

Effect of pore characteristics of $\text{AlO}(\text{OH})$ nano gel on crystal growth of $\alpha\text{-Al}_2\text{O}_3$ platelets by molten salt precipitation

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To precipitate the complex gel of a flux and an aluminum hydroxides gel, an aqueous solution of a mixture of Na_2CO_3 and $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ was added with stirring into an aqueous solution of a mixture of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, Na_2SO_4 and K_2SO_4 , and then the complex gel was aged in 0~30 h at 90°C. As aging time passed, the aluminum hydroxides contained in the complex gel were grown to a acicular $\text{AlO}(\text{OH})$ nano gel. Also, aging time had an effect on the physical properties of the $\text{AlO}(\text{OH})$ nano gel and on the crystal growth of the $\alpha\text{-Al}_2\text{O}_3$ platelets prepared by molten-salt precipitation. In this study, the complex gel was crystallized in the temperature range of 400~1,200°C and after drying at 110°C, the effect of aging time on precipitation temperature, the size, thickness, morphology and particle size distribution of the $\alpha\text{-Al}_2\text{O}_3$ platelets were investigated. As aging time passed, the $\alpha\text{-Al}_2\text{O}_3$ platelets showed a tendency toward an increase in size and thickness as a result of an increase in BET surface area and pore volume of the $\text{AlO}(\text{OH})$ nano gel.

Key words: $\text{AlO}(\text{OH})$ gel, $\alpha\text{-Al}_2\text{O}_3$ platelets, molten salt precipitation, pearlescent substrate, insulator.

Introduction

$\alpha\text{-Al}_2\text{O}_3$ platelets have been used as an insulator, a reinforcing agent to improve mechanical properties of ceramic materials, an additive to improve thermal conductivity, and a substrate for a pearl pigment [1-3]. Among these, to become a proper substrate for a pearl pigment, it should have a flake shape with a thickness of less than 0.3 μm and an aspect ratio of more than 50, and has to be colorless and possible for light transmission, without aggregation, twin crystals, and edge growth. Also, if the thickness of crystal is thick or the surface is not uniform, light is scattered and the pearl luster characteristic is lowered when coated with metal oxides, and thus it is important to manufacture crystals of a thin thickness and a uniform surface finish.

$\alpha\text{-Al}_2\text{O}_3$ has a hexagonal, flaky, compact structure with 1.7 refractive index, 0.1~1.5 μm thickness, 2~60 μm in size, and melting point of 2,050°C, and is not dissolved in acidic or alkaline solutions. Either opaque or transparent flaky crystals are produced depending on the characteristics of the $\text{AlO}(\text{OH})$, a precursor, and the complex gel of flux, Na_2SO_4 and K_2SO_4 , and the action of the molten salt, and this is greatly affected by the grain morphology, pore structure, and physical properties of the $\text{AlO}(\text{OH})$ gel. As with precursors of $\alpha\text{-Al}_2\text{O}_3$ platelets, it is useful to use the complex gel of

$\text{AlO}(\text{OH})$ and flux, which is obtained through the hydrolysis of a mixed solution of $\text{Al}_2(\text{SO}_4)_3$ and Na_2SO_4 and K_2SO_4 with alkali by a sol-gel method. The $\text{AlO}(\text{OH})$ goes through a phase transition to $\gamma\text{-Al}_2\text{O}_3$ at above 400°C and $\alpha\text{-Al}_2\text{O}_3$ is precipitated at above 850°C [4-7], and Na_2SO_4 and K_2SO_4 melt at about 840°C to form a molten salt. The $\alpha\text{-Al}_2\text{O}_3$ platelets for the pearl pigment are made by heating $\text{AlO}(\text{OH})$ or $\gamma\text{-Al}_2\text{O}_3$ to 1,000~3,000°C in a molten salt solution, during which nucleation and crystal growth are followed [8-11].

In general, if the complex gel produced by the sol-gel method is crystallized by a molten salt method, the platelet crystals with a large aspect ratio and very uniform surface finish are generated, and thus it is very appropriate as a substrate for a pearl pigment.

