Influence of Addition of AlF₃ on Thermal Decomposition of Gibbsite and Phase Transition of the Intermediate Alumina to α-Al₂O₃

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The addition of aluminum fluoride to gibbsite retarded the phase change to boehmite by chemisorption of hydrogen fluoride on gibbsite particles. In the specimen with addition of aluminum fluoride, the spinel type phase transformed directly to α-Al₂O₃, without passing through κ- and θ-Al₂O₃ phases. The formed α-Al₂O₃ consisted of clear, hexagonal plate-like particles about 1 μm, Without taking over a relic of the gibbsite particle. The formation of automorphic crystals suggests that a surface diffusion also contributes to the mechanism of this material transport in addition to the vapor phase transport.

1. Introduction

Most commercial aluminas are produced through the Bayer process,[1] in which aluminum trihydrates are precipitated from a supersaturated sodium aluminate liquor, washed, dried, and fired to form α-alumina above 1100°C. Gibbsite is the normal precipitated phase. As the relics of trihydrate particles result after firing, pulverizing operation for the fired alumina powders is usually conducted. The origin of relics would be based on the orientation relationship between gibbsite and intermediate phases having spinel type structure, such as χ-, γ-, η- and δ-Al₂O₃. Coarse gibbsite particles about 100 μm in size change to boehmite, aluminum monohydrate phase, intermediately before the transformation to alumina during heating. Boehmite also has the orientation relationship with spinel type structure of intermediate aluminas. The orientation relationships are as follows;[2] the (110) diffraction spot of gibbsite is coincident with the (220) spot of spinel structure, and the (200) spot of boehmite with the (440) spot of spinel structure and the (020) spot of boehmite with the (400) spot of spinel structure. Relic-free powders or weak aggregate powders, which are easily broken or pulverized, are better for many ceramic applications.

Magnesium hydroxide (brucite) also leaves the hexagonal plate-like relics after formation of MgO. The relics are not desirable for sintering of MgO. There are several reports investigating the effects of addition of magnesium halides on the decomposition of $Mg(OH)_2$ and crystal growth of MgO. The addition of $MgCl_2 \cdot 6H_2O$ to $Mg(OH)_2$ produces relic-free, round and sinterable MgO powders after the decomposition process.[3],[4] Crystallite of MgO is promoted with presence of Cl^- ion.[5] Brucite chemisorbs hydrogen fluoride on the edge and the decomposition shifts to higher temperature side.[6] Fluorine ion inhibits crystal growth of MgO at temperature below 900°C, but promotes above 1000°C.[5],[7] On the other hand, the addition of chloride to bayerite, one of aluminum trihydrates, is not effective to break their relics.[8] The presence of fluorine ion accelerates transformation of intermediate alumina to α-Al₂O₃,[9] but the details are not clear. Daimon and Kato[10] reported that the addition of 25 mass% of AlF₃ to η-Al₂O₃, which was prepared by the thermal decomposition of hydrated aluminum sulfate, directly transformed it to hexagonal plate particles of α-Al₂O₃ under the firing conditions at 1100°C for 1 h or 900°C for 20 h via a vapor transport mechanism.

In this paper, the influence of addition of AlF₃ on thermal decomposition of coarse gibbsite particles and phase transition of the intermediate alumina to α-Al₂O₃ is investigated, anticipating the formation of relic-free particles or weak aggregates.

2. Experimental procedure

Coarse gibbsite powder was offered by Sumitomo Chemical Co., Ltd., (CW–375HT, 99.9% pure, mean particle size; about 75 μm). Aluminum fluoride (chemical pure grade) as an additive was also offered by Nippon Light Metal Co., Ltd. The main crystal of fluoride is β-AlF₃ and contains a small amount of β-AlF₃·3H₂O. The fluoride powders were elutriated and the fine powders under 1 μm were collected. The amount of addition was determined, evaluating the weight loss by TG/DTA measurement (EXSTAR6000, Seiko Instruments).

