

High Purity, Fine α -Alumina Powder Obtained by Thermal Decomposition of Ammonium Dawsonite

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Abstract

The preparation and the characteristics of ammonium dawsonite which is a precursor of very sinterable α -alumina powder are described in detail. The advantage of ammonium dawsonite as the precursor is discussed in terms of its morphology including fine primary agglomerates which flock to make secondary loose agglomerates. The examples of ceramic preparation using the dawsonite-derived α -alumina powder are also briefly reviewed.

1. Introduction

A high-purity, fine α -alumina powder has been prepared by the thermal decomposition of ammonium dawsonite ($\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$). An ammonium dawsonite is synthesized by the reaction of ammonium hydrogen carbonate solution and ammonium alum solution. The dawsonite-derived alumina powder is very deagglomeratable. The alumina powder which is milled simply is agglomerate-free and has very fine particle size (about $0.1 \mu\text{m}$).

The compacts of the powder can be sintered to nearly theoretical density at the temperatures between 1250°C and 1300°C . The sintering at low temperatures results in uniform microstructure with fine grain size, which leads to excellent properties such as high flexural strength and high resistance to wear and corrosion.

The ease of deagglomeration depends on powder morphology. The formation process of such deagglomeratable alumina powder has not yet been clearly understood, since the formation process includes the θ - to α -transformation which remains unclear. Therefore, it is worthwhile to present one plausible interpretation on the θ - to α -transformation process, and hence the formation process of the fine deagglomeratable powder.

In this paper, the formation process of the deagglomeratable powder is described in terms of the synthesis of the ammonium dawsonite and the morphology change during the θ - to α -transformation. Moreover, the various problems occurred during the fabrication process using this alumina powder and the properties of the sintered alumina are discussed.

2. Ammonium Dawsonite

2.1 Characteristics of Ammonium Dawsonite

Ammonium dawsonite is one of the dawsonite compounds and expressed as $\text{NH}_4\text{Al}(\text{OH})_2\text{CO}_3$ [1]. A family of dawsonite type compounds, in which alkali site is exchangeable, has been known and most of the dawsonites are only artificially synthesized, except for a sodium dawsonite which occurs in nature. It is also possible to substitute Fe or Cr ion in a dawsonite for Al ion.

The crystal structure of an ammonium dawsonite is orthorhombic symmetry as shown in Figure 1 [2], and is made up of the chains of Al-O-OH octahedra attached with CO_3 group parallel to the c-axis and the chains of octahedra are cross-linked by ammonium ions. Ammonium dawsonite is less stable than sodium dawsonite, and has considerably lower decomposition temperature of 230°C than the other precursors of alumina powder.

In addition, it seems to be less hydrophylic than the other aluminum hydrates due to CO_3 ions occupying half of the sites of oxygen in the Al-O-(OH) octahedra chains. Therefore, the dawsonite does not contain substantial amounts of water in its precipitates, resulting in good perviousness. It is very preferable property for the industrial powder processing such as filtration, washing, and drying.

The ammonium dawsonite as the precursor of "sinterable" alumina powder is prepared only by the rapid reaction. Contrarily, the reaction under more moderate conditions, i.e., the aging of a boehmite gel in the ammonium hydrogen carbonate solution, results in the different morphology of the precipitates,

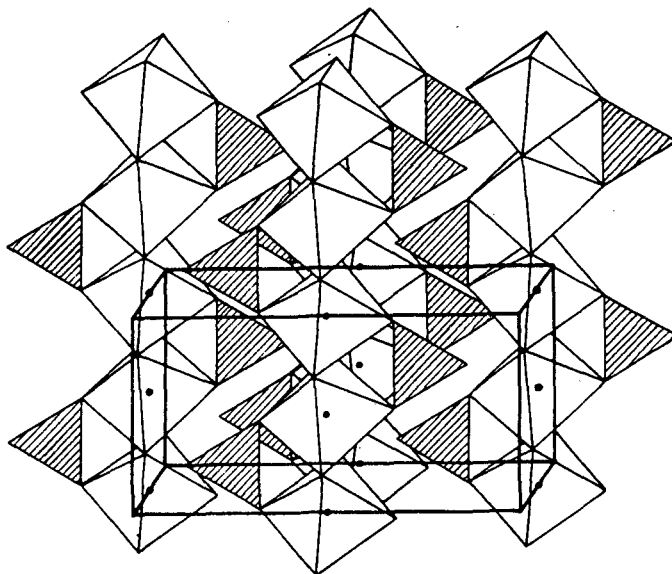
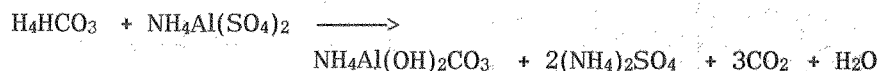


Figure 1. Schematic of ammonium dawsonite crystal structure. CO_3 group (shaded triangle) is attached to Al-O-(OH) octahedra.

ch as rice-like [3] or needle-like particles [4], which are not suitable starting powders for the dense ceramics.

2 Synthesis of Ammonium Dawsonite

Ammonium dawsonite can, in general, be prepared by adding an aluminum nitrate solution to an ammonium hydrogen carbonate solution. The reaction using ammonium alum as aluminum salt is expressed as follows: [1]



Conversely, the addition of the ammonium hydrogen carbonate solution to an ammonium alum solution yields a boehmite gel [3], one of the aluminum hydroxide with low crystallinity. The boehmite gel converts to the ammonium dawsonite during aging in the ammonium hydrogen carbonate solution.

Various morphologies of the ammonium dawsonite are observed. It depends on the precipitation conditions. For example, the gel-like precipitates with poor crystallinity are obtained at a very high precipitation rate and diamantly grown needle-like crystals at a low precipitation rate.

The particle size and the degree of deagglomeration of the α -alumina powder after the calcination are strongly affected by the morphology and the crystallinity of ammonium dawsonite. Consequently, the morphology of ammonium dawsonite is one of our major concerns.

Figure 2(A) shows the appearance of the ammonium dawsonite agglomerate which consists of a collection of "rod-like" particles. Figure 2(B) demonstrates the secondary agglomerates consisting of nearly spherical primary agglomerates of about 100 nm in diameter. This secondary structure is a characteristic feature of the dawsonite. It gives important implication concerning the mechanisms of the agglomeration. If these particles were separately created, it was difficult to understand why they were clustered into spherical agglomerates. This suggests that individual "particles" within the primary agglomerates may all have formed from a single nucleus. That is, all of the rod-like particles are not generated by homogeneous nucleation in solution, but by the precipitation reaction which is likely to proceed by repeating nucleation and growth on the crystal surface of the rod-like particles.

The smallest fragments obtained by ultrasonic dispersion for the preparation of TEM observations have similar size to the primary agglomerate. This suggests that the interparticle bond of the rod-like particles in the primary agglomerates seems to have the considerable strength, which might contribute to the individuality of the primary agglomerate.

The extent to which they can grow, e.g., the size of the primary agglomerates (approximately 100 nm), might be limited by the ratio of the material

