

DESCRIPTION

TITLE

SPHERICAL ALUMINA PARTICLES, PRODUCTION METHOD OF SAME, AND RESIN
COMPOSITE COMPOSITION COMPRISING SAME

FIELD

[0001]

The present invention relates to spherical alumina particles, in particular spherical alumina particles reduced in surface residual Na^+ concentration and with small agglomeration, a method of production of the same, and a resin composite composition containing the same.

BACKGROUND

[0002]

In recent years, due to the increasingly higher functions and higher speeds of mobile phones and other electronic equipment, the amount of heat generated from the electronic components inside electronic equipment has been increasing. For normal operation of electronic equipment, efficient dissipation of the generated heat to the outside has become an important issue. For heat dissipation, much use is made of what are called “heat dissipation sheets” and “heat dissipation adhesives”. These are adhered or coated and press bonded between a heat generating body and heat dissipating fins to eliminate the gaps between the heat generating body and heat dissipating fins and enable efficient dispersion of the heat. Further, inside of the electronic components, the semiconductors themselves also remarkably generate heat due to their increasingly higher functions and speeds. A heat dissipation ability is also sought to be imparted to the sealants protecting the semiconductors.

[0003]

In general, heat dissipation sheets, heat dissipation adhesives, and semiconductor sealants are comprised of a thermal conductive inorganic filler and a resin. As the thermal conductive inorganic filler, inexpensive aluminum hydroxide or aluminum oxide (below, “alumina”) and, furthermore, materials from which high thermal conductivity can be expected such as silicon carbide, boron nitride, and aluminum nitride are being used. In particular, alumina is inexpensive and is chemically stable, therefore is often used as a thermally conductive inorganic filler.

[CITATIONS LIST]

[PATENT LITERATURE]

[0004]

[PTL 1] Japanese Unexamined Patent Publication No. 2012-21710

[PTL 2] Japanese Unexamined Patent Publication No. 2008-120673

[TECHNICAL PROBLEM]

[0005]

As the method for production of alumina, the Bayer process is widely known. In the Bayer process, bauxite is treated by caustic soda (sodium hydroxide) to dissolve aluminum as sodium aluminate and make the impurities of iron, titanium, silicon, etc. precipitate as red mud. This is filtered, hydrous alumina $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is seeded in the filtrate (sodium aluminate solution), and the result agitated for several days to make the hydrous alumina precipitate in the solution and recover the same. The recovered hydrous alumina is calcined to enable high purity alumina Al_2O_3 to be obtained.

[0006]

In the Bayer process, since caustic soda (sodium hydroxide) is used for treatment, sometimes sodium remains in the finished product alumina. If sodium is present on the filler surface in large amounts, it reacts with the resin or the moisture in the air and hydroxide ions are released. The hydroxide ions react with the epoxy groups present at the epoxy resin and obstruct the polymerization reaction between resins and becomes a cause of defective curing. Further, if sodium ions or potassium ions are present in the resin composition prepared by being kneaded with the epoxy groups, the voltage resistance is impaired. From the following viewpoint, the smaller the amount of sodium, the more desirable. To remove or reduce the sodium, the alumina is washed, then dried.

[0007]

PTL 1 discloses an apparatus enabling a powder such as alumina to be efficiently washed, filtered, and dried inside the same container. More specifically, it proposes to introduce a compressed gas into a container and thereby perform the washing, filtration, and drying of the powder to be performed in the same container without requiring stirring blades inside the container. Further, it discloses improving the speed of drying using heating by electricity or steam or microwaving.

[0008]

In this way, when drying the washed alumina slurry, it is often heated to dry. However, the long heating in the heat drying treatment causes sodium ions remaining inside the alumina to move to the outside and to liable to end up being eluted to the surface of the alumina cleaned by the washing. Further, the smaller the particle size of the alumina particles contained in the slurry, the more the particles agglomerate due to the heat drying and the dried matter forms strong agglomerated clumps. Due to such agglomerated clumps, crushing is necessary for forming a

powder. Along with the crushing, foreign matter from the crusher is liable to enter (contaminate) the product alumina powder.

[0009]

Further, PTL 2 discloses fine particle size spheroidal aluminum oxide powder made using fine particle size low sodium aluminum oxide as a starting material and having a maximum particle size of 7 μm or less and an average particle size of 0.2 to 0.9 μm in range. It discloses that by powerfully crushing this starting material powder before introducing it into a flame and continuously introducing the agglomerated particles into the flame right after fully crushing and dispersing the same, spherical inorganic oxide powder with no coarse particles and with an average particle size of less than 1 μm are stably obtained. However, in the same way as PTL 1, along with crushing, the product alumina powder is liable to have foreign matter from the crusher enter (contaminate) it. Note that it does not disclose the concentration of the sodium constituent in the powder.

[0010]

The present invention was made considering the above situation and has as its object the provision of spherical alumina particles with a low surface residual Na^+ concentration and a small agglomeration, a method of production of the same, and a resin composite composition including the same.

[SOLUTION TO PROBLEM]

[0011]

The inventors discovered that by drying this washed alumina slurry by a predetermined method, it is possible to directly dry and powderize the slurry without crushing.

[0012]

Based on the above discovery, the gist of the present invention is as follows:

- [1] Spherical alumina particles having an average particle size of 0.4 to 1.9 μm , a specific surface area of 1.0 to 5.0 m^2/g , a surface residual Na of 20 ppm or less, a contained Na_2O of 1000 ppm or less, an agglomeration degree of 1.0% or less, and a roundness of 0.9 or more.
- [2] The spherical alumina particles according to [1] having an α -phase ratio of 10.0% or less.

