

DESCRIPTION

TITLE

SPHERICAL CRYSTALLINE SILICA PARTICLES, METHOD FOR PRODUCING SAME,
AND RESIN COMPOSITE COMPOSITION AND RESIN COMPOSITE CONTAINING SAME
FIELD

[0001]

The present invention relates to spherical crystalline silica particles, in particular spherical crystalline silica particles with a low lithium content and a high quartz crystallization rate and a method of producing the same and to a resin composite composition and resin composite containing those spherical crystalline silica particles.

BACKGROUND

[0002]

Silica particles are being used as fillers for resin use, for example, are being used as fillers for sealing materials of semiconductor chips. If the silica particles are sharply angular in shape, their fluidity, dispersibility, and fillability in the resin will deteriorate. To improve these, spherical silica particles are being widely used.

[0003]

In general, the thermal spraying method is being used as the method for producing spherical silica. In thermal spraying, particles are passed through a flame or other high temperature region whereby the particles melt and surface tension causes the particles to become spherical. The particles made spherical by melting are recovered while being conveyed by a stream of gas so that the particles do not fuse together, but after thermal spraying, the particles are rapidly cooled. Since being rapidly cooled from the melted state, the silica will not include much crystals at all but will have an amorphous structure. It forms glass shaped particles called "quartz glass".

[0004]

Since the spherical silica obtained by thermal spraying is amorphous, it is low in thermal expansion coefficient and thermal conductivity. These physical properties are considered equal to the thermal expansion coefficient of quartz glass - which does not have a crystalline structure, but has an amorphous structure. The thermal expansion coefficient is around 0.5 ppm/K while the thermal conductivity is 1.4W/mK.

[0005]

In general, since spherical silica particles used in sealing materials etc. are amorphous, they are low in thermal expansion coefficient. For this reason, when mixed with a resin, they have the effect of lowering the thermal expansion coefficient of the mixture (resin composition). Due to this, it is possible to make the thermal expansion coefficient of the resin composition approach that of

the semiconductor chip. Further, when using a resin composition for a sealing material etc., it is possible to keep down the deformation occurring at the time of heating and cooling in the curing process of the resin etc. However, the thermal conductivity of amorphous silica is not that high. On the other hand, along with the increase in the amount of heat generated accompanying the higher performance of semiconductors, it has been sought to more efficiently disperse the heat generated. Therefore, spherical silica particles with higher thermal conductivity have been considered necessary.

[0006]

Compared with amorphous silica, crystalline silica has a regular, close-packed structure, thus is high in thermal conductivity. As crystal structures of silica, there are cristobalite, quartz, tridymite, etc. Silica having these crystal structures is known to have a higher thermal expansion coefficient and thermal conductivity compared with amorphous silica. In particular, quartz has a more closely packed crystal structure than the other crystals, thus the thermal conductivity is a high 12.8W/mK. Spherical silica particles containing a large amount of quartz are believed to give a high thermal conductivity.

[0007]

Means for obtaining crystalline silica particles have been the subject of various studies up to now.

[0008]

PTL 1 discloses to add a Zn compound to an amorphous silica gel produced by the sol-gel method and heat treat the mixture at 900 to 1100°C to thereby obtain a porous powder mainly comprised of SiO₂, containing the Zn compound, and having a main crystal phase comprised of quartz. It should be noted that the heat treatment is performed in the air atmosphere etc. and no particular pressing is performed. Further, the ratio of content of the crystal phase is not disclosed.

[0009]

PTL 2 discloses spherical crystalline silica particles having a crystal phase as 90 mass% or more of the whole, having quartz crystals as 70 mass% or more of the whole, containing lithium in 0.4 to 5 mass% in oxide equivalent, and/or containing calcium in 1 to 5 mass% in oxide equivalent. The spherical crystalline silica particles are obtained by heat treating the powder material at 800 to 1300°C and then cooling. It should be noted that the heat treatment is performed in an electric furnace, gas furnace, etc. No particular pressing is performed.

[0010]

PTL 3 relates to spherical crystalline silica particles and discloses that the ratio of the crystalline silica phase in the spherical crystalline silica particles is 40.0% or more, the ratio of quartz in the crystalline silica phase is 80.0 mass% or more, lithium is contained in 0.02 mass% or more and less than 0.40 mass% in oxide equivalent, and calcium is contained in 0.004 mass% or more and less than 1.0 mass% in oxide equivalent. The spherical crystalline silica particles are

obtained by heat treating the powder material at 850 to 1150°C. It should be noted that the heat treatment can be performed in an inert gas atmosphere of nitrogen, argon, etc. Further, the atmospheric pressure is considered to be preferably the air pressure since large amounts are heat treated industrially. No particular pressing is performed.

[0011]

PTL 4 relates to a cured product for dental use and discloses that the spherical crystallinity controlled powder contained in the dental use cured product has a content of silicon dioxide of 97 mass% or more and 100 mass% and is comprised of an amorphous part and crystalline part mixed together. The ratio of the amorphous part and crystalline part is controlled by heat treating an amorphous powder material at 600°C to 1700°C. It should be noted that, in the heat treatment, no particular pressing is performed. PTL 4 describes that pressing may be performed at the time of curing, but the specific pressure is not described. Further, the type and ratio of content of the crystals are not particularly specified.

[0012]

PTL 5 discloses powder for spherical silica filler use containing a keatite phase in 80 mass% or more. Keatite is not a general crystal phase like quartz or cristobalite and is mainly synthesized under a high temperature, high pressure, and high steam pressure. In PTL 5, no particular pressing is performed. Spherical amorphous silica particles and a lithium compound are mixed and the mixture is heated at 650 to 725°C for 3 to 20 hours to thereby obtain the powder for spherical silica filler use.

[CITATIONS LIST]

[PATENT LITERATURE]

[0013]

[PTL 1] Japanese Unexamined Patent Publication No. 2002-20111

[PTL 2] WO2018/186308

[PTL 3] WO2021/235530

[PTL 4] Japanese Patent No. 5616672

[PTL 5] Japanese Unexamined Patent Publication No. 2019-52051

SUMMARY

[TECHNICAL PROBLEM]

[0014]

In a semiconductor product, efficient dispersion of the heat generated is sought. In particular, to deal with the increase in the amount of heat generated along with higher performance, high heat conducting materials enabling heat to be dispersed more easily are being sought in semiconductor sealing materials and other peripheral members are well. For this reason, as the filler used for

sealing materials etc., spherical crystalline silica high in thermal conductivity and enabling a high filling rate is useful. Silica includes various crystal forms. In particular, quartz is high in thermal conductivity and preferable.

[0015]

As the method for obtaining spherical crystalline silica, the method has been disclosed of adding an element for promoting crystallization to amorphous spherical silica and heat treating the mixture at a high temperature to crystallize it. However, in general, added elements are liable to affect the properties of the spherical crystalline silica. In particular, in applications of semiconductor sealing material fillers, it is concerned that alkali metals will harm the reliability of electronic devices. Therefore, in spherical crystalline silica, further reduction of lithium is being sought.

[0016]

Further, from the viewpoint of improving the thermal conductivity, in spherical crystalline silica, it is required that the content of crystal be a certain extent or more. This is because if the amorphous content is high, the thermal conductivity will approach that of amorphous silica and sometimes the thermal conductivity will be unable to be sufficiently improved. On top of this, it is required that the main type of crystal be specified. Depending on the type of crystal, the property of thermal conductivity will differ. Therefore, if a plurality of types of crystal are mixed together, the thermal conductivity will fluctuate and the desired thermal conductivity will sometimes be unable to be obtained.

[0017]

PTLs 1 and 4 do not specify the contents of the crystals and the types of the crystals. Further, in the powder for silica filler use of PTL 5, the content of the keatite phase is disclosed to be 80 mass%, but the content of the crystal phase in the powder is not clear. Therefore, in these prior art, sufficient thermal conductivity is liable to be unable to be obtained.

[0018]

The spherical crystalline silica particles of PTL 2 contain a crystal phase in 90 mass% or more of the total. Quartz crystals account for 70 mass% or more of the whole, thus sufficient thermal conductivity can be expected. However, lithium is included in 0.4 to 5 mass% in oxide equivalent. Further, the spherical crystalline silica particles of PTL 3 contain calcium in 0.004 mass% or more and less than 1.0 mass% in oxide equivalent whereby lithium is reduced to 0.02 mass% or more and less than 0.40 mass% in oxide equivalent. However, further reduction of lithium is desired.

[0019]

In view of the above situation, the present invention has as its object the provision of spherical crystalline particles with a low lithium content and a high quartz crystallization rate and a method of producing the same and also a resin composite composition and resin composite containing those spherical crystalline silica particles.