The nucleation of $\alpha\text{-Al}_2\text{O}_3$ platelets is divided into homogeneous nucleation, in which typical nucleation by atomic diffusion while relying on the supersaturation of the solution in the molten salt solution, and heterogeneous nucleation, in which nucleation is formed on the surface of the container holding the solution or the surface of other solids and contaminants in the solution [12]. However, most of the nuclei of $\alpha\text{-Al}_2\text{O}_3$ platelets are made by heterogeneous nucleation, in which nucleation is formed on the surface of solids such as the crucible or contaminant particles and the interfacial energy is much smaller than that for homogeneous nucleation so that the activation energy is lowered for much easier heterogeneous nucleation. In the heterogeneous nucleation, the activation energy is greatly changed depending on the wetting angle, which

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is formed between the solution and the solid surface, with the smaller the wetting angle, the smaller the driving force required for nucleation, and thus the easier the nuclei form. However, nucleation is difficult even though the wetting angle is small, because the chemical affinity or physical properties on the surface is more important than the wetting angle. Therefore, nucleation becomes easier if there are micro-pores or grooves on the solid surface or there is chemical activation between the nucleation material and the solid surface, than on a smooth surface [13].

When $\alpha\text{-Al}_2\text{O}_3$ crystals grow in the molten salt solution, the phase transition temperature is lowered by 200–400°C, and a solid state nucleus is formed in the liquid state and grows by the supersaturation of the solution and the diffusion of oxygen, and thus the values of surface free energy and volume free energy are decreased to greatly lower the activation energy required for $\alpha\text{-Al}_2\text{O}_3$ crystal growth. Because this molten salt is water-soluble, solid state $\alpha\text{-Al}_2\text{O}_3$ platelets can be easily obtained by dissolving the salt in water, filtering, and washing.

In this study, $\text{Al}_2(\text{SO}_4)_3 \cdot 14\sim 18\text{H}_2\text{O}$ and a mixed solution of Na_2SO_4 and K_2SO_4 were hydrolyzed by a mixed solution of Na_2CO_3 and $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ to produce precursors and dried, and then $\alpha\text{-Al}_2\text{O}_3$ platelets were produced by a molten salt solution precipitation method [14] at 1,200°C. Also, aggregation and twin crystals were inhibited and $\alpha\text{-Al}_2\text{O}_3$ platelets with a thin thickness, a uniform surface finish, and a large aspect ratio were made by investigating the effect of gel aging time on the crystal growth of $\alpha\text{-Al}_2\text{O}_3$ platelets which are used as abrasives, ceramic materials, insulators, and substrates for pearl pigments.

Experimental Methods

Starting materials

$\text{Al}_2(\text{SO}_4)_3 \cdot 14\sim 18\text{H}_2\text{O}$ (Aldrich) was used as a starting material for $\alpha\text{-Al}_2\text{O}_3$ platelets and Na_2SO_4 and K_2SO_4 (Jin Chem. Co. Ltd., Korea) were used as a flux, and Na_2CO_3 (Shinyo Chem. Co. Ltd., Japan) and $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (Sigma-Aldrich Co., USA) were used as an alkali for the hydrolysis. The $\text{Al}_2(\text{SO}_4)_3 \cdot 14\sim 18\text{H}_2\text{O}$ contained a trace amount of heavy metal ions and Fe ions.

Preparation of $\alpha\text{-Al}_2\text{O}_3$ platelets

A sample of 2,470 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ solution, 340 g of Na_2SO_4 and 280 g of K_2SO_4 was placed in a 5 l reaction container and dissolved at 60°C to produce a mixed acid solution, while 1,220 g of Na_2CO_3 solution and a small amount of $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ were placed in a 1 l reaction container and dissolved at 60°C to produce a mixed alkali solution. The mixed alkali solution was added with stirring into the mixed acid solution and hydrolyzed at pH 7.0 to precipitate the complex gel of

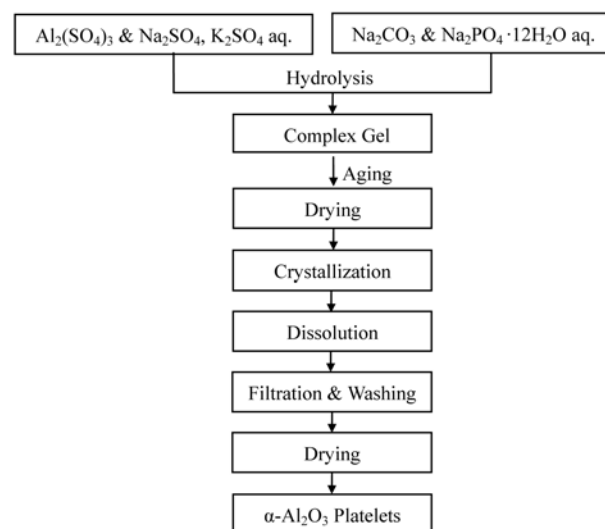


Fig. 1. Process diagram for the experimental procedure.