[0013]

- [3] A method of production of spherical alumina particles comprising an aqueous slurry preparation step for mixing a starting material spherical alumina and water to prepare an aqueous slurry containing a starting material spherical alumina and a drying step for drying the aqueous slurry.
- [4] The method of production of spherical alumina particles according to [3], further comprising a starting material spherical alumina washing step for washing by water the starting

material spherical alumina before the aqueous slurry preparation step.

[0014]

[5] A resin composite composition containing spherical alumina particles according to [1] or [2].

5 [6] The resin composite composition according to [5], further comprising at least one or more inorganic fillers selected from amorphous spherical silica particles, crystalline spherical silica particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, and carbon fiber.

10 **[ADVANTAGEOUS EFFECTS OF INVENTION]**

[0015]

According to the present invention, spherical alumina particles with a low surface residual Na^+ concentration and a small agglomeration and a resin composite composition containing the same are obtained. The spherical alumina particles are low in surface residual Na^+ concentration, therefore when used as a filler, it is possible to avoid defective curing and loss of voltage resistance. Further, the agglomeration degree is small, so crushing is unnecessary and entry of (contamination by) foreign matter due to crushing can be avoided. Furthermore, the method of production of one aspect of the present invention enables the spherical alumina particles to be easily produced.

20

BRIEF DESCRIPTION OF DRAWINGS

[0016]

FIG. 1 is a view schematically showing the states of alumina particles in the case of conventional heat drying and in the case of freeze drying of the present embodiment.

25

DESCRIPTION OF EMBODIMENTS

[0017]

[Spherical Alumina Particles]

[0018]

30 (Average Particle Size)

The spherical alumina particles of one embodiment of the present invention have an average particle size of 0.4 to 1.9 μm . If the average particle size is less than 0.4 μm , the agglomerating ability of the particles becomes greater and, when used as a filler etc., the fluidity of the resin composition remarkably falls, therefore this is not preferable. If the average particle size is more than 1.9 μm , in the increasingly smaller size and greater thinness semiconductor packages etc., particles end up catching at the narrow parts between the mounting board and chip, the fluidity

35

of the liquid sealant becomes poorer, and the shapeability sometimes falls.

[0019]

Here, the “average particle size” indicates the average particle size (D50) and means the median size D50 with a cumulative volume of 50% in the particle size distribution based on volume measured by the laser diffraction/scattering type particle size distribution measurement method. Note that the laser diffraction/scattering type particle size distribution measurement method is the method of firing a laser at a dispersion in which spherical alumina particles are dispersed and finding the particle size distribution from the intensity distribution pattern of diffracted/scattered light emitted from the dispersion. In the present invention, a laser diffraction/scattering type particle size distribution measurement apparatus “Mastersizer 3000” (made by Malvern) is used. Note that the average particle size can also be found in the same way for the starting material of the spherical alumina particles.

[0020]

(Specific Surface Area)

In one embodiment of the present invention, the spherical alumina particles have a specific surface area measured by the BET method of $1.0 \text{ m}^2/\text{g}$ or more and $5.0 \text{ m}^2/\text{g}$ or less.

[0021]

If the specific surface area of the spherical particles is less than $1.0 \text{ m}^2/\text{g}$, it becomes difficult for the particles to form a fine packed structure, therefore sometimes the fluidity of the liquid sealant containing the particles will fall. On the other hand, if the specific surface area of the spherical particles is more than $5.0 \text{ m}^2/\text{g}$, the tendency for the particles to agglomerate increases and similarly sometimes the fluidity of the liquid sealant will fall.

[0022]

The specific surface area can be measured by the BET method. Typically, the specific surface area is measured by the following procedure.

About 5 g of a sample is measured out and dried in vacuo at 250°C for 5 minutes. Next, the sample is set in an automatic specific surface area measurement apparatus (Macsorb made by Mountec Co., Ltd.) Using pure nitrogen and a nitrogen-helium mixed gas (mixed ratio nitrogen 30% and He 70%), the nitrogen gas absorbance at a 77K measurement temperature and relative pressure P/P_0 of 0.291 in value is measured and the one-point method used to calculate the BET specific surface area.

[0023]

(Surface Residual Na)

In one embodiment of the present invention, the spherical alumina particles have a surface residual Na of 20 ppm or less. The “surface residual Na” referred to here means the Na remaining adhered to the alumina surfaces and measured by ion chromatography.

If there is a large amount of sodium present at the filler surface, that is, the alumina surface, it reacts with the resin or the moisture in the air and releases hydroxide ions. The hydroxide ions react with the epoxy groups present in the epoxy resin and obstruct the polymerization reaction of the resins with each other thereby becoming the cause of defective curing. Further, if there are sodium ions or potassium ions in the resin composition prepared by kneading with epoxy groups, the voltage resistance becomes impaired. If sodium is 20 ppm or less, it is possible to avoid defective curing and loss of voltage resistance. From the above viewpoint, the lower the sodium, the more preferable, but complete removal is large in load in cost, therefore is made 0.1 ppm or more.

