation rate of titanium(IV) measured at a constant temperature remarkably depended on the temperature; marked changes in the particle size distribution and mean particle size were observed during the reaction. The precipitation rate was well expressed by the rate equation based on the rate-determining step of the surface chemical reaction. The apparent activation energy was 111 kJ mol^{-1}. Although no effects of coexisting cations such as iron(III) and aluminium(III) were recognized, the presence of sulfate and fluoride ions significantly affected the particle shape and size of such precipitates. Anatase-type hydrous titanium(IV) oxide consisting of spherical particles of narrow size distribution was also obtained in the presence of fluoride ion.

As a new manufacturing process of titanium(IV) oxide, the authors previously proposed the Chloride Process,[1,2] in which both production of titanium(IV) oxide and recovery of iron compounds in higher state of purity were expected. This process is based on the leaching of ilmenite ore in concentrated hydrochloric acid solutions and on the selective recovery of titanium(IV) and iron(III) from the resulting leach liquor by solvent extraction with tributyl phosphate (TBP). In this process, ilmenite ore, which occurs abundantly in nature, can be used. The other important feature is that using hydrochloric acid as the leachant allows easier recovery of useful free acid from its waste solution than using sulfuric acid does.[3–5] The kinetics of leaching of ilmenite ore[1] and the solvent extraction of titanium(IV) and iron(III) using TBP[2] have been already studied. As the third unit process for producing hydrous titanium(IV) oxide from the back-extracted solution containing titanium(IV), the thermal decomposition[5,6] or the thermal hydrolysis[7,8] can be useful. In the conventional manufacturing process, *i.e.*, the sulfate process, thermal hydrolysis is extensively used.[9]

It is generally known that the rutile-type hydrous titanium(IV) oxide is produced in hydrochloric acid solutions by the thermal hydrolysis.[10] Recently Matijević *et al.*[11,12] also studied the thermal hydrolysis of titanium(IV) in hydrochloric acid solutions to clarify the optimum conditions for the preparation of titanium(IV) oxide hydrosol of narrow size distribution. On the other hand, the effect of various additives such as NO_3^-, Cl^-, SO_4^{2-}, and F^- ions on the crystal structure of the resulting hydrous titanium(IV) oxide was also investigated in the hydrolysis of titanium(IV) chloride,[7,10] in the aerial oxidation of titanium(III) chloride,[13] and in the hydrothermal treatment of amorphous titanic acid.[14] In addition, from the viewpoint of the kinetics of the hydrolysis[8] and of the mechanism of the particle growth,[15] the thermal hydrolysis of titanium(IV) chloride has been investigated. However, in the course of our development of the Chloride Process, further information about the factors influencing the particle properties of the hydrous titanium(IV) oxide precipitated by the thermal hydrolysis of titanium(IV) in hydrochloric acid solutions was necessary. This study will deal with the effect of process variables such as heating rate, heating temperature, aging time, and coexisting ions on the particle shape, size, crystal form, crystalline size, and content of water of the precipitates. The relation between the particle growth behavior and the precipitation rate of titanium(IV) was also investigated.

Experimental

Reagents. Commercial extra-pure titanium(IV) chloride (Wako Pure Chem. Ind., Ltd.) was purified by distillation at 61 °C and 64 mmHg (1 mmHg≈133.322 Pa) before being used. The titanium(IV) chloride stock solution was prepared by dissolving a 25 cm^3 portion of the distillate in 200 cm^3 analytical grade concentrated hydrochloric acid (Wako Pure Chem. Ind., Ltd.) and then by filtrating through a 0.66 μm teflon millipore filter to remove insoluble materials as impurities. The reaction solution used in the experiment was prepared by diluting the stock solution with hydrochloric acid solution. Additive ions were previously added as sodium salts in the case of anion and as chloride in the case of cation to the hydrochloric acid solution. All other reagents were of the highest purity grade available.