the flux and aluminum hydroxides, and then aged at 90°C for 0–30 h. The complex gel after aging was dried at 110°C for 24 h and pulverized to less than 5 mm, and then crystallized by heating at 400–1,200 °C. It was cooled down to room temperature to separate the flux and $\alpha\text{-Al}_2\text{O}_3$ platelets, and then dissolved in water, filtered, washed, and dried to produce $\alpha\text{-Al}_2\text{O}_3$ platelet powder. All experimental procedures are shown in Fig. 1.

Analysis & observation

Morphological changes as a function of the aging time of aluminum hydroxides and $\text{AlO}(\text{OH})$ gel included in the complex gel were observed using a transmission electron microscope (TEM, TECNAI G²), and changes of surface area, pore volume, and pore size were measured by the N_2 BET method (ASAP 2000, Micro. Inst.), and the crystal structure was identified by performing X-ray diffractometry (XRD, D/MAX-IIIB, Rigaku Denki). Differential thermal analysis (TGA-DTA, SDT 2960, TA Instruments, USA) was performed to investigate the phase transition temperature of the flux and $\text{AlO}(\text{OH})$ mixed gel, and a laser particle size analyzer (PSA, Malvern Instruments Ltd., Malvern, UK) was used for the measurement of particle distribution changes of the $\alpha\text{-Al}_2\text{O}_3$ platelets as a function of aging time. Morphological changes, size, and thickness of the $\alpha\text{-Al}_2\text{O}_3$ platelets were measured using scanning electron microscopy (SEM, JSM-840A, JEOL Co., Japan).

Results and Discussion

Crystal structure and morphological changes of $\text{AlO}(\text{OH})$ gel

The crystal structure of $\text{AlO}(\text{OH})$ gel forms a unit lattice with oxygen atoms coordinated on the edge of an octahedron with an aluminum ion in the center, and such a unit lattice is connected to form $(\text{AlOOH})_2$

layers and hydrogen bonds are formed between these layers. $\text{AlO}(\text{OH})$ has the same crystal structure as boehmite, which has 1 mole of water per 1 mole of Al_2O_3 , and contains 1.1–1.8 moles of water molecules per 1 mole of Al_2O_3 between the layers of chain-like $[\text{AlO}(\text{OH})]_2$. The crystal size is about 5–10 nm and the X-ray diffraction pattern has a characteristic peak with a wide full width at half maximum at the same diffraction angle as boehmite crystal [15–20].

When a mixed solution of $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and Na_2SO_4 and K_2SO_4 was slowly hydrolyzed with a mixed solution of Na_2CO_3 and $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ at above 60°C , $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ was precipitated as aluminum hydroxide gel. When the hydrolysis temperature was lower than 60°C , dissolved $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and Na_2SO_4 and K_2SO_4 were precipitated to inhibit the hydrolysis, and thus the temperature should be maintained at above 60°C . After the hydrolysis, Na_2SO_4 and K_2SO_4 contained in the complex gel were dissolved in water and completely eliminated through filtering and washing to observe the crystal structure and morphological changes of aluminum hydroxide gel. When it was not aged as shown in Fig. 2(a), the X-ray diffraction pattern was similar to an $\text{AlO}(\text{OH})$ crystal but precipitated as needle-like aluminum hydroxide gel without observation of the main peak near 14° . As shown in Fig. 2(b), (c), and (d), when precipitated aluminum hydroxide gel was aged at 90°C , it grew into needle-like $\text{AlO}(\text{OH})$ crystals. The crystal growth of $\text{AlO}(\text{OH})$ gel is determined by the OH^- existing between the layers of $[\text{AlO}(\text{OH})]_2$, and the lower the hydrolysis pH is, the lower the aging temperature is and the lower the $\text{H}_2\text{O}/\text{Al}_2(\text{SO}_4)_3$ mole ratio is, there are more OH^- ions existing between the layers of $[\text{AlO}(\text{OH})]_2$. At this time, if the rate of OH^- existing between the layers of $[\text{AlO}(\text{OH})]_2$ to condense into water and being separated is low, the distance between the layers is increased to induce the distortion of the $[\text{AlO}(\text{OH})]_2$ layers and to slow down the crystal growth [21]. The reason that Fig. 2(b), (c), and (d) showed similar X-ray diffraction intensity is because the hydrolysis pH was low and the $\text{H}_2\text{O}/\text{Al}_2(\text{SO}_4)_3$ mole ratio was low, and thus the activation energy for crystal growth was low and the rate of crystal growth