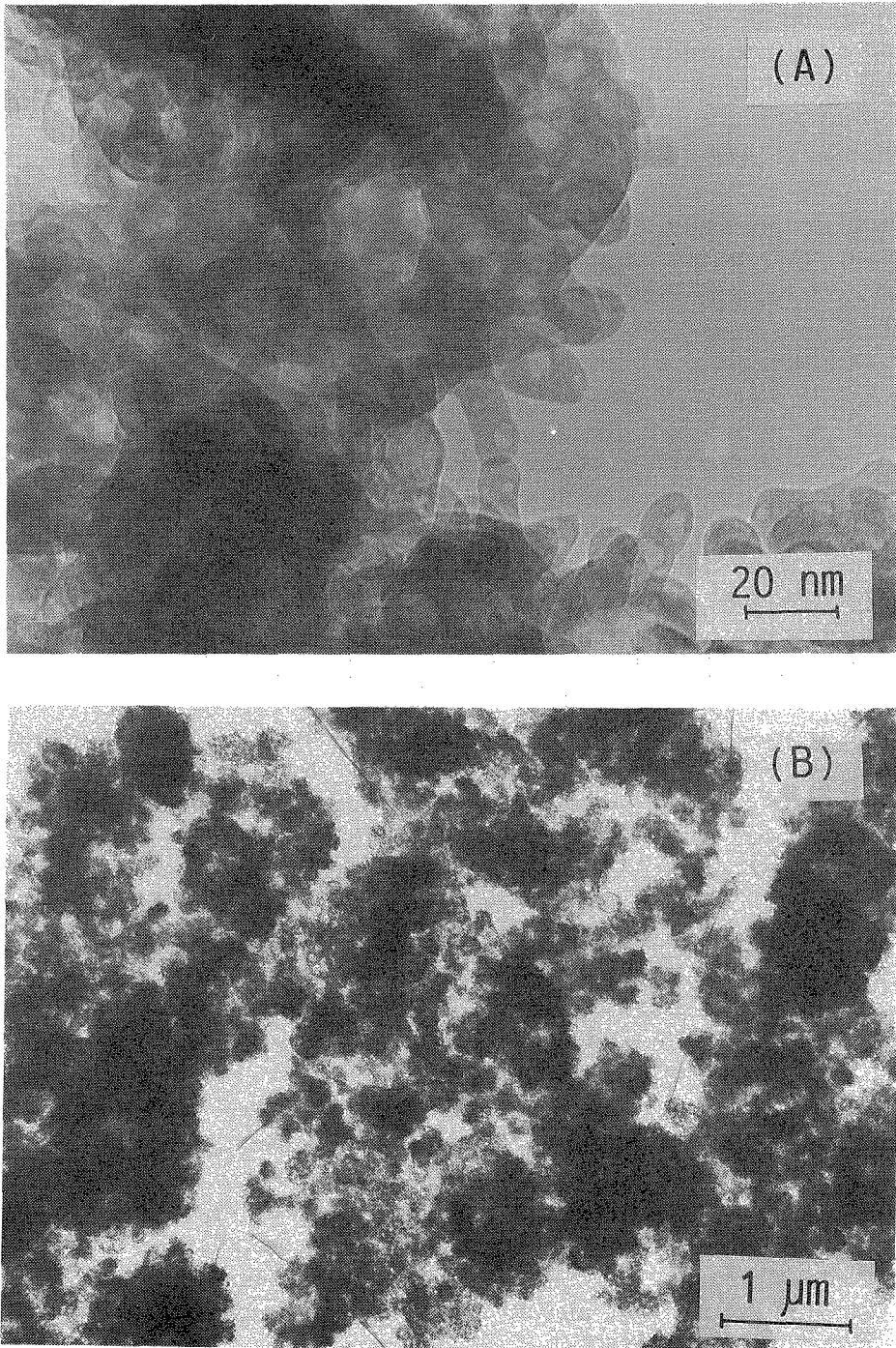


Figure 2. TEM of ammonium dawsonite.

(A) high magnification: agglomerate consisting of rod-like primary particles.

(B) low magnification : primary and secondary agglomerates.

transport to the reaction rate, and by the density of the homogeneous nucleation. With regard to the ratio, the deficit of ions that should be supplied to the reaction fronts by diffusion as the precipitation proceeds, can play an important role in limiting the agglomerate size.

As previously mentioned, the primary agglomerates of ammonium dawsonite flock into the secondary agglomerates during the formation reaction. The secondary agglomerates have a wide variety of shapes and sizes showing no regularity, though the extent of the variety seems to vary depending on the pH of the solution and the reaction temperature during the formation process. The characteristics of the secondary agglomerates have very important influence upon the fabrication process such as filtration of the dawsonite precipitates and the deagglomeration of the calcined α -alumina powder. However, it is not clear how the secondary agglomeration is affected by the synthetic conditions.

2.3 Formation Region of Ammonium Dawsonite

Kato *et al.* [1] demonstrated that the formation of ammonium dawsonite requires the ammonium hydrogen carbonate solution with higher concentration than about 1 mol/l, as shown in Figure 3. The use of the solution with lower concentration results in the formation of boehmite gel. They explained the results in terms of the concentration of hydrogen carbonate ion which might be directly related to the formation of the ammonium dawsonite.

Hayashi *et al.* [5] determined the boundary of the dawsonite formation as a function of pH and temperature. They found that the ammonium dawsonite was formed in the solutions with the pH higher than 7 - 8 (shown in Figure 4). These experimental results enable us to determine the critical ion species whose concentrations control the formation of ammonium dawsonite in this reaction system, and to estimate the critical concentration range of the ion. Aluminate ion concentration cannot be critical factor for forming the ammonium dawsonite. An aluminum ion introduced to an ammonium hydrogen carbonate solution, even if the amount of aluminum ion is small, forms ammonium dawsonite or boehmite gel immediately after mixing, without forming an aluminate ion.

Table I shows all of the ion concentrations in the ammonium hydrogen carbonate solution at 25°C as a function of pH, which were calculated by Hayashi *et al.* [5] using the equilibrium constants of the ions. The concentration of ammonium ion decreases with increasing pH up to basic region, where the ammonium dawsonite is predominantly formed. Therefore, the concentration of ammonium ion as the critical factor for the formation of ammonium dawsonite can also be excluded. The hydrogen carbonate ion concentration in equilibrium varies with pH. It increases with pH up to 7, but after reaching maximum, it turns to decreasing, and the concentration of the solution with pH = 5, in

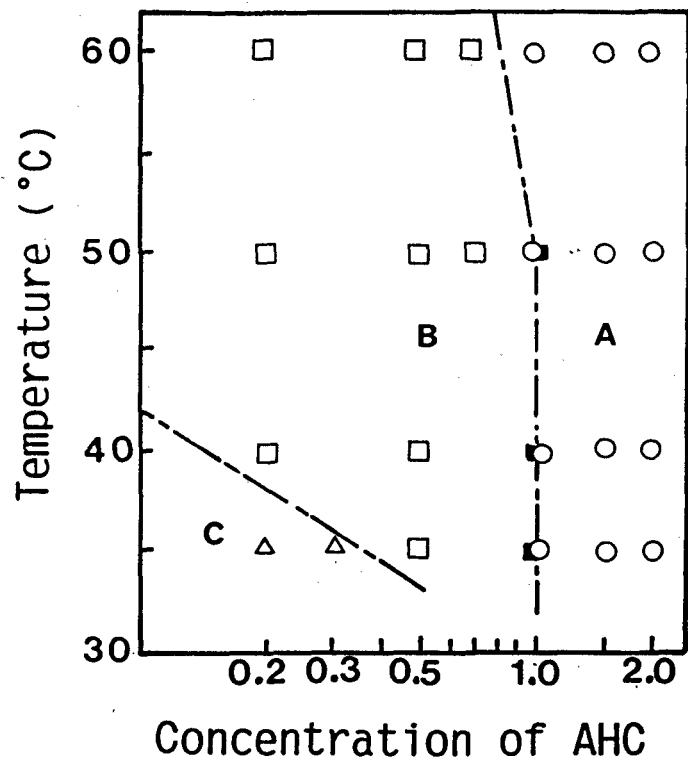


Figure 3. Formation map on the field of AHC concentration and temperature (after Kato et al.)

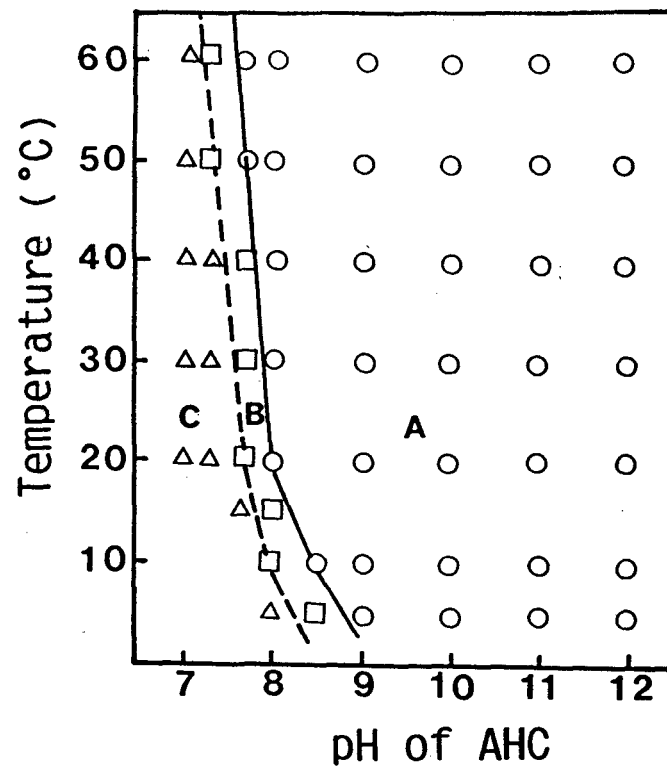


Figure 4. Formation map on the field of pH and temperature (after Hayashi et al.)