The sodium remaining at the surface is measured by ion chromatography. Typically, it is measured by the following procedure:

To a centrifuge tube, 4 g of a sample and 40 ml of distilled water were added, then the tube was capped and fully shaken to mix the contents. After mixing, a centrifuge was used to separate the sample and the sample solution. The sample solution was taken and an ion chromatograph used to analyze the sodium ions. As the ion chromatograph, an ion chromatograph made by Sysmex Corporation was used.

[0024]

(Contained Na₂O)

In one embodiment of the present invention, the spherical alumina particles have a contained Na₂O of 1000 ppm or less.

The “contained Na₂O” referred to here is the total amount of the Na part present at the surface and inside of the alumina and is assessed as oxide Na₂O by atomic absorption spectrometer.

If Na₂O is present in alumina in a large amount, sodium will be present not only at the alumina surface, but also the inside. When heat treating alumina, the sodium constituent ends up freed at the particle surface, therefore the surface residual Na is liable to become higher. If the contained Na₂O is 1000 ppm or less, the sodium part is low and it is possible to reduce the freedom of migration to the particle surfaces. The lower the contained Na₂O, the more preferable, but complete removal is difficult in production control, therefore the lower limit value may be made 50 ppm or more.

In the method of measurement of the contained Na₂O, the amount of sodium oxide which the alumina particles contain may be determined using an elemental analysis method known to persons skilled in the art. For example, it may be determined by an atomic absorption spectrometer and converted to oxides.

[0025]

(Agglomeration Degree)

In an embodiment of the present invention, the spherical alumina particles have an agglomeration degree of 1.0% or less.

The “agglomeration degree” referred to here is an indicator showing if the particles have agglomerated and is measured by a method of measurement by sieving.

5 By heat drying the washed slurry of alumina, the particles agglomerate with each other and end up forming large clumps. Due to the agglomeration, crushing is necessary to separate the particles. By crushing, the equipment becomes worn by contact with the crushing apparatus and costs end up being incurred. Further, due to the particles agglomerating, they are insufficiently dispersed in the resin, so the resin composition is liable to deteriorate in fluidity and viscosity. If
10 the agglomeration degree is 1.0% or less, it means there are few clumps and means that a crushing operation becomes unnecessary. From the above viewpoint, the lower the agglomeration degree, the more desirable, but complete prevention of agglomeration is difficult, therefore the lower limit value may be made 0.0001% or more.

The method of measurement of the agglomeration degree is as follows.

15 Standard sieves of two types of mesh of 4.75 mm and 212 μ m were stacked in that order. The stacking order had a 212 μ m mesh sieve placed at the bottom most position, then sieves were placed over it so that the mesh gradually became larger. On the uppermost 4.75 mm mesh sieve, 50 g of the sample was placed and the assembly was set in a sieve shaker. The sieve shaker used was an OCTAGON 200 made by Endecotts. After setting the sieves, the settings of
20 the sieve shaker were made an amplitude 5 and shake time of 3 minutes. After finishing shaking, the particles remaining on each sieve net and the particles passing through the 212 μ m mesh were measured for weight. When designating the amount of particles on the net of the 4.75 mm mesh as Ag, the amount of particles on the net of the 212 μ m mesh as Bg, and the amount of particles on the net of the 212 μ m mesh as Cg, (agglomeration degree)= $A/(B+C) \times 100(\%)$ was
25 calculated.

[0026]

(Roundness)

In one embodiment of the present invention, the spherical alumina particles may have a roundness of 0.90 or more.

30 The higher the roundness of the spherical particles, the more the viscosity of the resin composite composition containing the alumina particles can be lowered and the more the shapeability can be improved. The roundness may be 0.91 or more, may be 0.92 or more, or may be 0.93 or more. The upper limit of the roundness is theoretically 1.0, but from the viewpoint of production control, it may also be 0.98 or less or 0.95 or less.

[0027]

The roundness can be measured using an electron microscope or an optical microscope and

an image analysis apparatus. For example, FPIA made by Sysmex Corporation etc. may be used. These apparatuses are used to measure the roundness of the particles (circumference of equivalent circle/circumference of projected image of particle). 100 or more particles are measured for roundness and the average value of the same is made the roundness of the powder.

5 **[0028]**

(α -phase Ratio)

In one embodiment of the present invention, the spherical alumina particles may have an α -phase ratio of 10.0% or less. Here, the “ α - phase ratio” indicates the ratio of α -alumina crystals in the crystalline phase. The fact that alumina becomes crystalline is known. As typical
10 crystalline forms, α -alumina, θ -alumina, and δ -alumina are known. The spherical alumina particles of one embodiment of the present invention, while details will be explained later, can be produced by running the starting material through a flame to make it melt, then rapidly cooling it. In this case, the obtained alumina can be made greater in ratio of the amorphous state and spherical alumina particles with an α - phase ratio of 10.0% or less can be easily obtained. The
15 upper limit of the α - phase ratio may be 5.0%, may be 3.0%, and may be 1.0%. The lower limit of the α - phase ratio is not particularly prescribed and may also be 0.0%, but from the viewpoint of the load in production control and the viewpoint of the thermal conductivity of the resin composition, it may also be 0.1% and may also be 0.4%.

[0029]

20 The α - phase ratio of the alumina particle powder is measured using a powder X-ray diffraction apparatus. The integral area of the obtained diffraction peaks is found and the ratio of the diffraction peak area derived from α -alumina to the total is analyzed by the Rietveld method. Specifically, a D2PHASER made by Bruker is used to obtain the X-ray diffraction pattern at a 2θ of 10° to 90° in range. The obtained pattern is used to calculate the α - phase ratio by the
25 Rietveld method using a DIFFRAC.TOPAS made by Bruker. At the time of calculation, the analysis is conducted assuming that there are only three types of crystal phases of α -alumina, δ -alumina, and θ -alumina present and calculating the content of the α -alumina.

