DESCRIPTION

TITLE

SPHERICAL ALUMINUM OXIDE PARTICLE MIXTURE AND RESIN COMPOSITE COMPOSITION CONTAINING SAME

FIELD

[0001]

The present invention relates to a spherical alumina particle mixture, in particular a spherical alumina particle mixture provided with both a high thermal conductivity and fluidity and a resin composite composition and resin composite containing the spherical alumina particle mixture.

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 spaces 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 similar increasingly higher functions and speeds. A heat dissipation ability is also sought to be imparted to the encapsulants protecting the semiconductors.

[**0003]**

In general, heat dissipation sheets, heat dissipation adhesives, and semiconductor encapsulants are comprised of a thermal conductive inorganic filler and a resin. The thermal conductive inorganic filler, for example, alumina filler etc. form particle size distributions by combination of several particle sizes. By forming a particle size distribution, it is known that the spaces between filler particles (porosity) are reduced and therefore the fluidity and thermal conductivity are improved.

[0004]

PTLs 1 to 3 disclose alumina or other inorganic particle compositions having a particle size distribution combining several particle sizes. In a typical example, the particle size distribution

spreads over a range of a fine size of several μm to a coarse one of several hundred μm.

[0005]

On the other hand, in recent years, the spacings at heat dissipation sheets and adhesives have been becoming smaller. Further, semiconductors also have become increasingly fine. The spacing of interconnects connecting semiconductors and the outside are becoming narrower. Therefore, if using a filler mixture containing coarse particles as a filler of a heat dissipation sheet or adhesive, sometimes it becomes no longer possible to compress the mixture to the target thickness. Further, if such a coarse filler mixture is used for an encapsulant, the filler cannot pass through the spacing between the interconnects and the structure inside of the semiconductor is liable to end up breaking. Therefore, a smaller particle size of the filler itself is being sought.

[0006]

PTL 4 discloses a spherical amorphous silica powder having a maximum particle size of several μm or less and states that this silica powder satisfies the requirements for high fillability, low viscosity, and high permeability.

[0007]

However, amorphous silica has an extremely low thermal conductivity, therefore is unsuitable for encapsulating power semiconductors or heat dissipation applications of highly integrated IC chips in the future. Further, in the particle size distribution described in PTL 4, there are also the problems that the viscosity of the compound ends up rising at the time of kneading with a resin and various shaping operations become difficult.

[0008]

PTL 5 proposes use of alumina powder containing predetermined alumina particles as a filler. More specifically, it prescribes alumina particles having a predetermined particle size distribution, having a predetermined particle size and water content, etc. It describes that due to this, suitable fluidity of the resin composition is obtained and, further, deformation of interconnects can be suppressed at the time of semiconductor encapsulating.

[CITATION LIST]

[PATENT LITERATURE]

[0009]

[PTL 1] Japanese Patent No. 7325670

[PTL 2] WO2020/153505

[PTL 3] WO2022/071140

[PTL 4] Japanese Patent No. 4112470

[PTL 5] WO2021/200485

SUMMARY

[TECHNICAL PROBLEM]

[0010]

As shown in the above PTLs 1 to 3, to improve the fluidity and thermal conductivity, control of the particle size distribution of particle compositions is being studied. In addition, semiconductor technology is advancing with every passing day. Along with this, the amount of heat dissipation from semiconductors has been increasing and, further, sizes are being reduced. For this reason, as shown in PTL 4, limiting the maximum particle size is also being studied. Further, as shown in PTL 5, it has also been proposed to control the water content etc. to obtain a suitable fluidity in addition to the particle size distribution. However, materials with higher heat dissipation and fluidity are being sought.

[0011]

Therefore, the present invention has as its technical problem to provide a spherical alumina particle mixture enabling the smaller size of semiconductors etc. to be dealt with by limiting the maximum particle size in the particle size distribution and, further, improving the thermal conductivity and suppressing the viscosity (raise the fluidity) of a resin composition formed when kneading it with a resin and to provide a resin composition containing the same.

[SOLUTION TO PROBLEM]

[0012]

The present invention was made as a result of intensive study to solve the above-mentioned problem and has as its gist the following content as described in the claims.

[1] A spherical alumina particle mixture having

an average particle size (D50) by a laser diffraction/scattering method of 0.5 μm or more and 10.0 μm or less,

particles of 25.0 μm or more comprising 0.04 wt% or less of a particle size distribution measured by a wet type particle size test method,

a specific surface area of 0.30 m^2/g or more and 2.00 m^2/g or less,

a circularity of 0.85 or more, and

an α-conversion rate of less than 50.0%.

[2] The spherical alumina particle mixture according to [1], wherein

in a number of particles of 1 μm or more and 30 μm or less detected by a Coulter counter, a number frequency of particles of 10 μm or more is 100 ppm or less.

[3] The spherical alumina particle mixture according to [1] or [2], wherein a water content by coulometric Karl Fischer titration is less than 20 ppm.

[4] The spherical alumina particle mixture according to any one of [1] to [3],

containing

spherical alumina particles (a) with an average particle size (D50) of 7.0 μm or more and 10.0 μm or less and a circularity of 0.85 or more and

spherical alumina particles (b) with an average particle size (D50) of 2.4 μm or more and 6.0 μm or less and a circularity of 0.85 or more,

containing

the spherical alumina particles (a) in 50 wt% or more and 95 wt% or less and

the spherical alumina particles (b) in 5 wt% or more and 45 wt% or less, and

having a total of spherical alumina particles (a) and spherical alumina particles (b) of 90 wt% or more.

[5] The spherical alumina particle mixture according to any one of [1] to [4],

containing

spherical alumina particles (b) with an average particle size (D50) of 2.4 μm or more and 6.0 μm or less and a circularity of 0.85 or more and

spherical alumina particles (c) with an average particle size (D50) of 0.4 μm or more and 2.2 μm or less and a circularity of 0.85 or more,

containing

the spherical alumina particles (b) in 50 wt% or more and 90 wt% or less and

the spherical alumina particles (c) in 5 wt% or more and 20 wt% or less, and

having a total of spherical alumina particles (b) and spherical alumina particles (c) of 90 wt% or more.

[6] The spherical alumina particle mixture according to any one of [1] to [5],

containing

spherical alumina particles (a) with an average particle size (D50) of 7.0 μm or more and 10.0 μm or less and a circularity of 0.85 or more,

spherical alumina particles (b) with an average particle size (D50) of 2.4 μm or more and 6.0 μm or less and a circularity of 0.85 or more, and

spherical alumina particles (c) with an average particle size (D50) of 0.4 μm or more and 2.2 μm or less and a circularity of 0.85 or more**,**

containing

the spherical alumina particles (a) in 50 wt% or more and 90 wt% or less,

the spherical alumina particles (b) in 5 wt% or more and 20 wt% or less, and

the spherical alumina particles (c) in 5 wt% or more and 30 wt% or less, and

having a total of spherical alumina particles (a), spherical alumina particles (b), and spherical alumina particles (c) of 90 wt% or more.

[7] A resin composite composition comprising a resin containing a spherical alumina particle

mixture according to any one of [1] to [6].

[8] The resin composite composition according to [7], further containing at least one type or more of inorganic filler selected from amorphous spherical alumina particles, crystalline spherical silica particles, alumina particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, and carbon fiber.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0013]

According to one embodiment of the present invention, a spherical alumina particle mixture enabling the smaller size of semiconductors etc. to be dealt with by limiting the maximum particle size in the particle size distribution and, further, improving the thermal conductivity and suppressing the viscosity (raise the fluidity) of the resin composition formed when kneading it with a resin and a resin composition containing the same are provided. Further, according to one embodiment of the present invention, spherical alumina particles having an excellent hue index and a resin composition containing the same are provided and improvement of the beauty and visual impact of products containing the same can be contributed to.

