



New technology and application development of alkoxide-derived high purity alumina

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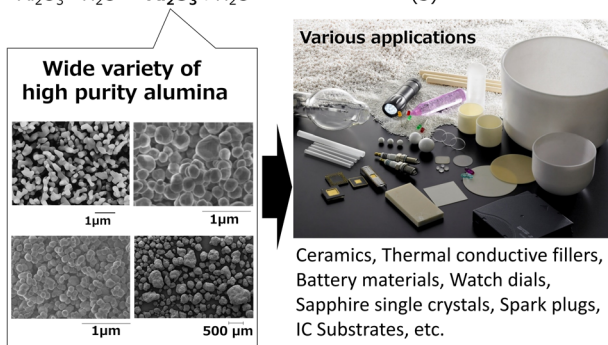
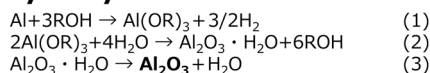
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Abstract

High purity alumina, alumina with a purity of 99.99% or higher, has been widely used for various applications, for instance, ceramics, thermally conductive fillers, battery materials and sapphire single crystals. Among several manufacturing methods for high purity alumina, we have established mass-production technology using hydrolysis of aluminum alkoxide. In some applications of high purity alumina, there are technical problems to be solved. Two applications are described in this article. First, higher mechanical strength and corrosion resistance are required for ceramic parts of semiconductor manufacturing equipments. In order to obtain these properties, we have developed nano-sized α -alumina which has round and uniform particle shape with sharp particle size distribution. This alumina, NXA-150, can be sintered at a low temperature. Second, in the thermal interface material application, demands for electrical insulating and thermally conductive fillers are increasing. We have developed large size alumina (260 μm) which can reduce filler/resin interface and increase thermal conductivity of filler/resin composites.

Graphical abstract

Hydrolysis of aluminum alkoxide



Keywords High purity alumina, Sintered body · Filler · Thermal conductivity · Thermal interface materials

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Highlights

- We have established a technology for mass-producing high purity alumina by the aluminum alkoxide hydrolysis.
- Fine alumina can produce dense sintered bodies for various applications such as semiconductor devices.
- Large-size alumina can produce composites with high heat dissipation performance.

1 Introduction

Aluminum has the third highest Clarke number of all elements, indicating that it is relatively abundant in the earth's crust. Alumina is one of the most common metal oxides, and also has excellent physical and chemical properties, such as heat resistance, electric insulation, wear resistance, and corrosion resistance.

In general, alumina can be obtained by extracting sodium aluminate from bauxite ore using caustic soda, crystallizing a supersaturated solution of the extracted sodium aluminate to form aluminum hydroxide, and calcining the obtained aluminum hydroxide. This method is known as the Bayer process. The purity of alumina obtained by this method is 99.6–99.9% [1], and it is used in a variety of products such as refractories [2], spark plugs [3], and IC substrates [4].

In contrast, alumina with a purity of 99.99% (4N) or higher is called high purity alumina, and is used in sapphire glass for LED substrates [5] and watch dials [6], fine ceramic materials such as translucent tubes for high-pressure sodium lamps [7] and high-strength ceramic tools [8], coatings for lithium-ion battery separators [9], and high-intensity phosphorus [10]. Alumina with a small and uniform particle size is used as a polishing filler for magnetic tapes and as a precision polishing material for metals and plastics [11].

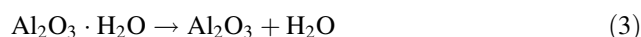
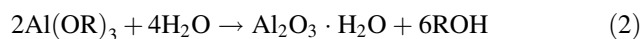
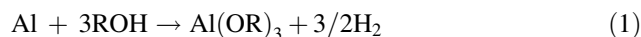
We have established a technology for mass production of high purity alumina by the aluminum alkoxide hydrolysis method [12]. Since entering this market in 1981, we have expanded our business by developing a variety of high purity alumina products to meet the customer needs.

This article outlines the characteristics and applications of our products, as well as the development status and future prospects for new alumina products.