The fixed amounts of aluminum fluoride were wet-mixed with gibbsite powders using ethanol and an agate mortar. The amounts of additive were 1, 2, 5 and 10 mass% (converted into the amount of Al₂O₃). Dried mixtures were supplied to DTA measurement and the temperature shift of the endothermic peak with the amount of addition was examined. Influence of addition of AlF₃ on phase transition of intermediate aluminas to α-Al₂O₃ was investigated for the specimen containing 2 mass% of additive. The specimen about 3 g was put in an alumina covered crucible of 0.03 dm³ volume and heated at 6°C/min to a given temperature in an electric furnace and quenched by the cut of electric current. Identification of crystal phases in heat-treated specimens was done by powder X-ray diffractometry (XRD) (Model RU–200, Rigaku Co.) and the microstructure was observed by SEM (T–300, JEOL). In the case of the specimens which were heat-treated in no-covered crucible, the data obtained were not stable, influenced with the amount of specimen. Chemical analysis of residual fluorine in heat-treated specimens was conducted by the ion chromatography method after alkali fusion and steam distillation separation treatments (commissioned to Sumitomo Metal Technology, Inc.).

3. Results and discussion

Figure 1 is the SEM photographs of a gibbsite particle as a raw material and the specimen converted to α-Al₂O₃ by firing at 1200°C for 1 h. Both massive figures are the similar image, indicating that strong relics of gibbsite are preserved after the conversion to α-Al₂O₃.
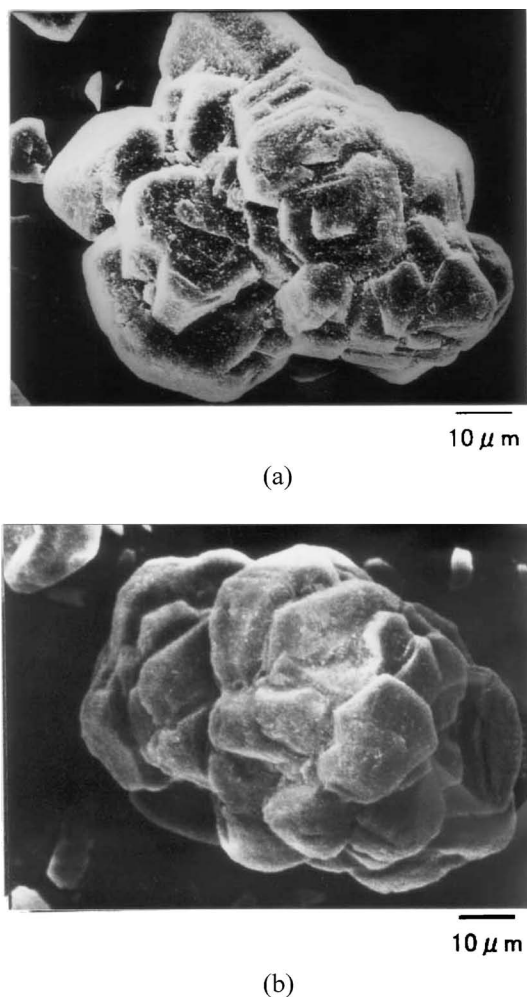
(a)

(b)

Fig. 1. SEM photographs of a gibbsite particle and the fired specimen at 1200°C for 1 h. (a) Gibbsite, (b) Fired specimen
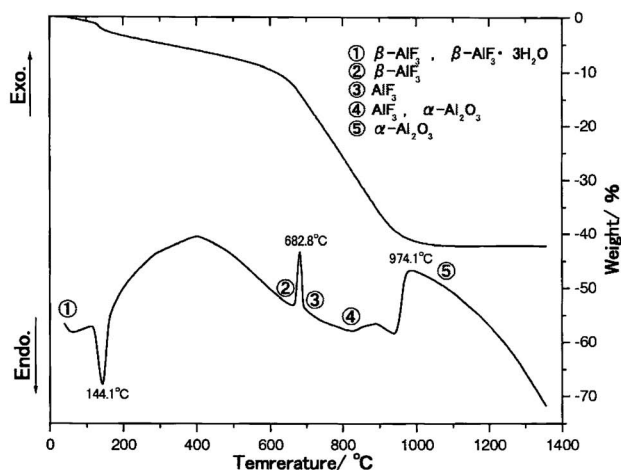

Fig. 2. TG/DTA curves of aluminum fluoride as an additive. ①room temperature, ②605°C, ③689°C, ④843°C and ⑤1020°C.