[0030]

(Purity)

30 The purity of the aluminum oxide of the alumina particles is preferably 99.99% or less and 100.00% or less. If the purity of the aluminum oxide is less than 99.99%, the alumina particles easily become irregular in shape.

[0031]

As a specific example of an apparatus for measuring the purity of alumina fine particles,
35 ICP spectroscopy enabling quantification of the level of impurities by a high sensitivity and an analytical apparatus such as AES and SIMS can be used. The amount of impurities in the

alumina particles in the present embodiment was measured by ICP spectroscopy and atomic absorption spectroscopy. Note that the measurement of the different metal oxides was performed by the following methods of the JIS standards:

· Fe₂O₃ (%):sulfuric acid (1+3) pressure acid decomposition, ICP method

(JIS R 1649)

· SiO₂ (%):sodium carbonate-boric acid dissolution, ICP method

(JIS H 1901)

· Na₂O (%):sulfuric acid (1+3) pressure acid decomposition, atomic absorption spectrometry

(JIS R 1649)

Further, the purity of the alumina particles was calculated by the following formula:

Further, it was defined as the value after rounding to 3 decimal places.

[0032]

Purity of alumina particles [Al₂O₃ (%)] = 100(%) - [Fe₂O₃ (%)] - [SiO₂ (%)] - [Na₂O (%)]

[0033]

[Method of Production of Spherical Alumina Particles]

In one embodiment of the present invention, a method of production of spherical alumina particles is provided. This method of production is a method enabling suitable production of the above-mentioned alumina particles and includes the following steps:

(1) step of producing starting material alumina,

(2) step of making starting material alumina spheroidal to produce starting material spherical alumina,

(3) aqueous slurry preparation step of mixing starting material spherical alumina and water to prepare an aqueous slurry including the starting material spherical alumina, and

(4) drying step of drying the aqueous slurry.

[0034]

(Starting Material Alumina)

As the method of production of the starting material alumina, the method of pyrolysis of ammonium aluminum carbonate, gas phase oxidation method, deflagration method, Bayer process, method of hydrolysis of aluminum alkoxide, etc. is used to produce it.

[0035]

(Starting Material Spherical Alumina)

The starting material alumina can be made spheroidal by the flame melting method to be made the starting material spherical alumina.

The flame melting method is one type of the known thermal spraying method. It sprays particles into a flame to make the particles spheroidal. At this time, it is possible to adjust the average spheroidal degree by the amount of introduction into the flame per time and the type of

the combustion gas. Further, by adjusting the particle size of the particles used, it is possible to adjust the particle size of the spherical alumina powder. The refrigerant is not particularly limited, but from the viewpoint of not allowing the purity of the spherical particles to fall, a low impurity, low activity air or nitrogen, argon, or other gas is preferable.

Further, it is also possible to produce the starting material spherical alumina by the deflagration method of forming a chemical flame by a burner in an atmosphere containing oxygen, running metal aluminum powder into that chemical flame in an amount sufficient for forming a dust cloud, and causing deflagration to obtain spherical alumina particles.

[0036]

(Aqueous Slurry)

The above-mentioned starting material spherical alumina and water are mixed to prepare an aqueous slurry containing starting material spherical alumina. The mixed water, from the viewpoint of not lowering the purity of the spherical particles, is desirably distilled water or ion exchange water not containing sodium, chlorine ions, etc. as impurities. The amount of mixing can be suitably adjusted considering the viscosity etc. of the slurry.

[0037]

(Washing)

Before the aqueous slurry preparation step, a starting material spherical alumina washing step for washing the starting material spherical alumina by water may be performed. The washing water, in the same way as slurry water, may be made distilled water or ion exchange water not containing sodium ions, chlorine ions, etc. as impurities. Alternatively, in accordance with matter desired to be removed by washing, a cleaning agent, surfactant, etc. may be used for washing. It is possible to suitably adjust the temperature, frequency, duration, and other conditions of the washing so as to render the alumina particles the desired washed state.

Typically, it is possible to obtain the desired surface residual Na^+ concentration and contained Na_2O concentration. After washing, a filter etc. can be used to dehydrate the particles until reaching any concentration. By dehydration, it is possible to wash away the Na constituent dissolved in the water or cleaning agent so as to prevent redeposition after drying. Further, it is also possible to add water to the washed starting material spherical alumina and dissolve the residual impurity constituents in water. If adding water, by again dehydrating the particles, it is possible to wash away the impurity constituents deposited on the alumina particle surface. In addition to higher purity, it is possible to control the particles to any concentration so as to raise the efficiency of drying in the later steps.

[0038]

(Drying)

To take out from spherical alumina from the aqueous slurry containing the starting material

spherical alumina, the moisture is dried off. Conventional drying causes moisture to be evaporated from the slurry by heating the standing slurry over a long period of time. At this time, along with the progress in heating, the moisture in the slurry evaporates and is reduced, so that inside the slurry, the distance between the alumina particles becomes narrower. When the moisture is completely removed from the slurry, the alumina particles contact each other and a strong agglomerate is formed. Further, by heating the slurry over a long period of time, sometimes the sodium constituent migrates to the surface from the inside of the spherical alumina particles contained in the slurry and sometimes is freed at the particle surface. As opposed to this, in the present embodiment, the aqueous slurry containing the starting material spherical alumina is airflow heat dried or freeze dried.