Procedure. Hydrochloric acid solution containing titanium(IV) (0.2 mol dm^{-3} in Ti(IV); 2 mol dm^{-3} in HCl) was transferred in a Vitro Dynamics rectangular parallelepiped microslide (inner size: 0.3 mm×3.0 mm×50 mm) and then both ends of the slide were sealed using epoxy resin adhesive. After this procedure, the slide was heated in the small-sized silicone oil bath equipped with a Sinku Riko HPC-5000 thermal program controller for the hydrolysis of titanium(IV). The oil bath was designed to allow us to observe the precipitation behavior of titanium(IV) in the slide. After the lapse of a fixed time, the slide was taken out and rapidly quenched to room temperature. Subsequently, the slide was destroyed and the precipitate which had formed on the inner side of the slide was washed with 2 mol dm^{-3} hydrochloric acid and distilled water, and then dried over diphosphorus pentaoxide under reduced pressure. As an experiment to measure the precipitation rate of titanium(IV), the thermal hydrolysis was similarly carried out using a cylindrical glass sealed tube (36 cm^3 in volume). The resulting suspension was first quenched and then centrifuged. The supernatant solution was withdrawn to analyze for titanium ion. The percentage precipitation of titanium(IV) was calculated from the titanium ion concentrations in solution before and after the hydrolysis. The precipitate was washed and dried by the procedures described above.

Analysis. The observation of the particle shape and the measurement of the particle size distribution of the precipitate were performed using a Hitachi-Akashi MSM 4C-102 Scanning Electron Microscope. The X-ray diffraction patterns were obtained using a Rigaku Denki Geigerflex 2013 with Ni filtered Cu $K\alpha$ radiation, with 30 kV and 10 mA. The crystalline size of the precipitate was obtained by the line-broadening method,[16] based on the half-value width of X-ray diffraction peaks of $2\theta=27.42°$ (110) for the rutile and of $2\theta=25.28°$ (101) for the anatase, respectively. DTA and TG were obtained using a Rigaku Denki Thermoflex over the range from room temperature to 1200 °C. The rate of temperature rise was 10 °C min^{-1}. The concentrations of titanium ion and hydrochloric acid were analyzed by colorimetric method[17] and neutralization, respectively.

Results and Discussion

Effect of Heating Rate. Hydrochloric acid solution containing titanium(IV) was heated from room temperature with the heating rates of 0.2, 1.0, and 2.0 °C min^{-1}. The turbidity point is defined here as the temperature at which turbidity was observed in the solution by the hydrolysis of titanium(IV). The turbidity points observed were 77, 87, and 97 °C, respectively. Scanning electron micrographs of the precipitated particles obtained at the turbidity point or above under the heating rate of 1.0 °C min^{-1} are shown in Fig. 1. The particle shape of the precipitate obtained at the turbidity point was that of a distorted ellipsoid, an aggregate of two or three small particles. As the temperature was raised further, the shape changed to sphericity with an increase in the particle size. A similar result was obtained under the heating rate of 0.2 °C min^{-1}. X-Ray diffraction revealed that all these precipitates were rutile-type hydrous titanium(IV) oxide.

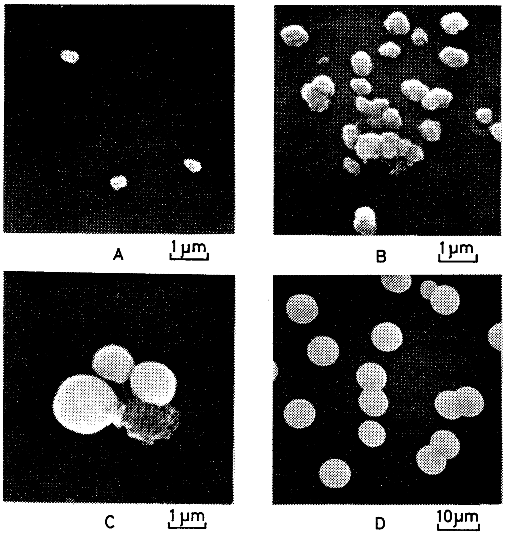

Fig. 1. Scanning electron micrographs of the precipitated particles obtained at different temperatures.
HCl: 2.10 mol dm^{-3}, Ti(IV): 0.230 mol dm^{-3}, heating rate (°C min^{-1})—1.0(A: 87 °C (turbidity point), B: 95 °C, C: 105 °C), 0.2(D: 105°C).

