Development of New High-Purity Alumina

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Sumitomo's high-purity alumina has been manufactured by the method of hydrolysis of aluminum alkoxide since 1981, and the present production capacity is 1500t/Y. High-purity alumina is used in areas such as displays, energy, automobiles, semiconductors and computers and demand for it is growing steadily.

In this paper, a general view of recent applications for high-purity alumina is introduced, and our newly developed high-purity alumina products are also described.

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Introduction

Alumina (Al_2O_3) is widely used in a variety of applications, because it has superior physical and chemical properties which is high heat resistance, excellent electrical isolation, abrasion resistance and high corrosion resistance.

Generally alumina is manufactured with a purity of 99.6 – 99.9% mainly by the Bayer process with bauxite as the starting material. It is used in refractory products, spark plugs and IC substrate and so on.

High purity alumina, which has a purity of more than 99.99% and has an uniform fine particle has been widely used in translucent tubes for high-pressure sodium lamps, single crystal materials such as sapphires for watch covers, high-strength ceramic tools, abrasives for magnetic tape and the like.

In recent years, the demand of high purity alumina is expanding in fields which are expected to show a high growth rate e.g. display materials, energy, automobiles, semiconductors and computers.

To attend to these needs, Sumitomo Chemical established mass production technology of high purity alumina using an unique process of hydrolysis of aluminum alkoxide. In 1981, a 250 ton per year plant was constructed, and after that, there were increases in capacity. In 2004, it was increased to 1500 tons per year.

Furthermore we have developed high quality powders to attend to the needs of many applications.[1)–10)]

In this paper, the current state and future outlook for production technology and development of applications for high purity alumina are described.

High Purity Alumina Production Technology

There are many industrial methods for producing high purity alumina, thermal decomposition of ammonium alum,[11)] thermal decomposition of ammonium aluminum carbonate hydroxide (AACH),[12)] underwater spark discharge with aluminum,[13)] vapor-phase oxidation[14)] and the like. In this section, production technology of hydrolysis of aluminum alkoxide and its recent progress are introduced.

1. Hydrolysis of Aluminum Alkoxide

Fig. 1 shows the manufacturing process of high purity alumina by aluminum alkoxide method. High purity aluminum alkoxide is synthesized from aluminum metal and alcohol, and hydrated alumina is produced by hydrolysis of alkoxide, and finally high purity alumina is obtained by calcination.

$$Al + 3ROH \rightarrow Al(OR)_3 + 3/2H_2 \quad (1)$$

$$2Al(OR)_3 + 4H_2O \rightarrow Al_2O_3 \cdot H_2O + 6ROH \quad (2)$$

$$Al_2O_3 \cdot H_2O \rightarrow Al_2O_3 + H_2O \quad (3)$$

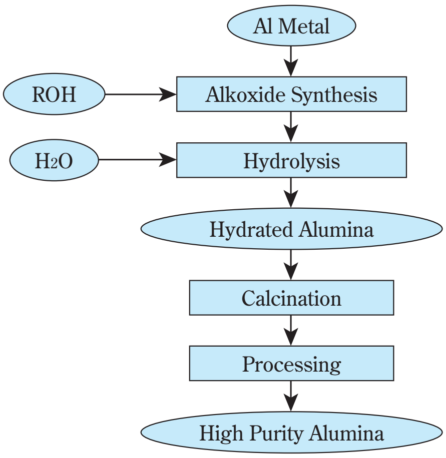


Fig. 1 Manufacturing process of High Purity Alumina by alkoxide method

In this method, aluminum alkoxide is purified by distillation and so on.

In addition, it is important to control the conditions during hydrolysis and to avoid producing rigid agglomerates during drying. Because the hydrolysis rate for aluminum alkoxide is extremely fast, it produces fine particle hydrated alumina which easily become rigid agglomerates.

α-Al_2O_3, which is a stable phase at high temperatures, is obtained by calcination of hydrated alumina (boehmite, for example) via γ, δ, θ-Al_2O_3. The various phases of alumina other than α-Al_2O_3, which is a stable phase at high temperatures, are called intermediate alumina, and its original particles are super fine particles of several tens of nanometers.