A: ammonium dawsonite B: boehmite gel C: amorphous
 AHC: ammonium hydrogen carbonate

Table I. Concentration of the ions in ammonium hydrogen carbonate solution at various pH for concentration of 1.5 mol/l. Note that the concentration of HCO_3^- at pH 6 where boehmite is stable is higher than that at pH 11 where the ammonium dawsonite is stable.

pH	$[\text{NH}_4^+]$	$[\text{CO}_3^{--}]$	$[\text{HCO}_3^-]$	$[\text{NH}_4^+][\text{CO}_3^{--}]$
4	1.5×10^0	8.0×10^{-9}	2.0×10^{-2}	1.2×10^{-8}
5	1.5×10^0	7.0×10^{-7}	1.0×10^{-1}	1.1×10^{-6}
6	1.5×10^0	2.0×10^{-5}	7.0×10^{-1}	3.0×10^{-5}
7	1.5×10^0	7.0×10^{-4}	1.2×10^0	1.1×10^{-3}
8	1.5×10^0	1.0×10^{-2}	1.5×10^0	1.5×10^{-2}
9	1.0×10^0	1.0×10^{-1}	1.5×10^0	1.0×10^{-1}
10	4.0×10^{-1}	9.0×10^{-1}	1.0×10^0	3.6×10^{-1}
11	6.0×10^{-2}	1.5×10^0	2.0×10^{-1}	9.0×10^{-2}
12	7.0×10^{-3}	1.5×10^0	4.0×10^{-2}	1.1×10^{-2}
13	6.0×10^{-4}	1.5×10^0	5.0×10^{-3}	9.0×10^{-4}
14	7.0×10^{-5}	1.5×10^0	6.0×10^{-4}	1.1×10^{-4}

(mol/l)

Table II. Concentrations of the ions in ammonium hydrogen carbonate solution of various concentrations at pH 8.

Concentration	$[\text{NH}_4^+]$	$[\text{CO}_3^{--}]$	$[\text{HCO}_3^-]$	$[\text{NH}_4^+][\text{CO}_3^{--}]$
0.5	5.0×10^{-1}	3.3×10^{-3}	5.0×10^{-1}	1.7×10^{-3}
0.7	7.0×10^{-1}	4.7×10^{-3}	7.0×10^{-1}	3.3×10^{-3}
1.0	1.0×10^0	6.7×10^{-3}	1.0×10^0	6.7×10^{-3}
1.2	1.2×10^0	8.0×10^{-3}	1.2×10^0	9.6×10^{-3}
1.5	1.5×10^0	1.0×10^{-2}	1.5×10^0	1.5×10^{-2}
1.7	1.7×10^0	1.1×10^{-2}	1.7×10^0	1.9×10^{-2}
2.0	2.0×10^0	1.3×10^{-2}	2.0×10^0	2.7×10^{-2}

(mol/l)

which boehmite gel forms, equals to that of the solution with pH = 11 in which dawsonite forms. Therefore the hydrogen carbonate ion is not regarded as critical one. Only the concentration of the carbonate ion in ammonium hydrogen carbonate solution increases as pH increases. These results suggest that the concentration of the hydrogen carbonate ion is not responsible for determining the formation range, but that of the carbonate ion is.

The concentration of carbonate ion and the product of the concentrations

of ammonium ion and carbonate ion are shown in Table II as a function of the concentration of ammonium hydrogen carbonate solution at pH = 8. The concentration of carbonate ion which is needed to form the ammonium dawsonite was estimated to be higher than $6-7 \times 10^{-3}$ mol/l.

Hayashi and co-workers reported that the crystallite size of dawsonite (estimated from line broadening of X-ray powder diffraction) is a function of pH, which shows minimum at pH = 10 [6] (Figure 5). The results are very interesting, since the crystallite size of dawsonite is believed to affect on the nucleation frequency of α -alumina. They interpreted the effect of pH on the crystallite size in terms of the product of the concentrations of all ions concerning the reaction, that is, $[\text{NH}_4^+][\text{AlO}(\text{OH})_2^-][\text{HCO}_3^-]$, shown in Figure 5, because the smaller crystallite size may result from the higher reaction rate which is proportional to the product of the ion concentrations.

However, as has been shown, the critical ion for the formation of the dawsonite is the carbonate ion, but not the hydrogen carbonate ion. And when the concentration of the aluminum ion introduced to the reaction system

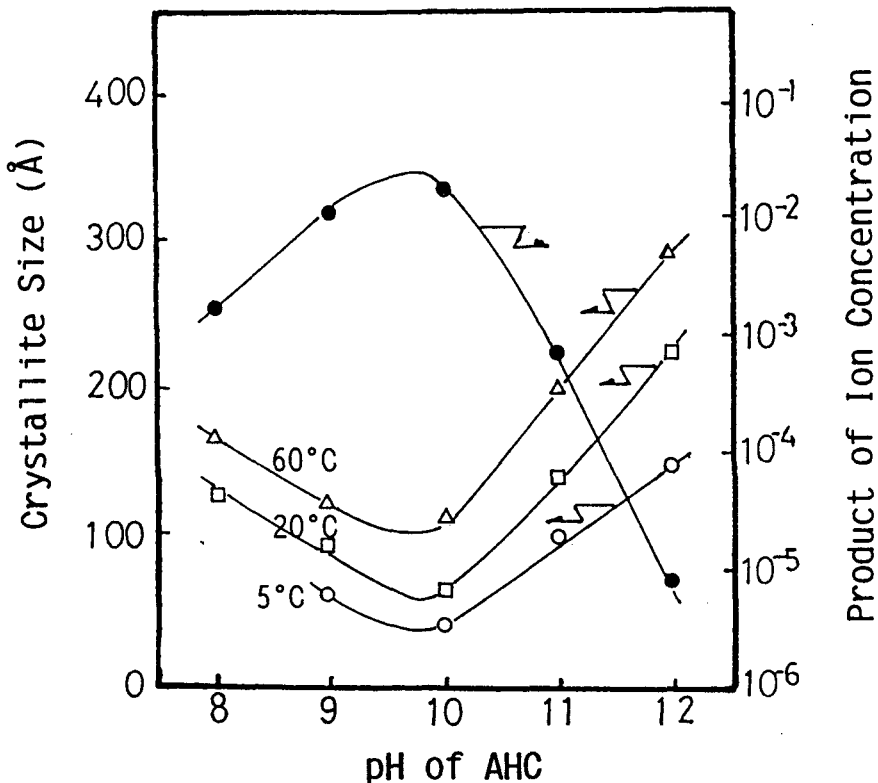


Figure 5. Crystallite size of ammonium dawsonite as a function of pH at various temperatures (after Hayashi et al.)

can be considered to be constant, the reaction rate may be proportional to the product of the ammonium ion and carbonate ion. The products as a function of pH (as shown in Table II) have a maximum at pH 10, which is consistent with the experimental results obtained by Hayashi *et al.* [6].

1. Fine Particle Formation Process

The size of α -alumina particles and its agglomerate morphology are largely determined during the transformation of intermediate- to α -alumina. In order to control the properties of alumina powder, therefore, it is important to understand the microstructural changes occurred in the transformation steps.

Before examining the reason why the use of ammonium dawsonite as a tarting compound has an advantage for forming the fine, deagglomeratable alumina powder, we first present a brief review of the transformation sequence of alumina.

1.1 θ - to α -Transformation

There are a variety of transition aluminas such as γ -, δ -, θ -, η -, χ -, and κ -alumina. These transition aluminas, formed by thermal decomposition of aluminum salts or aluminum hydroxides, eventually transform to a stable α -alumina at the temperatures between 1000°C and 1300°C [6,7,8,9].

Many researchers have observed that the powder agglomerates are created during the formation of α -alumina from the θ -alumina.* Hence, the investigation of the microstructural changes during the θ - to α -alumina transformation is very helpful to understand the agglomerate characteristics.

Dynys and Halloran [8] gave the detailed descriptions on the α -alumina formation process, which are mostly consistent with the observations by Daimon *et al.* [10,11] and our observations [7,9] on the transformation study of the transition alumina derived from aluminum sulfate.

Figure 6 shows the SEM micrograph of the powder agglomerates obtained by calcination of aluminum sulfate at 1200°C, which indicates the morphological changes during the transformation from the θ -alumina (finer particles at lower right) to α -alumina (coarser particles at upper left).

The continuous vermicular α -alumina appears to be a single crystal, because the electron diffraction pattern of the coarse particle region is that of single crystal. The similar observations were reported by Dynys and Halloran [8] and Daimon and Kato [10]. The transformation proceeds by the growth

θ -alumina is the phase obtained by thermal decomposition of alum or dawsonite, immediately before transforming to α -alumina.