[SOLUTION TO PROBLEM]

[0020]

The inventors engaged in intensive studies so as to solve the above problem and as a result came up with the following idea:

By adding calcium to amorphous silica particles and heat treating the mixture, crystallization to quartz is promoted. That is, calcium is a crystallization promoting element to quartz. However, crystallization to quartz occurs only at the surroundings where calcium is present. That is, the effect of phase transition to quartz by the addition of calcium is local or limited.

In addition, if performing heat treatment to cause crystallization of amorphous silica particles, overall crystallization to cristobalite also occurs. Therefore, in the range to which the effect of addition of calcium does not reach, typically inside of the amorphous silica particles, crystallization not to quartz, but cristobalite proceeds. To promote phase transition of the amorphous silica particles as a whole to quartz, calcium has to be dispersed to the insides of the particles by heat, but the coefficient of dispersion of calcium in amorphous silica is small.

As a result, with merely addition of calcium, the quartz crystallization rate is low. This becomes remarkable in particular in the case of silica particles with a large particle size (typically D50: 10 μm or more). This is because the larger the size of silica particles, the more the specific surface area falls and the more the contact area with calcium falls.

In this way, there are limits to improving the rate of crystallization of quartz by merely the addition of calcium.

On the other hand, it is known that pressure affects the crystallization of amorphous silica, but there are almost no reports in which this is investigated in detail.

Therefore, the inventors conducted crystallization experiments changing the types and amounts of addition of additives to amorphous silica particles and the atmospheric pressure at the time of heat treatment. In particular, the atmospheric pressure was changed up to the high pressure region in high pressure, high temperature treatment using a hot isostatic pressing (HIP) apparatus. As a result, it was discovered that silica with a high quartz crystallization rate can be obtained even if reducing the amount of addition of the lithium element to substantially the level of zero.

[0021]

The gist of the present invention is as follows:

[1] Spherical crystalline silica particles having a circularity of 0.80 or more, having an average particle size (D50) of 1.0 μm or more and 100.0 μm or less, containing lithium in 0.05 mass% or less in oxide equivalent, containing calcium in 0.10 to less than 1.00 mass% in oxide equivalent, having 50.0% or more of the whole comprised of crystalline silica, and having 90.0% or more of the crystalline silica comprised of quartz.

[2] The spherical crystalline silica particles according to [1], containing lithium in 0.02 mass% or

less in oxide equivalent.

[3] The spherical crystalline silica particles according to [1] or [2], wherein cristobalite comprises 5.0% or less of the whole.

[4] The spherical crystalline silica particles according to any one of [1] to [3], containing aluminum in 90 to 9000 ppm.

[5] The spherical crystalline silica particles according to any one of [1] to [4], wherein the average particle size (D50) is 10.0 μm or more.

[6] A method of producing spherical crystalline silica particles comprising a powder material preparing step of mixing a calcium material with spherical amorphous silica particles or mixing in a calcium material and lithium compound particles to obtain a powder material and

a heat treatment step of heat treating the powder material obtained in the powder material preparing step at a temperature of 1125°C or more and 1300°C or less and a pressure of 125 MPa or more using a hot isostatic pressing apparatus for 1 hour or more to form spherical crystalline silica particles, wherein

the ratios of mixture of the calcium material or the calcium material and lithium compound particles in the powder material preparing step are adjusted to make the calcium be present in 0.10 to 1.00 mass% in oxide equivalent and the lithium be present in 0.05 mass% or less in oxide equivalent in the spherical crystalline silica particles formed in the heat treatment.

[7] A resin composite composition comprising a resin in which are contained spherical crystalline silica particles according to any one of [1] to [5].

[8] A resin composite comprised of the resin composite composition according to [7] which has been cured.

[ADVANTAGEOUS EFFECTS OF INVENTION]

[0022]

According to the present invention, spherical crystalline particles with a low lithium content and a high quartz crystallization rate and a method of producing the same and also a resin composite composition and resin composite containing those spherical crystalline silica particles are provided.

DESCRIPTION OF EMBODIMENTS

[0023]

The spherical crystalline silica particles of the present invention have a circularity of 0.80 or more, have an average particle size (D50) of 1.0 μm or more and 100.0 μm or less, contain lithium in 0.05 mass% or less in oxide equivalent,

contain calcium in 0.10 to less than 1.00 mass% in oxide equivalent,
have 50.0% or more of the whole comprised of crystalline silica, and
have 90.0% or more of the crystalline silica comprised of quartz. Below, each identifying
matter will be explained.

[0024]

The spherical crystalline silica particles of the present invention are spherical. The means for
rendering them spherical is not particularly limited. Crushing, polishing, and other means may be
used. In particular, the means of thermal spraying before crystallization is high in productivity and
enables spheroidization at a low cost. Spherical silica particles, when utilized as filler for
semiconductor sealing material use etc., are high in fluidity, dispersibility, and fillability and,
further, enable wear of equipment for manufacturing the sealing material to be suppressed.

[0025]

(Circularity: 0.80 or More)

More specifically, the spherical crystalline silica particles of the present invention may have
an average circularity of 0.80 or more, preferably 0.85, more preferably 0.90 or more. The
circularity can be measured by a commercially available flow type particle image analyzer. When
the circularity = 1, it is a true circle. That is, the closer the circularity to 1, the nearer to a true circle.
The average circularity is calculated as the average value of the circularity measured for 100 or
more particles. If the average circularity is less than 0.80, if utilized as a filler for semiconductor
sealing material use etc., sometimes the fluidity, dispersibility, and fillability are not sufficient or
wear of the equipment for manufacturing the sealing material is promoted.

The upper limit of the circularity may be 1.0 as well, but actually making the circularity 1.0 is
de facto difficult. If trying to realize it, the production costs and management costs become high. In
accordance with the application etc., the upper limit of the circularity may be 0.98, preferably 0.95.

[0026]

To obtain the above average circularity, it is possible to adjust the circularity of the amorphous
spherical silica particles (particles before crystallization) used as the starting material. If using
thermal spraying means, it is possible to easily make the silica powder into high circularity
particles. Further, the average circularity of the spherical crystalline silica particles of the present
invention does not fall much at all before and after heat treatment for crystallization. This is
because spherical crystalline silica particles of the present invention are rendered crystalline at 1125
to 1300°C and, in that temperature range, the circularity does not fall much at all. Further,
amorphous silica particles sometimes bond with each other by fusion or sintering at 1125 to
1300°C or so, but the spherical crystalline silica particles of the present invention are crystalline
(are already not amorphous), thus bonding by fusion or sintering at 1125 to 1300°C or so is
sufficiently suppressed. If bonding, the circularity falls, but bonding of the spherical crystalline
silica particles of the present invention is sufficiently suppressed, thus the average circularity does

not fall much at all. Therefore, the spherical crystalline silica particles of the present invention can raise the fluidity, dispersibility, and fillability when used as filler for a semiconductor sealing material etc.

[0027]

(Average Particle Size (D50): 1.0 μm or More and 100.0 μm or Less)

The spherical crystalline silica particles of the present invention have an average particle size (D50) of 1.0 to 100.0 μm . 10.0 μm or more is also possible. If the average particle size is more than 100.0 μm , if utilized as filler for a semiconductor sealing material etc., the particle size becomes too large and sometimes gate clogging or mold wear is easily caused. If the average particle size is less than 1.0 μm , the particles become too small and sometimes the viscosity of the resin composition comprised of the silica particles and resin mixed together is excessively raised and filling in a large amount becomes no longer possible. It should be noted that, the average particle size here can be found by measurement of the particle size distribution by the wet laser diffraction method (laser diffraction scattering method).

The “average particle size” referred to here is referred to as the “median size”. The particle size when measuring the particle size distribution by the laser diffraction method and when the cumulative frequency of the particle size becomes 50% is made the average particle size (D50).

[0028]

To make the particle size this range, it is possible to adjust the particle size of the amorphous spherical silica particle material (particles before crystallization). If using the thermal spraying means, it is possible to easily adjust the particle size. In other words, the average particle size of the spherical crystalline silica particles of the present invention does not change much at all before and after the heat treatment for crystallization. Amorphous silica particles soften even at 1125 to 1300°C or so and sometimes bond by fusion or sintering, but the spherical crystalline silica particles of the present invention are crystalline and do not soften like amorphous particles, thus are sufficiently kept from bonding by fusion or sintering at 1125 to 1300°C or so. In particular, particles bond by fusion or sintering more easily the larger the surface area ratios of the particles, i.e., the smaller the particle sizes. However, the spherical crystalline silica particles of the present invention are crystalline, therefore even if the average particle size is 1.0 μm , the particles do not bond by fusion or sintering and are resistant to agglomeration. Therefore, the spherical crystalline silica particles of the present invention can raise the fluidity, dispersibility, and fillability when utilized as filler for semiconductor sealing material use etc.

Further, the temperature at which particles fuse or sinter changes due to the particle size of the amorphous spherical silica material and the type and amount of addition of the added constituents, thus heat treatment is desirably performed at a suitable temperature where no fusing or sintering occurs, depending on the materials and added constituents, even in the 1125 to 1300°C temperature range.