[0039]

(Freeze Drying)

In freeze drying, the moisture is immobilized by freezing. Along with this, the alumina particles are also immobilized. Due to the freeze drying, the moisture is gradually removed from the system (slurry) by sublimation, but since the alumina particles are immobilized, the distances between the alumina particles are maintained to a certain extent and contact and agglomeration are suppressed. That is, when drying is complete and moisture has completely been removed from the slurry, the content between alumina particles becomes minimal and agglomeration becomes difficult. FIG. 1 is a view schematically showing the state of alumina particles in the case of conventional heat drying and in the case of freeze drying of the present embodiment. In this way, if performing freeze drying of the present embodiment, the obtained alumina particles are kept from agglomerating and there is no need for crushing the agglomerated clumps of alumina particles. In general, a mill or other crushing apparatus is used for crushing the agglomerates and entry of (contamination by) foreign matter from the crushing apparatus is liable to be caused. However, in the present embodiment, there is also no need for crushing, therefore only naturally, entry of (contamination by) foreign matter due to crushing is suppressed. Furthermore, the heating temperature is low (10 to 90°C, the more preferable upper limit is 80°C), therefore seepage of sodium constituents from the inside of the particles is kept to a minimum extent, therefore less sodium is freed and is redeposited at the surface of the powder after drying.

[0040]

(Airflow Heat Drying)

Airflow heat drying is a method of spraying slurry into a 100 to 300°C high temperature air flow to make only the moisture evaporate and thereby take out the spherical alumina powder from the slurry. The slurry is sprayed by a nozzle like a two fluid nozzle to into a high temperature air flow. The sprayed slurry becomes fine droplets by the effect of dispersion in the

air flow. Compared with the conventional heat drying method, the airflow heat drying method uses a nozzle to render the slurry into droplets and thereby results in an extremely large surface area. The amount of heat received by the slurry is proportional to the surface area of contact between the heat source and the slurry, therefore the moisture of the droplets instantaneously
5 dries by evaporation. Compared with the conventional heat drying method, the drying time is short (0.01 second to 10 seconds or so), therefore seepage of the sodium constituent from the inside of the particles is kept down to the minimum extent, therefore less sodium is freed and is redeposited at the surface of the powder after drying. Furthermore, the spherical alumina powder is sprayed into the air flow, therefore agglomeration of the spherical alumina powder is
10 suppressed and there is no need to crush agglomerated clumps of alumina particles.

[0041]

[Resin Composite Composition]

According to one embodiment of the present invention, it is possible to produce a composite composition of the finally obtained spherical alumina particles and resin. The composition of the
15 resin composite composition will be explained in more detail below.

[0042]

A slurry composition containing the spherical alumina particles and a resin can be used to obtain a semiconductor sealant (in particular, a solid sealant), interlayer insulating film, or other resin composite composition. Furthermore, by curing these resin composite compositions, it is
20 possible to obtain a sealant (cured), semiconductor package board, or other resin composite.

[0043]

If producing a resin composite composition, for example, in addition to the spherical alumina particles and resin, a curing agent, curing accelerator, flame retardant, silane coupling agent, etc. are mixed in along with need and a composite formed by kneading or another known
25 method. Further, the mixture is shaped into pellets, a film, etc. in accordance with the application.

[0044]

Further, if producing a resin composite composition, in addition to the spherical alumina particles and resin, another inorganic filler may be mixed in. As the inorganic filler, amorphous
30 spherical silica particles, crystalline spherical silica particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, and carbon fiber may be mentioned. The blending ratio of the inorganic filler can be suitably adjusted in accordance with the application of the resin composite composition.

[0045]

Furthermore, if curing the resin composite composition to produce a resin composite, for
35 example, heat is applied to the resin composite composition to melt it, the composition is worked

into the shape corresponding to its application, and a heat higher than the time of melting is applied to cause the composition to completely cure. In this case, the transfer mold method or other known method can be used.

[0046]

5 For example, when producing a package board or interlayer insulating film or other semiconductor related material, as the resin used for the resin composite composition, a known resin can be used, but employing an epoxy resin is preferable. The epoxy resin is not particularly limited, but, for example, a bisphenol A type epoxy resin, bisphenol F type epoxy resin, biphenyl type epoxy resin, phenol novolac type epoxy resin, cresol novolac type epoxy resin, naphthalene type epoxy resin, phenoxy type epoxy resin, etc. can be used. It is possible to use one type among these alone or to use two types or more having different molecular weights together. Among these as well, from the viewpoint of the curability, heat resistance, etc., an epoxy resin having two or more epoxy groups in a molecule is preferable. Specifically, a biphenyl type epoxy resin, phenol novolac type epoxy resin, o-cresol novolac type epoxy resin, phenol types and aldehyde types of novolac resins which are epoxylated, bisphenol A, bisphenol F, bisphenol S, and other glycidyl ethers, glycidyl ester acid epoxy resins obtained by reaction of a phthalic acid, dimer acid, or other polybasic acid and epichlorohydrin, linear aliphatic epoxy resin, alicyclic epoxy resin, heterocyclic epoxy resin, alkyl modified polyfunctional epoxy resin, β -naphthol novolac type epoxy resin, 1, 6-dihydroxynaphthalene type epoxy resin, 2, 7-dihydroxynaphthalene type epoxy resin, bishydroxybiphenyl type epoxy resin, an epoxy resin in which bromine or other halogen is introduced to impart flame retardance, etc. may be mentioned. Among these epoxy resins having two or more epoxy groups in a molecule, in particular a bisphenol A type epoxy resin is preferable.