The TG/DTA curves of aluminum fluoride to be an additive are shown in **Fig. 2**. On the DTA curve, a sharp endothermic peak at 144.1°C, a sharp exothermic peak at 682.8°C and complicated curves above 800°C were observed. Five tem-

peratures on the curve were selected and the crystalline phases in the specimens heated up to these temperatures were examined (①room temperature, ②605°C, ③689°C, ④843°C and ⑤1020°C). The results are also shown in Fig. 2. The endothermic peak at 144.1°C is related to the decomposition of β-$AlF_3 \cdot 3H_2O$ to anhydride and the exothermic peak at 682.8°C to the phase transition of β-AlF_3 to AlF_3. The DTA curve above 800°C could not be analyzed. The weight loss heated up to 1350°C was about 42%. If all AlF_3 is converted to α-Al_2O_3 by the oxidation, the theoretical weight loss is 39.3%. The difference would be attributed to the dehydration of adsorbed water on powders and the decomposition of β-$AlF_3 \cdot 3H_2O$ to anhydride. The amount of adsorbed water is about 1 mass% from the estimation of the weight loss up to around 120°C. As the theoretical weight loss of the conversion of $AlF_3 \cdot 3H_2O$ to AlF_3 is 39.1%, the content of β-$AlF_3 \cdot 3H_2O$ in additive powder is evaluated to be about 5 mass%. On the TG curve, the weight loss increased gradually over about 3% above the decomposition temperature of β-$AlF_3 \cdot 3H_2O$, of which value is equivalent to the total of adsorbed water and weight loss based on the decomposition of β-$AlF_3 \cdot 3H_2O$ to anhydride. The increase of weight loss means that the decomposition of β-AlF_3 progresses slowly to generate hydrogen fluoride even at the low temperature range below the phase transition temperature of β-AlF_3 to AlF_3, though the decomposition product is unknown. As there is a possibility that water vapor acts to decompose AlF_3 to form Al_2O_3, a free energy of the following reaction at 500 K (227°C) was estimated from the JANAF data.[11] In this calculation, the value of γ-Al_2O_3 for Al_2O_3 was used.

$$2AlF_3(g) + 3H_2O(g)$$
$$\longrightarrow Al_2O_3(s) + 6HF(g) \quad \Delta G = -137.5 \text{ kJ}$$
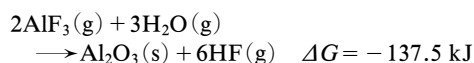
From the result the decomposition of β-AlF_3 would be caused by the attack of water vapor generated during the decomposition of β-$AlF_3 \cdot 3H_2O$, though a vapor pressure of β-AlF_3 must be very low. Above the phase transition temperature of β-AlF_3 to AlF_3, a weight loss of fluoride increased rapidly, indicating the decomposition of AlF_3 to form α-Al_2O_3. The weight loss stopped around 1000°C.

Figure 3 shows the DTA curves of specimens with and without 2 mass% of aluminum fluoride additive. On the curve of the specimen without additive, a large endothermic peak at 316.2°C, a small endothermic peak at 532.5°C and a small exothermic peak at 1234°C were observed. The endothermic peak at lower temperature is related to the phase change of gibbsite to boehmite and the endothermic peak at higher temperature to the decomposition of boehmite to γ-Al_2O_3. The exothermic peak at high temperature is corresponding mainly to the transition of κ-Al_2O_3 to α-Al_2O_3, supporting XRD results of the specimens heated to the temperatures before and after the exothermic peak. These phase transitions will be discussed later. On the curve of the specimen with additive, an exothermic peak at high temperature did not appear. Disappearance of the exothermic peak suggests that the transition to α-Al_2O_3 progresses slowly.