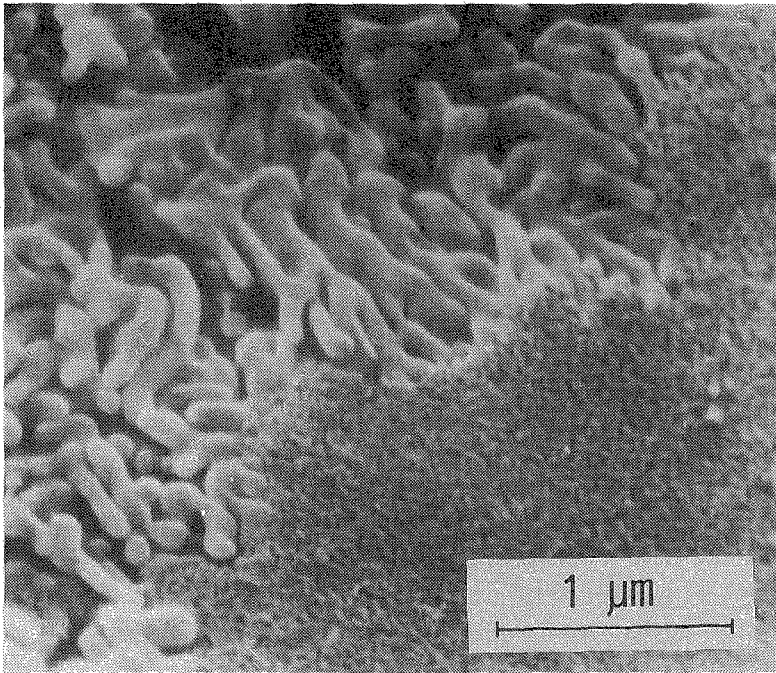


Figure 6. TEM of θ - to α -transformation in aluminum sulfate-derived θ -alumina agglomerate.

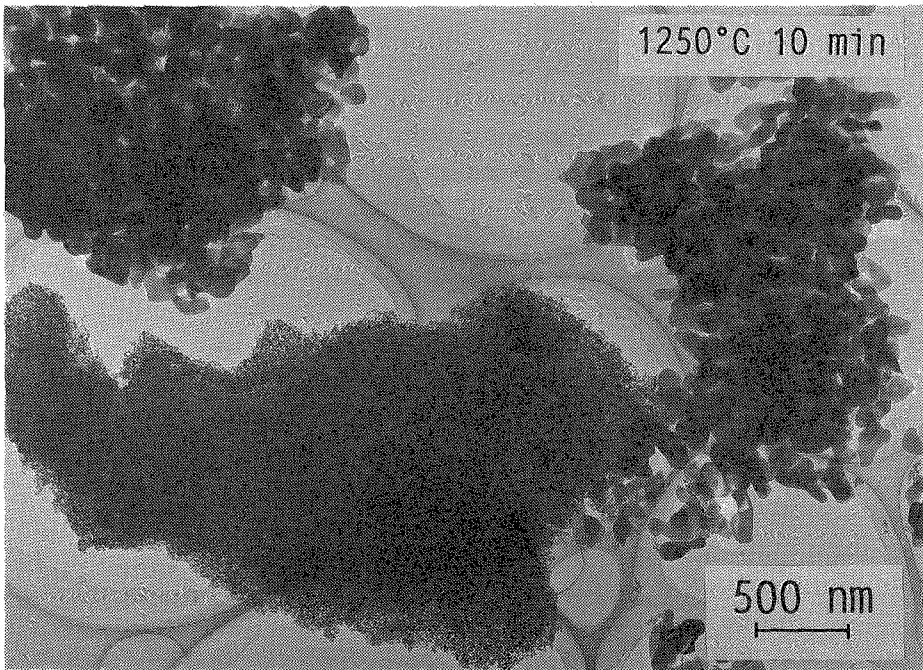


Figure 7. TEM of alumina powder derived from alum.

of α -alumina nuclei formed in the θ -alumina agglomerates, resulting in the wormy interconnected morphology. Figure 7 shows the coexistence of typical two types of agglomerates. The one is the agglomerate consisting of completely transformed α -alumina particles, and the other is the one consisting of θ -alumina that did not commence the transformation due to the lack of α -nuclei. From these experimental results, it is likely that the transformation proceeds only within individual agglomerates, and that the nucleation in the agglomerates of the transition alumina is followed by comparatively rapid transformation. Thus the total transformation rate probably depends on the nucleation frequency.

A number of nucleation in the agglomerates enables to complete the transformation to α -alumina in a short time, resulting in fine size of α -alumina particles. On the other hand, if the nucleation frequency is low, it takes more time to complete the transformation. This causes a broad particle size distribution due to the growth of the previously transformed particles.

Whereas the importance of the nucleation as the major controlling factor of the transformation rate has been recognized, the reasonable explanation of the nucleation mechanism has not been given as pointed out by Dynys and Halloran [8].

Some explanations on the nucleation mechanisms have been given based on the experimental results, in which the experimental handling such as mechanical treatment enhances the transformation by increasing the nucleation frequencies. The enhancement of the nucleation accompanied by the imperfection of the precursor crystals synthesized under rapid precipitation conditions was observed in the transformation of the alumina derived from aluminum sulfate [9] or ammonium dawsonite [3,6].

The transformation was also encouraged by the mechanical treatment of milling for a variety of alumina precursors such as aluminum sulfate hydrate [10] aluminum sulfate anhydrate [11], η -alumina [10] and θ -alumina [8] etc. The transformation kinetics of alumina mostly show sigmoidal curves [6,8,10,12] with the induction period ascribed to the delay for nucleation. The induction period is shortened by milling, suggesting the effect of the mechanical treatment on the nucleation. Dynys and Halloran [8] also reported that the mechanical compaction of the as-calcined powder (which is obtained by the calcination of alum at 1000°C), exhibits some extent of nucleation enhancement.

Before discussing the effects of the milling of precursor on the nucleation, we assume the "critical particle size" to which the growth of the transition alumina particles is necessary to initiate the nucleation for the transformation.

The concept of the "critical particle size" is firstly suggested by Wynnyckyj and Morris [12]. Hayashi *et al.* [6] determined it for the transformation of the thermally decomposed alumina of the ammonium dawsonite. If we accept the critical particle size for the transformation, the transformation mechanism could be interpreted simply in terms of the grain growth within the

transition alumina powders. However, it is difficult to explain how the particles with the critical size are converted into the α -alumina nuclei.

The synchro-shear mechanism proposed by Bye and Simpkin [13], Wynnickyj and Morris [12], and Hayashi *et al.* [6] might be one of the possible mechanisms interpreting a mode of direct atom movements of nucleation. However, another mechanism might also be possible, in which the embryo of α -alumina generated in the part of random structures grows up to nucleus by the short range diffusion mechanism.

Although it is not possible to definitely ascertain the rearrangement mechanism in the crystal lattice, the reason why the θ -particles above the critical size can convert α -phase, could be explained by the surface energy to volume effect. That is, for the θ -alumina particles which size was kept below the critical size (several nm), the weak bond strength in crystal structure allows the strain within the unstable transition alumina crystal. If the particle grows over the critical size, the strains in the particle cause to break the θ -alumina crystal structure.

Since the particle size of the transition alumina obtained by the calcination of the milled precursor is smaller than 10 nm, it is reasonable to consider that the milling of the precursor did not give any change on such fine particulates themselves, but give changes in the arrangement of fine particles in agglomerates [8]. The disturbance of the particle packing by milling treatment was reported by Daimon and Kato [10]. This is evidenced by the fact that the micropore distribution of the transition alumina prepared by milling of aluminum sulfate anhydrate was broader than that without milling. The milling treatment of the anhydrate enhanced the transformation of θ - to α -alumina.

As previously mentioned, the agglomerates of the transition alumina obtained by calcination of a precursor comprise the fine particulates under 10 nm and preserve the macroscopic morphology of the precursor fragments. The ultimate particles in the agglomerates appears to be strongly linked together by the interparticle bridges. The presence of interparticle bond was supported by the TEM observation that even in the powder immediately after decomposition, no remnant severely broken into pieces could be found. Hence, the particles in the agglomerate can be considered to be restrained in their positions at the beginning of the decomposition. In addition, for the agglomerate of θ -alumina derived from ammonium alum, TEM micrograph shows that there is no local difference in the particle packing density (Figure 8), suggesting very regular arrangement of particles.