Figure 2 shows the effect of the heating rate on the particle size distribution of the precipitates obtained at the turbidity points. No marked differences can be detected in the distribution histogram and mean particle size, δ. Therefore, it was concluded that the particle shape and size of the hydrous titanium(IV) oxide were not affected by the heating rate. In the experiments conducted in 4 mol dm^{-3} hydrochloric acid, the same results were obtained, except for a rise in the turbidity point of about 10 °C.

Effect of Aging Time. Hydrochloric acid solution containing titanium(IV) was heated at a rate of 1.0 °C min^{-1}, and then maintained at the desired temperatures in all subsequent experiments. Figure 3 shows the effect of the aging time on the particle size distribution at 95 °C. The mean particle size increased with the duration of the aging. The other impressive feature was that the tailing phenomenon was recognized in the distribution histograms after the lapse of 1—3 h and then disappeared after the lapse of 6 h. These precipitates were all spherical in shape, having the rutile structure. The results obtained in the experiments conducted at 88 °C were approximately the same as those described above.

The precipitation rate of titanium(IV) measured at 88, 91, and 95 °C are shown in Fig. 4. A rapid precipitation step was found at 2—4 h for 88 °C, and also at 1—3 h for 95 °C. It is noticeable here that these rapid precipitation steps correspond to the time at which the tailing phenomenon shown in Fig. 3 appeared. The disappearance of the tailing phenomenon at 6 h also seemed

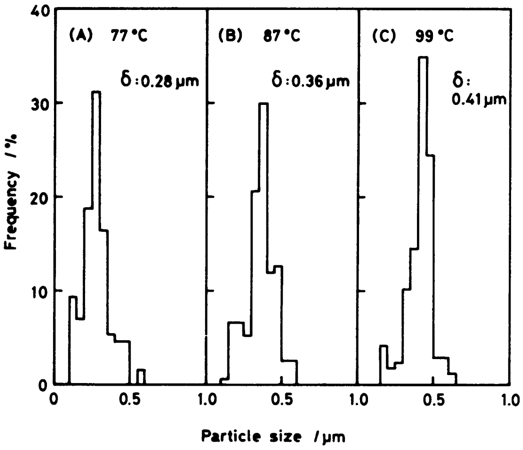

Fig. 2. Effect of heating rate on the particle size distribution of the precipitates obtained at the turbidity point.
HCl: 2.10 mol dm^{-3}, Ti(IV): 0.230 mol dm^{-3}, heating rate (°C min^{-1})—A: 0.2, B: 1.0, C: 2.0.

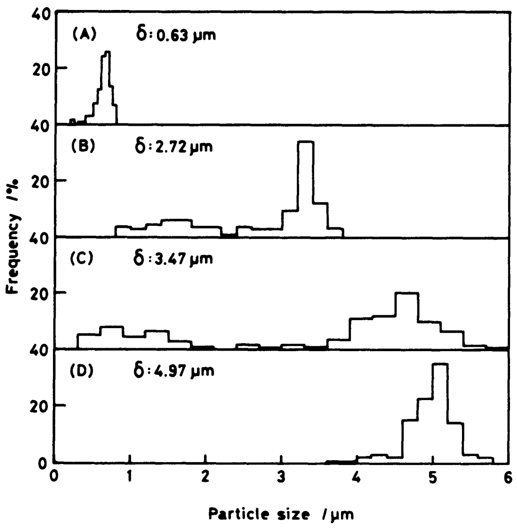

Fig. 3. Effect of aging time on the particle size distribution of the precipitates.
HCl: 2.13 mol dm^{-3}, Ti(IV): 0.220 mol dm^{-3}, temperature: 95 °C, aging time (h)—A: 0, B: 1, C: 3, D: 6.