[0029]

(Lithium Content: 0.05 Mass% or Less in oxide equivalent)

The spherical crystalline silica particles of the present invention contain lithium in 0.05 mass% or less in oxide equivalent based on the total mass of the spherical crystalline silica particles.

5 Lithium is one type of alkali metal. An alkali metal is liable to detract from the reliability of electronic devices. Therefore, the lower the lithium content of the silica particles, the better the reliability of an electronic device using those silica particles as a filler. On this point, the lower the lithium content, the better. In oxide equivalent, it may be less than or equal to or less than 0.03 mass%, may be less than or equal to or less than 0.02 mass%, and may be less than or equal to or
10 less than 0.01 mass%. Further, the lower limit of the lithium content is not prescribed and may even be 0. The lithium in the present invention is not limited to one which is proactively added and may also be an impurity contained in the amorphous silica particle materials etc. Further, to adjust the lithium content, lithium or a lithium compound may be mixed with the amorphous silica particle materials etc. The lithium compound may be an oxide, carboxide, hydroxide, nitrate, etc., i.e., is not
15 particularly limited in form at the time of addition.

In general, lithium can be present inside silica particles in which crystallization is to be promoted in the form of an oxide, carboxide, hydroxide, nitrate, etc. or composite oxide with silica. The majority of it is substantially present in the form of an oxide. Therefore, unless particularly indicated otherwise, in the present invention, the lithium content is calculated in oxide equivalent.
20 Specifically, the content of lithium is obtained by measuring the content by ICP mass spectrometry (ICP-MS) and converting the content to oxides.

[0030]

(Calcium Content: 0.10 Mass% or More and Less Than 1.00 Mass% in oxide equivalent)

The spherical crystalline silica particles of the present invention contain calcium in 0.10
25 mass% or more and less than 1.00 mass% in oxide equivalent based on the total mass of the spherical crystalline silica particles. Calcium promotes the crystallization of amorphous silica by heating it together with the amorphous silica. If the calcium content is less than 0.10 mass%, the crystallization is liable to not sufficiently proceed. The higher the calcium content, the higher the effect of promotion of crystallization. From that viewpoint, the calcium content may be made 0.20
30 mass% or more. However, if the content of calcium is 1.00 mass% or more, if heating it with amorphous silica, the calcium and silica will react and for example a silicic acid compound such as $\text{Ca}_2(\text{SiO}_4)$ becomes easily formed. In particular, if a high pressure, that possibility becomes further higher. Such a compound is easily formed at the outer circumference of the silica particles thereby causing the particles to deform in shape and lower the circularity of the particles, or the silicic acid
35 compound becomes present as irregular fine particles, thus is liable to cause the fluidity to drop when mixed with the resin. Therefore, the upper limit of the calcium content is less than 1.00 mass%, preferably less than or equal to or less than 0.90 mass%, more preferably less than or equal

to or less than 0.80 mass% or less.

It should be noted that to adjust the calcium content, calcium or a calcium compound may be mixed with the amorphous silica particle material etc. The calcium compound may be an oxide, carboxide, hydroxide, nitrate, etc., i.e., is not particularly limited in form at the time of addition.

The silica used as the material for the amorphous silica particles often contains calcium compounds as impurities, thus it is also possible to prepare a silica material or amorphous silica particles with suitable ranges of content in oxide equivalent and adjust them to the above preferable ranges.

In general, calcium can be present inside silica particles in which crystallization is to be promoted in the form of an oxide, carboxide, hydroxide, nitrate, etc. or composite oxide with silica. The majority of it is substantially present in the form of an oxide. Therefore, unless particularly indicated otherwise, in the present invention, the calcium content is calculated in oxide equivalent. Specifically, the content of calcium is obtained by measuring the content by ICP mass spectrometry (ICP-MS) and converting the content to oxides.

[0031]

(Aluminum)

In one aspect of the present invention, the spherical crystalline silica particles may contain 90 to 9000 ppm of aluminum in metal aluminum equivalent based on the total mass% of the spherical crystalline silica particles.

If using calcium for promoting crystallization of amorphous silica particles, it is preferable to include 90 to 9000 ppm of aluminum in metal aluminum equivalent. While not being bound by any specific theory, aluminum acts as an agent for forming crystal nuclei at the time of heat treatment and, when used together with calcium, gives rise to the effect of production of a large amount of quartz crystals. However, if aluminum is less than 90 ppm in metal aluminum equivalent, a sufficient effect of promoting crystallization cannot be obtained. Further, if aluminum becomes greater than 9000 ppm in metal aluminum equivalent, composite oxides containing calcium, aluminum, and the silicon contained in silica become easily formed, therefore, the effect of promotion of crystallization by addition of calcium becomes smaller and cristobalite becomes easily formed due to the increase in Al. That is, excessive aluminum is liable to reduce the amount of formation of quartz crystals. Based on the above, the aluminum content may also be made 100 ppm or more and may be made 8200 ppm or less.

It should be noted that, to adjust the aluminum content, aluminum or an aluminum compound may be mixed in the amorphous silica particle material etc. As the aluminum compound, aluminum oxide, aluminum hydroxide, etc. may be used. The silica used as the material for the amorphous silica particles often contains aluminum compounds as impurities, thus it is also possible to prepare a silica material or amorphous silica particles with a suitable range of content in metal aluminum equivalent to adjust them to the above preferable ranges.

Further, the content of aluminum is obtained by measurement by ICP mass spectrometry (ICP-

MS).

[0032]

Furthermore, in one aspect of the present invention, the spherical crystalline silica particles may contain metal impurities in a range not affecting the crystallinity. Typically, as metal
5 impurities, alkali metals (potassium, sodium, etc.), alkali earth metals (magnesium, barium, etc.) etc. may be mentioned.

[0033]

(Crystalline Silica: 50.0% or More of Spherical Crystalline Silica Particles)

In the spherical crystalline silica particles of the present invention, crystalline silica comprises
10 50.0% or more as a whole. In this case, “as a whole” indicates the spherical crystalline silica particles as a whole.

If the crystalline silica comprises less than 50.0%, the ratio of amorphous silica becomes 50.0% or more. The thermal conductivity of amorphous silica is a low 1.4W/mK, thus sometimes if containing amorphous silica in 50.0% or more, the thermal conductivity of the silica particles end
15 up being lowered. The higher the ratio of crystalline silica, the higher the thermal conductivity becomes, thus the more preferable. Therefore, the ratio of crystalline silica may be 60.0% or more, preferably may be 70.0% or more, more preferably may be 80.0% or more, still more preferably may be 90.0% or more. The upper limit of the ratio of crystalline silica is not particularly prescribed. In accordance with the application, typically, it may be adjusted in accordance with the
20 desired thermal conductivity. Therefore, the upper limit of the ratio of crystalline silica may be 100% and may be 95% or less or may be 90% or less, may be 85% or less, and may be 80% or less.

The contents of the crystal phase and amorphous phase can be quantitatively analyzed by X-ray diffraction. In quantitative analysis by X-ray diffraction, by using a method of analysis such as the Rietveld method, it is possible to perform quantitative analysis without using standard
25 specimens.

More particularly, the ratio of crystalline silica with respect to the spherical crystalline silica particles as a whole (below, sometimes also called the “crystallinity”) is determined by finding the integrated areas of amorphous peaks and crystalline peaks by X-ray diffraction and deeming the ratio of crystalline areas to be the crystallinity. That is, the crystallinity is calculated as the
30 integrated area of crystalline peaks/(integrated area of amorphous peaks+integrated area of crystalline peaks).

[0034]

(Quartz: 90.0% or More of Crystalline Silica)

In the spherical crystalline silica particles of the present invention, quartz comprises 90.0% or
35 more of the crystalline silica. Quartz has a thermal conductivity of 12.8W/mK or far larger than the thermal conductivity of 1.4W/mK of amorphous silica. In the spherical crystalline silica particles of the present invention, crystalline silica comprises 50.0% or more of the particles as a whole and

quartz crystal comprises 90.0% or more of the crystalline silica, thus a desirable high thermal conductivity can be obtained.

Crystalline silica may contain cristobalite, tridymite, and other crystal forms as a crystal phase other than quartz. These crystals also have thermal conductivities of 10W/mK or so. While lower
5 than the 12.8W/mK of quartz, they have thermal conductivities higher than amorphous silica.

However, if the content of quartz is less than 90.0%, in other words, if the content of cristobalite, tridymite, etc. is 10.0% or more, a phase transition from α -cristobalite $\rightarrow\beta$ -cristobalite or a phase transition from α -tridymite $\rightarrow\beta$ 1 tridymite $\rightarrow\beta$ 2 tridymite occurs. Due to the expansion of volume accompanying the phase transitions, when used mixed with a resin, sometimes gaps are
10 formed between the resin and silica particles and become causes of fracture or cracks. For this reason, it is important that 90.0% or more of the crystalline silica be made quartz and that the content of cristobalite or tridymite be made smaller. On this point, the smaller the content of cristobalite, tridymite, etc., the more preferable. Therefore, in one aspect of the present invention, the content of cristobalite and/or tridymite may be 5.0% or less of the spherical crystalline silica
15 particles as a whole.