DESCRIPTION OF EMBODIMENTS

[0014]

The spherical alumina particle mixture provided by an embodiment of the present invention has

an average particle size (D50) by a laser diffraction/scattering method of 0.5 μm or more and 10.0 μm or less,

particles of 25.0 μm or more comprising 0.04 wt% or less of a particle size distribution measured by a wet type particle size test method,

a specific surface area of 0.30 m^2/g or more and 2.00 m^2/g or less,

a circularity of 0.85 or more, and

an α-conversion rate of less than 50.0%.

[0015]

(Spherical Alumina Particle Mixture)

The spherical alumina particle mixture in the present embodiment contains spherical alumina particles of a several particle sizes mixed together and has the properties explained below:

[0016]

(Average Particle Size (D50) by Laser Diffraction/Scattering Method of 0.5 μm or More

and 10.0 μm or Less)

The spherical alumina particle mixture of one embodiment of the present invention has an average particle size of 0.5 μm or more to 10.0 μm or less. If the average particle size is less than 0.5 μm, the agglomerating ability of the particles becomes greater and the resin composition remarkably falls in fluidity, so this is not preferable. If the particle size is more than 10.0 μm, in semiconductor packages made smaller in size and greater in thinness etc., the particles end up becoming caught in the narrow parts between the mounting board and chip, the fluidity of the liquid encapsulant becomes poorer, and sometimes the shapeability falls.

[0017]

<Measurement of Average Particle Size (D50)>

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 particle mixture.

0018]

(In Particle Size Distribution Measured by Wet Type Particle Size Test Method, Particles of 25.0 μm or More Being 0.04 wt% or Less)

The spherical alumina particle mixture according to the present embodiment contains particles of 25.0 μm or more in 0.04 wt% or less. Below, the reasons will be explained.

[0019]

The spherical alumina particle mixture is generally mixed with a resin and used as a semiconductor encapsulant. An encapsulated semiconductor chip sometimes has many interconnects arranged in a high density. The spaces between interconnects sometimes becomes narrow. The spherical alumina particle mixture is liable to be unable to run through the narrow spaces between interconnects if, in the particle size distribution, particles of 25.0 μm or more are present in more than 0.04 wt%. Note that, the weight ratio here is based on the spherical alumina particle mixture as a whole, that is, 100 wt%. Particles of 20.0 μm or more are more preferably present in 0.04 wt% or less.

[0020]

Similarly, a spherical alumina particle mixture is generally mixed with a resin and

sometimes used for a heat dissipation sheet, heat dissipation adhesive, or other heat dissipation member. Such a heat dissipation member is compressed by pressure, etc. and thereby is sometimes used to facilitate transfer of heat to another member. If the spherical alumina particle mixture has a particle size distribution in which particles of 25.0 μm or more are present in more than 0.04 wt%, at the time of compression, compression is liable to be hindered by coarse particles of 25.0 μm or more.

[0021]

Therefore, the spherical alumina particle mixture according to the one present embodiment contains particles of 25.0 μm or more in 0.04 wt% or less so that it can run through even the narrow spaces between interconnects or so that the heat dissipation member can be sufficiently compressed. Further, it substantially has no distribution at 25.0 μm or more. Note that the maximum value of the particle size distribution may also be suitably adjusted in accordance with the spaces between interconnects, thickness compressed, and other aspects of the usage environment. For example, the maximum value of the particle size distribution may be made 20.0 μm, may be made 19.0 μm, or may be made 18.0 μm. In other words, in the particle size distribution, particles of 20.0 μm or more may be present in 0.04 wt% or less, particles of 19.0 μm or more may be present in 0.04 wt% or less, and particles of 18.0 μm or more may be present in 0.04 wt% or less.

[0022]

<Wet Type Particle Size Test Method>

The wet type particle size test method will be explained. In that test method, a container is filled with 10 g of the spherical alumina particle mixture to be tested and with water and ultrasonic waves are used to make the spherical particles sufficiently dispersed to prepare a slurry. The slurry is transferred on to the mesh of a test sieve and sieved. The particles remaining on the mesh of the test sieve are taken in a suitable container, a hot plate etc. is used to make the sample evaporate to dryness, the weight of the residue is measured, and the ratio of weight of particles separated by sieving in the spherical alumina particle mixture 10 g to be tested is calculated.

[0023]

(α-Conversion Rate of Less Than 50.0%)

Alumina is known to differ in thermal conductivity depending on the crystal system. α-alumina is a crystal with the highest thermal conductivity. Therefore, by using alumina powder containing a large amount of α-alumina, it is possible to improve the thermal conductivity of the insulating resin composition. On this point, the higher the α-conversion rate (ratio of α-alumina in crystals contained in alumina particle mixture) of the spherical alumina particle mixture itself, the higher the thermal conductivity of that alumina particle mixture and the more preferable.

[0024]

On the other hand, α-alumina is obtained by treating a starting material at a high temperature to make its crystals grow. For example, the general practice is to obtain it by heating aluminum hydroxide or alumina at a high temperature. The heating method can be performed by firing in a furnace or heating by high temperature hot water etc. Further, from the viewpoint of efficiently obtaining α-particles having the desired particle size, the general practice is to crush or disintegrate α-particles coarsened after heating. For this reason, α-alumina particles with small particle sizes are mostly aspherical particles low in circularity. In other words, selecting and collecting just spherical particles having the desired circularity from α-alumina particles with small particle sizes is difficult. Trying to realize this would require a high cost burden.

[0025]

The inventors discovered that by controlling, in addition to the α-conversion rate, the specific surface area, circularity, etc. of the spherical alumina particle mixture itself, it is possible to obtain the desired thermal conductivity and excellent fluidity.

[0026]

The upper limit of the α-conversion rate is preferably made less than 50.0% from the viewpoint of controlling the specific surface area of the spherical alumina particle mixture and irregularities (or circularity) of the particle surface and improving the affinity with a resin. Due to this, the resin composition obtained by mixing with that spherical alumina particle mixture can realize a sufficiently high thermal conductivity. Further, the α-conversion rate may also be suitably adjusted so that the desired thermal conductivity is obtained. For example, the upper limit of the α-conversion rate may be made less than or equal to 45%, may be made less than or equal to 40%, may be made less than or equal to 38%, and may be made less than or equal to 36%. The lower limit of the α-conversion rate may be made more than or equal to 20% or may be made more than or equal to 30%. Note that, if suitably adjusting the α-conversion rate to the desired value, it is possible to adjust the α-conversion rate to the desired value by measuring in advance the α-conversion rates of the spherical alumina particles to be mixed and using the measured α-conversion rates to calculate the blending ratios.

[0027]

<Measurement of α-Conversion Rate>

The α-conversion rate is measured using a powder X-ray diffraction apparatus. The integrated areas of the obtained diffraction peaks are 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 an X-ray diffraction pattern at a 2θ of 10° to 90° in range. The obtained pattern is used to calculate the α-conversion rate by the 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.

[0028]

(Specific Surface Area of 0.30 m^2/g or More and 2.00 m^2/g or Less)

The spherical alumina particle mixture has a specific surface area measured by the BET method of 0.30 m^2/g or more and 2.00 m^2/g or less.