Figure 4 illustrates DTA curves of the specimens with and without additive around the temperature range of two endothermic peaks. The large endothermic peak related to the phase change of gibbsite to boehmite shifted to the high temperature side with the amount of additive. Temperature of the top of peak was 322.7°C for the specimen with 2 mass% of additive and 325.8°C for the specimen with 10 mass%, compared with 316.2°C for the specimen without additive. As a part of aluminum fluoride additive is supposed to decompose

already around these temperatures, it is inferred that hydrogen fluoride generated through the decomposition retards the phase change of gibbsite to boehmite. That is, gibbsite particles chemisorb hydrogen fluoride, and as the result the phase change to boehmite is restrained and the temperature shifts to higher temperature side. The decomposition of aluminum fluoride would be supported by its disappearance in the specimen heated up to 400°C and the free energy change of the decomposition reaction with water vapor as described above.

Figure 5 shows XRD patterns of the fired specimens with and without 2 mass% of additive. The patterns of specimen without additive heated above 1100°C are illustrated to be compared with the data of κ-Al₂O₃[12),13)] and θ-Al₂O₃.[14)] In both specimens heated up to 400°C, main sharp peaks belonging to boehmite were observed, while peaks belonging to a spinel type phase were broad and a small amount of gibbsite remained. The peaks belonging to β-AlF₃ were not observed in

the specimen with additive. In specimens with and without additive heated up to 900 and 950°C, the patterns were similar to show spinel type phase. In the specimen without additive, small peaks belonging to κ-Al₂O₃ newly appeared by heating up to 1000°C, in addition to a main phase of κ-Al₂O₃ θ-Al₂O₃ was also formed by heating up to 1100°C and 1200°C, and all peaks belonged to α-Al₂O₃ by heating up to 1300°C. On the other hand, in the specimen with additive, a main product was α-Al₂O₃ already by heating up to 1000°C. In this specimen, a small amount of spinel type phase remained. These results suggest that spinel type phase transformed directly to α-Al₂O₃ without passing through κ- and θ-Al₂O in the specimen with additive.

Both χ- and γ-Al₂O₃ have a spinel type structure and their diffraction peaks are broad and similar. Their distinction is difficult only on the XRD pattern, though the main difference
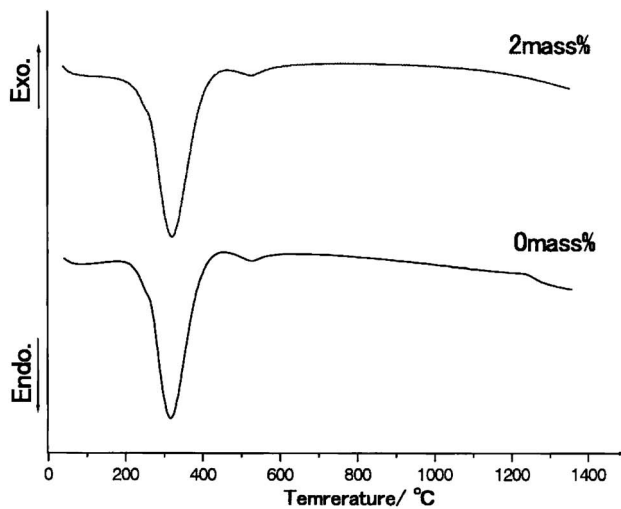
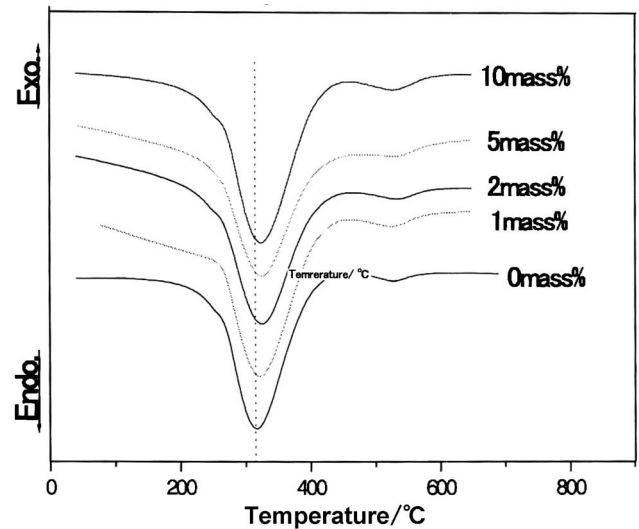Fig. 3. DTA curves of specimens with and without 2 mass% of aluminum fluoride.