[0047]

25 Further, as the resin used for applications other than composite materials for semiconductor sealant use, for example, prepregs for printed boards, various engineering plastics, and other resin composite compositions, resins other than epoxy types can also be applied. Specifically, in addition to epoxy resins, a silicone resin, phenol resin, melamine resin, urea resin, unsaturated polyester, fluororesin, polyimide, polyamide imide, polyether imide, or other polyamide; polybutylene terephthalate, polyethylene terephthalate, or other polyester; polyphenylene sulfide, aromatic polyester, polysulfone, liquid crystal polymer, polyether sulfone, polycarbonate, maleimide modified resin, ABS resin, AAS (acrylonitrile-acryl rubber-styrene) resin, and AES (acrylonitrile-ethylene-propylene-diene rubber-styrene) resin may be mentioned.

[0048]

35 As the curing agent usable in the resin composite composition, any curing agent known for curing a resin may be used, but, for example, a phenolic curing agent can be used. As a phenolic

curing agent, a phenol novolac resin, alkylphenol novolac resin, polyvinyl phenol, etc. can be used alone or in combinations of two or more types.

[0049]

The blended amount of the phenol curing agent is preferably, by equivalent ratio with the epoxy resin (phenolic hydroxy group equivalent/epoxy group equivalent), 0.1 or more and less than 1.0. Due to this, no more unreacted phenolic curing agent remains and the moisture absorption heat resistance is improved.

[0050]

The amount of addition of the spherical alumina particles of the present invention in the resin composite composition is preferably large from the viewpoint of the heat resistance and thermal expansion coefficient, but usually 70 mass% or more and 95 mass% or less, preferably 80 mass% or more and 95 mass% or less, and more preferably 85 mass% or more and 95 mass% or less are suitable. This is because if the blended amount of spherical alumina particles is too small, the effects of improvement of the strength of the sealant, suppression of thermal expansion, etc. become hard to obtain. Further, if too great, despite surface treatment of the spherical alumina particles, at the composite material, segregation easily occurs due to agglomeration of the spherical alumina particles, the viscosity of the composite material becomes too large, and other issues arise, therefore practical application as a sealant becomes difficult.

[0051]

Further, in addition to a resin, an added material, for example, a silane coupling agent, curing agent, coloring agent, retardant, or other known additive, can be used.

[0052]

Further, for the silane coupling agent, a known coupling agent may be used, but one having epoxy-based functional groups is preferable.

[0053]

A slurry composition containing spherical alumina particles and a resin can be used to obtain a heat dissipation sheet, heat dissipation grease, etc.

[0054]

When obtaining a heat dissipation sheet, in addition to the spherical alumina particles and resin, an additive is suitably blended and the mixture is formed into a composite by kneading or other known method. The obtained composite is shaped into a sheet by a known method.

[0055]

For example, when producing a heat dissipation sheet, as the resin used for the resin composite composition, a known resin can be applied, but specifically a silicone resin, phenol resin, melamine resin, urea resin, unsaturated polyester, fluororesin, polyimide, polyamide imide,

polyether imide, or other polyamide; polybutylene terephthalate, polyethylene terephthalate, or other polyester; polyphenylene sulfide, aromatic polyester, polysulfone, liquid crystal polymer, polyether sulfone, polycarbonate, maleimide modified resin, ABS resin, AAS (acrylonitrile-acryl rubber-styrene) resin, and AES (acrylonitrile-ethylene-propylene-diene rubber-styrene) resin may be mentioned. Among these as well, a silicone resin is preferably used. The silicone resin is not particularly limited, but, for example, a peroxide curing type, addition curing type, condensation curing type, ultraviolet curing type, etc. can be used.

[0056]

Further, in addition to a resin, an added material, for example, a silane coupling agent, curing agent, coloring agent, curing retardant, or other known additive can be used.

[0057]

When obtaining heat dissipation grease, in addition to the spherical alumina particles and resin, an additive is suitably blended and the mixture is formed into a composite by kneading or other known method. Here, the resin used for the heat dissipation grease is also called the “base oil”.

[0058]

For example, if producing heat dissipation grease, as the resin used for the resin composite composition, a known resin is possible, but specifically a silicone resin, phenol resin, melamine resin, urea resin, unsaturated polyester, fluororesin, polyimide, polyamide imide, polyether imide, or other polyamide; polybutylene terephthalate, polyethylene terephthalate, or other polyester; polyphenylene sulfide, aromatic polyester, polysulfone, liquid crystal polymer, polyether sulfone, polycarbonate, maleimide modified resin, ABS resin, AAS (acrylonitrile-acryl rubber-styrene) resin, AES (acrylonitrile-ethylene-propylene-diene rubber-styrene) resin, mineral oil, synthetic hydrocarbon oil, ester oil, polyglycol oil, silicone oil, and fluorine may be mentioned.

[0059]

Further, in addition to the resin, an added material, for example, a silane coupling agent, coloring agent, thickener, or other known additive can be used. As the thickener, calcium soap, lithium soap, aluminum soap, calcium complex, aluminum complex, lithium complex, barium complex, bentonite, urea, PTFE, sodium terephthalate, silica gel, organic bentonite, or other known ones can be used.