2 Production technologies for high purity alumina

Known mass-production methods for producing high purity alumina include hydrolysis of aluminum alkoxide, pyrolysis of ammonium alum [13], pyrolysis of aluminum ammonium carbonate (AACH) [14], spark discharge of aluminum in water [15], and gas-phase oxidation [16]. Here, we introduce the hydrolysis of aluminum alkoxide, which is adopted as our mass-production technology of high purity alumina.

The hydrolysis method of aluminum alkoxide is shown in reaction Eqs. (1)–(3) below. In this method, high purity alumina is synthesized by reacting metallic aluminum and alcohol to form aluminum alkoxide, hydrolyzing the aluminum alkoxide to obtain alumina hydrate (boehmite), and then calcining it.



The hydrolysis rate of aluminum alkoxide is very fast, so small particles of alumina hydrates (boehmite) are easily formed. It is important to prevent the formation of strong agglomerated particles at hydrolysis/condensation and drying steps. α -alumina, which is the thermodynamically stable form of alumina, is obtained by calcining of the aluminum hydrate (boehmite) through intermediate alumina of γ , δ , and θ -alumina [17].

Table 1 lists various properties of some of our high purity alumina products, and Fig. 1 shows SEM images of some of our high purity alumina products, which have a

Table 1 Various properties of Sumitomo's high purity alumina

	Crystal structure	Purity (%)	Particle size (μm)	Loose bulk density (g/cm^3)	BET specific surface area (m^2/g)	Impurity level				
						Si (ppm)	Na (ppm)	Mg (ppm)	Cu (ppm)	Fe (ppm)
AKP-20	α	>99.99	0.4~0.6	0.7~1.1	4~6	≤ 40	≤ 10	≤ 10	≤ 10	≤ 20
AKP-30	α	>99.99	0.3~0.5	0.7~1.0	5~10	≤ 40	≤ 10	≤ 10	≤ 10	≤ 20
AKP-50	α	>99.99	0.1~0.3	0.6~1.1	9~15	≤ 25	≤ 10	≤ 10	≤ 10	≤ 20
AKP-3000	α	>99.995	0.4~0.7	0.3~0.6	4~8	≤ 20	≤ 10	≤ 10	≤ 10	≤ 10
AA-03	α	>99.99	0.4	0.5	5.6	4	3	1	1	2

peculiar shape, small amount of impurities, α -type crystal, and submicron particle size. These are used in ceramic sintered bodies, coatings for lithium ion battery separators, abrasives, and many other fields. Nano-sized alpha alumina, NXA, and large size alumina particles, both of which are described later, have been developed based on our high purity alumina mentioned here.

3 Application of high purity alumina

3.1 Fine alumina for sintered bodies

We have commercialized many types of fine alumina product and some of them are shown in Fig.1 and Table 1. Hereafter, “small particle size” is described as “fine”. Among them, nanoscale and other fine particles have a larger specific surface area than micrometer-sized particles and exhibit excellent chemical and physical properties [18]. Tough and non-brittle alumina ceramics can be obtained by molding and sintering nano-sized crystalline alumina. This process allows to prepare a dense sintered body at temperatures as low as 1150 °C [19]. Ceramic materials made from dense sintered alumina body have excellent heat and corrosion resistance, and are therefore used in internal components for plasma and chemical solutions in semiconductor manufacturing equipment that are exposed to severe environments. The market in this field is expected to grow with the spread of 5G, the next-generation communication standard. As semiconductor circuits become increasingly miniaturized, manufacturing conditions are becoming more severe by generating plasma, and further resistance to such conditions are required for ceramic

components. Thus, nano-sized fine alumina particles that can make dense sintered bodies with high reliability and excellent plasma resistance will be in greater demand than ever before.