The transition to α-Al_2O_3 from the intermediate alumina requires high temperatures of over 1200°C, because it needs rearrangements of the oxygen packing (cubic closest-packed structure → hexagonal closest-packed structure). The generation of α crystal nuclei is a rate determining step for the α phase transition, and that the density of α crystal nuclei is low. But once nuclei are generated, a sudden grain growth occurs because of mass transfer from the surrounding intermediate alumina, and dendritic α-Al_2O_3 particles of micron size are obtained.

Therefore, in order to obtain α-Al_2O_3 particles which are fine and have a uniform particle size distribution, it is important to eliminate factors such as inhomogeneous generation of α-Al_2O_3 nuclei and to complete phase transition at as low a temperature as possible in addition to strict control of the uniformity of temperature distribution during calcination.

It is known that the α phase transition temperature is greatly affected by addition of seed crystals,[15)–18)] water vapour pressure in the calcination atmosphere[18), 19)] and elemental impurities.[20), 21)] The addition of α-Al_2O_3 crystal seeds give low energy sites for generation and growth of α phase, and the water content in the atmosphere promotes surface diffusion and accelerates the grain growth in the intermediate alumina. Along with these, the activation energy for the α phase transition is lowered, and it has the effect of lowering the temperature for the α phase transition.

α-Al_2O_3 particles, which is obtained by strictly controlling the conditions for hydrolysis, drying and calcination are in an agglomerate state, so deagglomeration process are necessary for getting particles of narrow particle size distribution. A ball mill, vibration mill, jet mill, media agitating mill or other type of mill can be used for the deagglomeration process.

In alumina ceramics applications, the presence of the agglomerates gives rise to local nonuniformity in a green body, and it causes residual pores in a sintered body. Particularly in translucent alumina ceramics applications for high pressure sodium lamps, the residual pores in the sintered body reduce the translucency. And for magnetic tape application, the presence of agglomerates makes for poor surface smoothness in the magnetic tape and causes damage to magnetic heads while the tape is running and lowers the electromagnetic conversion characteristics. By making refinement of various processes to reduce the agglomerates in high purity alumina powder, we have developed alumina powders suitable for various applications.[22), 23)]

Recently high-efficient jet mills and wet medium agitation mills for nanoparticles are developed,according to the trend to get high-functional submicron particles and nanometer particles.

Generally speaking, the process of deagglomeration of powders must be done with a great deal of caution. Because the smaller the original particles are, the more necessity for avoiding both regeneration of agglomerates and contamination are required.

Sumitomo Chemical has developed high purity alumina powders for a variety of applications by controlling these production conditions in a suitable manner.

Table 1 and **Fig. 2** show the characteristic and SEM photographs of the representative grades of Sumitomo Chemical's high purity alumina, respectively.

Table 1 Character of Sumitomo's high purity alumina

		AKP-20	AKP-30	AKP-50	AKP-3000	AKP-G008	AKP-G015	HIT-50
Crystal Form		α	α	α	α	θ	γ	α
Purity	(%)	> 99.99	> 99.99	> 99.99	> 99.995	> 99.995	> 99.995	> 99.95
Particle Size	(μm)	0.4 ~ 0.6	0.3 ~ 0.5	0.1 ~ 0.3	0.4 ~ 0.7	< 0.1	< 0.1	~ 0.25~
Loose Bulk Density	(g/cm^3)	0.7 ~ 1.1	0.7 ~ 1.0	0.6 ~ 1.1	0.3 ~ 0.6	–	–	–
BET Surface Area	(m^2/g)	4 ~ 6	5 ~ 10	9 ~ 15	4 ~ 8	~ 80 ~	~ 150 ~	6 ~ 13
Impurity Level	Si (ppm)	≤ 40	≤ 40	≤ 25	≤ 20	≤ 8	≤ 8	≤ 50
	Na (ppm)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 3	≤ 3	≤ 10
	Mg (ppm)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 3	≤ 3	≤ 10
	Cu (ppm)	≤ 10	≤ 10	≤ 10	≤ 10	≤ 3	≤ 3	≤ 10
	Fe (ppm)	≤ 20	≤ 20	≤ 20	≤ 10	≤ 8	≤ 8	≤ 30