EXAMPLES

[0060]

The present invention will be explained through the following examples and comparative examples. However, the present invention should not be interpreted limited to the following

examples.

[0061]

The starting material spherical alumina particles (Material 1 to Material 4) described in Table 1 were prepared and mixed with water to obtain aqueous slurries. The mixing rates of the ion exchange water and particles when preparing the aqueous slurries were, in the case of using the Materials 1 and 2, mixing 200 kg of particle powder with respect to 1000 liters of water. When using Material 3, it was made 300 kg of particle powder with respect to 1000 liters of ion exchange water. When using Material 4, it was made 200 kg of particle powder with respect to 1000 liters of ion exchange water. In each case, the aqueous slurry was mixed and agitated for 20 minutes to 1 hour or so, then a suitable filter was used for filtration. The filtration was performed until the amount of moisture became 60 to 80 wt% or so.

[0062]

(Examples 1 to 3)

The prepared slurries were preliminarily frozen once at -40°C. After that, the slurries were deaerated in vacuo in the apparatus while being freeze dried at 80°C for 24 hours.

[0063]

(Example 4)

The prepared slurry was airflow dried at 200°C using a Jet Turbo Dryer made by Hiraiwa Iron Works Co., Ltd.

[0064]

(Comparative Examples 1 to 3)

The prepared slurries were allowed to stand in an oven in a state with no air flow and dried by the heat drying method. The drying conditions were made drying under conditions of 230°C and 40 hours.

[0065]

(Comparative Example 4)

A slurry obtained by using the Material 4 was freeze dried under conditions similar to Example 1.

[0066]

(Comparative Example 5)

A slurry prepared using the Material 1 was preliminarily frozen once under a -40°C condition. After that, it was freeze dried at 95°C for 24 hours while deaerating the inside of the apparatus.

[0067]

(Comparative Example 6)

A slurry obtained by using the Material 1 was airflow dried at 350°C using conditions

similar to Example 1 using a Jet Turbo Dryer made by Hiraiwa Iron Works Co., Ltd.

[0068]

(Example 5)

The spherical alumina particles obtained in Example 1 and aluminum nitride particles
5 (D50=30 μm) were mixed to give (blended weight of spherical alumina particles):(blended
amount of aluminum nitride particles)=90:10 to prepare a spherical alumina particle mixture A.
Furthermore, the spherical alumina particle mixture A and the silicone resin CY52-276A
solution made by Dow-Toray were mixed so that the amount of addition of the spherical alumina
particle mixture A in the resin composite composition became 90 mass%. This was vacuum
10 kneaded by a vacuum kneader "Awatori Rentaro" made by Thinky to obtain a resin composite
composition. The kneading conditions were a preliminary kneading of 15 seconds and vacuum
kneading of 90 seconds. After kneading, the plastic container in which the kneaded matter was
contained was placed in a water bath adjusted to 25°C and cooled for 1 hour. 10 g of this resin
composite composition was placed on the smooth surface of an iron plate which was then tilted
15 by 60° with respect to the horizontal direction to confirm the degree of flow of the resin
composite composition. As a result, 5 hours after tilting, the resin composite composition flowed
by 15 cm or more and good fluidity was exhibited.

[0069]

(Example 6)

The spherical alumina particles obtained in Example 2 and boron nitride particles (D50=20
20 μm) were mixed to give (blended weight of spherical alumina particles):(blended amount of
boron nitride particles)=90:10 to prepare a spherical alumina particle mixture B. Furthermore,
the spherical alumina particle mixture B and the silicone resin CY52-276A solution made by
Dow-Toray were mixed so that the amount of addition of the spherical alumina particle mixture
25 B in the resin composite composition became 90 mass%. This was vacuum kneaded by a
vacuum kneader "Awatori Rentaro" made by Thinky to obtain a resin composite composition.
The kneading conditions were a preliminary kneading of 15 seconds and vacuum kneading of 90
seconds. After kneading, the plastic container in which the kneaded matter was contained was
placed in a water bath adjusted to 25°C and cooled for 1 hour. 10 g of this resin composite
30 composition was placed on the smooth surface of an iron plate which was then tilted by 60° with
respect to the horizontal direction to confirm the degree of flow of the resin composite
composition. As a result, 5 hours after tilting, the resin composite composition flowed by 15 cm
or more and good fluidity was exhibited.

[0070]

35 The values of the physical properties of the (dried) spherical alumina particles obtained
under the respective conditions are shown in Table 2.

[0071]

[Table 1]

Table 1

	Unit	Material 1	Material 2	Material 3	Material 4
Average particle size	μm	0.9	0.8	1.9	0.7
Specific surface area	m ² /g	3.2	3.3	1.6	3.4

5

[0072]

[Table 2]

Table 2

	Unit	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6
Material		Material 1	Material 2	Material 3	Material 1	Material 1	Material 2	Material 3	Material 4	Material 1	Material 1
Drying style		Freeze drying	Freeze drying	Freeze drying	Airflow drying	Heat drying	Heat drying	Heat drying	Freeze drying	Freeze drying	Airflow drying
Average particle size	μm	1.1	0.8	1.9	0.9	1	0.9	2	0.9	2.1	0.9
Specific surface area	m ² /g	3.24	3.4	1.6	3.5	3.1	3.3	1.5	3.7	3.1	3.6
Roundness	-	0.913	0.941	0.923	0.91	0.931	0.952	0.914	0.94	0.924	0.913
α- phase ratio	%	0.73	0.54	9.4	0.77	0.68	0.58	9.73	0.92	0.75	0.86
Surface residual Na	ppm	14.4	16.3	0.9	17.6	14.6	15	0.9	18.3	16.2	38.1
Na ₂ O	ppm	749	490	190	715	740	468	173	1342	730	681
Agglomeration degree	%	0.427	0.561	0.062	0.051	44.87	50.32	10.776	0.82	49.183	0.042