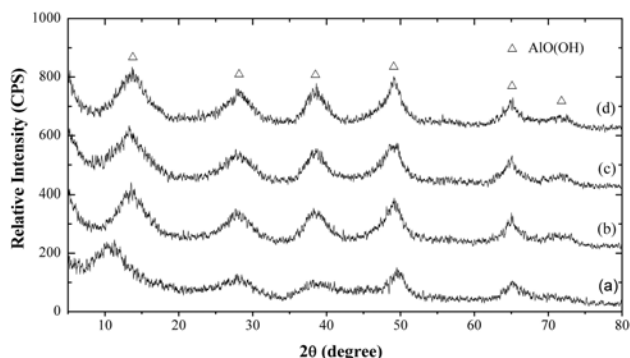


Fig. 2. XRD patterns of aluminum hydroxides and an $\text{AlO}(\text{OH})$ gel as a function of aging time: (a) 0 h, (b) 10 h, (c) 20 h and (d) 30 h.

was slow resulting in no difference in diffraction intensity.

Figure 3 showed the TEM micrographs of morphological changes of needle-like particles with aging time. As shown in this figure, small and thin needle-like crystals grew into long and thick needle-like crystals without aggregation as the aging time passed. Therefore, no difference was observed in the X-ray diffraction characteristics with aging time, except for the case of no aging, and only the morphology of the crystals was changed.

Changes in micro-pore structure of $\text{AlO}(\text{OH})$ gel

$\text{AlO}(\text{OH})$ has a very large BET surface area as much as $300\text{--}500\text{ m}^2/\text{g}$ and pore Volume as much as $0.6\text{--}1.2\text{ m}^3/\text{g}$, and if calcinated at $400\text{--}600^\circ\text{C}$, it shows a maximum 30% of weight reduction due to the break away of crystal water and surface-adsorbed water, resulting in the phase transition to $\gamma\text{-Al}_2\text{O}_3$.

The aging time of the complex gel for optimal precipitation of $\alpha\text{-Al}_2\text{O}_3$ platelets in the molten salt can be found by examining the changes in micro-pore structure of $\text{AlO}(\text{OH})$ gel with aging time. Figure 4 shows plots of N_2 ads./des. isotherms of aluminum hydroxides and $\text{AlO}(\text{OH})$ gel, which were obtained by filtering and sufficiently washing the hydrolyzed complex gel, at liquid nitrogen temperature after being dried at 110°C for 24 h. In this figure, in the case of no aging, an aluminum hydroxide gel with almost no BET surface area and pores was precipitated. This is because the gel could not grow into $\text{AlO}(\text{OH})$ crystals as seen in Fig. 2(a) and Fig. 3(a). Figure 4(b), (c), and (d) show isotherms with increased adsorption volume and Inconsistent adsorption/desorption because the precipitated amorphous gel grew into $\text{AlO}(\text{OH})$ crystals and pores

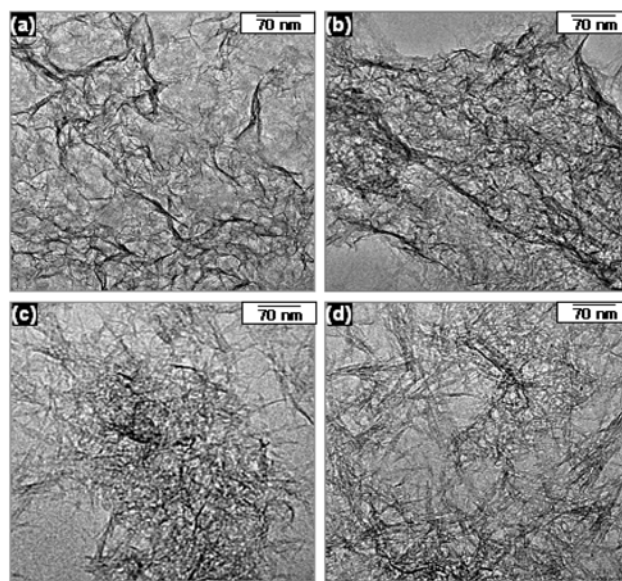


Fig. 3. TEM micrographs of aluminum hydroxides and an $\text{AlO}(\text{OH})$ gel as a function of aging time: (a) 0 h, (b) 10 h, (c) 20 h and (d) 30 h.