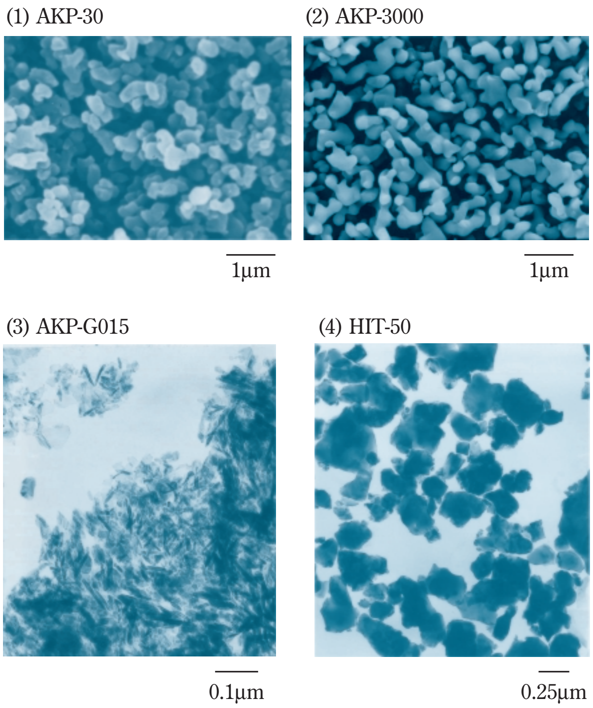


Fig. 2 SEM and TEM images of Sumitomo's high purity alumina

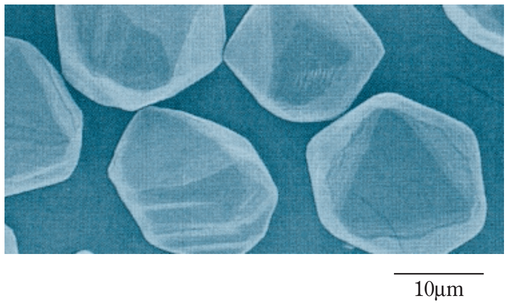


Fig. 3 SEM image of Sumicorundum®

2. In-situ Chemical Vapor Deposition[24)]

"In-situ Chemical Vapor Deposition", which is Sumitomo Chemical's original synthesis method is a technique for in-situ growing grains via gas phase by calcination of hydrated alumina, which is the raw material, in a special atmosphere.

"Sumicorundum®", consisting of single crystal α-Al_2O_3 particles manufactured by this synthesis technique, has grain diameters from submicron to several microns with uniform shape and excellent distribution characteristics.

A typical SEM photograph of Sumicorundum® is shown in **Fig. 3**.

3. Manufacturing Methods for Nano Sized α-Al_2O_3

In recent years there are great expectations for the future prospects surrounding nanotechnology.

It is difficult to synthesize nano sized α-Al_2O_3 with good dispersibility because the particle size can easily get too large and sintering between particles can occur at phase transition temperatures of approximately 1200°C.

There are a lot of examples of research for overcoming this problem, but the main point is lowering the phase transition temperature.

For the synthesis of nano sized α-Al_2O_3, many attempts have been made at lowering the phase transition temperature to 1000°C or less by adding various very small crystals to the alumina precursor.

Rajendran[25)] has reported synthesizing α-Al_2O_3 powder of 60 nm or less by calcination of hydrated alumina that contains α-Al_2O_3 seed crystals and ammonium nitrate at 950°C. Furthermore, Krell and Ma et al.[26)–28)] have reported obtaining approximately 50nm of nano sized α-Al_2O_3 by hydrolysis of an aqueous solution of aluminum nitrate with 0.1μm or less seed crystals (Diaspore or α-Al_2O_3) dispersed and calcination of that amorphous hydrolysate.