In the agglomerate having such considerably strong bonding and homogeneity, the particles should not change the relative positions during calcination, hence it is hard to consider that some particles grow faster than the other particles within the agglomerate. It is closely analogous to the situation where the grains in a porous compact can hardly grow during sintering. Namely, the strong interparticle bond and homogeneous arrangement of particles retard the grain growth of the transition alumina and hence inhibits the

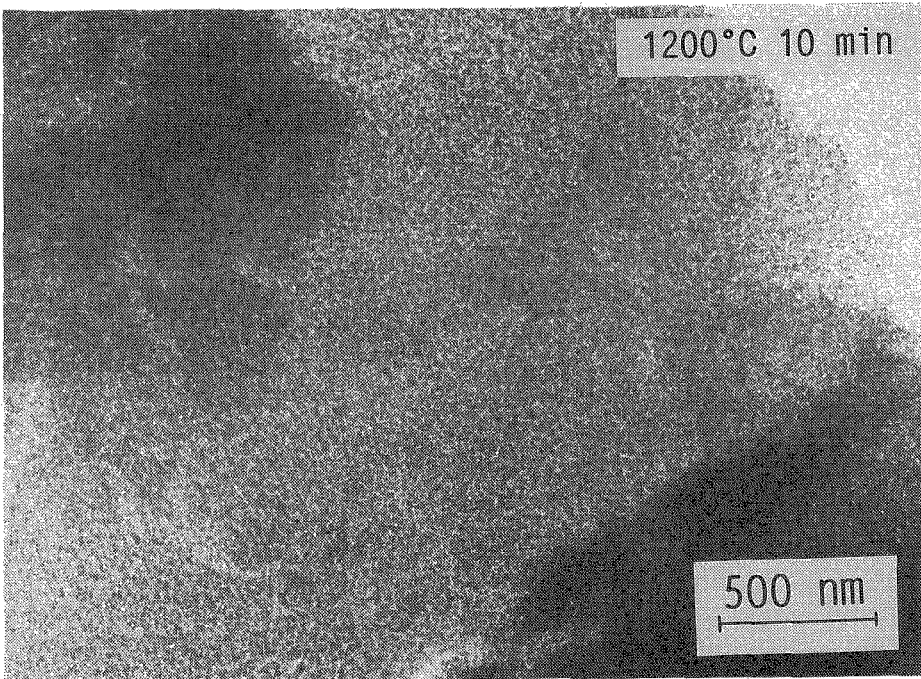


Figure 8. TEM of alum-derived θ -alumina agglomerate which reveals homogeneous particle packing.

nucleation of α -alumina. This is the reason why the nucleation in homogeneous agglomerate such as that in alum-derived powder is difficult to occur. However, even in these homogeneous agglomerates, some nucleation may occur during prolonged heating. It could be ascribed to the inhomogeneity originally occurred in the arrangement of particles, which is magnified to some extent during heating and aroused the stress to fracture the bonds between the particles, resulting the growth of some of the particles to the critical size.

Therefore, it may be reasonable to presume that the frequency of nucleation increases with increasing the part having the different particle packing density from the neighborhood in the transition alumina agglomerates. That is, any irregularities of the particle arrangement in the agglomerates caused by milling of the precursor or the transition alumina powder, or by the imperfection of the precursor crystals, resulting in the discontinuity of the agglomerates, might help to produce the particles to grow without stress exerted from neighboring particles and to nucleate. The nucleation opportunity increases with increasing the discontinuous portions of the particle arrangement in the agglomerate, hence the higher transformation rate results. In consequence, the transformation rate is significantly enhanced by the treatment to introduce the disorder of the particle arrangement.

Figure 6 clearly shows that the transformation after nucleation proceeds by diffusion between the θ -particles and α -particles, both particles are continuous on the front of the transformation. The growth of α -alumina would be terminated, when the α -alumina particle is forced to separate from θ -alumina particles. Since the separation between θ - and α -alumina particles often took place in the agglomerates with the low particle packing density, the small α -alumina particles resulted from the θ -alumina agglomerates with such a packing density. And such conditions are preferred to prepare the readily deagglomeratable powders. Consequently, the size and the morphology of the α -alumina particles are greatly dependent on the agglomeration state of the transition alumina.

The sinterable alumina powders have been fabricated by the calcination of alum rather than hydroxide, because the agglomerate density of an alum-derived transition alumina is probably lower than that of a hydroxide-derived one. It is obvious from the above mentioned results that the transformation rate including nucleation is greatly structure-sensitive of the agglomerate of the transition alumina. The contradiction between the kinetic data on the transformation of alumina in the literature can be explained in terms of the agglomeration structure which varies with the kinds of precursor and the preparation conditions. The effect of the agglomeration structures on the transformation of alumina should be taken into account when one studies the transformation mechanisms.

3.2 Formation of Fine Alumina Powder

In the previous section, the morphological change during the transformation of alumina was mainly discussed based on the results reported in the literature. In this section, we would attempt to describe how the finely deagglomerated alumina powder can be obtained from ammonium dawsonite, with regard to the nucleation density and the particle packing density distribution within the agglomerates.

3.2.1 Nucleation Density

Figure 8 shows the uniform packing of the very fine particles in the alum-derived θ -alumina agglomerate. In contrast, nonuniform packing structure is shown in Figure 9 for the θ -alumina agglomerates derived from ammonium dawsonite, that is, the particles larger than surroundings are prominent, indicated by the arrows. This means that the grain growth for nucleation is easier in the dawsonite-derived alumina than in the alum-derived alumina.

Because the ammonium dawsonite particle tends to have the concave

surface probably due to its crystal structure and has the crystallite size of several nm, less orientation of the crystallite in the agglomerates should be expected. Then the transition alumina particles formed by the thermal decomposition of such a precursor might tend to arrange irregularly in the agglomerates. This irregular particle arrangement may cause the interparticle stress during heating, leading to the discontinuous particle growth and hence to the nucleation at comparatively lower temperatures and to the high nucleation density. The high nucleation density may accomplish the entire transformation in a short time, thus the particle size of the resulting α -alumina would remain small.

3.2.2 Primary Particle Size of α -Alumina

As stated in the before section, the nucleation at low temperatures and the high frequency of the nucleation would contribute to the formation of the small primary particle size of α -alumina. However, the particle packing density and its fluctuation in the agglomerates of θ -alumina would also be important factors controlling the primary particle size of α -alumina.

As the θ - to α -transformation progresses, the separation of α -alumina particle from θ -particles may often occur in the agglomerates with the low packing density of θ -alumina matrix, inhibiting further growth of the α -alumina particles. The particle packing density of the agglomerates is believed to depend on the volume fraction of aluminum component in the precursor. The agglomerates of θ -alumina derived from the ammonium dawsonite as well as the ammonium alum have the low packing density, because the large amounts of gaseous components are evolved during calcination.

The growth of α -alumina in the θ -alumina agglomerates with the homogeneous packing density, such as that derived from the alum, tends to be continuous, i.e., finger-like. On the contrary, the shape and the size of the primary agglomerates of the ammonium dawsonite, which were created in the dawsonite formation process, are preserved throughout the entire calcination, resulting in the fluctuation of the θ -alumina particle packing density. The extent of the fluctuation in the secondary agglomerates parallels to the primary particle size of α -alumina. It is clearly revealed by comparing Figure 2(B) and Figure 10.

The changes in the bond area corresponding to the variety of packing density in the agglomerates interrupt the interparticle connections of α -alumina particles formed during the transformation and then control the primary particle size to $0.1 \mu\text{m}$.

3.2.3 Deagglomeration to Ultimate Particles

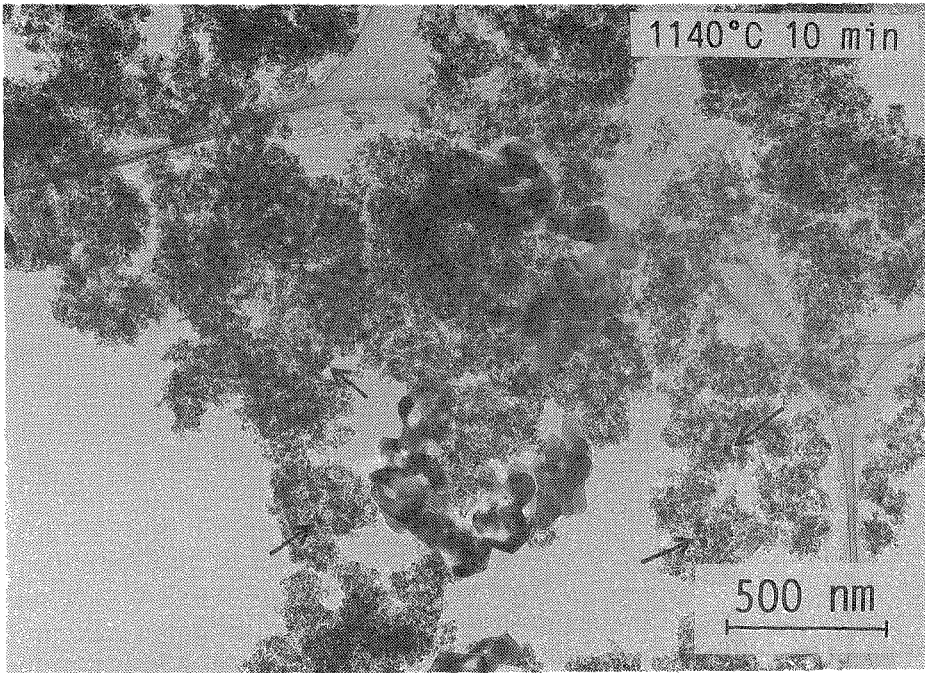


Figure 9. Dawsonite-derived θ -alumina. Inhomogeneous particle packing increases local densification and hence facilitates the nucleation.