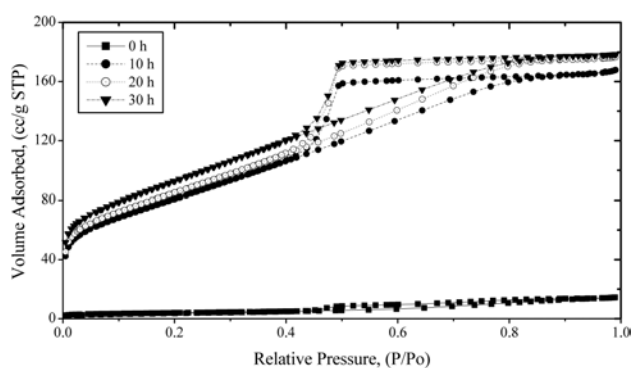


Fig. 4. N_2 ads./des. isotherms of aluminum hydroxides and an $\text{AlO}(\text{OH})$ gel as a function of aging time.

Table 1. Pore Characteristics of $\text{AlO}(\text{OH})$ Nano Gel as a Function of Aging Time

Aging Time (h)	BET Surface Area (m^2/g)	Pore Volume between 30–40 (cc/g)	Total Pore Volume (cc/g)
0	13.90	0.01	0.02
10	291.98	0.16	0.26
20	305.14	0.18	0.27
30	334.27	0.04	0.28

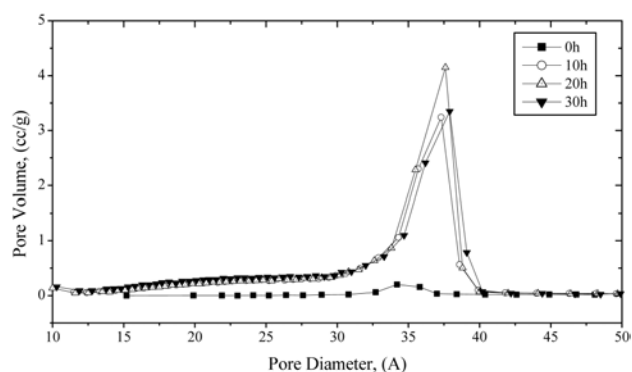


Fig. 5. Pore size distributions of aluminum hydroxides and an $\text{AlO}(\text{OH})$ gel as a function of aging time.

were developed as time passed. As shown in Fig. 3, Fig. 4, and Table 1, in the case when it was aged at 90°C , it can be seen that needle-like crystals grew and the BET surface area and pore volume were increased as the aging proceeded. However, as shown in Fig. 5, pores in the range of 30–40 Å developed mostly when aged for 20 h and then decreased afterwards, which is because $\text{AlO}(\text{OH})$ crystals have continuously produced micro-pores in the range of 30–40 Å for up to 20 h and then micro-pores fused with each other to develop into bigger pores due to continuous crystal growth.

Changes in crystals of $\text{AlO}(\text{OH})$ gel as a function of heating temperature

DTA curves as a function of aging time of the complex gel are shown in Fig. 6. In this figure, the endothermic peak near 270°C appeared because Na_2SO_4

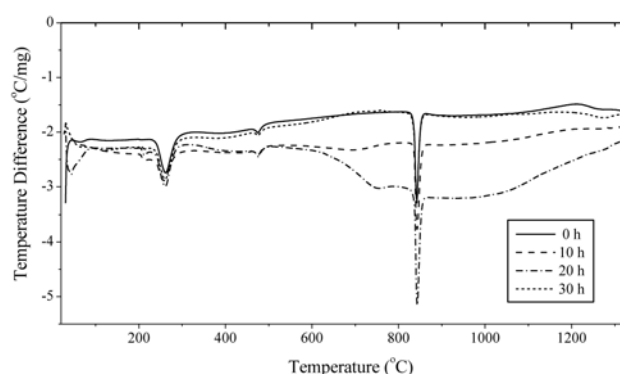


Fig. 6. DTA curves of aluminum hydroxides and an $\text{AlO}(\text{OH})$ gel as a function of aging time.