[0029]

If the specific surface area of the spherical particles is less than 0.30 m^2/g, it becomes difficult for the particles to form a close-packed structure, therefore sometimes the fluidity of the liquid encapsulant containing the particles will fall. On the other hand, if the specific surface area of the spherical particles is more than 2.00 m^2/g, the tendency for the particles to agglomerate increases and similarly sometimes the fluidity of the liquid encapsulant will fall. The preferable upper limit is 0.90 m^2/g.

[0030]

<BET Method>

The specific surface area is measured by the BET method. Typically, the following procedure is used to measure the specific surface area.

About 5 g of the sample is measured out and is 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 Mountech) and a pure nitrogen and nitrogen-helium mixed gas (mixed ratio of nitrogen 30%, He70%) is used to measure the value of the nitrogen gas adsorption at a 77K measurement temperature and relative pressure P/P0 of 0.291. The one-point method is used to calculate the BET specific surface area.

[0031]

(Circularity of 0.85 or More)

The spherical alumina particle mixture in the present embodiment is spherical. “Spherical” means the circularity as a spherical alumina particle mixture is 0.85 or more. Preferably, it is 0.9 or more. This is because if the circularity of the alumina particle mixture is less than 0.85, sometimes the hardness of the shaped body formed by kneading that alumina particle mixture and resin and the viscosity of the liquid kneaded material will end up greatly deteriorating. Particles like angular particles with low circularity are more easily formed with flat faces at the particle surfaces compared with truly spherical particles. Therefore, when particles contact each other, truly spherical particles will contact each other at points while particles like angular particles with low circularity will be formed with planar contacts and easily suffer from friction. For this reason, if the particles try to flow, the large friction angular particles will find it difficult to move and the hardness of the shaped body and viscosity will end up deteriorating. These

inconveniences become harder to occur the higher the circularity. Therefore, the higher the circularity, the more preferable. It may be 0.90 or more and further may be 0.91 or more. On the other hand, the circularity theoretically has an upper limit of 1.0, but making the circularity 1.0 is difficult in practice. Further, from the viewpoint of controlling the specific surface area and irregularities of the particle surfaces and improving the affinity with the resin, the upper limit of the circularity may also be 0.99 or less, 0.98 or less, or 0.97 or less. The circularity of the spherical alumina particle mixture (or the spherical alumina particles forming the spherical alumina particle mixture) can be adjusted using thermal spraying (flame fusion method) etc. Specifically, this can be adjusted by holding the temperature of the flame at the melting point of alumina or more. If becoming a temperature of the melting point of alumina or less, the alumina starting material will no longer melt and the circularity will deteriorate. The temperature of the flame can be adjusted by the flow rate of the fuel gas used etc. Note that the spherical alumina particles forming the spherical alumina particle mixture, in all particle sizes are preferably alumina particles with circularities of 0.85 or more, more preferably alumina particles of 0.9 or more.

[0032]

(Measurement of Circularity)

The circularity 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 circularity of the particles (circumference of equivalent circle/circumference of projected image of particle). 100 or more particles are measured for circularity and the average value of the same is made the circularity of the powder.

[0033]

(Number Frequency of 10 μm or More Particles in Number of Particles of 1 μm or More and 30 μm or Less Detected by Coulter Counter: 100 ppm or Less)

In one embodiment of the present invention, the spherical alumina particles may have a number frequency of particles of 10 μm or more in the number of particles of 1 μm or more and 30 μm or less detected by a Coulter counter of 100 ppm or less.

[0034]

A Coulter counter, as explained in detail later, uses the electrical resistance method referred to as the “Coulter principle” to measure particles. There is none of the errors in surface forms, internal structures, refraction indexes, color, etc. of the particles such as seen in the optical measurement method and a high measurement precision is obtained. In particular, the particle size obtained by this method can be expressed by a number distribution (/ml and /g). Precision management of the particle size distribution becomes possible.

[0035]

“100 ppm or less”, for example, means that when there are 100,000 particles of 1 μm or more and 30 μm or less, there are 10 or less particles of 10 μm or more among them. If the number frequency of coarse particles of 10 μm or more becomes more than 100 ppm, such coarse particles will clog the narrow parts between a mounting board and chip and as a result the defect rate at the semiconductor product in which the particles are filled is liable to rise.

[0036]

The greater the number density of coarse particles of 10 μm or more, the more the fluidity is improved, so the more preferable. On the other hand, if the number of coarse particles becomes greater, as explained above, the defect rate at the semiconductor product will end up rising. For this reason, the number frequency may be less than or equal to 90 ppm, less than or equal to 80 ppm, less than or equal to 70 ppm, less than or equal to 60 ppm, less than or equal to 50 ppm, less than or equal to 40 ppm, less than or equal to 30 ppm, less than or equal to 20 ppm, less than or equal to 18 ppm, less than or equal to 16 ppm, less than or equal to 14 ppm, less than or equal to 12 ppm, or less than or equal to 10 ppm. The number frequency of coarse particles of 10 μm or more may be 0 ppm, but cutting those coarse particles completely, that is, rendering them 0 ppm, would sometimes impose a large burden in production control and would be difficult, therefore the frequency may be made several ppm, specifically 1 ppm or more, 2 ppm or more, 3 ppm or more, 4 ppm or more, or 5 ppm or more. The lower limit of the number frequency may also be adjusted in accordance with the actual application or the allowable range of the target yield.

[0037]

Classification may be performed to obtain the desired particle size distribution. For classification, a conventionally known method can be employed. For example, the method of using a sieve having predetermined mesh openings and/or a precision wind classifier to cut the coarse powder side and fine powder side may be illustrated. In classification control, the number frequency by a Coulter counter may be measured. By precision management of the particle size distribution, excellent properties of the spherical alumina particle mixture, for example, fluidity, can be contributed to.

[0038]

<Measurement by Coulter Counter>

A Coulter counter uses the electrical resistance method referred to as the “Coulter principle” to measure particles. There is none of the errors in surface forms, internal structures, refraction indexes, color, etc. of the particles such as seen in the optical measurement method and a high measurement precision is obtained. In particular, the particle size obtained by this method can be expressed by a number distribution (/ml and /g). Precision management of the particle size distribution becomes possible.

[0039]

Specifically, a 200 ml glass beaker is filled with the sample spherical alumina particle mixture and an electrolytic solution in 150 ml. An ultrasonic homogenizer (ULTRA SONIC HOMOGENIZER UH-300 made by SMT) is used to disperse the particles for 30 seconds. Then, this dispersion is added to an electrolytic solution prepared in a separate beaker to adjust it in concentration. The dispersion adjusted in concentration is examined by a Coulter counter (Multisizer 3 made by Beckman Coulter) using an aperture size of 50 μm to measure the particle sizes of the spherical alumina particle mixture. At this time, the number of particles measured per measurement is made about 100,000. The same sample is repeatedly measured three times. Among these, the number of particles with a particle size of 10 μm or more is calculated and made the frequency (ppm) of coarse particles to the total number of measurements.

[0040]

(Water Content by Coulometric Karl Fischer Titration of Less Than 20 ppm)

In an embodiment of the present invention, the spherical alumina particle mixture may have a water content by coulometric Karl Fischer titration (below, sometimes simply referred to as the "water content") of less than 20 ppm.

[0041]

Coulometric Karl Fischer titration, details of which will be explained later, is a known method of quantifying water utilizing a Karl Fischer reaction (reaction of 1 mole each of iodine and water).

[0042]

The smaller the water content by coulometric Karl Fischer titration, the more the agglomeration of particles is suppressed, therefore the dispersion when mixing a filler with a resin is improved, so this is preferable. Therefore, that water content is preferably less than 20 ppm, more preferably 15 ppm or less, still more preferably 10 ppm or less, even more preferably less than 10 ppm.