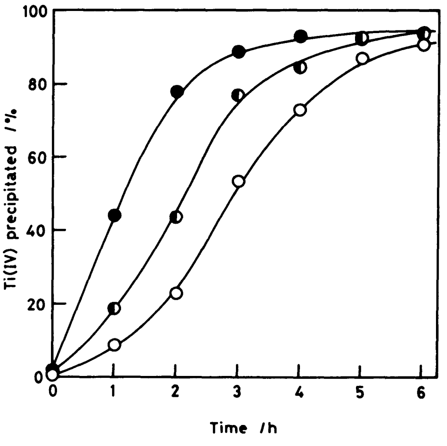

Fig. 4. Effect of temperature on the precipitation rate of Ti(IV) in HCl solution.
HCl: 2.16 mol dm^{-3}, Ti(IV): 0.219 mol dm^{-3}, temperature (°C)—○: 88, ◐: 91, ●: 95.

to be due to the growth of the particles by the dissolution-reprecipitation or by the annexation of small particles on the bigger ones.

Analysis of Particle Growth Rate. The analysis of the particle growth was carried out using the crystal growth theory. This analysis is based on the assumption that nucleation is finished at once in the beginning step of the crystal growth. In the case that the particle growth is limited by the surface chemical reaction, the precipitation rate is written as follows:[18]

$$\frac{dX}{dt} = \alpha X^{2/3}(1-X). \tag{1}$$

Here

$$\alpha = \{36\pi V^2(C_o-C_e)^2N\}^{1/3}G, \tag{2}$$

where X is the molar fraction of precipitation (—), t the time (h), V the volume per unit molar of precipitate (m^3 kg mol^{-1}), C_o the initial solute concentration in bulk solution (kg mol m^{-3}), C_e the solubility of the precipitate (kg mol m^{-3}), N the particle number per unit volume (m^{-3}), and G the transfer coefficient (m h^{-1}). By integration of Eq. 1, Eq. 3 was obtained:

$$\alpha t = \int_o^{X^{1/3}} \frac{3}{1-y^3}dy = I. \tag{3}$$

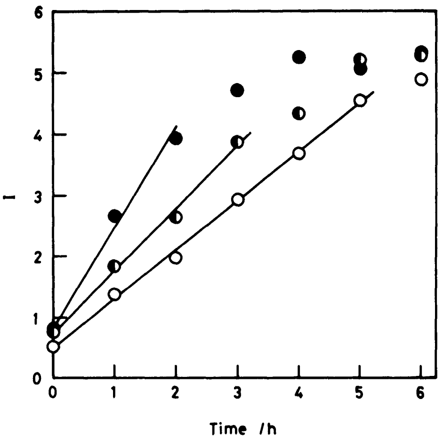

Fig. 5. Effect of temperature on the precipitation rate of Ti(IV) in HCl solution—I *versus* t.
HCl: 2.16 mol dm^{-3}, Ti(IV): 0.219 mol dm^{-3}, temperature (°C)—○: 88, ◐: 91, ●: 95.

Figure 5 shows the relationship between I and t. At 88 °C a good linear dependence of I on t was observed. This means that the precipitation rate of titanium(IV) is well expressed by Eq. 1. The linear dependence was also observed at early steps at 91 and 95 °C. However, there was not a linear relationship between I and t in the precipitation curves after 3 h at 91 °C or after 2 h at 95 °C. This deviation from the rate equation was thought to be dependent on the change in the rate-determining step from the surface chemical reaction process to the diffusion process of titanium(IV). The apparent activation energy calculated from the Arrhenius plots of α, which was given from the slope of the straight lines in Fig. 5, was 111 kJ mol^{-1}. This value indicates the reasonability of the assumption used in this analysis that the particle growth is limited by the surface chemical reaction.