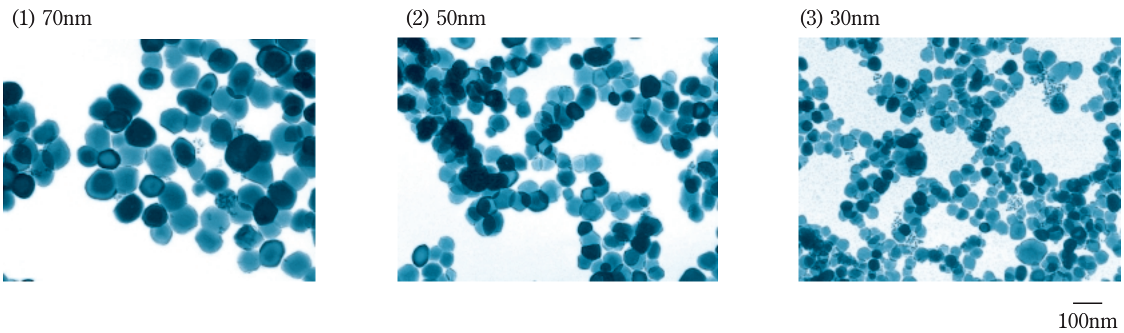


Fig. 4 TEM images of Sumitomo's nano-sized α-Al_2O_3 powders

At Sumitomo Chemical, we have optimized the industrial processes of nano sized α-Al_2O_3 with a good dispersion and only few coarse agglomerated particles.

Fig. 4 shows TEM images of nano sized α-Al_2O_3 powders developed at Sumitomo Chemical. Control of the particle size is possible by optimizing the processes, and there are expectations for new various applications.

Development of Applications for High Purity Alumina

In recent years, the demand of high purity alumina is expanding in fields which are expected to show a high growth rate e.g. display materials, energy, automobiles, semiconductors and computers. In the following, we will discuss new development of applications for high purity alumina.

1. Sapphire Single Crystal Applications

Sapphire single crystal, with a corundum structure of Al_2O_3 has been manufactured by the Verneuil process with γ-Al_2O_3 as the starting materials for a long time. It has been widely used for gem, and watch cover applications.

However, the sapphires obtained by the Verneuil process have poor crystallinity which limit their applications. Therefore, the edge-defined film-fed growth (EFG) process has been developed for the purpose of producing a high crystallinity sapphire and establishing industrial productivity. The sapphire obtained by EFG process has disseminated widely in applications such as substrates for high brightness light emitting diodes (LEDs), and support plates[29] for polarizers in liquid crystal projectors. In particular, among the high brightness LEDs, white LEDs is expected to widely used for advertisement lighting, displays, automobile headlights, home illumination and especially the backlights in mobile phones, which is their current main application.[30]

LED devices are manufactured by crystal growth of GaN (Ⅲ–V groups compound) on a substrate. Sapphire is used for this substrate, since it has superior characteristics as a base substrate, such as close lattice constant with GaN and high heat resistance at crystal growth temperature.[31]

The starting materials for sapphire are required not only to have high purity but also to minimize amount of absorbed water. Water causes oxidation of Mo crucible during the melting process at a high temperature of over 2000°C in the manufacturing process. In addition, in case of α-Al_2O_3 being continuously supplied into the process, it is necessary that particles of starting material such as α-Al_2O_3 do not fuse to each other in order not to cause any clogging in the manufacturing apparatus.[32]

High purity alumina AKQ-10, which is spherical in a size of approximately 2 mm, is widely used as a starting material of sapphire that satisfies these quality requirements. Recently single crystal growth technique of Czochralski has been improved[33], the requirements have increased for improving the bulk density of starting material. High bulk density of starting materials can improve industrial productivity of manufacturing sapphire. To respond to these requirements, Sumitomo Chemical has developed a new high density α-Al_2O_3 for starting materials of sapphire manufacturing that has a high bulk density of 2.0 g/cm^3 by improving the particle density and increasing of the packing properties by optimizing the particle size distribution.