and K_2SO_4 were dehydrated from the hydrate to anhydride, and the endothermic peak near 450°C appeared because of the phase transition of $\text{AlO}(\text{OH})$ to $\gamma\text{-Al}_2\text{O}_3$, and the endothermic peak near 840°C was due to melting of Na_2SO_4 and K_2SO_4 . In this figure, no endothermic peaks near 600°C were observed in samples with no aging and samples with 30 h of aging, but endothermic peaks were observed in samples with 10 and 20 h of aging. From this, an aging time in the range of 10–20 h precipitated $\alpha\text{-Al}_2\text{O}_3$ platelets even at a low temperature at which a molten salt is not formed. As in Fig. 5, the precipitation temperature of $\alpha\text{-Al}_2\text{O}_3$ crystals was greatly lowered when crystallizing $\text{AlO}(\text{OH})$ crystals with maximally developed micro-pores in the range of 30–40 Å by the molten salt solution precipitation method. When an $\text{AlO}(\text{OH})$ gel of the metastable phase contained in the complex gel was aged at 90°C , micro-pores in the range of 30–40 Å inside the needle-like crystals were continuously made and grown to a maximum, in which $\text{AlO}(\text{OH})$ gel was in the state of high energy due to many micro-pores contained in the crystals, and thus the precipitation of $\alpha\text{-Al}_2\text{O}_3$ platelets in the molten salt by inter-particle condensation was easier. Thus, when $\alpha\text{-Al}_2\text{O}_3$ platelets were produced by the molten salt solution precipitation method from the complex gel of $\text{AlO}(\text{OH})$ and Na_2SO_4 and K_2SO_4 precipitated by the sol-gel method, aging was required to precipitate $\alpha\text{-Al}_2\text{O}_3$ crystals even at a low temperature, and when it was aged at 90°C for 20 h, the precipitation temperature for $\alpha\text{-Al}_2\text{O}_3$ platelets was the lowest. Figure 7 shows the XRD patterns of samples obtained by crystallization of the complex gel at 400°C , 600°C , and $1,000^\circ\text{C}$ for 1 h and then dissolved in water and filtered and washed, and Fig. 8 shows the micrographs of crystals at 400°C , 600°C , and $1,000^\circ\text{C}$. This figure shows $\gamma\text{-Al}_2\text{O}_3$ crystal structure up to 400°C , but $\alpha\text{-Al}_2\text{O}_3$ crystals were precipitated after 600°C . However, as the crystallization temperature was lowered, Na_2SO_4 and K_2SO_4 used as the flux were not well dissolved and were adhered to the particle surface to cause particle aggregation, and when the crystallization temperature was increased above $1,000^\circ\text{C}$, the

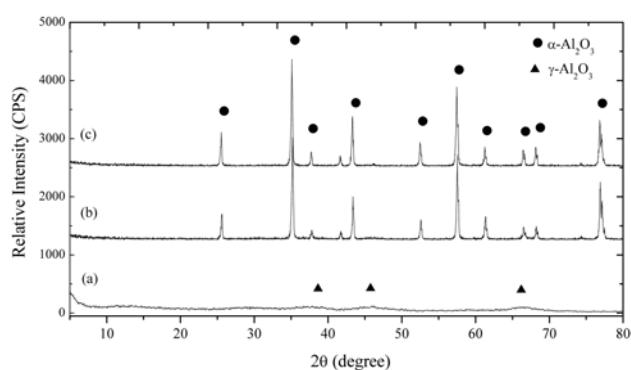


Fig. 7. XRD patterns for the α - Al_2O_3 platelets precipitated from the complex gel aged in 20 h at 90°C as a function of heating temperature: (a) 400°C, (b) 600°C and (c) 1,000°C.