[0043]

<Coulometric Karl Fischer Titration >

Coulometric Karl Fischer titration is a known method of measuring water using a Karl Fischer reaction (reaction of iodine and water in one mole each). In a coulometric titration method, iodine ions of an electrolytic cell anolyte are electrolyzed to generate iodine. Iodine is generated proportionally to the amount of electricity, and iodine and water react 1:1, so the water content can be found from the amount of electricity required for titration.

[0044]

As a specific example, the spherical alumina particle mixture is set in a Karl Fischer water content meter for coulometric titration use (CA-200 (measurement apparatus), VA-122

(vaporization apparatus) made by Nittoseiko Analytic), raised in temperature from 25°C to 500°C, held at 500°C, and checked when no further formation of water can be seen. After that, the temperature is further raised and the water content formed at 500°C or more and 900°C or less is measured.

[0045]

(Blending of Spherical Alumina Particle Mixture)

The spherical alumina particle mixture can be obtained by blending spherical alumina particles having different average particle sizes. The blending ratios can be suitably adjusted in accordance with the properties of the spherical alumina particles blended (specific surface area, α-conversion rate, etc.) to thereby obtain the desired properties of the spherical alumina particle mixture itself.

[0046]

As the spherical alumina particles blended, spherical alumina particles (a) to (c) having the following average particle sizes can be used:

Spherical alumina particles (a): Spherical alumina particles with average particle size (D50) of 7.0 μm or more and 10.0 μm or less and with circularity of 0.85 or more.

Spherical alumina particles (b): Spherical alumina particles with average particle size (D50) of 2.4 μm or more and 6.0 μm or less and with circularity of 0.85 or more.

Spherical alumina particles (c): Spherical alumina particles with average particle size (D50) of 0.4 μm or more and 2.2 μm or less and with circularity of 0.85 or more.

The spherical alumina particles (a) to (c) can be classified in the order of larger average particle sizes. The spherical alumina particles (a) to (c), for convenience, are sometimes respectively called “large particles” (or “coarse powder”), “medium particles” (or “medium powder”), and “fine particles” (or “fine powder”).

[0047]

<Measurement of Average Particle Size>

The average particle size of the alumina particles was measured by the laser diffraction/scattering type method. The apparatus used was an “MS3000” made by Malvern. Water was used as the dispersion medium. The “average particle size” referred to in this Description, unless otherwise particularly indicated, is what is called the “median size”. The laser diffraction/scattering type method or other method is used to measure the particle size distribution. The particle size giving a cumulative volume of particle size of 50% is defined as the “average particle size (D50)”.

[0048]

The spherical alumina particle mixture preferably contains at least two types or more of particles selected from the above spherical alumina particles (a) to (c). The spherical alumina

particles (a) to (c) differ in average particle sizes from each other. Particles with small average particle sizes can enter into the spaces between particles with large average particle sizes whereby the thermal conductivity of those spaces is improved. This is because heat can be conducted not through the spaces, that is, spaces, but through the entering small particles.

[0049]

Further, the spherical alumina particles (a) to (c) all have circularities of 0.85 or more, therefore the spherical alumina particle mixture obtained by mixing these also can be given a circularity of 0.85 or more. By the circularity being 0.85 or more, as explained above, it is possible to avoid major deterioration of the hardness of a shaped body formed by kneading together that alumina particle mixture and a resin or the viscosity of the liquid kneaded matter.

[0050]

The spherical alumina particles (a) to (c) can be suitably adjusted in blending ratios (ratios of composition) to enable the desired properties of the spherical alumina particle mixture itself to be obtained. As typical blending ratios, the following Blending Ratios (Composition Ratios) 1 to 3 can be used.

[0051]

Blending Ratio 1:

Containing spherical alumina particles (a) in 50 wt% or more and 95 wt% or less and spherical alumina particles (b) in 5 wt% or more and 45 wt% or less and

having total of spherical alumina particles (a) and spherical alumina particles (b) of 90 wt% or more.

Preferably, the total of the spherical alumina particles (a) and spherical alumina particles (b) is 95 mass% or more, more preferably 98 mass% or more, still more preferably 100 mass%.

To enable the desired properties to be obtained, the spherical alumina particles (a) may be made 55 wt% or more or 60 wt% or more and may be made 85 wt% or less or 80 wt% or less and the spherical alumina particles (b) may be made 10 wt% or more, 20 wt% or more, or 30 wt% or more and may be made 35 wt% or less or 30 wt% or less.

[0052]

Blending Ratio 2:

Containing spherical alumina particles (b) in 50 wt% or more and 90 wt% or less and spherical alumina particles (c) in 5 wt% or more and 20 wt% or less and

having total of spherical alumina particles (b) and spherical alumina particles (c) of 90 wt% or more.

Preferably, the total of the spherical alumina particles (b) and spherical alumina particles is 95 mass% or more, more preferably, 98 mass% or more, still more preferably 100 mass%.

To enable the desired properties to be obtained, the spherical alumina particles (b) may be

made 55 wt% or more or 60 wt% or more and may be made 85 wt% or less or 80 wt% or less and the spherical alumina particles (c) may be made 10 wt% or more or 12 wt% or more and may be made 18 wt% or less or 16 wt% or less.

[0053]

Blending Ratio 3:

Containing the spherical alumina particles (a) in 50 wt% or more and 90 wt% or less, the spherical alumina particles (b) in 5 wt% or more and 20 wt% or less, and the spherical alumina particles (c) in 5 wt% or more and 30 wt% or less and

having total of spherical alumina particles (a), spherical alumina particles (b), and spherical alumina particles (c) of 90 wt% or more.

Preferably, the total of the spherical alumina particles (a), spherical alumina particles (b), and spherical alumina particles (c) is 95 mass% or more, more preferably, 98 mass% or more, still more preferably 100 mass%.

To enable the desired properties to be obtained, the spherical alumina particles (a) may be made 55 wt% or more or 60 wt% or more and may be made 85 wt% or less or 80 wt% or less, the spherical alumina particles (b) may be made 10 wt% or more or 12 wt% or more and may be made 18 wt% or less or 15 wt% or less; and the spherical alumina particles (c) may be made 10 wt% or more, 12 wt% or more, or 15 wt% or more and may be made 25 wt% or less or 20 wt% or less.

[0054]

The spherical alumina particle mixtures blended by the above blending ratios 1 to 3 enable the desired specific surface area and other properties to be obtained. More specifically, the specific surface area etc. of the spherical alumina particle mixture itself is 0.30 m^2/g or more and 2.00 m^2/g or less, preferably 0.90 m^2/g or less.

[0055]

The above blending ratios 1 to 3 have the following blending effects of the particles.

[0056]

The blending ratio of the alumina spherical particles (a) is confirmed by the two effects of the effect of formation of thermal conduction paths such as the conduction of heat in the filler and the lowering of the viscosity. This is because if the blending ratio of the alumina spherical particles (a) is small, the amount of small particles relatively increases, paths of thermal conduction are formed by contact of the small particles with each other, and the thermal conductivity falls. Furthermore, the specific surface area unnecessarily increases and becomes a cause of deterioration of the viscosity. Further, if the blending ratio of the alumina spherical particles (a) becomes excessive, the amount of small particles relatively decreases, large spaces are easily formed between filler parts, resin is caught in the spaces, and the viscosity deteriorates

caused by this.