In the same way as the contents of the crystal phase and amorphous phase, the contents of quartz, cristobalite, tridymite, and other crystals can be quantitatively analyzed by X-ray diffraction. In quantitative analysis by X-ray diffraction, by using a method of analysis such as the Rietveld method, it is possible to perform quantitative analysis without using standard specimens.

More particularly, the ratios of the different crystal forms with respect to the crystalline silica are found by finding the integrated areas of the peaks of the different crystal forms by X-ray diffraction and finding the ratios from the ratios of the areas of these crystals. As one example, the ratio of crystals of quartz is calculated as the integrated area of peaks of quartz/(integrated area of peaks of quartz+integrated area of peaks of cristobalite+integrated area of peaks of
20 tridymite+integrated area of peaks of other crystal forms).

[0035]

(Method of Production)

The spherical crystalline silica particles of the present invention can be produced by a method including the following steps. That is, the method of production of spherical crystalline silica
30 particles of the present invention comprises

a powder material preparing step of mixing a calcium material with spherical amorphous silica particles or mixing in a calcium material and lithium compound particles to obtain a powder material and

a heat treatment step of heat treating the powder material obtained in the powder material preparing step at a temperature of 1125°C or more and 1300°C or less and a pressure of 125 MPa or more using a hot isostatic pressing apparatus for 1 hour or more to form spherical crystalline silica particles, wherein
35

the ratio of mixture of the calcium material or the calcium material and lithium compound particles in the powder material preparing step is adjusted to make the calcium be present in 0.10 to 1.00 mass% in oxide equivalent and the lithium be present in 0.05 mass% or less in oxide equivalent in the spherical crystalline silica particles formed in the heat treatment step.

[0036]

(Spherical Amorphous Silica Particles)

The spherical amorphous silica particle material can be fabricated by the thermal spraying method etc. For example, in the thermal spraying method, silica powder crushed to adjust it to the desired particle size is passed through a flame whereby the particles melt and surface tension causes the particles to become spherical.

[0037]

To prevent the particles melted and made spherical by thermal spraying from fusing with each other, the thermally sprayed particles may be rapidly cooled. In this case, since they are rapidly cooled from the molten state, the spherical silica particles do not have crystalline structures, but have amorphous structures. Since the spherical silica particles are thermally sprayed, they may also be nonporous. Nonporous spherical silica particles are dense and are expected to become high in thermal conductivity.

[0038]

Using thermal spraying etc., the spherical amorphous silica particles can be given an average circularity of 0.80 or more. The subsequent heat treatment for crystallization features a maximum temperature of 1300°C or so, therefore the circularity of the spherical silica particles does not change much at all. The circularity sometimes changes due to sticking in the process of transition from amorphous silica particles to crystalline silica particles, but if crushing the particles, it is possible to obtain crystalline silica particles of substantially the same circularity as the original amorphous silica particles. That is, if using amorphous silica particles with a circularity of 0.80 or more, the crystalline silica particles obtained by heat treatment also become particles with a circularity of 0.80 or more in range. The crushing may be performed by a tumbling ball mill, rocking mixer, bead mill, or other general mixer or mill. If the circularity changes by heat treatment, it is possible to confirm the rate of change of the circularity by advance tests or advance investigation and adjust the circularity of the spherical amorphous silica particles before heat treatment based on the results of confirmation. Further, with the thermal spraying means, it is possible to easily obtain spherical amorphous silica particles with a high average circularity. For this reason, with the method of the present invention, spherical crystalline silica particles with a circularity of 0.8 or more can be easily realized. Only naturally, if using spherical amorphous silica particles with an average circularity of less than 0.80, the method of the present invention can be used to obtain spherical crystalline silica particles with an average circularity of less than 0.80.

[0039]

The spherical amorphous silica particles obtained by thermal spraying etc. may have an average particle size (D50) of 1.0 to 100.0 μm or 10.0 μm or more. The subsequent heating and cooling steps for crystallization feature a maximum temperature of 1300°C or so, therefore the particle size of the spherical silica particles does not change much at all. The average particle size D50 sometimes changes due to sticking in the process of transition from amorphous silica particles to crystalline silica particles, but if crushing the particles, it is possible to obtain crystalline silica particles with substantially the same average particle size as the original amorphous silica particles. That is, if using amorphous silica particles with a D50 of 1.0 μm or more and 100 μm or less, the crystalline silica particles obtained by heat treatment also become particles with a D50 of 1.0 μm or more and 100 μm or less in range. Due to heat treatment, silica powder sometimes lightly sticks together, but by crushing, it becomes powder of equal to the original average particle size. The crushing may be performed by a tumbling ball mill, rocking mixer, bead mill, or other general mixer or mill. If the average particle size (D50) changes by heat treatment, it is possible to confirm the rate of change of the average particle size (D50) by advance tests or advance investigation and adjust the average particle size (D50) of the spherical amorphous silica particles before heat treatment based on the results of confirmation. Further, with the thermal spraying means, it is possible to easily adjust the particle size of spherical amorphous silica particles. For this reason, with the method of the present invention, spherical crystalline silica particles with an average particle size (D50) of 1.0 to 100.0 μm can be easily realized. Further, spherical crystalline silica particles with an average particle size (D50) of 10.0 μm or more can be easily realized. Only naturally, if using spherical amorphous silica particles with an average particle size (D50) of less than 1.0 μm , the method of the present invention can be used to obtain spherical crystalline silica particles with an average particle size (D50) of less than 1.0 μm . Further, if using spherical amorphous silica particles with an average particle size (D50) of 10.0 μm or more, it is possible to obtain spherical crystalline silica particles with an average particle size (D50) of 10.0 μm or more by the method of the present invention. Furthermore, if using spherical amorphous silica particles with an average particle size (D50) of more than 100.0 μm , it is possible to obtain spherical crystalline silica particles with an average particle size (D50) of more than 100.0 μm by the method of the present invention.

[0040]

Further, the silica powder may be prepared so that the silica powder before thermal spraying includes 90 to 9000 ppm of aluminum. While not being bound by any specific theory, aluminum is believed to act as an agent for forming crystal nuclei at the time of heat treatment. Through the thermal spraying step (melting), the aluminum is evenly dispersed in the silica particles. Aluminum is believed to act as an agent for forming crystal nuclei at the time of the subsequent heat treatment step. By being evenly dispersed in the silica particles, crystal growth is realized evenly and at a lower temperature and shorter time than the past.

Further, with alumina, obtained by oxidation of aluminum, the effect of improving the chemical durability (oxidation resistance etc.) of silica particles can also be expected. If the content of aluminum is less than 90 ppm, sometimes the effect of promotion of crystallization or the effect or improvement of chemical durability will not be sufficient. On the other hand, aluminum and alumina are known to have the effect of lowering the melting point of silica. For example, the melting point of alumina silica glass is lower than the melting point of pure silica glass. For this reason, if the content of aluminum becomes more than 9000 ppm, the melting point of the silica particles falls and, during heat treatment, the silica particles will easily bond together by fusion or sintering. If the particles continue to be bonded together, when utilized as filler for semiconductor sealing material use etc., the fluidity, dispersibility, and fillability will not be sufficient and, further, wear of the equipment for producing the sealing material will also be promoted. Further, in a semiconductor sealing material, in general a high purity is considered necessary. Adding aluminum in 9000 ppm or more sometimes is not suitable.

Further, the presence of aluminum has the effect of promoting crystallization when causing crystallization of amorphous silica particles by mixing in calcium.

Further, the content of aluminum can be measured by ICP mass spectrometry (ICP-MS).

The content of aluminum does not change much at all even at the stage of heat treatment for causing crystallization. Further, the mass of the silica particles also does not change much at all before and after heat treatment. For this reason, it is possible to use spherical silica particles containing 90 to 9000 ppm of aluminum to obtain the effect of promotion of crystallization. If the content of aluminum changes due to the heat treatment, it is possible to confirm the rate of change of the content of aluminum by advance tests or advance investigation and adjust the content of aluminum of the spherical amorphous silica particles before heat treatment based on the results of confirmation.

[0041]

Further, the silica powder before thermal spraying may include metal impurities in a range not affecting crystallization. Typically, as metal impurities, alkali metals (potassium, sodium, etc.), alkali earth metals (magnesium, barium, etc.) etc. may be mentioned.