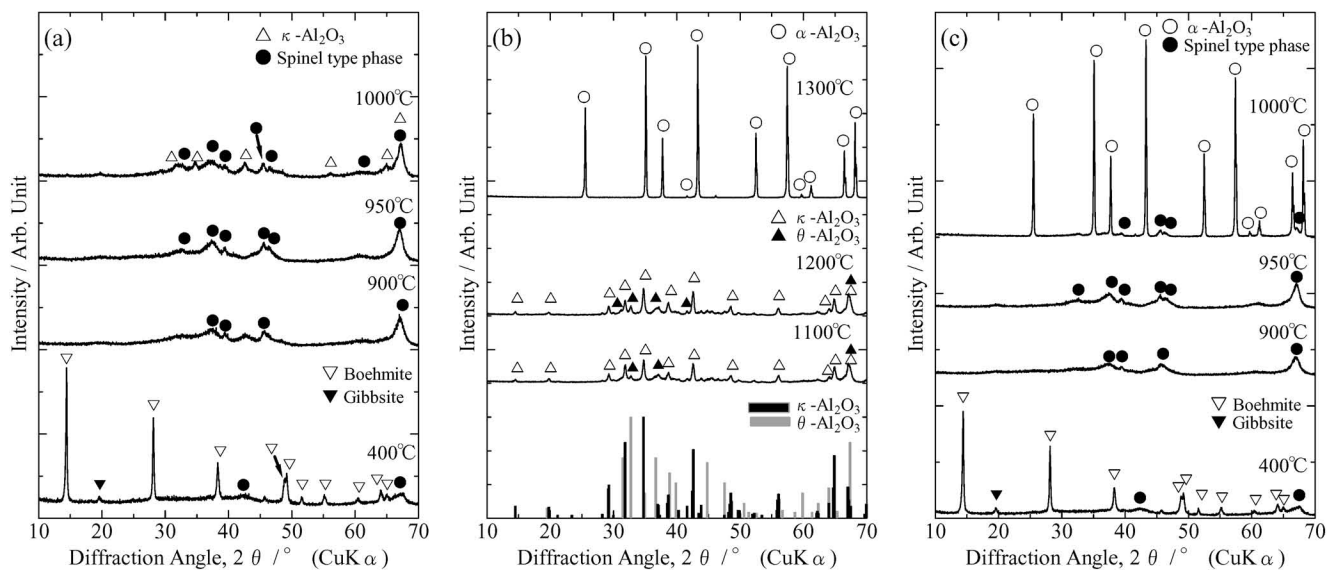Fig. 4. DTA curves of specimens with and without additive around the two endothermic peaks.

Fig. 5. XRD patterns of specimens with and without 2 mass% of additive heated up to various temperatures. (a) Specimen without additive (below 1000°C), (b) Specimen without additive (above 1100°C), χ-Al₂O₃: standard peaks position of χ-Al₂O₃[12)] θ-Al₂O₃: standard peaks position of θ-Al₂O₃[14)], (c) Specimen with additive.

10 μm
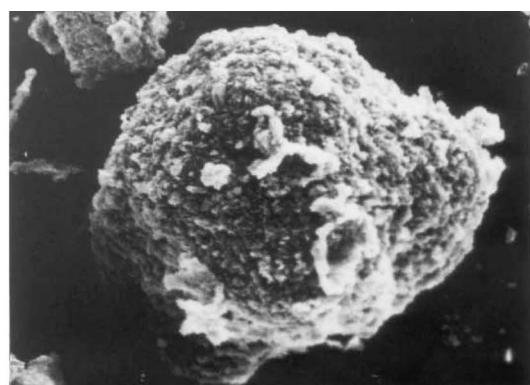
Low magnification

1 μm

High magnification

Fig. 6.   SEM photographs of the specimen with 2 mass% of additive heated up to 1000°C.

1 μm

Fig. 7.   SEM photograph of fired specimen of gibbsite at 1200°C for 1 h.