Inorganic oxides other than alumina have also become highly functional in recent years due to recent trends toward finer and nano-sized particles. Pulverizers, dispensers, classifiers, and other devices, which are essential for developing new materials, are being created in rapid succession. By optimizing production conditions with these devices, it is possible to develop nano-sized alumina powders suitable for a variety of applications. In general, the smaller the primary particles are, the more likely they are to aggregate, and it is important to develop additives that suppress this aggregation. Nano-sized fine alumina is effective in a wide range of applications, including use in ceramic sintered bodies, coating layers in lithium-ion battery separators, and highly active catalysts and homogeneous composite materials [20].

As mentioned earlier, there are various methods for the synthesis of alumina. Generally, the transition temperature of alumina crystals, which changes from intermediate alumina to α -alumina, is as high as about 1200 °C [21]. As necking between particles proceeds, the particles grow and aggregate. Therefore, it is said to be difficult to manufacture nano-sized α -alumina with high dispersibility [22].

There are several methods for synthesizing nano-sized α -alumina at the laboratory-scale, including the gas-phase method [16], alkoxide sol-gel method [23], hydrothermal method [24], coprecipitation method [23], and polymerization complex method [25]. Among them, the sol-gel method has the advantage of obtaining high purity particles with a large specific surface area [26]. Technically, it is

Fig. 1 SEM image of Sumitomo’s high purity alumina

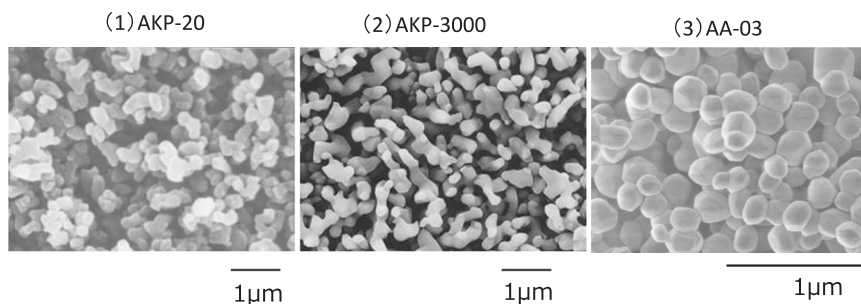
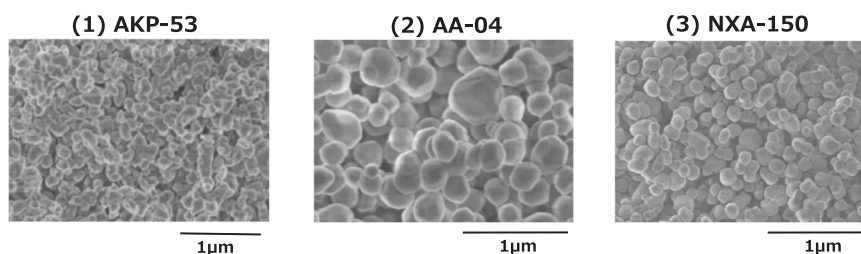