[0042]

(Calcium Material)

For the calcium material, the carboxide CaCO_3 or hydroxide Ca(OH)_2 may be used. CaCO_3 and Ca(OH)_2 are more chemically stable compared with the oxide CaO and are lower in danger safety-wise, thus handling is comparatively easy. Further, if using CaCO_3 or Ca(OH)_2 , the decomposition temperature of CaCO_3 is 825°C . Compared with this, Ca(OH)_2 breaks down into CaO at the lower 580°C temperature. For this reason, it is believed that use of Ca(OH)_2 has the effect of promoting crystallization since it breaks down into CaO at a low temperature and gives rise to the effect of crystallization to quartz as a low temperature type of crystal of silica.

[0043]

(Lithium Compound Particles)

For the lithium compound particles, the carboxide Li_2CO_3 may be used. Li_2CO_3 is low in solubility and low in danger safety-wise if mixed with water, thus handling is relatively easy.

Further, Li_2CO_3 melts at 710°C , but it is believed it reacts with SiO_2 at the melting point or less temperature and is taken into the SiO_2 particles. By Li being taken into SiO_2 at such a low temperature, the effect of promotion of crystallization at a low temperature can be expected. On the other hand, lithium is one type of alkali metal. An alkali metal is liable to detract from the reliability of electronic devices. For this reason, lithium compound particles need not be proactively added. They are optionally mixed together with the spherical amorphous silica particles. Further, the lithium included in the spherical crystalline silica particles after heat treatment may also be derived from the impurities included in the amorphous silica particle material etc.

[0044]

(Powder Material Preparing Step)

In the powder material preparing step, a calcium material is mixed with the spherical amorphous silica particles or a calcium material and lithium compound particles are mixed with them to obtain the powder material.

[0045]

The calcium material and lithium compound particles mixed with the spherical amorphous silica particles may be oxides, carboxides, hydroxides, nitrates, etc., i.e., are not particularly limited in the form when added. If uniformly mixed with amorphous spherical silica particles, they may be added in the form of powder, aqueous solutions, etc. The method of mixture is not particularly limited so long as the materials are mixed uniformly dispersed in the mixture. The mixing may also be performed by a powder mixer. Due to the mixing, the calcium material and lithium compound particles contact at least part of the spherical amorphous silica whereby crystallization of the spherical amorphous silica, in particular crystallization to quartz, is promoted in the next heat treatment step.

[0046]

Here, the ratios of mixture of the calcium material or the calcium material and lithium compound particles are adjusted so that in the spherical crystalline silica particles produced in the heat treatment, the calcium becomes 0.10 to 1.00 mass% in oxide equivalent and the lithium becomes 0.05 mass% or less in oxide equivalent. It should be noted that the above mass% is based on the total of the mass of the spherical crystalline silica particles as 100 mass%. The powder material obtained by this mixing has generally the same mass ratios even at the subsequent stage of heat treatment for causing crystallization. However, the total amount of the mixed calcium material and lithium compound particles is sometimes not contained in the spherical crystalline silica particles after heat treatment, thus the ratios of mixture are adjusted considering the yield.

Typically, if there are differences in the compositions of the powder material and spherical crystalline silica particles, it is possible to confirm the differences in composition by advance tests or advance investigation and adjust the ratios of mixture of calcium material or the calcium material and lithium compound particles in the powder material before heat treatment based on the results of confirmation. It should be noted that adjustment of these includes “no adjustment” depending on the results of advance confirmation. As a specific example, it is possible to conduct tests on reducing the lithium and calcium used under the heat treatment conditions for crystallization under the same conditions in advance to find the conditions for operation. Therefore, by using the powder material, it is possible to obtain the lithium content and calcium content in the spherical crystalline silica particles of the present invention.

[0047]

(Heat Treatment Step)

The powder material obtained by mixing is heat treated using a hot isostatic pressing apparatus at 1125°C or more and 1300°C or less under an atmospheric pressure of 125 MPa or more for 1 hour or more. In the heat treatment step, the calcium material and/or lithium compound particles contained in the powder material disperse to the insides of the spherical amorphous silica particles, therefore crystallization of the spherical amorphous silica particles to quartz is promoted.

[0048]

The heat treatment temperature is 1125°C or more and 1300°C or less.

If less than 1125°C, the crystallization of the amorphous silica is not sufficiently promoted and sometimes spherical crystalline silica particles where 50.0% or more of the whole comprises crystalline silica is not obtained. Further, if more than 1300°C, the crystallization of the amorphous silica is sufficiently promoted, but in the obtained crystalline silica, crystals other than quartz, in particular cristobalite, are sometimes contained in large amounts. That is, spherical crystalline silica particles where 90.0% or more of the crystalline silica comprises quartz sometimes cannot be obtained. The rate of temperature rise until the heat treatment temperature is not particularly limited, but if the rate of temperature rise is too slow, the productivity will sometimes fall while if the rate of temperature rise is too fast, excessive equipment performance becomes necessary, thus the rate may be 2°C/min to 20°C/min.

[0049]

The atmospheric pressure is 125 MPa or more. The crystallization of amorphous silica is sufficiently promoted by suitable heat treatment, but in crystalline silica obtained by a low atmospheric pressure, sometimes crystal forms other than quartz, in particular cristobalite, are included in large amounts. That is, at less than 125 MPa, sometimes spherical crystalline silica particles where 90.0% or more of the crystalline silica is comprised of quartz cannot be obtained. It is believed that the higher the pressure, the more the formation of quartz is promoted. The atmospheric pressure may also be 147 MPa or more. The upper limit of pressure is not particularly

prescribed, but there are limits to the capacity of apparatuses. Typically, the upper limit may be approximately 200 MPa or may be 196 MPa.

[0050]

The heat treatment time is 1 hour or more.

5 If the heat treatment time is less than 1 hour, the crystallization of the amorphous silica will not sufficiently be promoted and sometimes spherical crystalline silica particles where 50.0% or more comprises crystalline silica will not be obtainable. In general, the longer the heat treatment time, the more crystallization is promoted. On the other hand, there is also a possibility of cristobalite and other crystal forms to be formed besides quartz. Therefore, the heat treatment time
10 can be suitably adjusted so that the desired crystallization rate and quartz formation rate are obtained. For this reason, the upper limit of the heat treatment is not particularly prescribed, but considering productivity etc., it may be made 24 hours or less, 20 hours or less, 16 hours or less, or 12 hours or less.

[0051]

15 In the present invention, the heat treatment is performed by a hot isostatic pressing apparatus. A hot isostatic pressing apparatus is a pressing apparatus utilizing the synergistic effects of pressure and temperature. Typically, a treated object can be treated by simultaneously applying a high temperature of several 100 to 2000°C and an isotropic pressure of several 10 to 200 MPa.

[0052]

20 While not desiring to be bound by any specific theory, the reason why high temperature, high pressure heat treatment enables spherical crystalline silica particles having a high quartz formation rate to be obtained is believed to be as follows:

It is known that even under ordinary pressure (not under high pressure), by heat treating amorphous silica, crystallization of the amorphous silica is promoted. Furthermore, by mixing a
25 calcium material into amorphous silica, the calcium contained in the calcium material promotes crystallization, in particular quartz formation. However, the effect by calcium is limited to locations contacting the amorphous silica particles. For this reason, crystallization (quartz formation) inside the amorphous silica particles is difficult to promote. On the other hand, inside the amorphous silica particles, sometimes cristobalite formation is promoted due to the effects of heat treatment
30 (temperature). That is, spherical crystalline particles with a high quartz crystallization rate become hard to obtain. According to the present invention, by performing heat treatment at a pressure of 125 MPa or more, calcium easily disperses by the heat to the inside of the amorphous silica particles and crystallization (quartz formation) is promoted even inside the amorphous silica particles. As a result, it is believed that spherical crystalline silica particles having a high quartz
35 formation rate are obtained.

Further, in general, the larger the particle size of particles, the smaller the specific surface area becomes, the more heat dispersion of calcium is not promoted, and the more difficult it is to obtain

spherical crystalline silica particles having a high quartz formation rate. According to the present invention, it is possible to obtain a high quartz formation rate even with such large particle size particles, typically even if the average particle size (D50) is 10.0 μm or more.

[0053]

(Applications of Spherical Crystalline Silica Particles)

According to one aspect of the present invention, it is possible to produce a composite composition of the finally obtained spherical crystalline silica particles and resin and further a resin composite obtained by curing the resin composite composition. The composition of the resin composite composition will be explained below.

[0054]

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

[0055]

If producing the resin composite composition, for example, in addition to the spherical crystalline silica particles and resin, a curing agent, curing accelerator, flame retardant, silica coupling agent, etc. are blended in accordance with need and formed into a composite by kneading or other known method. Further, the composite is shaped into pellets, a film, etc. in accordance with the application.

[0056]

Furthermore, if curing the resin composite composition to produce a resin composite, for example, heat is added to the resin composite composition to make it melt, the composition is worked into a shape suitable for the application, and a heat higher than the time of melting is applied to make the composition completely cure. In this case, it is possible to use the transfer mold method or other known method.