[0073]

The methods for measurement of the various physical properties are described below:

[0074]

(Average Particle Size by Laser Diffraction/Scattering Method)

5 The laser diffraction/scattering type particle size distribution measurement method is the method of firing a laser at a dispersion in which spherical alumina particles are dispersed and finding the particle size distribution from the intensity distribution pattern of diffracted and scattered light emitted from the dispersion. In the present invention, a laser diffraction/scattering type particle size distribution measurement apparatus "Mastersizer 3000" (made by Malvern)
10 was used.

[0075]

(Specific Surface Area)

The BET theory was applied to an adsorption isotherm measured by the gas adsorption method to find the specific surface area (BET value) (BET method). As the specific surface area
15 measurement apparatus, a product name "Macrosorb Model HM-1208" made by Mountec Co., Ltd. is used in the measurement.

[0076]

(Surface Residual Na)

20 The amount of ionic impurities deposited on the surface can be measured using an ion chromatograph. To the centrifuge tube, 4 g of a sample and 40 ml of distilled water were added, then the tube was capped and fully shaken to mix the contents. After mixing, a centrifuge was used to separate the sample and the sample solution. The sample solution was taken and an ion chromatograph used to analyze the sodium ions. As the ion chromatograph, an ion chromatograph made by Sysmex Corporation was used.

[0077]

(Contained Na_2O)

0.5 g of a sample was added to a pressure container, 10 ml of sulfuric acid (1+3) was added, the container was capped, then the container was heated in a heat drying furnace at 230°C in
30 temperature for 16 hours. The heated solution was allowed to cool, then the solution as diluted to 100 ml, then it was measured by an atomic absorption spectrometer.

Note that "sulfuric acid (1+3)" indicates a solution comprised of concentrated sulfuric acid 1 diluted by addition of pure water by a volume ratio of 3.

[0078]

(Agglomeration Degree)

35 Standard sieves of two types of mesh of 4.75 mm and 212 μm were stacked in that order. The stacking order had a 212 μm mesh sieve placed at the bottom most position, then the sieves

were placed over it so that the mesh gradually became larger. On the uppermost 4.75 mm mesh sieve, 50 g of the sample was placed and the assembly was set in a sieve shaker. The sieve shaker used was an OCTAGON 200 made by Endecotts. After setting the sieves, the settings of the sieve shaker were made an amplitude 5 and shake time of 3 minutes. After finishing shaking, the particles remaining on each sieve net and the particles passing through the 212 um mesh were measured for weight. When designating the amount of particles on the net of the 4.75 mm mesh as Ag, the amount of particles on the net of the 212 um mesh as Bg, and the amount of particles on the net of the 212 um mesh as Cg, (agglomeration degree)= $A/(B+C) \times 100(\%)$ was calculated.

[0079]

It was confirmed through the above examples that spherical alumina particles with a low surface residual Na⁺ concentration and a small degree of agglomeration were obtained. Further, a resin composite composition containing the spherical alumina particles was obtained.

[INDUSTRIAL APPLICABILITY]

[0080]

The spherical alumina particles of the present invention have a low surface residual Na⁺ concentration, therefore when used as a filler, defective curing and loss of voltage resistance can be avoided. Further, the degree of agglomeration is small, therefore crushing is unnecessary and entry of (contamination by) foreign matter due to crushing can be avoided. For this reason, they can be utilized well as fillers for semiconductor packages made smaller in size and greater in thinness. Furthermore, according to the method of production of one aspect of the present invention, the spherical alumina particles can be easily produced. A resin composite composition containing the spherical alumina particles exhibits excellent quality and can be used not limited to semiconductor sealants, but also used for other applications. Specifically, it can be used for preregs for printed circuit board use, various engineering plastics, etc.

CLAIMS

[Claim 1]

5 Spherical alumina particles having an average particle size of 0.4 to 1.9 μm , a specific surface area of 1.0 to 5.0 m^2/g , a surface residual Na of 20 ppm or less, a contained Na_2O of 1000 ppm or less, an agglomeration degree of 1.0% or less, and a roundness of 0.9 or more.

[Claim 2]

10 The spherical alumina particles according to claim 1 having an α - phase ratio of 10.0% or less.

[Claim 3]

15 A method of production of spherical alumina particles comprising an aqueous slurry preparation step for mixing a starting material spherical alumina and water to prepare an aqueous slurry containing a starting material spherical alumina and a drying step for drying the aqueous slurry.

[Claim 4]

20 The method of production of spherical alumina particles according to claim 3 further comprising a starting material spherical alumina washing step for washing by water the starting material spherical alumina before the aqueous slurry preparation step.

[Claim 5]

25 A resin composite composition containing spherical alumina particles according to claim 1 or 2.

[Claim 6]

30 The resin composite composition according to claim 5, further comprising at least one or more inorganic fillers selected from amorphous spherical silica particles, crystalline spherical silica particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, and carbon fiber.