Table 1.   Amount of Remaining Fluorine in Specimens Heated up to 950°C and 1000°C

Specimen	Fluorine content (mass%)
Heated specimen up to 950°C	0.80
Heated specimen up to 1000°C	0.25

is a peak around 42–43° (CuKα 2θ) and χ-Al$_2$O$_3$ has it, while γ-Al$_2$O$_3$ has not.[15] As gibbsite decomposes not to form γ-Al$_2$O$_3$ directly, fine gibbsite powder under 1 μm in size decomposes to form χ-Al$_2$O$_3$ above 300°C and boehmite decomposes to form γ-Al$_2$O$_3$ above 500°C,[1),15)] spinel type phase in the specimens heated up to 400°C would be χ-Al$_2$O$_3$. Since χ-Al$_2$O$_3$ transforms to κ-Al$_2$O$_3$ above 850°C and γ-Al$_2$O$_3$ transforms to θ-Al$_2$O$_3$ through δ-Al$_2$O$_3$ above 1050°C,[1),15)] the spinel type phase in the specimen heated up to 900 and 950°C is inferred to be a mixture of χ- and γ-Al$_2$O$_3$. Although a large amount of boehmite was observed in the specimen heated up to 400°C, κ-Al$_2$O$_3$ was a main phase rather than θ-Al$_2$O$_3$ in the specimen without additive heated up to above 1100°C. The reason is not clear.

Figure 6 is the SEM photographs of the specimen with additive heated up to 1000°C. The specimen consists of clear, hexagonal plate-like particles about 1 μm and the massive figure is rounded, suggesting a different image from a relic of gibbsite particle, while a specimen without additive fired at 1200°C for 1 h consists of fine cocoon-like particles about 0.3 μm (Fig. 7). These photographs indicate that the addition of aluminum fluoride to gibbsite particles accelerates the crystal growth of α-Al$_2$O$_3$ to form the automorphic crystals.

The amount of remaining fluorine in the specimens heated up to before and after the transition temperature to α-Al$_2$O$_3$ is

listed in **Table 1**. By the way, the amount of fluorine is calculated to be 2.23 mass% in the original mixture specimen with 2 mass% additive. The fired specimens were prepared by heating about 9 g of the original specimen in an alumina covered crucible up to 950°C and 1000°C. A part of the specimen was supplied for the XRD test and the residual part of about 5 g for the chemical analysis. A very small amount of α-Al$_2$O$_3$ was detected besides spinel type phase in the specimen heated up to 950°C, while α-Al$_2$O$_3$ single phase in the specimen heated up to 1000°C. The results show that a remaining amount of fluorine decreases considerably during the transition to α-Al$_2$O$_3$ and that 0.25 mass% of fluorine remains even after the transition to α-Al$_2$O$_3$. Supposing that fluorine ions connect with aluminum ions on α-Al$_2$O$_3$ surface by the correspondence of 1 : 1 and that α-Al$_2$O$_3$ crystal is 1 μm width and 0.1 μm thickness, an amount of chemisorbed fluorine ion on α-Al$_2$O$_3$ was estimated. In this estimation, total number of aluminum ions on the crystal surface was calculated, also supposing that the basal plane of one corundum unit cell consists of two aluminum ions and three oxygen ions, though these aluminum ions and oxygen ions are not positioned exactly on the same basal plane. The calculated result was 0.20 mass%. This value is corresponding to the value by the chemical analysis (0.25 mass%), imaging that many α-Al$_2$O$_3$ crystals are smaller than 1 μm width and that a part of fluorine ions might be engulfed into α-Al$_2$O$_3$ crystals. These results suggest that a considerable amount of fluorine remains on the surface of alumina particles even after the conversion to α-Al$_2$O$_3$.