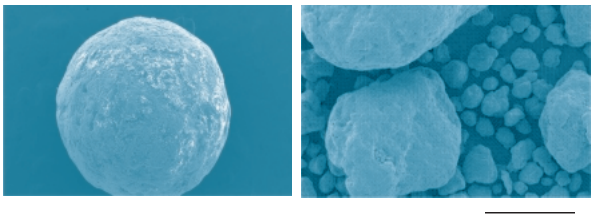
Table 2 and **Fig. 5** show the characteristics and SEM images of Sumitomo Chemical α-Al_2O_3 for sapphire single crystal growth, respectively.

When sapphire single crystals are grown by newly

Table 2 Character of α-Al_2O_3 for sapphire single crystal

		AKQ-10	High Density New Alumina
Crystal Form		α	α
Purity	(%)	> 99.99	> 99.99
Loose Bulk Density	(g/cm^3)	1 ~	≥ 2
BET Surface Area	(m^2/g)	~ 3 ~	≤ 1
Impurity Level	Si (ppm)	≤ 10	≤ 10
	Na (ppm)	≤ 10	≤ 10
	Mg (ppm)	≤ 10	≤ 10
	Cu (ppm)	≤ 10	≤ 10
	Fe (ppm)	≤ 10	≤ 10
	Ca (ppm)	≤ 10	≤ 10

(1) AKQ-10 (2) High Density New Alumina



1mm

Fig. 5 SEM images of α-Al_2O_3 for sapphire single crystal

developed α-Al_2O_3 as starting materials, it is possible to get better productivity than conventional and to get high quality sapphire single crystal, because the amount of α-Al_2O_3 that can be stocked in the growth apparatus is increased. So we expect new α-Al_2O_3 widely used for manufacturing sapphire single crystal.

2. Phosphor Applications

In recent years, plasma display panels (PDP) have been receiving attention as large flat panel displays that are thin with flat screens and as devices that can be made thinner and lighter. The principle of operation[34] for PDPs are the emitting of phosphor exited by the vacuum ultraviolet (VUV) that was generated by Xe molecular beam radiation with a wavelength of 147 nm and the Xe resonance line with a wavelength of 172 nm. In addition, in the cold cathode fluorescent lamps that are widely used as backlights of LCD, Red, Green and Blue phosphors are excited by ultraviolet ray with a wavelength of 254 nm which are emitted by mercury atoms.

Among these phosphors, it is known that $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM), which is used as commercial blue phosphor, is most unstable. The decrease of luminescence intensity and color tone shift of BAM has been enhanced by the heating in the panel manufacturing processes and the VUV irradiation when the panels are driven in PDP applications. Investigations into increasing the luminescence intensity and improving the deterioration characteristics are continuing.[35]

Generally, aluminate phosphors including BAM are typically manufactured by mixing high purity alumina, Ba-, Mg-, Eu-compound, and fluoride flux as starting materials and calcining the mixture. It is usually called solid reaction method. However reaction is not so simple, so the phosphor manufacturers have the know-how in the details of these production processes.[36)–38] For example, conventional phosphors using fluoride flux is a square sheet shape, and the particle size distribution is broad, however Oshio et al.[39] synthesized aluminate phosphors, which spherical shape and size were similar to starting alumina powder without fluoride flux. And that the chromaticity of this spherical phosphor was the same as that of conventional products and the luminosity was improved by 5% over conventional products. Furthermore, thermal degradation of phosphor was able to reduced.

As described above, aluminate phosphors are used for the next generation material of display, and in the future it is expected that the demand will broaden.

In the field of phosphors, high purity alumina is one of the materials that controls the characteristics of phosphors and has an important position. Sumitomo Chemical is continuing development of alumina powders suitable for these needs.