Effect of Coexisting Ions. The effect of sulfate and fluoride ions, both which have stronger complexing ability for titanium(IV) than chloride ion does, on the particle shape, size, crystal form, crystalline size, and content of water of the precipitate was investigated in detail. Scanning electron micrographs of the precipitated particles obtained in the presence of these anions at 95 °C after 6 h are shown in Fig. 6, together with that obtained in the absence of these anions. The precipitated particles were perfectly spherical in shape; X-ray diffraction revealed that crystal form corresponded to rutile-type hydrous titanium(IV) oxide. On the other hand, the particle shape of the precipitate was irregular plate-like in the presence of sulfate ion and slightly distorted spherical in the presence of fluoride ion. The reason for this difference is as yet unclear. The other important feature was that both precipitates were ana-

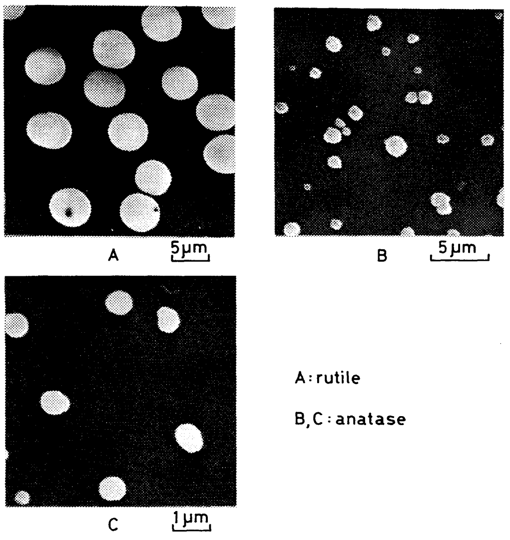

Fig. 6. Scanning electron micrographs of the precipitated particles obtained in the presence of sulfate and fluoride ions.

HCl: 2.13 mol dm^{-3}, Ti(IV): 0.220 mol dm^{-3}, temperature: 95°C, anion added—A: none, B: 0.480 mol dm^{-3} Na_2SO_4, C: 0.112 mol dm^{-3} NaF.

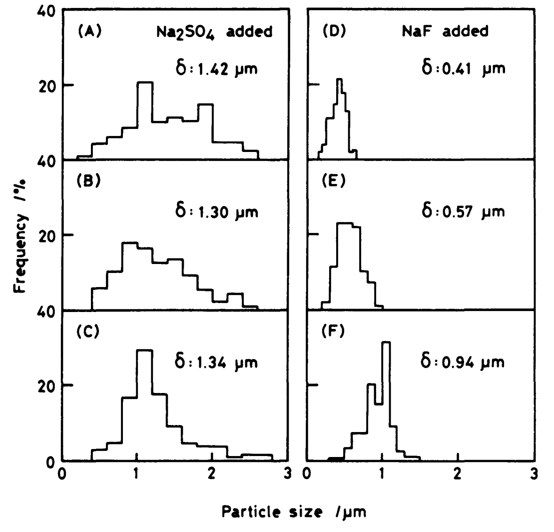

Fig. 7. Effect of coexisting anions on the particle size distribution of the precipitates.

HCl: 2.13 mol dm^{-3}, Ti(IV): 0.220 mol dm^{-3}, temperature: 95 °C, anion added—A—C: 0.480 mol dm^{-3} Na_2SO_4, D—F: 0.112 mol dm^{-3} NaF, Aging time (h)—A,D: 1, B,E: 3, C,F: 6.

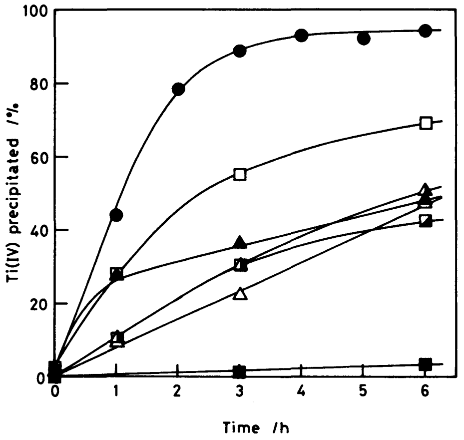

Fig. 8. Effect of coexisting anions on the precipitation rate of Ti(IV) in HCl solution.