[0057]

For example, if producing package boards, interlayer insulating films, or other semiconductor related materials, resins known as resins used for resin composite compositions can be applied, but an epoxy resin is preferably employed. 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 also possible to use single types among these alone or use two types having different molecular weights or more together. Among these in particular, from the viewpoint of the curability, heat resistance, etc., an epoxy resin having two or more epoxy groups in one molecule is preferable. Specifically, a biphenyl type epoxy resin, phenol novolac type epoxy

resin, o-cresol novolac type epoxy resin, phenol type and aldehyde type novolac resin which is epoxylated, bisphenol A, bisphenol F, bisphenol S, or other glycidyl ether, a glycidyl ester acid epoxy resin obtained by a reaction of phthalic acid or dimer acid or other polybasic acid and epichlorohydrin, linear aliphatic epoxy resin, alicyclic epoxy resin, heterocyclic epoxy resin, alkyl-
5 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, further, an epoxy resin in which bromine or other halogen is introduced for imparting flame retardancy, etc. may be mentioned. Among epoxy resins having two or more epoxy groups in a single molecule, in particular a bisphenol A type epoxy resin is
10 preferable.

[0058]

Further, as the resin used for applications other than composite materials for semiconductor sealing material use, for example, prepregs for printed circuit board use, various engineering plastics, and other resin composite compositions, resins other than epoxy types can also be used.
15 Specifically, in addition to epoxy resins, silicone resins, phenol resins, melamine resins, urea resins, unsaturated polyesters, fluororesins, polyimides, polyamide imides, polyether imides, and other polyamides; polybutylene terephthalates, polyethylene terephthalates, and other polyesters; polyphenylene sulfides, aromatic polyesters, polysulfones, liquid crystal polymers, polyether sulfones, polycarbonates, maleimide modified resins, ABS resins, AAS (acrylonitrile-acrylic
20 rubber-styrene) resins, and AES (acrylonitrile-ethylene-propylene-diene rubber-styrene) resins may be mentioned.

[0059]

As the curing agent used for the resin composite composition, a known curing agent may be used to cure the resin, but for example a phenolic curing agent can be used. As the phenolic curing
25 agent, a phenol novolac resin, alkylphenol novolac resin, polyvinyl phenols, etc. can be used alone or in combinations of two or more types.

[0060]

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

[0061]

The amount of addition of the spherical crystalline silica particles of the present invention in the resin composite composition is preferably large from the viewpoint of the heat resistance and
35 thermal expansion coefficient, but is 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. This is because if the amount of the spherical crystalline silica particles is too small, the

improvement of the sealing material strength, suppression of thermal expansion, and other effects become hard to obtain, while conversely if too large, regardless of the surface treatment of the spherical crystalline silica particles, segregation easily occurs due to agglomeration of spherical crystalline silica particles at the composite material, the viscosity of the composite material also becomes too great, and other problems arise due to which practical application as a sealing material becomes difficult.

[0062]

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

EXAMPLES

[0063]

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

[0064]

(Example 1 to Example 4)

Amorphous silica particles were prepared by the thermal spraying method. In the thermal spraying, powder obtained by mixing in calcium in 0.80 mass% in oxide equivalent with respect to the mass of the total of the mass of crushed shaped silica and mass of calcium in oxide equivalent was used as a material. The spherical amorphous silica particles (average particle size d₅₀: 27.8 μm, circularity 0.92) were filled in containers made of BN (boronitride) and heat treated under isotropic pressure by a hot isostatic pressing (HIP) apparatus of Kobe Steel Corporation using nitrogen gas as a pressure medium. The holding temperatures were made 1150°C in Example 1, 1200°C in Example 2, 1250°C in Example 3, and 1300°C in Example 4. The samples were held for 12 hours in Example 1, 8 hours in Example 2 and Example 3, and 1 hour in Example 4. The rates of temperature rise were made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 196 MPa.

[0065]

(Example 5 to Example 17)

The amorphous spherical silica powder used was the one used in Example 1 to Example 4. Lithium carbonate powder was mixed with the amorphous spherical silica. Lithium carbonate particles were mixed in by 0.01 mass% in Example 5 to Example 8, 0.02 mass% in Example 9, 0.03 mass% in Example 10 to Example 13, and 0.05 mass% in Example 14 to Example 17 in oxide equivalent with respect to the mass of the total of the mass of spherical amorphous silica and mass of lithium in oxide equivalent. The mixed powders were filled in containers made of BN and heat treated under isotropic pressure by an HIP apparatus using nitrogen gas as a pressure medium. The

holding temperatures were made 1125°C in Example 14, 1150°C in Example 15, 1200°C in Example 5, Example 6, Example 9, Example 10, Example 11, and Example 16, 1250°C in Example 7, Example 12, and Example 17, and 1300°C in Example 8 and Example 13. The holding times were made 1 hour in Example 5, Example 8, Example 9, Example 10, Example 13, and Example 17 and 8 hours in Example 6, Example 7, Example 11, Example 12, Example 14, Example 15, and Example 16. The rates of temperature rise were made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 196 MPa.

[0066]

(Example 18)

The amorphous spherical silica powder used in Example 1 to Example 4 was used. The amorphous spherical silica powder was filled in a container made of BN and heat treated under isotropic pressure by an HIP apparatus using nitrogen gas as a pressure medium. The holding temperature was made 1250°C, the holding time was made 8 hours, and the rate of temperature rise was made approximately 600°C/h. The nitrogen gas holding pressure at the holding temperature was made 147 MPa.

[0067]

(Example 19 and Example 20)

The amorphous spherical silica powder used in Example 1 to Example 4 was used. Lithium carbonate powder was mixed with the amorphous spherical silica powder. Lithium carbonate particles were mixed in by 0.01 mass% in oxide equivalent with respect to the mass of the total of the mass of spherical amorphous silica and mass of lithium in oxide equivalent. The mixed powders were filled in containers made of BN and heat treated under isotropic pressure by an HIP apparatus using nitrogen gas as a pressure medium. The holding temperatures were made 1250°C, the holding times were made 8 hours, and the rates of temperature rise were made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 147 MPa in Example 19 and 125 MPa in Example 20.

[0068]

(Example 21 to Example 31)

Amorphous silica particles were prepared by the thermal spraying method. Calcium hydroxide and lithium carbonate were mixed with the spherical amorphous silica particles (average particle size d₅₀: 30.2 μm, circularity 0.91). Calcium hydroxide particles were mixed in by 0.20 mass% in oxide equivalent and lithium carbonate by 0 mass% in Example 21, 0.01 mass% in Example 22 to Example 24, 0.03 mass% in Example 25, and 0.05 mass% in Example 26 to Example 31 in oxide equivalent with respect to the mass of the total of the mass of spherical amorphous silica and mass of calcium in oxide equivalent and mass of lithium in oxide equivalent. The mixed powders were filled in containers made of BN and heat treated under high isotropic pressure by a HIP apparatus using nitrogen gas as a pressure medium. The holding temperatures were made 1250°C and the

holding times were made 8 hours in Example 21, Example 23, Example 25, Example 29, and Example 31, the holding temperature was made 1150°C and the holding time was made 12 hours in Example 22, the holding temperatures were made 1300°C and the holding times were made 1 hour in Example 24 and Example 30, the holding temperature was made 1125°C and the holding time was made 12 hours in Example 26, the holding temperatures were made 1200°C and the holding time were made 8 hours in Example 27 and Example 28, and the rates of temperature rise were made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 196 MPa in Example 21 to Example 27, Example 29, and Example 30, 147 MPa in Example 31, and 125 MPa in Example 28.

[0069]

(Example 32 to Example 40)

Amorphous silica particles were prepared by the thermal spraying method. To those spherical amorphous silica particles (average particle size d₅₀: 2.20 μm, circularity 0.93), calcium hydroxide and lithium carbonate were mixed. The calcium hydroxide was mixed in by 0.90 mass% in oxide equivalent and the lithium carbonate by 0 mass% in Example 32 to Example 35, 0.01 mass% in Example 36, 0.03 mass% in Example 37, and 0.05 mass% in Example 38, Example 39, and Example 40 in oxide equivalent with respect to the mass of the total of the mass of spherical amorphous silica and mass of calcium in oxide equivalent and of lithium in oxide equivalent. The mixed powders were filled in containers made of BN and heat treated under high isotropic pressure by an HIP apparatus using nitrogen gas as a pressure medium. The holding temperature was made 1125°C and the holding time was made 12 hours in Example 38, the holding temperature was made 1150°C and the holding time was made 12 hours in Example 32, the holding temperature was made 1200°C and the holding time was made 8 hours in Example 33, the holding temperatures were made 1250°C and the holding times were made 8 hours in Example 34, Example 36, Example 37, Example 39, and Example 40, the holding temperature was made 1300°C and the holding time was made 1 hour in Example 35, and the rates of temperature rise were made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 196 MPa in Example 32 and Example 34 to Example 39, 147 MPa in Example 40, and 125 MPa in Example 33.