[0057]

The blending ratio of the alumina spherical particles (b) is enough so that the large spaces between large particles are buried and points of contact between filler parts increase resulting in the effect of improvement of the thermal conductivity. The alumina spherical particles (b) have a smaller specific surface area compared with the alumina spherical particles (c), therefore even if increasing the blended amount, there is almost detrimental effect on the viscosity. However, if a certain amount or more is blended, the spaces between large sized alumina spherical particles (a) are almost completely buried and the excess medium sized alumina spherical particles (b) make the specific surface area increase and cause the viscosity to deteriorate.

[0058]

The alumina spherical particles (c) have the effect of lowering the viscosity by adjusting the specific surface area of the spherical alumina particle mixture itself and burying the small spaces. However, as explained above, if making the blending ratio greater, the specific surface area becomes too large and causes the viscosity to end up deteriorating.

[0059]

Note that, in the above blending ratios 1 to 3, particles other than the compositions forming the blending ratios 1 to 3 (below, referred to as "other particles") may be contained in extents not detracting from the effects of blending the spherical alumina particles (a) to (c) or the properties of the spherical alumina mixtures blended by the blending ratios 1 to 3.

As the above other particles, known inorganic particles can be used. $CaCO_3$, $BaSO_4$, talc, mica, kaolin clay, wollastonite, sepiolite, hydrotalcite, montmorillonite, potassium titanate, aluminum borate, silica, titanium oxide, zinc oxide, alumina, magnesium oxide, aluminum hydroxide, magnesium hydroxide, boron nitride, aluminum nitride, carbon black, and graphite may be mentioned. Preferably, it is silica, zinc oxide, alumina, magnesium oxide, boron nitride, and aluminum nitride due to which excellent dimensional stability or thermal conductivity can be expected at the time made a resin composite, more preferably it is alumina.

[0060]

The blended amount of the other particles is, from the viewpoint of not detracting from the properties of the spherical alumina mixture, 10 wt% or less or less than 10 wt% of the spherical alumina mixture, more preferably less than 5 wt%, still more preferably less than 2 wt%, still more preferably 0 wt%.

[0061]

The average particle size D50 of the other particles is not limited so long as in a range not detracting from the properties of the spherical alumina mixture, but preferably is 0.1 to 150 μm.

[0062]

(Starting Material of Spherical Alumina Particles)

For the starting material of the spherical alumina particles, alumina powder, aluminum hydroxide powder, etc. is used. Further, metal aluminum may also be used.

[0063]

(Method of Production of Spherical Alumina Particles)

The spherical alumina particles can be produced by the flame fusion method or the VMC method.

The flame fusion method is one type of known thermal spraying method. It sprays the starting material particles in a flame to make the starting material spheroidal. At this time, it is possible to adjust the average spheroidicity by the amount charged into the flame per time and the type of fuel gas. Further, by adjusting the particle size of the starting material powder used, it is possible to adjust the particle size of the spherical alumina particles. The content of α-alumina can be improved by holding the temperature in the melting furnace high. The temperature in the melting furnace is preferably 1200°C or more from the viewpoint of promoting crystal growth of α-alumina. Further, by rapidly cooling the spherical particles right after solidifying them by air, water, or another refrigerant, the content can be lowered. The refrigerant is not particularly limited, but from the viewpoint of not causing the purity of the spherical particles to fall, air or distilled water or ion exchanged water not containing sodium ions or chlorine ions as impurities is desirable.

[0064]

The VMC method is the method of forming a chemical flame by a burner in an atmosphere containing oxygen, charging metal powder into this chemical flame in an amount by which a powder dust cloud is formed, and causing deflagration to obtain spherical oxide particles. Due to the VMC method (deflagration method), the aluminum or other metal material and the oxygen react to obtain alumina or other metal oxide.

[0065]

The spheroidized alumina particles can be separated by a cyclone separator etc. into coarse particles and fine particles. The thus obtained spherical alumina particles can be stripped of particles of 10.0 μm or more and classified into particles of the desired average particle size by a sieve having a predetermined mesh opening or using a wind classifier. The mesh openings of the mesh used are not particularly limited so long as 10.0 μm or less.

[0066]

(Mixing)

Spherical alumina particles of several particle sizes can be mixed to obtain the spherical alumina particle mixture. For the mixing method, a rocking mixer, V-type mixer, air blender, or other known method is used for mixing. At the time of mixing, the mixing conditions may be

suitably adjusted to keep from lowering the circularity of the spherical alumina particles and from preventing the desired circularity of the spherical alumina particle mixture from being obtained. Typically, the mixing time, mixing density, etc. may also be adjusted.

[0067]

Measurement of the thermal conductivity and fluidity (viscosity) of the spherical alumina particle mixture itself is difficult. Therefore, for the thermal conductivity, that spherical alumina particle mixture is mixed with a resin under predetermined conditions, the thermal conductivity of the resin composition obtained is measured, and the thermal conductivity of the spherical alumina particle mixture is evaluated based on the measurement results. Further, for the fluidity (viscosity), that spherical alumina particle mixture is mixed with a resin under predetermined conditions, the fluidity (viscosity) of the resin composition obtained is measured, and the fluidity (viscosity) of the spherical alumina particle mixture is evaluated.

[0068]

<Measurement of Thermal Conductivity>

More specifically, the following procedure is used to measure the thermal conductivity. A spherical alumina particle mixture in 92 parts by mass, silicone resin (CY-52-276A made by Toray Dow Corning) in 4 parts by mass, and silicone resin B (CY-52-276B made by Toray Dow Corning) in 4 parts by mass are mixed by a vacuum kneader, the obtained resin composition is poured into a mold, and the composition is heated and press-formed to give any thickness. The shaping conditions are a pressure of 6 MPa and heating at a temperature of 120°C for 1 hour. After heating, the shaped sheet is taken out from the mold and then heated by a 140°C dryer. The post heated sheet is cooled. The prepared sheet is cut to 20 mm square and measured for thermal conductivity using the ASTM-D5470 method under conditions of a pressure of 1.25 kgf/cm^2.

In examples using the spherical alumina particle mixture according to the present embodiment, if the filler is filled to the maximum amount, the lower limit of the thermal conductivity may be 2.40W/m·K and may be 2.60W/m·K, may be 2.80W/m·K, may be 3.00W/m·K, may be 3.10W/m·K, may be 3.20W/m·K, may be 3.30W/m·K, may be 3.40W/m·K, and may be 3.50W/m·K. On the other hand, the upper limit of the thermal conductivity may be 8.00W/m·K, may be 4.00W/m·K, and may be 3.50W/m·K.

Further, if the maximum filled amount of the filler is 91 wt%, the lower limit of the thermal conductivity may be 2.9W/mK and preferably may be 3.0W/mK. On the other hand, the upper limit of the thermal conductivity may be 3.5W/mK.

[0069]

<Maximum Filler Filling Amount>

Maximum filler filling amount is determined in the following manner.

A spherical alumina particle mixture and a silicone resin A (CY-52-276A made by Toray

Dow Corning) mixed by a predetermined ratio are vacuum kneaded at any ratio and remainder of any filler not kneaded in the kneaded matter (spherical alumina particle mixture) is visually checked for. After the visual check, if no filler remains, it is deemed that the filler has been able to be filled in the resin. The maximum filler filling amount is found by increasing the blended amount of the filler until filling is no longer possible. The higher the maximum filler filling amount, the more filler can be filled in the resin, therefore this can be said to be a filler with a good fillability.