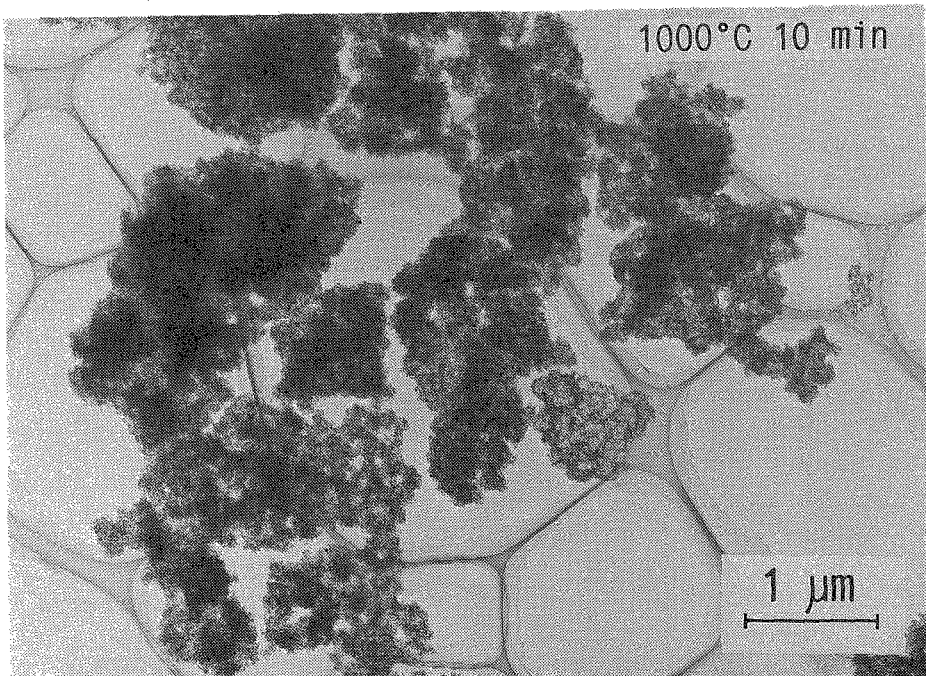


Figure 10. Transition alumina obtained by thermal decomposition of ammonium dawsonite.

The powder with interparticle bond formed in the agglomerates during calcination should be deagglomerated to the ultimate particles for ceramic use. The insufficient deagglomeration leads to low sinterability, even if the powder consists of very fine particles.

The θ -alumina agglomerates derived from ammonium dawsonite, have the packing density fluctuation of about $0.1 \mu\text{m}$, corresponding to the primary agglomerate of the dawsonite. This fluctuation leads to some of the particles to coarsen and consequently contributes to the high nucleation density. This results in the individual particles transformed from one nucleus. And also the fluctuation causes the formation of the well-separated particles during the transformation, so that the interparticle bond areas would be limited to very small. As a result, they can be readily deagglomerated into ultimate particles by milling.

4. Application of Commercial Alumina Powder

The high purity alumina powder derived from the ammonium dawsonite has been commercially manufactured for ceramic applications*. (* "Taimicron". Taimei Chemical Industry Co., Ltd.)

The typical characteristic features of the powder are summarized in Table III, in which particularly the fine particle size ($0.1\text{-}0.15 \mu\text{m}$) and high purity (99.99%) are very prominent features.

There are some technological difficulties in using such fine powders, in order to achieve the best performance of ceramics. Therefore, at present, it should be worthwhile to present the technical issues accompanied with the application of "Taimicron". Some of the ceramic processing techniques, which are successful attempts to use the powder, were demonstrated in this section.

4.1 *Shaping of the Fine Alumina Powder*

As mentioned before, the compacts of this alumina powder can be densified at much lower firing temperatures compared to that of the usual alumina powders. However, all of the compacts of fine powder are not necessarily sintered at the low temperatures. It is widely recognized that the powders deagglomerated to the ultimate fine particles tend to sinter at the lower firing temperatures. The presence of the aggregates in the powder prevents the close and uniform particle packing in the compacts and hence might be detrimental for densifying the compact at lower temperatures.

In general, it seems difficult to make an ideal powder compaction for lower temperature sintering using such fine powders. However, for taking advantage of this fine alumina powder effectively, we should develop the forming process to attain the very near close-packed compaction. Many stud

Table III. Typical Properties of TM-DA*

Phase	α -Al ₂ O ₃	
Purity	99.99	%
Surface area	14	m ² /g
Primary particle size	0.1	μ m
Average particle size ¹⁾	0.22	μ m
Apparent density	0.9	g/cm ³
Tap density	1.1	g/cm ³
Green density ²⁾	2.30	g/cm ³
Fired density ³⁾	3.96	g/cm ³
Impurity ⁴⁾	Na	3 ppm
	K	1 ppm
	Fe	8 ppm
	Ca	3 ppm
	Mg	2 ppm
	Si	10 ppm
	U	<4 ppb
Th	<5 ppb	

*Taimicron

1) Sedigraph

2) Mold pressed at 1000 kg/cm²

3) Fired at 1350°C for 1 h

4) Na,K: Flame spectrophotometry

Others: I.C.P. Emission spectrophotometry

ies and attempts to achieve uniform green microstructure which promises to fabricate the quality ceramics, have been made on a wide variety of ceramic processing using this alumina. Some of those results would be surveyed.

Miyashita *et al.* [14] observed, in the pressed compacts, the nonuniform structure due to the aggregates which persist after pressing. The nonuniform structure causes the crack-like faults which continue to expand to the large defects leading to failure during subsequent firing. On the other hand, in the slip casted specimens, they found more uniform, close-packed structures than that for the pressed compacts. Cold isostatic pressing (CIP) was often used after conventional pressing in order to improve the microstructural homogeneity of the green body. However, even the CIP process is not necessarily sufficient to achieve better microstructural homogeneity, because deficient pressure in CIP causes the surviving of granule structure leading to the growth of the linear defects during sintering [14,15,16].

The some degree of failure in the compacts is inevitable since the forming process involves collapsing "granules" which are essentially nonuniform in

itself. Annihilation of such defects during compaction, therefore, should not be expected. Next two approaches appear to be possible to reduce the defects caused by pressing. The one approach is improvement of the granule fabrication process, which includes the optimization of granule brittleness by developing the new binder systems, so that relatively lower pressure is sufficient to form the compacts free from the remnant of the granules. The other processing would be transient, but appeared to be useful for yielding the defect-free products, which involves the addition of MgO and CIP at high pressure. CIP process at relatively higher pressure would control the size of the defects and MgO addition would control the growth of defects during sintering, so as to achieve the uniform microstructures.

More uniform powder compacts could be obtained by injection molding process than by dry cold pressing. However, in order to gain uniformity in powder compacts by injection molding, some technical problems, such as thorough dispersion of the powder particles in the resin should be cleared since the inhomogeneity of the compacts is originated from the preparation step of pelletized chips for the injection.

Nozaki [17,18,19] found that the deficient structure of compacts has occurred during the granulation process after mixing, and he solved the trouble by freezing the mixture in liquid nitrogen before the chips are crushed into appropriate size. This process enables to prepare the uniform thin plate green body free from any strain, and to sinter the specimen without any deformation. Some other new injection molding processings were tried, for example, such that conducted in aqueous system by using water retention organic polymers [20], or that at low pressures by using paraffin wax [21].

The slip casting is a predominant forming process, which is characterized by the possibility of the relatively complex green body with high density and uniform microstructures. However, the low efficiency of fabrication and the contamination from plaster mold during slip casting processes have restricted its applications. With recent developments, these are very improved by using the resinoid molds which were designed to work at the combination of vacuum and pressure casting. The microstructural characteristics of the cakes may be dependent on the structure of the slip varied with the degree of deflocculation. Mizuta *et al.* [22,23,24] prepared the highly concentrated and well-dispersed slips for casting by using oligosaccharide alcohol as a dispersing agent. By the pressure casting using the slip thus prepared, they obtained the high density shape with the relative density of 62.9%.

Although "Taimicron" must be one of the well-deagglomerated powders which are commercially available, the perfect comminution to its ultimate particles was not yet achieved, i.e., a little population of the agglomerates consisting of a few particles appears to present. Inada *et al.* [25] investigated the densification behaviors and microstructural development of the slip casted compacts of the powder which is nearly completely divided into ultimate particles with the size of "Taimicron". They attained extremely high density of

green body (68.5% theoretical) by slip casting with the slurry from which the coarse component is removed by setting aside the well-dispersed slurry by adjusting pH 2 for one month. The green body can be sintered to full density at 1150°C, for 50 hours. The fired specimens have the very fine uniform microstructure with the grain size of 0.35 μm . This result reveals the level of the alumina powder commercially available at present and gives the target to be developed in the next step.

Alumina compacts become to a closed porous state at the relative density of about 95%. The closed pore compacts is possible to use isostatic hot-pressing (HIP) without capsule. When "Taimicron" is used as the starting powder, the advantage of HIP is manifest, because the grains in the closed porous components remained very small, and it enables to reduce the resistance to plastic deformation.