Fig. 2 SEM image of Sumitomo’s high purity alumina



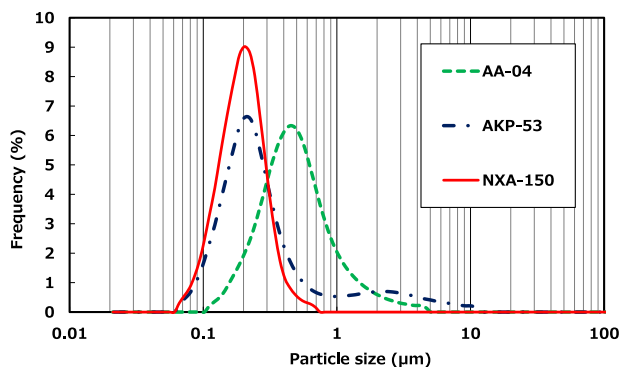


Fig. 3 Particle size distribution of Sumitomo's high purity alumina

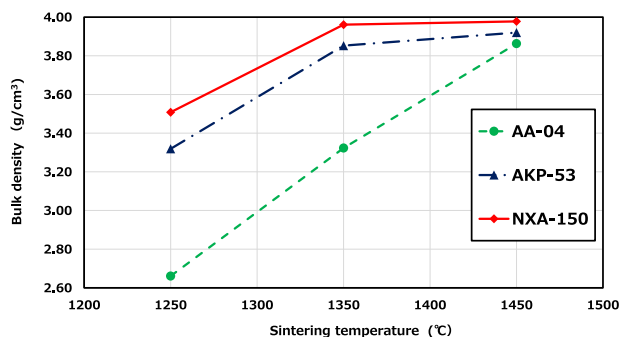


Fig. 4 Sintering curves of Sumitomo's high purity alumina

important to lower the temperature for the transformation to α -alumina. Several processes (e.g., addition of alumina precursors or some kind of species) have been carried out to achieve the transition to α -type crystals at low temperatures [27].

After extensive examination based on the know-how accumulated over the years, we have developed nano-sized α -alumina “NXA” and its industrially feasible production method. By optimizing this manufacturing process, the particle size can be controlled at the nano-size level, and crystalline α -spherical alumina is expected to be used for the various applications mentioned above.

Currently “NXA” series is under development, but, its expected performance is explained here by comparison with other alumina products of ours. Figures 2 and 3 show SEM image and particle size distribution, respectively, of NXA-150, AKP-53 and AA-04. Compared to AKP-53 and AA-04, NXA-150, which is one of “NXA” products, has round and uniform particle shape, and sharp particle size distribution (fine particle without aggregation).

The sintering curves of these alumina are shown in Fig. 4. NXA-150 shows higher sintering density at a lower temperature than AKP-53 and AA-04, which are adopted in the market using their characteristics and performance. In alumina ceramics applications, the agglomerates are not preferred because they are one of the causes of residual

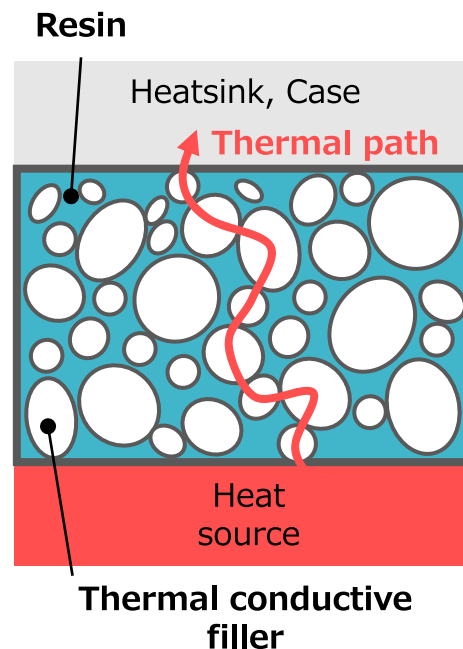


Fig. 5 Image of cross section of thermal interface material

pores in a sintered body by forming local non-uniformity (defects, pores, etc.) in a green body. The characteristics of “NXA”, which are round shape and uniform size without aggregation, reduce defects and pores in a green body. As a result, a highly dense sintered body can be obtained by using NXA-150.

3.2 Development of large-size alumina for thermal interface materials

In recent years, as typified by the automotive industry, equipments have become increasingly motorized and computerized, and the places where heat-generating components are installed have increased rapidly. Since the heat increases the probability of the failure and shortens the lifetime of the equipments, it is important to introduce thermal design and thermal countermeasures to ensure the reliability of systems (e.g., power control units). In general, thermal interface materials that transfer heat from a heat source to a heat sink or other devices are used as thermal countermeasures for electronic devices. As shown in Fig. 5, the thermal interface material is a composite material consisting of a matrix resin (silicone resin, epoxy resin, etc.) filled with thermally conductive fillers. In order to improve the thermal conductivity of thermal interface materials, it is important to select and adjust the thermally conductive fillers so that they make good contact with each other and form a thermal conduction path.