[0070]

(Comparative Example 1 to Comparative Example 9)

The amorphous spherical silica powder used in Example 1 to Example 4 was used. Powders comprised of this silica powder without lithium carbonate powder mixed in (Comparative Example 1, Comparative Example 2, and Comparative Example 7) and powders with lithium carbonate powder mixed in (Comparative Example 3 to Comparative Example 6, Comparative Example 8, and Comparative Example 9) were prepared. The lithium carbonate was mixed in to give contents of lithium carbonate of 0.01 mass% in Comparative Example 3, Comparative Example 5, and Comparative Example 8 and 0.05 mass% in Comparative Example 4, Comparative Example 6, and

Comparative Example 9 in oxide equivalent with respect to the mass of the total of the mass of spherical amorphous silica and mass of lithium in oxide equivalent. The powders without lithium carbonate powder mixed in and the powders with it mixed in were filled in containers made of BN and heat treated under isotropic pressure by an HIP apparatus using nitrogen gas as a pressure medium. The holding temperatures were made 1100°C in Comparative Example 1, Comparative Example 3, Comparative Example 4, and Comparative Example 7 and 1350°C in Comparative Example 2, Comparative Example 5, Comparative Example 6, Comparative Example 8, and Comparative Example 9. The holding times were made 12 hours in Comparative Example 1, Comparative Example 3, Comparative Example 4, and Comparative Example 7 and 1 hour in Comparative Example 2, Comparative Example 5, Comparative Example 6, Comparative Example 8, and Comparative Example 9. The rate of temperature rise was made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 196 MPa in Comparative Example 1 to Comparative Example 6 and 147 MPa in Comparative Example 7 to Comparative Example 9.

[0071]

(Comparative Example 10 to Comparative Example 13)

The amorphous spherical silica powder used in Example 1 to Example 4 was used. Powder comprised of this silica powder without lithium carbonate powder mixed in (Comparative Example 10) and powders with lithium carbonate powder mixed in (Comparative Example 11 to Comparative Example 13) were prepared. The lithium carbonate was mixed in to give contents of lithium carbonate of 0.01 mass% in Comparative Example 11, 0.03 mass% in Comparative Example 12, and 0.05 mass% in Comparative Example 13 in oxide equivalent with respect to the mass of the total of the mass of spherical amorphous silica and mass of lithium in oxide equivalent. The powder without lithium carbonate powder mixed in and the powders with it mixed in were filled in containers made of BN and heat treated under high isotropic pressure by an HIP apparatus using nitrogen gas as a pressure medium. The holding temperatures were made 1250°C. The holding times were made 8 hours in Comparative Examples 10 to 12 and 1 hour in Comparative Example 13. The rates of temperature rise were made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 118 MPa in Comparative Example 10 to Comparative Example 13.

[0072]

(Comparative Example 14 and Comparative Example 15)

The amorphous spherical silica powder used in Example 1 to Example 4 was used. Powder comprised of this silica powder without lithium carbonate powder mixed in (Comparative Example 14) and powder with lithium carbonate powder mixed in (Comparative Example 15) were prepared. The lithium carbonate was mixed in to give a content of lithium carbonate of 0.05 mass% in oxide equivalent with respect to the mass of the total of the mass of spherical amorphous silica and mass

of lithium in oxide equivalent. The powder without lithium carbonate powder mixed in and the powder with it mixed in were filled in containers made of alumina and heat treated in the air atmosphere (atmospheric pressure) using the electric furnace SUPER-BURN (made by KK Motoyama). The samples were raised in temperature by rates of temperature rise of approximately 600°C/h up to 1250°C and held there for 8 hours in Comparative Example 14 and 1 hour in Comparative Example 15. After that, they were cooled by rates of temperature fall of approximately 100°C/h down to room temperature.

[0073]

(Comparative Example 16 to Comparative Example 18)

The amorphous spherical silica powder used in Example 21 to Example 31 was used. Powder comprised of those spherical amorphous silica particles (average particle size d50: 30.2 μm) with only calcium hydroxide mixed in was prepared. Calcium was mixed in at 0.20 mass% in oxide equivalent with respect to the mass of the total of the mass of spherical amorphous silica and mass of calcium in oxide equivalent. The mixed powder was filled in containers made of BN and heat treated under isotropic pressure by an HIP apparatus using nitrogen gas as a pressure medium. The holding temperatures were made 1100°C in Comparative Example 16, 1350°C in Comparative Example 17, and 1250°C in Comparative Example 18. The holding times were made 12 hours in Comparative Example 16, 1 hour in Comparative Example 17, and 8 hours in Comparative Example 18. The rates of temperature rise were made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 196 MPa in Comparative Example 16 and Comparative Example 17 and 118 MPa in Comparative Example 18.

[0074]

(Comparative Example 19 to Comparative Example 22)

The amorphous spherical silica powder used in Example 21 to Example 31 was used. Powder comprised of those spherical amorphous silica particles (average particle size d50: 30.2 μm) into which both of calcium hydroxide and lithium carbonate were mixed (Comparative Example 19 to Comparative Example 22) was prepared. In powder comprised of amorphous silica particles into which only calcium hydroxide is mixed, calcium is mixed by a predetermined amount in oxide equivalent with respect to the mass of the total of the mass of the spherical amorphous silica and the mass of calcium in oxide equivalent. On the other hand, in powder made of powder comprised of spherical amorphous silica particles into which both calcium hydroxide and lithium carbonate are mixed, calcium hydroxide is mixed in by 0.20 mass% in oxide equivalent of calcium and further lithium carbonate is mixed in by 0.01 mass% in Comparative Example 19 and Comparative Example 21 and 0.05 mass% in Example 20 and Example 22 in oxide equivalent of lithium with respect to the mass of the total of the mass of the spherical amorphous silica and the mass of calcium in oxide equivalent and lithium in oxide equivalent. The mixed powders were filled in containers made of BN and heat treated under isotropic pressure by an HIP apparatus using

nitrogen gas as a pressure medium. The holding temperatures were made 1100°C in Comparative Example 19 and Comparative Example 20 and 1350°C in Comparative Example 21 and Comparative Example 22 and the holding times were made 12 hours in Comparative Example 19 and Comparative Example 20 and 1 hour in Comparative Example 21 and Comparative Example 22. The rates of temperature rise were made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 196 MPa

[0075]

(Comparative Example 23 to Comparative Example 25)

The amorphous spherical silica powder used in Example 32 to Example 40 was used. Powder comprised of the spherical amorphous silica particles (average particle size d50: 2.2 μm) into which only calcium hydroxide was mixed was prepared. Calcium was mixed into it by 0.90 mass% in oxide equivalent with respect to the mass of the total of the mass of spherical amorphous silica and mass of calcium in oxide equivalent. The mixed powder was filled in containers made of BN and heat treated under isotropic pressure by an HIP apparatus using nitrogen gas as a pressure medium. The holding temperatures were made 1100°C in Comparative Example 23, 1350°C in Comparative Example 24, and 1250°C in Comparative Example 25 and the holding times were made 12 hours in Comparative Example 23, 1 hour in Comparative Example 24, and 8 hours in Comparative Example 25. The rates of temperature rise were made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 196 MPa in Comparative Example 23 and Comparative Example 24 and 118 MPa in Comparative Example 25.

[0076]

(Comparative Example 26 to Comparative Example 29)

The amorphous spherical silica powder used in Example 32 to Example 40 was used. Powder comprised of the spherical amorphous silica particles (average particle size d50: 2.2 μm) into which both calcium hydroxide and lithium carbonate were mixed was prepared. Calcium hydroxide was mixed by 0.90 mass% in oxide equivalent of calcium and further lithium carbonate was mixed by 0.01 mass% in Comparative Example 26 and Comparative Example 28 and 0.05 mass% in Comparative Example 27 and Comparative Example 29 in oxide equivalent of lithium with respect to the mass of the total of the mass of the spherical amorphous silica and the mass of calcium in oxide equivalent and lithium in oxide equivalent. The mixed powders were filled in containers made of BN and heat treated under isotropic pressure by an HIP apparatus using nitrogen gas as a pressure medium. The holding temperatures were made 1100°C in Comparative Example 26 and Comparative Example 27 and 1350°C in Comparative Example 28 and Comparative Example 29. The holding times were made 12 hours in Comparative Example 26 and Comparative Example 27 and 1 hour in Comparative Example 28 and Comparative Example 29. The rates of temperature rise were made approximately 600°C/h. The nitrogen gas holding pressures at the holding temperatures were made 196 MPa.

[0077]

The silica particles obtained in the examples and comparative examples are respectively shown in Tables 1 and 2.