It has been demonstrated that the translucent alumina ceramic body can easily be obtained by HIP of the closed porous compacts prepared by slip casting [26,27,28], injection molding [29] or CIP [30]. These translucent ceramics have the linear transmittance of 40%, even their extremely fine textures (less than 1 μm mean grain size) which result in the notably high strength levels. Almost all of the data on flexural strength at room temperature fall in the range between 700 and 800 MPa, but exceptionally the case exceeding 1000 MPa is reported.

It is also reported that the higher prefiring temperature lead to the increase of large defect causing lower strength. And the higher temperature of HIP results in lower strength due to increasing grain sizes [31].

4.2. Sintering of "Taimicron"

4.2.1 Influence of Impurities on Sintering of High Purity Alumina

The high purity alumina powders have, in the first place, been developed in order to improve the ceramic characteristics. Impurity itself might be mainly expected to have the function as sintering aids for lowering the firing temperature. Thus purification of starting powders has been considered to lead to an elevated sintering temperature.

However, with the development of ultra-fine, high purity alumina powder which can be sintered to nearly full density at low temperatures, it was found that impurities effectively retarded the densification rate though the extent of the retardation was depending on those of the kinds and the amounts. In general, the sintering aid dopants have been considered to act as either liquid formation agent or grain growth inhibitor helping a porosity reduction through modifying a pore morphology. And the diffusion rate of materials may not be necessarily increased. It is believed that the addition of MgO [32], the most common additive for alumina sintering, decreases both the grain bound-

ary mobility and the densification rate. And the addition of a small amounts of ZrO_2 [33] also retards the grain boundary diffusion, though the effect of inhibition is not so conspicuous as observed in the silica addition.

The remarkable retardation effects of silica addition on the sintering and grain growth of high purity alumina were demonstrated by Iga and Shimamoto [33,34]. The increase of about $100^\circ C$ in sintering temperature was observed by the addition of 50 ppm Si to achieve the nearly full density. The log densification versus log time plots at various temperatures for the high-purity alumina and those with a small amount of silicon showed the same slopes, suggesting that the addition of silicon does not change the material transport mechanisms, but decreases the material transport rate. The grain growth kinetics are markedly depressed by the silicon addition. For example, in the specimen with 200 ppm Si annealed at $1500^\circ C$ for 5 hours, no appreciable grain growth was observed.

4.2.2 Characteristic Properties of Fired Body

The excellent properties of the alumina ceramics produced by using "Taimicron" are primarily ascribed to its high purity and fine grained uniform microstructures.

The properties such as the fewer strength degradation at high temperature, the high thermal conductivity, and the high in-line transmittance, may be attributed to high purity. The moderate decrease of the flexural strength up to $1100^\circ C$ for the products fabricated by HIP suggests no or very little grain boundary secondary phases. The high modulus of rupture (MOR) and high resistance to wear can be expected because of their fine grained microstructures.

The mechanical strength of ceramics depends sensitively on defect size. Types and size of the defect present in the compacts are mainly controlled by green body fabrication processes, though the powder characteristics may also be responsible for the formation of defects.

Sekiguchi *et al.* [31,35] demonstrated that the prefiring temperatures for HIP affect the size distribution of the defect, and that the strength estimated from the largest defect present in the body is in good agreement with the measured value. As stated in the section on the green body preparation, it is difficult to expect that the components fabricated by dry pressing have a high mechanical strength, because some granules may reside resulting in the intergranular boundaries after pressing.

Usually the MOR of the products prepared by pressing using "Taimicron" fall in about 600 MPa, though it varies with the size of the products. The products prepared by slip casting have the strength of 700 MPa. Though no measured strength of the products prepared by injection molding could be found, it can be expected to have a higher MOR because of the uniform micro-

structures with fine grains. The mechanical properties are expectedly improved by subsequent HIP.

Igarashi [30] has prepared the translucent alumina ceramics having the average flexural strength of 1066 MPa by HIP combined with CIP. The fabricated translucent alumina body showed several superior features, such as the in-line transmittance of 41.1% which enables to inspect the inner defects, twice

Table IV. Properties of high strength, translucent alumina (LX05)*

Density	3.98	g/cm ³
Hardness Hv (10 kg load)	18.6	GPa
Average flexural strength	1100	MPa
Fracture toughness	3.1	MPa·m ^{1/2}
Young's modulus	380	GPa
Thermal expansion coefficient	7.9 x 10 ⁻⁶	/K
Thermal conductivity	38	W/m·K
Transparency (in-line)(1 mm thickness)	41	%
Surface roughness Rmax	<0.03	μm

*Toshiba Tangaloy Co., Ltd.

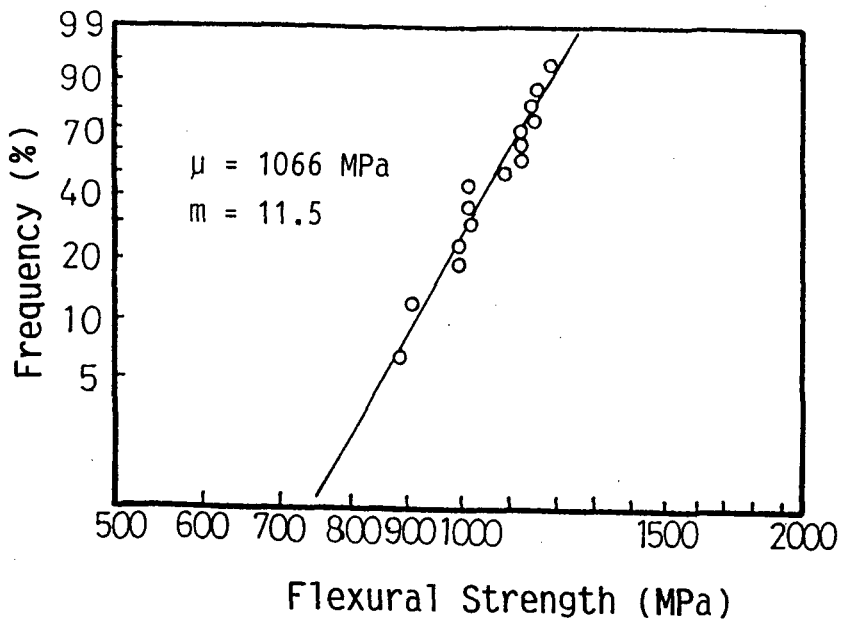


Figure 11. Weibull plot of translucent alumina.

times higher thermal conductivity than the commercial high-alumina ceramics, little degradation of high temperature strength which shows 300 MPa at 1500°C. The products also have good wear resistance comparable with the zirconia ceramics which are believed to be the best wear resistant materials at present. When the milling batch contains hard particles such as B_4C , the abrasion wear of zirconia milling media becomes higher than that of alumina, due to the lower hardness of zirconia than alumina. The typical characteristics of the high-strength and translucent alumina ceramics are shown in Figure 11 and Table IV.

4.2.3 Superplastic Deformation of the Alumina

There has been a very few studies on the superplastic deformation behaviors of alumina, because of the difficulties obtaining the alumina components with grain size as fine as zirconia ceramics.

Xue and Chen [36] investigated the superplastic deformation behavior for the specimens with grain size about $0.5 \mu m$ prepared by slip casting of the alumina powder and subsequent sintering at 1250°C. The pure alumina ceramics showed a marked dynamic grain growth during deformation causing strain hardening, which is different from zirconia ceramics. The material hardening induced by much strain and/or high strain rates leads to the cavitation and the cracks. As a result, it is not possible to achieve the superplastic deformation of the pure alumina ceramics.

Yoshizawa and Sakuma [37] studied the high-temperature deformation for the alumina specimens with a variety of additives. In the specimens with ZrO_2 , the grain growth is suppressed during deformation, but the plastic deformation is not observed at 1300°C. MgO-doped specimens exhibited extreme grain growth, and substantial strain hardening. In the case of lithium aluminate glass addition to alumina, the decrease in both the deformation stress and the strain hardening appeared to occur.

Xue and Chen [38] successfully demonstrated that it is possible to suppress the dynamic grain growth for the specimens by the addition of 300 ppm MgO or 10-vol%- ZrO_2 , proving the superplastic deformation.

4.2.4 Composite Materials

It is generally considered that alumina ceramics have a shortcoming of comparatively low toughness. To improve the toughness of alumina ceramics, many works on the composites of alumina matrix with other materials such as zirconia particles, SiC whisker and Si_3N_4 whisker have been carried out.

The fine powder was preferably used for producing the alumina based composites, giving favorable fine-grained matrix. Hayashi and Konishi [39]

obtained the zirconia toughened alumina composites prepared by HIP having the flexural strength of 1225 MPa and fracture toughness of 5 MPam^{1/2} at room temperature. Hirano and Inada [40] showed that the composites (Y,Ce)-PSZ/Al₂O₃ have the flexural strength over 2000 MPa and phase stability under hydrothermal condition (180°C, for 1 h).