3. Automotive Sensor Applications

In recent years, the market for the air to fuel ratio sensors (A/F sensors) that are used in controlling the air to fuel ratio in automotive engines is expanding. A/F sensors detect the air to fuel ratio for the combustion in the engine from the concentration of oxygen and the concentration of unburned combustible gases remaining in the exhaust, and carry out highly precise adjustments of the fuel injection. A combination of partially stabilized zirconia and alumina substrate endowed with heater are proposed for A/F sensors. Partially stabilized zirconia is an oxygen ion conductor and an alumina substrate is used for its excellent electrical insulating properties and high heat conductivity. Sintering to unitize the partially stabilized zirconia substrate and the alumina substrate is necessary, and to join these two disparate materials, the shrinkage in sintering and the coefficient of thermal expansion for these materials must be the same.[40] In addition, since there is a possibility that cracks happen at the interface between them because of the differences in thermal expansion in the actual usage environment. It is necessary to make the partially stabilized zirconia and alumina substrates have high density and a fine grain size[42] in addition to making the difference in thermal expansion small for the two.[41] It is been assumed that it is necessary to improve the low-temperature sintering properties of alumina for such requirements.

It is said that as the original grain size of the raw powder becomes smaller, the temperature at which shrinkage begins becomes lower. But a small original grain size lowers green density and easily become hard agglomerates and they causes low fired density of sintered body. Sumitomo Chemical has developed various types of sintering grade α-Al_2O_3 powder suitable for low temperature sintering.

Fig. 6 and **Fig. 7** show sintering behavior of Sumitomo Chemical's high purity alumina powders and a typical microstructure of sintered body, respectively. One can see that superior low-temperature sintering characteristics are exhibited according to the reduction of the size of the grain.

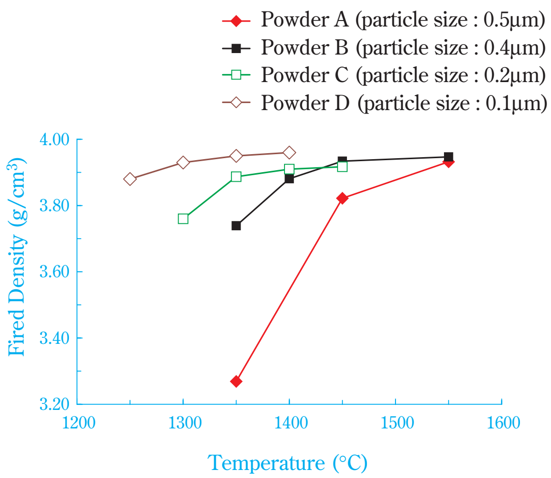


Fig. 6 Sintering behavior of Sumitomo's high purity alumina powders

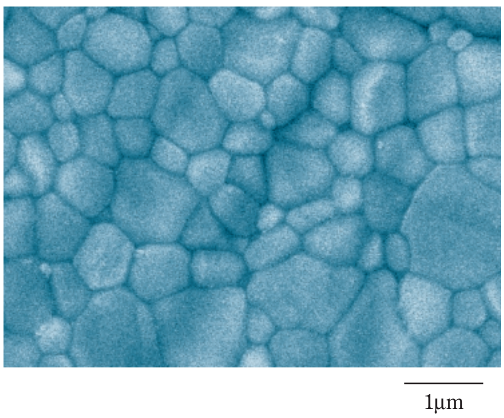


Fig. 7 Microstructure of Powder D (MgO = 500ppm addition) sintered body at 1300°C

4. Semiconductor Applications

In the fields of semiconductors manufacturing equipment and liquid crystal display manufacturing equipment, a large amount of α-Al_2O_3 components, which has a high level of plasma corrosion resistance, is used. In the case of sintered aluminum bodies, improvements in corrosion resistance are achieved by reducing the pores and impurities, and by using a fine grained product of Sumitomo Chemical's Sumicorundum®, it is possible to obtain a high bending strength and corrosion resistant alumina ceramic without residual pores.[24]

In addition, the demand for materials for forming plasma spray coatings of alumina on aluminum, nickel, chromium, zinc and zirconium or alloys of these and the like has been increasing.[43]

For plasma spray coating material for semiconductor tool, some properties are required as follows

- High purity
- Good fluidity such that the alumina particles can be supplied stably and constantly to plasma flame during spraying
- Shape of the particles must be maintained during supply and before melting in plasma flame
- Complete melting during spraying.