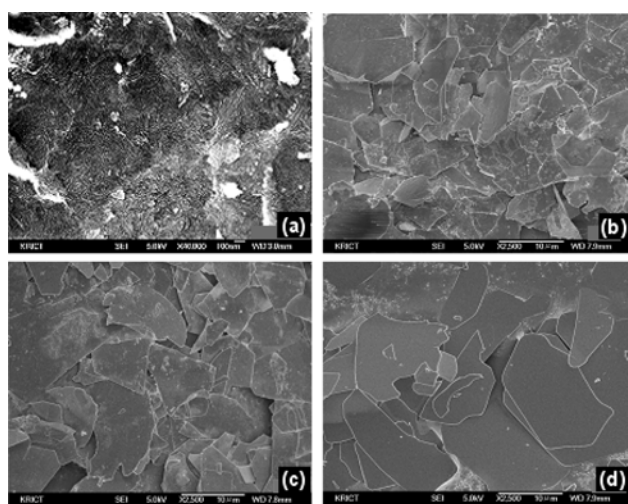


Fig. 8. SEM micrographs for the α - Al_2O_3 platelets precipitated from the complex gel aged in 20 h at 90°C as a function of heating temperature: (a) 400°C, (b) 600°C, (c) 800°C, and (d) 1,000°C.

surface tended to be clean and the particle size tended to increase. Therefore, it is desirable to maintain the crystallization temperature at above 1,000°C to obtain clean α - Al_2O_3 crystals without aggregation, with even surfaces.

Morphological changes in flaky α - Al_2O_3 crystal as function of aging time

Figure 9 shows the XRD diffraction patterns of the complex gel aged for 0, 10, 20, and 30 h at 90°C and crystallized for 5 h at 1,200°C. In this figure, these are peaks of Na_2SO_4 and K_2SO_4 used as the flux except for an α - Al_2O_3 peak. The α - Al_2O_3 peak was observed over all the aging times and the size of the diffraction intensity tended to increase as the aging time passed. Also, as shown in the SEM micrographs of Fig. 10 and Fig. 11 and Table 2, the particle size tended to increase as the aging time passed, and both the size and thickness of crystal tended to increase above 30 h aging. It is considered that this is because, as in the TEM micrographs of Fig. 3, the size and thickness of

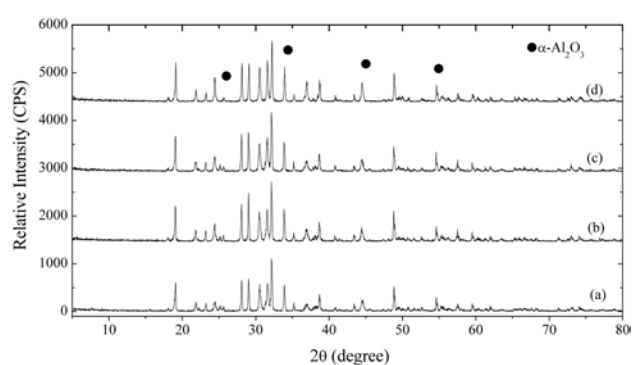


Fig. 9. XRD patterns of the complex gel heated 5 h at 1,200°C as function of aging time: (a) 0 h, (b) 10 h, (c) 20 h and (d) 30 h.

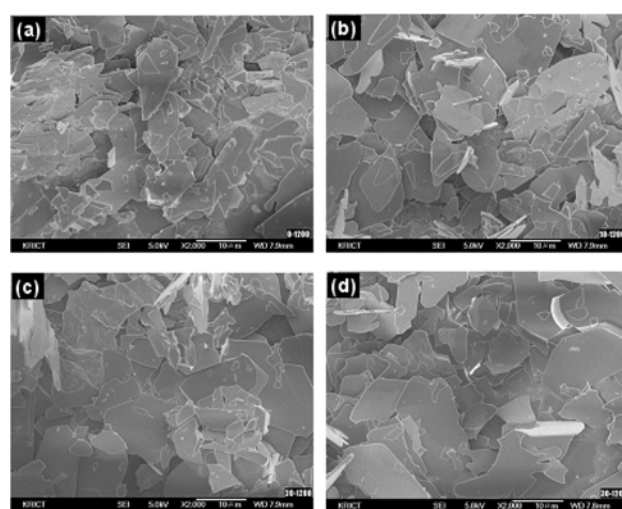


Fig. 10. SEM micrographs showing the morphology of the α - Al_2O_3 platelets precipitated at 1,200°C in a molten-salt as a function of aging time: (a) 0 h, (b) 10 h, (c) 20 h and (d) 30 h.