There are two types of thermally conductive fillers: electrically conductive fillers made of such as metal or carbon, and insulating fillers made of insulating materials

Table 2 Typical properties of thermal conductive materials

	Thermal conductivity	Cost	Handling ability	Particle size
Boron nitride	◎	× high	× Crystalline anisotropy	0.5–40 μm
Aluminum nitride	◎	× high	× Water resistance	1–80 μm
Spherical alumina	○ (×: Fine size)	○ (△: Fine size)	◎	<100 μm
Advanced alumina (AA)	○	△	○	0.2–18 μm

◎ excellent, ○ good, △ not bad, × poor

such as ceramics [28]. Electrically conductive fillers made of conductive materials generally have high thermal conductivity, but they can cause short circuits and electric shocks when they are used in areas where voltage is applied, such as IC chips or inverters. Therefore, they can only be used as fillers in limited areas. Insulating fillers, on the other hand, can withstand voltage, but their thermal conductivity is an order of magnitude smaller than that of electrically conductive fillers. When high thermal conductivity is required for thermal interface materials filled with insulating fillers, they must be densely filled to compensate for their inferior thermal conductivity.

With the improvement of the performance of electronic devices, the use of semiconductor devices that generate more heat is increasing. In addition, with the miniaturization of equipments, various devices are installed in high density, resulting in increase of thermal density [29]. For these reasons, thermal interface materials of higher thermal conductivity are required than ever before. Furthermore, thermal interface materials used in power semiconductors that operate at high voltages and high currents require more reliable insulation performance than ever before. Consequently, the use of ceramic fillers with high insulation performance will be increased.

Boron nitride, aluminum nitride, and alumina, shown in Table 2, are mainly used as ceramic fillers. These have relatively high thermal conductivity among the ceramic materials. The issue of using ceramic fillers for thermal interface materials is how to improve the heat dissipation of ceramic materials, which have lower thermal conductivity than conductive materials. Boron nitride and aluminum nitride have higher thermal conductivity than alumina and are expected to improve the thermal conductivity of thermal interface materials, but they have the disadvantage of being expensive. Also, boron nitride has crystal anisotropy in thermal conductivity. The thermal conductivity of in-plane direction in hexagonal boron nitride flake is high (250–360 W/mk), on the other hand, that of out of plane direction is small (2 W/mk) [30]. Aluminum nitride reacts with water to produce aluminum hydroxide and ammonia, making it difficult to handle [31]. Alumina is relatively inexpensive, has excellent electrical insulation properties, is

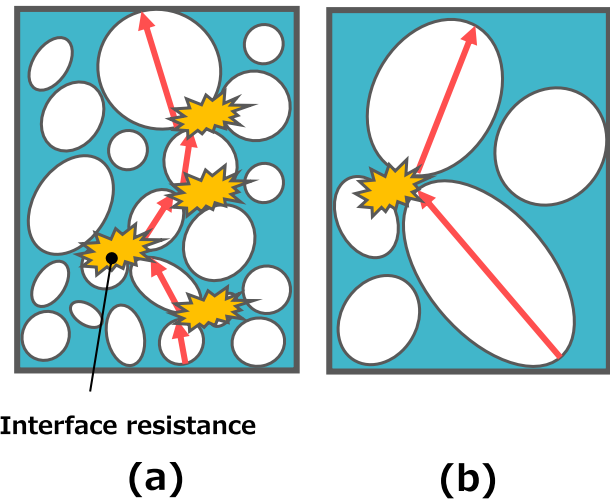


Fig. 6 Image of thermal dissipation in thermal interface material. **a** Conventional alumina. **b** Development of large sized alumina

chemically stable, and is highly reliable as a material for thermally conductive fillers. For these reasons, alumina is currently the most common material used as thermal interface material.

In order to improve thermal conductivity, it is important to fill the resins with fillers of high thermal conductivity as densely as possible. However, even when monodispersed spherical alumina particles are densely packed in a composite thermal interface material, the thermal conductivity of the composite will be as low as 4–6 W/mK while the thermal conductivity of α -alumina is 30–40 W/mK [32]. On the other hand, by mixing high performance alumina with different mean particle sizes at appropriate ratios, it is possible to fill the resins with alumina particles in more densely, resulting in high thermal conductivity of the composites.