Single crystal, and large grained α-Al_2O_3 Sumicorundum® is used as a material that matches these requirements, and there are expectations for an expansion in future demand.

5. New Applications of Ultra Fine α Alumina Powder

Nano sized α-Al_2O_3 is a new material, and it is a material that is expected to open up new applications in the future. We describe applications about abrasives, ceramics, precision separation membranes.

(1) Abrasives Applications

As one application, ultra fine α Alumina will be applied for abrasives based on high hardness of alumina.

At Sumitomo Chemical up to this point, we have developed the HIT series that have edge-shape particles by adjusting the manufacturing conditions. Fig. 1 – (4) shows a SEM photograph of Sumitomo Chemical's alumina powder.

These edge-shape particles of alumina are used in magnetic tape additives and abrasives for precision lapping and polishing abrasives of metal,[44)–47)] plastics and the like.

Magnetic tapes are widely used as a recording medium for consumer use, broadcast use and industrial use because of its high reliability, high volume recording density, high transfer speed and other characteristics, and there has been a focus on magnetic tapes that can store large volumes of data in recent years.

Magnetic tapes are produced by coating of a magnetic powder material on a PET or PEN film.[48)] The advantages are mass production and superior stability because the magnetic material is protected by polymers.

As is shown in **Fig. 8**, since the magnetic layer of magnetic tape passes rapidly over a magnetic head and is subjected to a rigorous state of abrasion, α-Al_2O_3 is added to the magnetic layer to increase the abrasion resistance of the magnetic layer and clean the adhesion materials (for example Fe and C) to prevent a magnetic head blockage. In recent years, there are requirements for higher volume and recording density in magnetic tape, and so problems arise when the magnetic layer is made thinner (100 nm or less), the magnetic material used is finer (forming nanoparticles) and the magnetic layer has to be made more uniform and smooth.[49)] Therefore, it is necessary to add α-Al_2O_3 nano particles to the magnetic layer.

At Sumitomo Chemical, we are currently investigating the nano sized α-Al_2O_3 abrasives with our knowledge in the development of magnetic tape abrasives. Furthermore, we are also considering development in the precision polishing known as chemical mechanical polishing (CMP), and are making further improvements in the physical properties of powders.

(2) Alumina Ceramics Applications

If agglomeration of the nano size α-Al_2O_3 powder is prevented and generation of defects in the green body is decreased, we can expect to obtain high density sintered bodies with fine grain sizes. Ma et al.[26), 27)] have shown that a high density sintered body with a submicron grain size and a relative density of 99% can be obtained by slip cast molding after ball mill processing of nano size α-Al_2O_3 powder and sintering at 1285°C.

The nano sized α-Al_2O_3 powder was developed by Sumitomo Chemical, by using a wet process, a high density sintered body with a density of 3.95 g/cm^3 (relative density 99.2%) has been obtained with a sintering temperature of 1250°C.

(3) Separation Membrane Applications

Using its chemical resistance and heat resistance, α-Al_2O_3 porous bodies are used in the applications such as ultrafiltration, gas separation membranes.

Among the gas separation membranes, the hydrogen separation membranes are incorporated in to a hydrogen production process based on the steam-reforming reaction shown in reaction equation (4). This makes it possible to lower the reaction temperature (800°C → 500°C) by drawing the produced hydrogen gas outside of the reaction system and unify the hydrogen production process and separation process. There are expectations for future development aimed at achieving hydrogen utilization systems in fuel cells and the like.

$$CH_4 + H_2O \rightarrow 3H_2 + CO \quad (4)$$

As shown in **Fig. 9**, the configuration of a hydrogen separation membranes is based on a structure that pro-