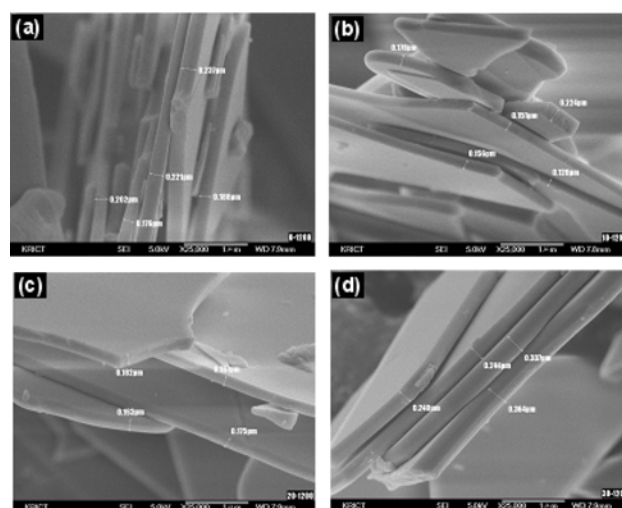
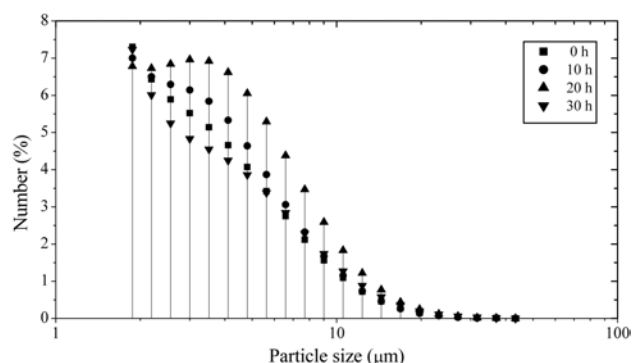


Fig. 11. SEM micrographs showing the thickness of the α - Al_2O_3 platelets precipitated at 1,200°C in a molten-salt as a function of aging time.

the needle-like $\text{AlO}(\text{OH})$ crystals increased as the aging time increased, and when the α - Al_2O_3 platelets

Table 2. Morphological Changes of the $\alpha\text{-Al}_2\text{O}_3$ Platelets as a Function of Aging Time

Aging Time (h)	Crystal Diameter (μm)	Crystal Thickness (μm)	Aspect Ratio	Aggregation
0	9.6	0.15~0.23	50	many
10	10.9	0.15~0.23	57	a little
20	11.6	0.15~0.23	61	little
30	12.8	0.23~0.35	46	little

**Fig. 12.** Particle size distributions of the $\alpha\text{-Al}_2\text{O}_3$ platelets precipitated at 1,200°C in a molten-salt as a function of aging time.

were precipitated in the molten salt by condensation of needle-like particles, the (0001) plane of the thickness direction and (2110), (1120), and (1210) planes of the length directions were also increased. As seen in Fig. 12, small particles were largely observed in cases of no aging and aging for 30 h. It is thought that the large distribution of small particles and bigger average particle size were due to the wide particle distribution. In this figure, samples with 10 or 20 h of aging showed a uniform distribution with smaller numbers of small particles. Therefore, with 10–20 h of aging, flaky $\alpha\text{-Al}_2\text{O}_3$ crystals with a uniform particle size with an average particle size of 12 μm could be made, and the thickness was 0.15–0.23 μm .

Conclusions

When flaky $\alpha\text{-Al}_2\text{O}_3$ crystals were made with the complex gel obtained by hydrolysis of a mixed solution of $\text{Al}_2(\text{SO}_4)_3 \cdot 14\sim 18\text{H}_2\text{O}$ and Na_2SO_4 and K_2SO_4 with a mixed solution of Na_2CO_3 and $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$, the aging time greatly affected the precipitation temperature and particle morphology of flaky $\alpha\text{-Al}_2\text{O}_3$ crystals, and the following conclusions were obtained.

1. The aluminum hydroxide gel precipitated by hydrolysis increased its size and thickness to grow into

needle-like $\text{AlO}(\text{OH})$ crystals as time passed and micro-pores in the range of 30–40 Å continuously developed until 20 h aging, and then decreased.

2. When the complex gel, which was aged for 20 h, was crystallized, the phase transition temperature was lowered and $\alpha\text{-Al}_2\text{O}_3$ platelets were precipitated at 600°C.

3. As the aging time of the complex gel was increased, the size of $\alpha\text{-Al}_2\text{O}_3$ platelets tended to increase and the thickness was also increased after 30 h.

4. When the complex gel was aged for 20 h, $\alpha\text{-Al}_2\text{O}_3$ platelets could be made with uniform particle size of 12 μm and a thickness of 0.15–0.23 μm .

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