HCl: 2.12 mol dm^{-3}, Ti(IV): 0.219 mol dm^{-3}, temperature: 95°C, anion added—None: ● Na_2SO_4 (mol dm^{-3}): △ 0.10, ◭ 0.20, ▲ 0.46, NaF (mol dm^{-3}): □ 0.10, ◪ 0.20, ■ 0.44.

tase-type hydrous titanium(IV) oxide; this result agrees with those reported by earlier workers.[7,10,13,14]

The effect of both anions on the particle size distribution is shown in Fig. 7. In the presence of sulfate ion, the distribution was broadened, although the mean particle size became smaller. However, in the presence of fluoride ion, the range of the distribution was extremely narrow, so that the particles can be regarded as monodispersed, whereas the mean particle size became even smaller. Although Matijević *et al.*[11,12] had reported the preparation method of rutile-type titanium(IV) oxide consisting of spherical particles of narrow size distribution, it was found here that a similar result on the formation of anatase-type titanium(IV) oxide could be obtained by the addition of fluoride ion.

Figure 8 also shows the effect of both anions on the precipitation rate of titanium(IV). In general, the precipitation rate decreased in the presence of these anions. The degree of the decrease in the precipitation rate was correlative with the stability constant of each titanium(IV) complex, as shown below (25 °C):

$$\frac{[\mathrm{TiOCl^+}]}{[\mathrm{TiO^{2+}}][\mathrm{Cl^-}]} = 3.55,^{19)} \tag{4}$$

$$\frac{[\mathrm{TiOSO_4}]}{[\mathrm{TiO^{2+}}][\mathrm{SO_4^{2-}}]} = 1.69\times 10^2,^{20)} \tag{5}$$

$$\frac{[\mathrm{TiOF^+}]}{[\mathrm{TiO^{2+}}][\mathrm{F^-}]} = 2.75\times 10^6.^{21)} \tag{6}$$

The precipitation rate decreased with increasing the concentration of fluoride ion. The initial precipitation rate oppositely increased with increasing the concentration of sulfate ion. This conflicting result can be explained by the phenomenon that sulfate ion exists mostly as HSO_4^- under the conditions of 90 °C and 2 mol dm^{-3} hydrochloric acid, as can be estimated from the following equation:

$$\frac{[\mathrm{SO_4^{2-}}]}{[\mathrm{HSO_4^-}]} = 3.97\times 10^{-4}.^{23)} \tag{7}$$

Namely, the increase in the initial precipitation rate seemed to be due to the actual decrease in acid concentration.

The time changes in the mean particle size of the precipitate obtained at different temperatures in the presence or absence of these anions are shown in Fig. 9. In general, the mean particle sizes increase with the duration of the aging, except in the case of the presence of sulfate ion, and decreased with an increase in the complexing ability of these anions for titanium(IV). It

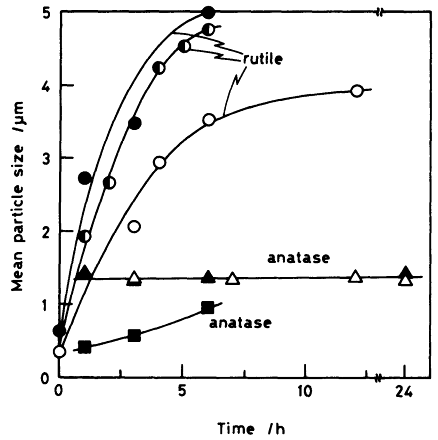

Fig. 9. Effects of temperature and coexisting anions on the mean particle size of the precipitates.
HCl: 2.13 mol dm^{-3}, Ti(IV): 0.220 mol dm^{-3},

	○ ◐ ●	△ ▲	■
Temperature/°C	78 88 95	78 95	95
Anion added	None	0.480 mol dm^{-3} Na_2SO_4	0.112 mol dm^{-3} NaF