Figure 8 is a SEM micrograph and XRD pattern of the coexisting specimen of spinel type phase and α-Al$_2$O$_3$. The specimen was prepared by heating the original mixture enclosed in a platinum foil envelop up to 930°C. On the XRD pattern, clear peaks belonging to κ- and θ-Al$_2$O were not observed. The result means that spinel type phase transformed directly to α-Al$_2$O$_3$ without passing through κ- and θ-Al$_2$O in the specimen with additive. On the micrograph, a part of gathering of hexagonal plate–like particles (α-Al$_2$O$_3$) with
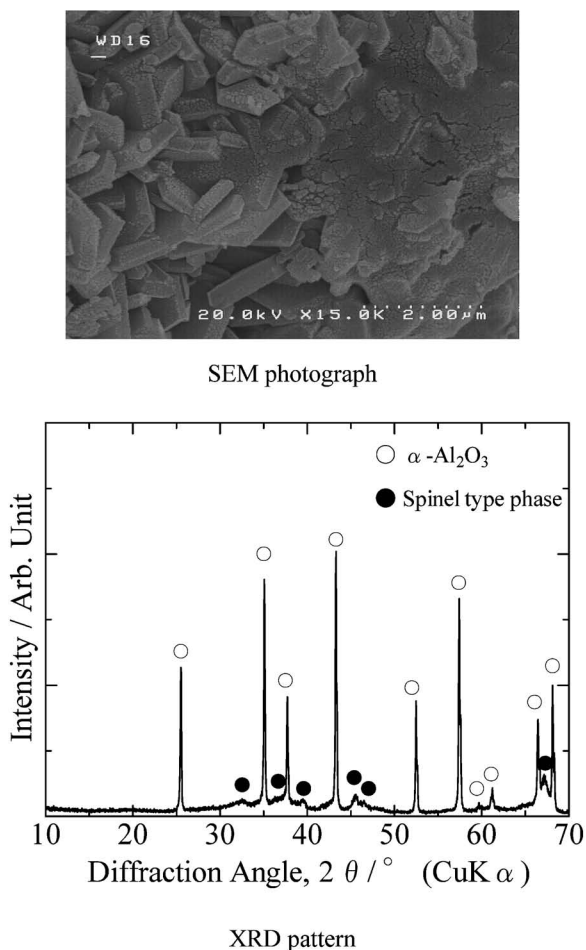
SEM photograph

XRD pattern

Fig. 8. SEM photograph and XRD pattern of specimen with 2 mass% of additive heated up to 930°C. Specimen was enclosed in a platinum foil envelop.

about 1 μm width and an obscure part (spinel type phase) were observed. Around the boundary area, some hexagonal particles seem to be buried in an obscure part. This figure suggests that hexagonal particles grew rapidly from an obscure part to the size about 1 μm width and that then the growth of particles stopped. Considering the short transport distance, it is better to understand that a surface diffusion also contributes to the mechanism of the material transport in addition of the vapor phase transport suggested by Daimon and Kato.[10] The surface diffusion of alumina would be accelerated by the presence of fluorine ion or hydrogen fluoride chemisorbed on fine spinel type phase particles.

An increase of the amount of specimen with additive put in an alumina covered crucible lowered the transition temperature of spinel type phase to α-Al₂O₃ as described above. And in the case of the specimen enclosed in a platinum foil envelop, the transition temperature was further lowered, as obtained the coexisting specimen of spinel type phase and α-Al₂O₃ by heating up to 930°C. These instances show that an increase of the concentration of fluorine in a container accelerates the phase transition of spinel type phase to α-Al₂O₃. Selecting a closed system for the firing process of aluminum hydroxide materials to α-Al₂O₃, the addition of a small amount of fluo-

ride gives effective results to obtain relic-free particles of original material and hexagonal plate-like particles of α-Al₂O₃, though hydrogen fluoride and fluorine are poisonous gases.

4. Conclusion

Influence of addition of AlF₃ on thermal decomposition of coarse gibbsite particles and phase transition of the intermediate alumina to α-Al₂O₃ was investigated.

（1） The addition of fluoride to gibbsite disappeared an exothermic peak corresponding to the transition of κ-Al₂O₃ to α-Al₂O₃ on the DTA curve.

（2） A small amount of aluminum fluoride decomposed slowly with water vapor to generate hydrogen fluoride even at the low temperature range below the phase transition point of β-AlF₃ to AlF₃. Gibbsite particles chemisorbed hydrogen fluoride, and as the result the phase change to boehmite was restrained and the phase change temperature shifted to higher temperature side.

（3） In the specimen with additive spinel type phase transformed directly to α-Al₂O₃, without passing through κ- and θ-Al₂O₃ phases. The formed α-Al₂O₃ consisted of clear, hexagonal plate-like particles about 1 μm, disappearing a relic of gibbsite particle. The formation of automorphic crystals suggests that a surface diffusion also contributes to the mechanism of this material transport in addition to the vapor phase transport.

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