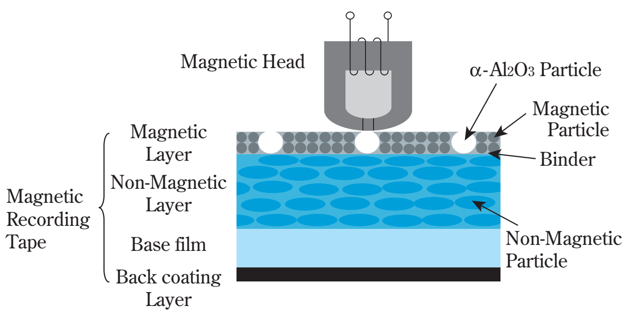


Fig. 8 Magnetic Recording System

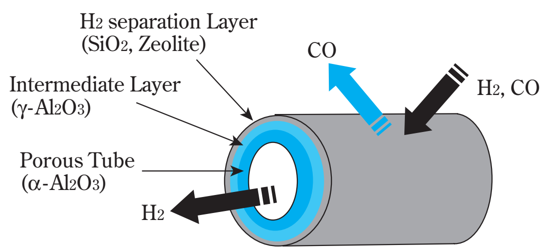


Fig. 9 Structure of Hydrogen separation element

vides a γ-Al_2O_3 intermediate layer on a pipe-shaped porous α-Al_2O_3 support substrate and, forms a silica, zeolite or palladium layer with hydrogen separation function on top.

However, in the steam atmosphere the grain growth and crystal transition of the γ-Al_2O_3 used in the intermediate layer are promoted, and so the use of α-Al_2O_3 is being considered. To get high performance of nano pore-sized α-Al_2O_3 layer, it is required to control both pore diameter according to the application and a sufficient porosity for assuring the flow rate of the fluid (moreover, assuming that the particles are closest packed, the pore diameter is approximately 1/5 of the grain diameter).

Krell and Ma et al.[28] have reported an α-Al_2O_3 layer had porosity of approximately 40% and an average pore diameter of 10 – 60 nm by dip-coat method using a nano sized α-Al_2O_3 slurry. In addition, an α-Al_2O_3 layer with an average pore diameter of 2 – 50 nm and a porosity of 30 – 40% being produced from a mixture of 10 – 100 nm fine α-Al_2O_3 and γ-Al_2O_3 or boehmite has been reported.[50]

The pore diameter distribution of green body in Sumitomo Chemical α-Al_2O_3 is shown in **Fig. 10**. The finer the original particle sizes of α-Al_2O_3 is, the finer the pore diameter becomes, and one can see that the average pore diameter with nano sized α-Al_2O_3 is reduced to 16 nm.

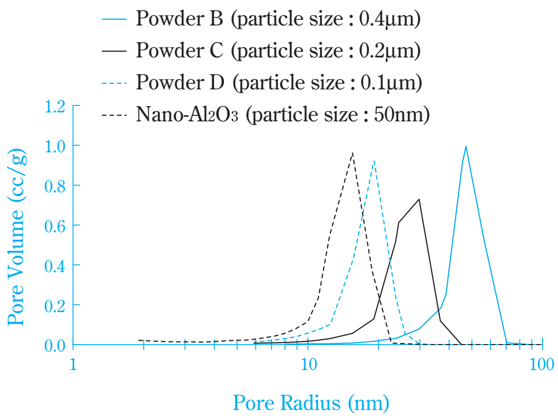


Fig. 10 Pore size distribution of high purity alumina powder compacts

We have described nano pore sized separation membrane applications focusing on hydrogen separation membrane. But for the other applications of precision filtration, which are not limited to gas separation, it is assumed that there will be made further improvements and they will be put to practical use in the future. So it is expected to brought further acceleration in the development of applications for α-Al_2O_3 nano particles.

Conclusion

As has been discussed in this paper, high purity alumina by controlling particle size and shape and particle size distribution is a hopeful inorganic material in the field such as display materials, energy, automobiles, semiconductors, computers, which the speed of technical innovations is very rapid.

With the increasing level of needs, we raw material makers must brush up the performance of high purity alumina powders to attend to these needs. In particular, nano sized grain dispersion technology is essential for promoting new development. In the future, we would like to carry out development on process technology for targeted markets and moving downstream.

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