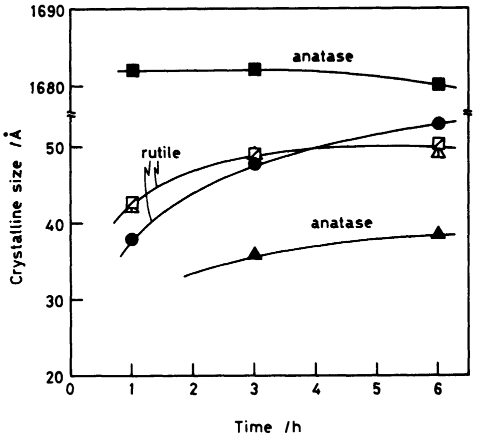

Fig. 10. Effect of coexisting ions on the crystalline size of the precipitates.
HCl: 2.2 mol dm^{-3}, Ti(IV): 0.22 mol dm^{-3}, temperature: 95 °C, ion added—●: none, ▲: 0.20 mol dm^{-3} Na_2SO_4, ■: 0.20 mol dm^{-3} NaF, ▨: 0.02 mol dm^{-3} $FeCl_3$, △: 0.01 mol dm^{-3} $AlCl_3$.

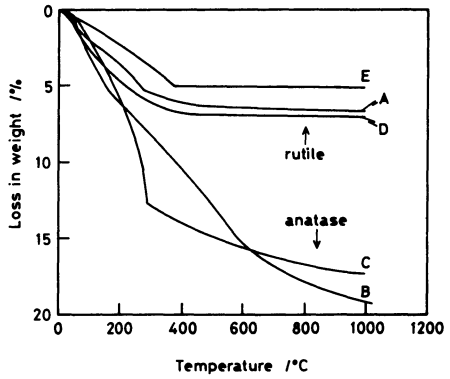

Fig. 11. TG curves of the precipitated particles obtained in the presence of various ions.
HCl: 2.2 mol dm^{-3}, Ti(IV): 0.22 mol dm^{-3}, temperature: 95 °C, ion added—A: none, B: 0.20 mol dm^{-3} Na_2SO_4, C: 0.20 mol dm^{-3} NaF, D: 0.01 mol dm^{-3} $FeCl_3$, E: 0.01 mol dm^{-3} $AlCl_3$.

was also found that the mean particle size increased with an increase in the heating temperature, as shown in Fig. 3, whereas no changes was observed in the case of the presence of sulfate ion.

The effect of coexisting cations such as iron(III) and aluminium(III), which would be contained in the hydrochloric acid leach liquor of ilmenite ore, was also investigated here. With regard to the coprecipitation behavior, about 5% of the initial concentration of iron(III) was incorporated in the hydrous titanium(IV) oxide precipitate, whereas no aluminium(III) was incorporated. Therefore, it is necessary to remove iron(III) from the leach liquor containing titanium(IV) by solvent extraction using TBP before the thermal hydrolysis.[2]

Figure 10 shows the effect of the coexisting ions on the crystalline size of the precipitates. No changes in the crystalline size were observed in the presence of these cations, although it varied drastically in the presence of anions. Especially in the presence of fluoride ion, the crystalline size became extremely large, and increased with increasing the concentration of fluoride ion. The enlargement in the crystalline size was observed in the fluoride ion concentration of 0.05 mol dm^{-3} or above, whereas time dependences were generally not recognized. On the contrary, the crystalline size became slightly smaller in the presence of sulfate ion.

TG curves of the precipitated particles obtained in the presence or absence of various additional ions are shown in Fig. 11. The rutile-type hydrous titanium(IV) oxides obtained in pure hydrochloric acid solution or in the presence of such cations were found to contain 5—7% of water. The anatase-type hydrous titanium(IV) oxides obtained in the presence of sulfate and fluoride ions indicated that a large weight loss occurred in the heating process. Since the sulfate ion decomposes at temperature higher than 700 °C, most of this weight loss (16—17%) of Sample B can be regarded as the release of water. However, the rapid weight loss of Sample C at about 285 °C corresponded with the close-neighboring peaks of sharp exothermic peak (293 °C) and endothermic peak (300 °C) on the DTA curve. Therefore, this rapid weight loss seemed to be dependent on the formation and sublimation of TiF_4. From these results, the content of F^- ion in the precipitate was calculated as 0.82%. It can be said that the anatase-type hydrous titanium(IV) oxide contains a larger amount of water than the rutile-type one.

The results show that the particle shape, size, crystal form, crystalline size, and content of water of the hydrous titanium(IV) oxide precipitated in hydrochloric acid solution can be controlled in the limited range by varying the heating temperature, aging time, and addition of such anions.

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