[0070]

<Measurement of Flow Rate>

The following procedure is used to measure the flow rate. The spherical alumina particle mixture in 87 parts by mass and an epoxy resin (Epicoat 801N) in 13 parts by mass are mixed by a kneader, the obtained resin composition is cooled by a water bath for 60 minutes, then a Flow Tester CFT-500D is used for measurement. 10 ml or so of the kneaded sample is extruded from a die of a diameter of 2.0 mm and length of 75.0 mm at temperature set at 28.5°C. The extrusion load is made 50.0 kgf. The ejection rate (ml/sec) from the point of time of extrusion of about 50% of the sample to completion of extrusion of 75% is measured.

In examples using the spherical alumina particle mixture according to the present embodiment, the lower limit of the flow rate may be 0.2 ml/sec, preferably may be 0.40 ml/sec. On the other hand, the upper limit may be 1.0 ml/s. This is because if the flow rate is too low, when used as an encapsulant, it becomes a cause of poor encapsulating. Further, even when used as an adhesive, grease, or other liquid heat dissipation material, the fluidity becomes insufficient and becomes a cause of worsening work efficiency. On the other hand, if the flow rate is too high, when used as an encapsulant, the material will leak out from the spaces in the mold causing the formation of burrs. Even when used as a liquid heat dissipation material, the material ends up leaking out from the coated object resulting in worsening work efficiency.

[0071]

(Hue Index (L∗ Value)/(C∗ Value) of 100 or More and 300 or Less)

The spherical alumina particle mixture according to one embodiment of the present invention has a hue index of 100 or more and 300 or less. Due to this, it is possible to contribute to improvement of the beauty and visual impact of the product containing the spherical alumina particle mixture.

[0072]

The “hue index” is defined as the ratio of the value of the lightness (L∗) and the value of the chroma (C∗) (L∗ value)/(C∗ value). The value of the lightness (L∗) and the value of the chroma (C∗) are found based on JIS Z8729. The L∗ value and C∗ value are indicators used for expressing the color of a measured object by the L∗a∗b∗ color space (CIE 1976). In this color

space, the L∗ value expresses the lightness, the C∗ value expresses the chroma, and the a∗ value and b∗ value are used for representing the index by the formula $(a^2+b^2)^{1/2}$.

[0073]

An increase of the lightness L∗ value means the whiteness increases in the color of the measured substance, while a drop in its numerical value means an increase in the black color. The larger the chroma C∗ value, the clearer the color of the measured object meant. On the other hand, if the C∗ value is small, it means close to no color or a colorless state.

[0074]

The chroma C∗ value is expressed using the a∗ value and b∗ value. The a∗ value and b∗ value are called chromaticness indexes and express the direction of colors. The a∗ value has 0 as a baseline. If its numerical value becomes minus, it means the green color increases in the hue of the measured substance, while if it becomes plus, it means the red increases. Further, the b∗ value has 0 as a baseline. If its numerical value becomes minus, it means the blue color increases in the hue of the measured substance, while if it becomes plus, it means the yellow increases. Note that, if both of the a∗ value and the b∗ value are 0, the result becomes no color or colorless. Further, the C∗ value expresses the chroma and is expressed by the formula $(a^2+b^2)^{1/2}$.

[0075]

The alumina particle mixture according to an embodiment of the present invention preferably has a hue index (L∗ value)/(C∗ value) of 100 or more and 300 or less. This generally corresponds to a high lightness L∗ value and low chroma C∗ value. The higher the lightness (L∗), the higher the whiteness and brilliance and the more improvement of the aesthetic appeal and visual impact of the product containing the alumina particle mixture can be contributed to. On the other hand, the lower the chroma (C∗), the more the effect of not interfering with the color of the coloring pigment contained in the final product is also obtained.

[0076]

The hue index (L∗ value)/(C∗ value) may be suitably adjusted in accordance with the beauty and visual impact desired in the products containing the alumina particle mixture. For example, the upper limit of the hue index (L∗ value)/(C∗ value) may be made less than or equal to 250 and less than or equal to 200. The lower limit of the hue index (L∗ value)/(C∗ value) may be made more than or equal to 130 or more than or equal to 160. Note that if suitably adjusting the desired hue index (L∗ value)/(C∗ value), the hue index (L∗ value)/(C∗ value) of the spherical alumina particles to be mixed can be measured in advance and the blending ratio adjusted to adjust them to the desired hue index (L∗ value)/(C∗ value).

[0077]

<Method of Measurement of Lightness (L∗) and Chroma (C∗)>

The lightness (L∗) and chroma (C∗) are measured using a whiteness meter (Nippon

Denshoku Industries Co., Ltd., NW-12). Specifically, the lightness (L*) value, $a^{*\ value}$, and $b^{*\ value}$ are measured and the chroma (C*) is calculated by $(a^2+b^2)^{1/2}$.

[0078]

(Resin Composite Composition Containing Spherical Alumina Particle Mixture)

According to one aspect of the present invention, a resin composite composition containing a spherical alumina particle mixture is provided. Furthermore, that resin composite composition can be cured to produce a resin composite. The composition of the resin composite composition etc. will be explained in more detail below.

[0079]

A slurry composition containing the spherical alumina particle mixture and a resin can be used to obtain a semiconductor encapsulant, interlayer insulating film (including a heat dissipation sheet or heat dissipation adhesive), or other resin composite composition. Furthermore, by curing these resin composite compositions, it is possible to obtain an encapsulant (cured), semiconductor package board, or other resin composite.

[0080]

If producing the resin composite composition, for example, in addition to the spherical alumina particle mixture 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 method. Further, the mixture is shaped into pellets, a film, etc. in accordance with the application.

[0081]

Further, if producing a resin composite composition, in addition to the spherical alumina particle mixture of one aspect of the present invention and resin, another inorganic filler may be mixed in. As the inorganic filler, amorphous spherical silica particles, crystalline spherical silica particles, alumina 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, but from the viewpoint of obtaining the effect of the spherical alumina particle mixture of the present invention, (blended weight of spherical alumina particle mixture):(blended weight of other inorganic fillers)=95:5 to 60:40 is preferable.

[0082]

Furthermore, if curing the resin composite composition to produce a resin composite, for 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,

compression mold method, or other known method can be used.

[0083]

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-dihydroxynapthalene type epoxy resin, 2,7-dihydroxynapthalene 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.

[0084]

Further, as the resin used for applications other than composite materials for semiconductor encapsulant 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.

[0085]

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.

[0086]

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.

[0087]

The amount of addition of the spherical alumina particle mixture 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 alumina particle mixture is too small, the effects of improvement of the strength of the encapsulant, suppression of thermal expansion, etc. become hard to obtain. Further, if too great, despite surface treatment of the spherical alumina particle mixture, at the composite material, segregation easily occurs due to agglomeration of the spherical alumina particle mixture, the viscosity of the composite material becomes too large, and other issues arise, therefore practical application as an encapsulant becomes difficult.

[0088]

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.

[0089]

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

[0090]

A slurry composition containing a spherical alumina particle mixture and a resin can be used to obtain a heat dissipation sheet, heat dissipation adhesive (also sometimes referred to as “heat dissipation grease”), etc.

[0091]

When obtaining a heat dissipation sheet, in addition to the spherical alumina particle mixture 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.

[0092]

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.

[0093]

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.

[0094]

When obtaining the heat dissipation adhesive or heat dissipation grease, in addition to the spherical alumina particle mixture 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 adhesive or heat dissipation grease is also called the "base oil".

[0095]

For example, if producing a heat dissipation adhesive or 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 oil may be mentioned.

[0096]

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

[0097]

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

examples.