This is probably because the resin with low thermal conductivity inhibits thermal conduction at the interface between the alumina and the resin, as shown in Fig. 6a. Therefore, to improve the thermal conductivity, it is necessary to form a thermal conduction path effectively. Using alumina of a large particle size makes the thermal conduction paths in the alumina particles longer as shown in Fig. 6b, and reduces the interface between the alumina and

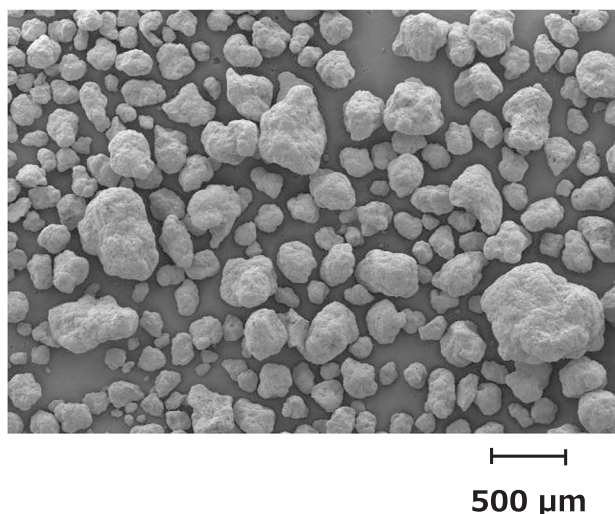


Fig. 7 SEM images of developed large size alumina

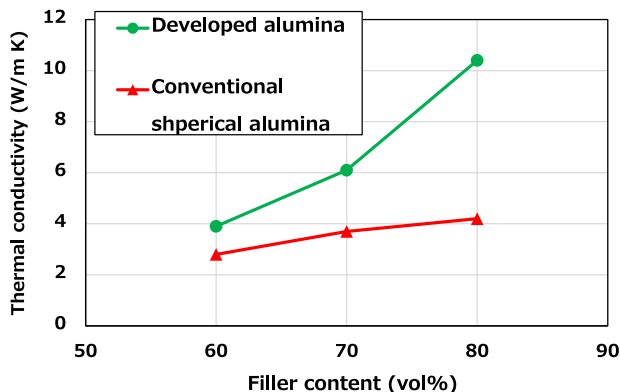


Fig. 8 Thermal conductivity of thermal interface materials containing conventional spherical fillers (70 μm in mean size) and developed large-size alumina fillers (210 μm in mean size)

the resin where heat transfer is inhibited. As a result, the thermal conductivity of the thermal interface material can be improved. The effect of the large alumina on improving the thermal conductivity of the thermal interface material was evaluated by comparing the newly developed large-size alumina with common spherical alumina as the filler

Figure 7 is SEM image of the developed large-size alumina, which has a mean particle size of 260 μm . It is larger than the spherical alumina (10–100 μm) commonly used as the filler [32]. The large-size alumina is a filler with high α -conversion rate (100%), high true density (3.87 g/cm^3), and high thermal conductivity.

The developed large-size alumina was mixed with epoxy resin to prepare a thermal interface material, and its thermal conductivity was evaluated by the laser flash method. The results are shown in Fig. 8. Using large-size alumina has the effect of improving the thermal conductivity, and the higher the filler filling ratio, the greater the effect. At a filler ratio of 80 vol%, the composites filled with large-size alumina

achieved a thermal conductivity of 10.4 W/m K. This is a very high value compared to the thermal conductivity of 5.0 W/m K when using conventional spherical alumina. This result indicates the potential use of large-size alumina as a filler in applications that require high thermal conductivity.

4 Conclusion

We have established a technology for mass-producing high purity alumina by the aluminum alkoxide hydrolysis, and developed various high purity alumina powders to meet customer requirements and expanded its business. In particular, this article describes fine alumina for sintered bodies and large-size alumina for thermally conductive filler. The former can produce dense sintered bodies, which can be used for various applications such as semiconductor devices. The latter, on the other hand, can produce composites with high heat dissipation performance and is expected to expand its applications in the future.

Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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