Tamari *et al.* [41] fabricated the Si₃N₄-whisker reinforced alumina composites by hot-pressing. The flexural strength and the fracture toughness of the composite containing 20 vol%-whisker were about 620 MPa and about 4.7 MPam^{1/2}, respectively. For the alumina body without any reinforcement the strength at 1300°C decreased to about 40% of the value at room temperature. In comparison, for the composites reinforced by whisker contained ranging from 30 vol% to 40 vol%, the strength at 1100°C is nearly the same at room temperature, and even at 1300°C retained that of 75% at room temperature, obviously showing the improving effects of reinforcements on the mechanical strength. The thermal shock resistance, one more deficient property for alumina ceramics, was also improved to the critical temperature difference of 300 K by the composition.

From the different point of insight, the composites with metals were attempted to give electrical conductivity [42,43,44], in addition to the improvement of the fracture toughness. Nawa *et al.* [45] reported on the high strength alumina/Mo nano composite materials prepared by hot-pressing having 884 MPa in average strength (fracture toughness; 3.3 MPam^{1/2}), in which the high strength might result from its fine-grained microstructure.

5. Summary

The finest α -alumina powder commercially available is fabricated by calcination of ammonium dawsonite, NH₄Al(OH)₂CO₃.

In this report, we described the formation process of ammonium dawsonite as a precursor of alumina powder for ceramic use, and gave the suggestion to the morphological changes during θ - to α -alumina phase transformation, which give very important influences on the alumina powder characteristics.

Some suggestions for the next development of powder characteristics for ceramics could be given through examining the synthetic process of the precursor and the polymorphic transformation process of alumina. And also we introduced some of the characteristic features of the ceramics produced by using this finely divided alumina powder. Possible dramatic improvement in the field of powder preparation and powder processing would be expected, with enthusiasm for development of high performance ceramics.

Acknowledgement

The authors wish to express their appreciation to M. Ohashi of the Government of Research Institute, Nagoya and T. Kamiyanagi of Taimei Chemicals for their valuable discussions and to K. Hayashi of Toto Ltd. and his co-workers of The Kyusyu University, and to Toshiba Tangaloy Co.,Ltd for their kind permission to use their data. The authors also wish to acknowledge Dr. Z. Nakagawa for a critical reading of the manuscript.

References

1. S. Kato, T. Iga, S. Hatano and Y. Izawa, *Yogyo Kyokai-Shi*, **84**, 215 (1976).
2. T. Iga and S. Kato, *Yogyo Kyokai-Shi*, **86**, [11] 509-512 (1978).
3. S. Kato and T. Iga, *Yogyo Kyokai-Shi*, **85**, [6] 253 (1977).
4. Y. Murase and T. Iga, *Yogyo Kyokai-Shi*, **95** [5] 556-561 (1987).
5. Koichi Hayashi, S. Toyota, K. Nakashima and K. Morinaga, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi*, **98**, [5] 444-449 (1990).
6. Koichi Hayashi, S. Toyota, H. Shikibu and K. Morinaga, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi*, **99**, [7] (1991).
7. K. Kato, T. Iga, S. Sano and E. Ishii, *Yogyo Kyokai-Shi*, **77**, 60 (1969).
8. F.W. Dynys and J.W. Halloran, *J. Am. Ceram. Soc.* **65**, [9] 442-448 (1982).
9. K. Kato and T. Iga, *Yogyo Kyokai-Shi*, **81**, 560 (1973).
10. K. Daimon and E. Kato, *Yogyo Kyokai-Shi*, **94**, [2] 273-280 (1986).
11. E. Kato, K. Daimon, A. Yamaguchi and T. Yamada, *Yogyo Kyokai-Shi*, **85**, [3] 134-140 (1977).
12. J.R. Wynnyckyj and C.G. Morris, *Metall. Trans. B* **16B** [6] 345-353 (1985).
13. G.C. Bye and G.T. Simpkin, *J. Am. Ceram. Soc.* **57** [8] 367-371 (1974).
14. M. Miyashita, Z. Kato, N. Uchida, K. Uematsu and K. Saito, *Nippon Seramikkusu Kyokai Annual Meeting*, pp.544 (1990).
15. M. Komuro, Z. Kato, N. Uchida, K. Uematsu and K. Saito, *Nippon Seramikkusu Kyokai Annual Meeting*, pp.178 (1991).
16. K. Uematsu, C. Kim, Z. Kato, N. Uchida and K. Saito, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi*, **98** [5] 515-516 (1990).
17. Y. Nozaki, *Nippon Kikai Gakkai Text*, 3,4 th July (1990).
18. Y. Nozaki, *Nippon Fukugo Zairyo Gakkai*, July (1990).
19. Y. Nozaki, Special Seminar 26 Nov. (1990).
20. H. Yoshimatsu, H. Kawasaki, S. Ohmori, Y. Miura, A. Osaka and Y. Uchiyama, *Nippon Seramikkusu Kyokai Annual Meeting*, pp.223 (1988).
21. K. Miyamoto, I. Inamura, K. Takahashi and T. Miyamoto, *Funtai Funmatsu Yakin Kyokai Koen Gaiyoshu*, Spring, pp.136 (1991).
22. H. Mizuta, Y. Oda, M. Maeda, Y. Shibasaki, M. Machida and K. Ohshima,

- Nippon Seramikkusu Kyokai Annual Meeting*, pp.182 (1991).
23. Y. Shibasaki, H. Mizuta, S. Sakai, M. Katagiri and H. Fujimoto, *Funtai Funmatsu Yakin Kyokai*, pp.134 (1988).
 24. H. Mizuta, K. Oda and Y. Shibasaki, *Nyu Seramikkusu*, 5, [7] 87-94 (1990).
 25. S. Inada, T. Kimura and T. Yamaguchi, *Ceram. Int.* 16, 369-37 (1990).
 26. M. Machida, Y. Tazaki, H. Mizuta, Y. Shibasaki and K. Ohshima, *Nippon Seramikkusu Kyokai Annual Meeting*, pp.37 (1990).
 27. K. Oda, H. Mizuta, M. Maeda, Y. Shibasaki, M. Machida and K. Ohshima, *Nippon Seramikkusu Kyokai Annual Meeting*, pp.183 (1991).
 28. Y. Shibasaki, K. Oda, H. Mizuta, M. Maeda, M. Machida and K. Ohshima, *Funtai Funmatsu Yakin Kyokai Koen Gaiyoshu*, pp.128 (1991).
 29. Koichi Hayashi and K. Morinaga, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi*, 97 [8] 868-871 (1989).
 30. T. Igarashi, *Tangaroi*, pp.42-46 (1989).
 31. M.Sekiguchi, M. Komuro, C. Kim, Z. Kato, N. Uchida, U. Uematsu and K. Saito, *Nippon Seramikkusu Kyokai Annual Meeting*, pp.38 (1990).
 32. Y. Izawa, *Yogyo Kyokai Genryo Bukai Koenkai*, 3-4, Dec. (1987).
 33. T. Iga and K. Shimamoto, *Nippon Seramikkusu Kyokai Annual Meeting*, pp.320 (1988).
 34. T. Iga, *Yogyo Kyokai Annual Meeting*, pp.75 (1986).
 35. M.Sekiguchi, C. Kim, Z. Kato, N. Uchida, U. Uematsu and K. Saito, *Nippon Seramikkusu Kyokai Tohoku Hokkaido Shibu Kenkyu Happyokai*, (1989).
 36. L.A. Xue and I-Wei Chen, *J. Am. Ceram. Soc.* 73 [11] 3518-3521 (1990).
 37. Y. Yoshizawa and T. Sakuma, *Nippon Seramikkusu Kyokai Annual Meeting*, pp.171 (1991).
 38. L.A. Xue and I-Wei Chen, *J. Am. Ceram. Soc.* 74 [4] 842-845 (1991).
 39. Katsura Hayashi and H. Konishi, *MRS Int'l, Mtg. on Adv. Mats.* Vol. 5, 5-10 (1989).
 40. M. Hirano and H. Inada, *J. Am. Ceram. Soc.* 74 [3] 606-611 (1991).
 41. N. Tamari, T. Tanaka, I. Kondo and S. Kose, *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi*, 99 [5] 370-375 (1991).
 42. H. Watanabe and O. Kimura, *Funtai Funmatsu Yakin Kyokai Koen Gaiyoshu*, Spring, pp.122 (1991).
 43. H. Watanabe and O. Kimura, *Funtai Funmatsu Yakin Kyokai Koen Gaiyoshu*, Spring, pp.148 (1990).
 44. H. Watanabe and O. Kimura, *Funtai Funmatsu Yakin*, 38 [3] 19-22 (1991).
 45. M. Nawa, T. Sekiguchi and K. Niihara, *Nippon Seramikkusu Kyokai Annual Meeting*, pp.558 (1991).