[0098]

(Example 1 to Example 14 and Comparative Examples A to G)

The starting material of the alumina particles was charged into a high temperature flame formed by LPG and oxygen and spheroidized. The particle size of the charged alumina particle starting material was controlled to produce spherical alumina particles. Further, the temperature inside the melting furnace was made 1200°C or more, then the cooling speed was controlled to obtain spherical alumina particles having a predetermined α-conversion rate. The obtained spherical alumina particles were separated by a cyclone separator into coarse particles and fine particles, both the coarse particles and fine particles were run through a sieve of any mesh opening, and only the parts under the sieve were collected to obtain the spherical alumina particles in Table 1. The properties of the obtained spherical alumina particles and the silica fine powder used in some of the examples are summarized in Table 1. The spherical alumina particles and silica fine powder in Table 1 were mixed in the blending ratios in Table 2 to obtain the spherical alumina particle mixtures of Examples 1 to 14 and Comparative Examples A to G.

[0099]

Table 2 shows the physical properties of the obtained spherical alumina particle mixtures. Note that in each of Example 1 to Example 14, the water content by coulometric Karl Fischer titration was less than 20 ppm. Further, in each of Example 1 to Example 14, the thermal conductivity at a filler filling amount of 88 wt% was 1.7 to 2.0W/m·K. Further, the thermal conductivity at the time of the respective filling amounts of the filler of maximum filling was 2.4 to 3.0W/m·K.

[0100]

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

[0101]

(Average Particle Size D50)

A laser diffraction/scattering type particle size distribution measurement apparatus “Mastersizer 3000” (made by Malvern) is used to measure the average particle size (D50).

[0102]

(Specific Surface Area)

The specific surface area is measured by the BET method. Specifically, the following procedure is used to measure the specific surface area.

About 5 g of the 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 measuring device (Macsorb made by Mountech) and a pure nitrogen and nitrogen-helium mixed gas (mixed ratio of nitrogen 30%, He70%) is used to measure the value of the nitrogen gas adsorption at a 77K measurement

temperature and relative pressure P/P0 of 0.291. The one-point method is used to calculate the BET specific surface area.

[0103]

(Particle Size Distribution Measured by Wet Type Particle Size Test Method)

In the wet type particle size test method, a container is filled with 10 g of the spherical alumina particles to be tested and with water and ultrasonic waves are used to make the spherical particles sufficiently dispersed to prepare a slurry. The slurry is transferred on to the mesh of a test sieve and sieved. The particles remaining on the mesh of the test sieve are taken in a suitable container, a hot press etc. is used to make the sample evaporate to dryness, the weight of the residue is measured, and the ratio of weight of particles separated by sieving in the spherical alumina particle mixture 10 g to be tested is calculated.

[0104]

(Measurement by Coulter Counter Method)

A 200 ml glass beaker is filled with the sample spherical alumina particle mixture and an electrolytic solution in 150 ml. An ultrasonic homogenizer (ULTRA SONIC HOMOGENIZER UH-300 made by SMT) is used to disperse the particles for 30 seconds. Further, this dispersion is added to an electrolytic solution prepared in a separate beaker to adjust it in concentration. The dispersion adjusted in concentration is examined by a Coulter counter (Multisizer 3 made by Beckman Coulter) using an aperture size of 50 μm to measure the particle sizes of the individual spherical alumina particles. At this time, the number of particles measured per measurement is made about 100,000. The same sample is repeatedly measured three times. Among these, the number of particles with a particle size of 10 μm or more is calculated and made the frequency (ppm) of coarse particles to the total number of measurements.

[0105]

(α-Conversion Rate)

The α-conversion rate is measured using a powder X-ray diffraction apparatus. The integrated areas of the obtained diffraction peaks are 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 an X-ray diffraction pattern at a 2θ of 10° to 90° in range. The obtained pattern is used to calculate the α-conversion rate by the 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.

[0106]

(Circularity)

The circularity is measured using an electron microscope or an optical microscope and an

image analysis apparatus. In the examples and comparative examples, FPIA made by Sysmex Corporation is used. These apparatuses are used to measure the circularity of the particles (circumference of equivalent circle/circumference of projected image of particle). 100 or more particles are measured for circularity and the average value of the same is made the circularity of the powder.

[0107]

<Measurement of Flow Rate>

The following procedure is used to measure the flow rate. The spherical alumina particle mixture in 87 parts by mass and an epoxy resin (Epicoat 801N) in 13 parts by mass are mixed by a kneader, the obtained resin composition is cooled by a water bath for 60 minutes, then a Flow Teste rCFT-500D made by Shimadzu is used for measurement. 10 ml or so of the kneaded sample is extruded from a die of a diameter of 2.0 mm and length of 75.0 mm at temperature set at 28.5°C. The extrusion load is made 50.0 kgf. The ejection rate (ml/sec) from the point of time of extrusion of about 50% of the sample to completion of extrusion of 75% is measured.

[0108]

<Measurement of Thermal Conductivity>

The following procedure is used to measure the thermal conductivity. A spherical alumina particle mixture in 92 parts by mass, silicone resin A (CY-52-276A made by Toray Dow Corning) in 4 parts by mass, and silicone resin B (CY-52-276B made by Toray Dow Corning) in 4 parts by mass are mixed by a vacuum kneader, the obtained resin composition is poured into a mold, and the composition is heated and press-formed to give any thickness. The shaping conditions are a pressure of 6 MPa and heating at a temperature of 120°C for 1 hour. After heating, the shaped sheet is taken out from the mold and then heated by a 140°C dryer. The post heated sheet is cooled. The prepared sheet is cut to 20 mm square and measured for thermal conductivity using the ASTM-D5470 method under conditions of a pressure of 1.25 kgf/cm^2.

[0109]

<Measurement of Water Content by Coulometric Karl Fischer Titration>

The following procedure is used to measure the water content by coulometric Karl Fischer titration. The spherical alumina particle mixture 0.5 to 1.0 g is set in a Karl Fischer water content meter for coulometric titration use (CA-200 (measurement apparatus), VA-122 (vaporization apparatus) made by Nittoseiko Analytic), raised in temperature from 25°C to 500°C, held at 500°C, and checked when no further formation of moisture can be seen. After that, the temperature is further raised and the water content formed at 500°C or more and 900°C or less is measured.

[0110]

The spherical alumina particle mixture in the range of the present invention has a particle

size distribution measured by the wet type particle size test method in which particles of 25.0 μm or more account for 0.04 wt% or less. On top of this, it was confirmed that excellent fluidity and thermal conductivity are obtained in that spherical alumina particle mixture. Furthermore, it was confirmed that an excellent hue index is obtained in that spherical alumina particle mixture.

[0111]

[Table 1]

Table 1. Properties of Spherical Alumina Particles and Silica Fine Powder

Name of material	Average particle size	Specific surface area	Circularity	α-conversion rate
	μm	m^2/g	-	%
Coarse Powder 1	8.1	0.46	0.96	50.4
Coarse Powder 2	19.7	0.31	0.93	49.7
Medium Powder 1	4.9	0.66	0.95	43.5
Medium Powder 2	3.6	0.78	0.96	32.1
Medium Powder 3	2.7	1.15	0.91	2.5
Fine Powder 1	1.9	1.70	0.91	1.6
Fine Powder 2	1.0	3.08	0.91	0.6
Fine Powder 3	1.2	3.24	0.92	0.6
Silica fine powder	2.1	8.00	0.98	0

[0112]

[Table 2]

Table 2. Properties of Spherical Alumina Particle Mixtures

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12	Ex. 13	Ex. 14
Coarse Powder 1		70%	80%	68%	60%	63%	56%	64%	95%	85%	70%			75%	50%
Coarse Powder 2															
Medium Powder 1						10%	20%	20%		5%					
Medium Powder 2												85%	85%		
Medium Powder 3		30%	20%	29%	40%	27%	24%	16%	5%	10%	10%			25%	20%
Fine Powder 1												15%			
Fine Powder 2															
Fine Powder 3											20%		15%		20%
Silica fine powder				3%											10%
Average particle size D50	μm	7.1	8.1	6.9	4.8	6.0	5.8	6.5	7.6	7.6	5.2	3.3	3.3	7.4	2.7
Specific surface area	m^2/g	0.71	0.62	0.89	0.88	0.71	0.78	0.72	0.52	0.54	1.10	0.97	1.16	0.62	1.84
Ratio of particles of 25 um or more by wet type particle size test method	wt%	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ratio of particles of 20 um or more by wet type particle size test method	wt%	0	0	0	0	0	0	0	0	0	0	0	0	-	-
Ratio of particles of 10 um or more by Coulter counter	ppm	-	-	-	-	-	-	-	-	-	-	0	30	-	-
α-conversion rate	%	36.6	39.4	33.9	32.1	33.1	35.4	37.7	43.5	41.7	40.6	23.3	22.5	48.9	36.9
Circularity	-	0.96	0.96	0.96	0.96	0.96	0.96	0.96	0.95	0.95	0.95	0.95	0.95	0.96	0.96
Flow rate	ml/s	0.84	0.74	0.96	0.82	0.69	0.75	0.69	0.54	0.61	0.72	0.45	0.52	0.89	0.96
Maximum filling amount	wt%	90.0	90.0	90.0	90.0	91.5	91.0	91.0	90.0	91.0	92.0	88.0	89.0	91.0	91.5
Thermal conductivity at time of maximum filling amount	W/mK	2.8	2.8	2.8	2.8	3.3	3.0	2.9	2.6	3.0	3.4	2.4	2.6	3.5	3.1
Hue index (L/c)	-	163.5	195.6	133.5	164	163.7	163.5	133.5	139.6	139.4	244.8	122.4	122.5	162.8	114.3

[0113]

[Table 3]

Table 2 (continued). Properties of Spherical Alumina Particle Mixtures

		Comp. Ex. A	Comp. Ex. B	Comp. Ex. C	Comp. Ex. D	Comp. Ex. E	Comp. Ex. F	Comp. Ex. G
Coarse Powder 1		100%	50%		97%	45%		65%
Coarse Powder 2				95%				
Medium Powder 1					3%	55%	45%	20%
Medium Powder 2								
Medium Powder 3			10%	5%				
Fine Powder 1								
Fine Powder 2								
Fine Powder 3			30%				55%	
Silica fine powder			10%					15%
Average particle size D50	μm	8.5	2.0	15.8	8.5	6.9	2.1	6.2
Specific surface area	m^2/g	0.48	2.03	0.26	0.47	0.57	2.15	1.63
Ratio of particles of 25 um or more by wet type particle size test method	wt%	0	0.33	0	0	0	0	0
Ratio of particles of 20 um or more by wet type particle size test method	wt%	0	-	8.85	-	-	-	-
Ratio of particles of 10 um or more by Coulter counter	ppm	-	-	-	-	-	-	-
α-conversion rate	%	51.0	35.2	44.0	56.7	54.2	30.5	54.1
Circularity	-	0.94	0.96	0.97	0.95	0.96	0.96	0.95
Flow rate	ml/s	Not measurable	0.91	0.86	0.43	0.42	0.39	0.52
Maximum filling amount	wt%	82.0	92.0	87.0	85.0	87.0	90.0	85.0
Thermal conductivity at time of maximum filling amount	W/mK	1.3	2.5	2.3	2.0	2.1	2.5	1.8
Hue index (L/c)	-	121.6	135.5	191.6	152.9	325.7	161.3	135.3

INDUSTRIAL APPLICABILITY

[0114]

The spherical alumina particle mixture and resin composite composition containing the same of the present invention can exhibit excellent fluidity and thermal conductivity and further an excellent hue index. The spherical alumina particle mixture and the resin composite combination containing the same are not limited to semiconductor encapsulants and can be used for other applications as well. Specifically, they can also be used for heat dissipation sheets, heat dissipation adhesives, etc.

CLAIMS

[Claim 1]

A spherical alumina particle mixture having

an average particle size (D50) by a laser diffraction/scattering method of 0.5 μm or more and 10.0 μm or less,

particles of 25.0 μm or more comprising 0.04 wt% or less of a particle size distribution measured by a wet type particle size test method,

a specific surface area of 0.30 m^2/g or more and 2.00 m^2/g or less,

a circularity of 0.85 or more, and

an α-conversion rate of less than 50.0%.

[Claim 2]

The spherical alumina particle mixture according to claim 1, wherein

in a number of particles of 1 μm or more and 30 μm or less detected by a Coulter counter,

a number frequency of particles of 10 μm or more is 100 ppm or less.

[Claim 3]

The spherical alumina particle mixture according to claim 1, wherein a water content by coulometric Karl Fischer titration is less than 20 ppm.

[Claim 4]

The spherical alumina particle mixture according to claim 1,

containing

spherical alumina particles (a) with an average particle size (D50) of 7.0 μm or more and 10.0 μm or less and a circularity of 0.85 or more and

spherical alumina particles (b) with an average particle size (D50) of 2.4 μm or more and 6.0 μm or less and a circularity of 0.85 or more,

containing

the spherical alumina particles (a) in 50 wt% or more and 95 wt% or less and

the spherical alumina particles (b) in 5 wt% or more and 45 wt% or less, and

having a total of spherical alumina particles (a) and spherical alumina particles (b) of 90 wt% or more.

[Claim 5]

The spherical alumina particle mixture according to claim 1,

containing

spherical alumina particles (b) with an average particle size (D50) of 2.4 μm or more and 6.0 μm or less and a circularity of 0.85 or more and

spherical alumina particles (c) with an average particle size (D50) of 0.4 μm or more and 2.2 μm or less and a circularity of 0.85 or more,

containing

the spherical alumina particles (b) in 50 wt% or more and 90 wt% or less and

the spherical alumina particles (c) in 5 wt% or more and 20 wt% or less, and

having a total of spherical alumina particles (b) and spherical alumina particles (c) of 90 wt% or more.

[Claim 6]

The spherical alumina particle mixture according to claim 1,

containing

spherical alumina particles (a) with an average particle size (D50) of 7.0 μm or more and 10.0 μm or less and a circularity of 0.85 or more,

spherical alumina particles (b) with an average particle size (D50) of 2.4 μm or more and 6.0 μm or less and a circularity of 0.85 or more, and

spherical alumina particles (c) with an average particle size (D50) of 0.4 μm or more and 2.2 μm or less and a circularity of 0.85 or more,

containing

the spherical alumina particles (a) in 50 wt% or more and 90 wt% or less,

the spherical alumina particles (b) in 5 wt% or more and 20 wt% or less, and

the spherical alumina particles (c) in 5 wt% or more and 30 wt% or less, and

having a total of spherical alumina particles (a), spherical alumina particles (b), and spherical alumina particles (c) of 90 wt% or more.

[Claim 7]

A resin composite composition comprising a resin containing a spherical alumina particle mixture according to any one of claims 1 to 6.

[Claim 8]

The resin composite composition according to claim 7, further containing at least one type or more of inorganic filler selected from amorphous spherical alumina particles, crystalline spherical silica particles, alumina particles, titania particles, magnesia particles, aluminum nitride particles, boron nitride particles, barium titanate particles, calcium titanate particles, and carbon fiber.