[0078]

5 The methods of measurement of the items in Tables 1 and 2 will be explained.

[0079]

(Constituent Phase Ratio)

10 The presence ratios of amorphous and crystalline silica of the silica particles obtained by heat treatment and the types of crystalline silica and the ratios of the same were found by XRD. In the present invention, an X-ray diffraction apparatus “D2 PHASER” (made by Bruker) was used. The crystal phases were quantitatively analyzed by the Rietveld method using the crystal structure analysis software “TOPAS” (made by Bruker).

15 If the spherical crystalline silica particles are comprised of amorphous and crystalline silica, the ratios of presence of the amorphous and crystalline silica and the types of the crystalline silica and their ratios can be found by XRD.

It is possible to find the ratio of the crystal phases by calculation by the following formula from the sum (I_c) of integrated intensities of the crystalline peaks and the integrated intensities (I_a) of the amorphous halo parts in XRD measurement. More specifically, the ratio of the phases of crystalline silica contained in spherical crystalline silica particles can be found.

20
$$X \text{ (ratio of crystal phases)} = I_c / (I_c + I_a) \times 100 \text{ (\%)}$$

In the present invention, the XRD measurement was performed in the range of $2\Theta = 10^\circ$ to 90° . The ratio of the crystal phases was found from the sum of the intensities of the crystalline peaks appearing in the 2Θ measurement range and the integrated intensities of the halo parts derived from broad amorphous structures appearing near $2\Theta = 22^\circ$.

25 Further, the quantitative analysis of the crystal phases using the Rietveld method was performed without using standard specimens.

[0080]

(Circularity)

30 The circularity was found by the flow type particle image analysis method. In the present invention, a flow type particle image analyzer “FPIA-3000” (made by Spectris) was used.

[0081]

(Average Particle Size)

35 The average particle size (D_{50}) of the spherical quartz particles was measured by the laser diffraction-scattering type particle size distribution measurement method. In the present invention, a laser diffraction-scattering type particle size distribution measurement apparatus “CILAS920” (made by Cilas) was used.

[0082]

(Amount of Impurities or Amount of Additives)

The contents of lithium, calcium, and other impurities or additive elements in the spherical silica particles of the present invention were measured by ICP mass spectrometry (ICP-MS). Specifically, measurement was conducted based on JIS-K0133 using ICP-MS (“7700X” made by Agilent). An aqueous solution obtained by completely dissolving silica particles by hydrofluoric acid was used as a sample. In this case, the contents of impurity elements contained in the silica particles were made the contents of impurity elements in the silica solution. The calibration line may also be obtained using a base solution of only the reagents.

[0083]

(Regarding Impurities of Amorphous Spherical Silica Particles)

The contents of zinc in the spherical amorphous silica particles produced by the thermal spraying method in the examples and comparative examples were less than 1.0 ppm in metal equivalent and further the totals of the alkali metals (Li, K, and Na) were 22 to 38 ppm in metal equivalent. The amorphous spherical silicas described in Example 1 to Example 18 and Comparative Example 1 to Comparative Example 15 at which calcium was added at the time of thermal spraying contained calcium in 7931 ppm, but the totals of the alkali earth metals (Ca+Mg+Ba) of the amorphous spherical silicas used for Example 19 to Example 28 and Comparative Example 16 to Comparative Example 27 were 11 to 32 ppm and aluminum metal was 97 to 8230 ppm.

[0084]

[Table 1]

Sample no.		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	Ex. 15	Ex. 16	Ex. 17	Ex. 18	Ex. 19	Ex. 20
Al content		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
ppm		1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237
Additive 1	Ca constituent	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray
	wt% (oxide eq.)	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Additive 2	Li constituent	Not added	Not added	Not added	Not added	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃
	Method of addition (oxide eq.)	Not added	Not added	Not added	Not added	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃
Heat treatment	Holding temperature	1150	1200	1250	1300	1200	1200	1250	1300	1200	1200	1200	1250	1300	1125	1150	1200	1250	1250	1250	1250
	Holding time	12	8	8	1	1	8	8	1	1	1	8	8	1	8	8	8	1	8	8	8
	Rate of temperature rise	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600
Atmospheric pressure		196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	196	147	147	125
Constituent phases	a. amorphous	48.6	42.9	12.8	9.2	45.2	29.9	1.3	1.1	28.6	13.6	8.0	2.7	1.2	35.2	13.3	1.8	1.3	12.6	1.8	16.3
	b. quartz	50.1	55.0	81.3	80.6	54.0	67.2	97.4	90.4	68.4	81.4	85.3	87.8	87.9	58.5	85.4	94.9	93.4	79.3	91.5	74.7
	c. cristobalite	0.9	1.2	5.0	8.9	0.4	2.1	0.9	7.2	2.2	3.9	5.8	8.1	9.6	6.1	1.1	2.9	4.8	7.2	6.0	8.3
	d. tridymite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	e. other crystals	0.4	0.9	0.9	1.3	0.4	0.8	0.4	1.3	0.8	1.1	0.9	1.4	1.3	0.2	0.2	0.4	0.5	0.9	0.7	0.7
Ratio of constituent phases	Ratio of crystalline silica in silica overall	51.0	56.2	86.3	89.5	54.4	69.3	98.3	97.6	70.6	85.3	91.1	95.9	97.5	64.6	86.5	97.8	98.2	86.5	97.5	83.0
	Ratio of quartz in crystalline silica b/(b+c+d)*100	98.2	97.9	94.2	90.1	99.3	97.0	99.1	92.6	96.9	95.4	93.6	91.6	90.2	90.6	98.7	97.0	95.1	91.7	93.8	90.0
Circularity and average particle size of silica after heat treatment	Circularity	0.90	0.89	0.88	0.86	0.92	0.91	0.89	0.87	0.92	0.92	0.91	0.91	0.88	0.92	0.92	0.90	0.89	0.91	0.89	0.89
	Average particle size	27.9	28.9	29.2	30.2	27.9	28.2	28.7	29.7	27.9	28.1	27.9	28.4	30.1	27.7	27.9	27.9	29.6	27.9	27.8	28.0
Am't of impurities of silica after heat treatment	wt% (oxide eq.)																				
	Li	(9 ppm)	(9 ppm)	(9 ppm)	(9 ppm)	0.009	0.008	0.008	0.009	0.018	0.028	0.027	0.028	0.028	0.048	0.048	0.048	0.047	(9 ppm)	0.009	0.009
	Ca	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79	0.79

Sample no.		Ex. 21	Ex. 22	Ex. 23	Ex. 24	Ex. 25	Ex. 26	Ex. 27	Ex. 28	Ex. 29	Ex. 30	Ex. 31	Ex. 32	Ex. 33	Ex. 34	Ex. 35	Ex. 36	Ex. 37	Ex. 38	Ex. 39	Ex. 40
Al content		21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
	ppm	8,230	8,230	8,230	8,230	8,230	8,230	8,230	8,230	8,230	8,230	8,230	97	97	97	97	97	97	97	839	40
Additive 1	Ca constituent	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂	Ca(OH) ₂
	wt% (oxide eq.)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90	0.90
Additive 2	Li constituent	None added	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Not added	Not added	Not added	Not added	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃	Li ₂ CO ₃
	Am't of addition (oxide eq.)	—	0.01	0.01	0.01	0.03	0.05	0.05	0.05	0.05	0.05	0.05	—	—	—	—	0.01	0.03	0.05	0.05	0.05
Heat treatment	Holding temperature	1250	1150	1250	1300	1250	1125	1200	1200	1250	1300	1250	1150	1200	1250	1300	1250	1250	1125	1250	1250
	Holding time	8	12	8	1	8	12	8	8	8	1	8	12	8	8	1	8	8	12	8	8
	Rate of temperature rise	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600
Atmospheric pressure		196	196	196	196	196	196	196	125	196	196	147	196	125	196	196	196	196	196	196	147
Constituent phases Ratio in silica overall	a. amorphous	24.8	48.6	20.1	9.0	9.8	40.4	17.2	20.2	3.7	3.3	7.2	45.5	31.4	11.1	9.2	8.6	3.9	48.7	2.8	3.6
	b. quartz	68.7	50.8	74.5	81.3	84.6	59.2	79.1	71.1	90.1	86.0	83.2	53.0	61.4	79.2	80.9	83.9	89.6	50.0	88.2	86.0
	c. cristobalite	5.7	0.4	4.5	8.6	4.6	0.2	2.8	7.9	5.1	9.4	8.5	1.1	6.8	8.8	8.9	6.6	5.6	0.9	7.9	9.3
	d. tridymite	0	0	0	0.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
	e. other crystals	0.8	0.2	0.9	1.1	1	0.2	0.9	0.8	1.1	1.3	1.1	0.4	0.4	0.9	1.0	0.9	0.9	0.4	1.1	1.1
Ratio of constituent phases	Ratio of crystalline silica in silica overall	74.4	51.2	79.0	89.9	89.2	59.4	81.9	79.0	95.2	95.4	91.7	54.1	68.2	88.0	89.8	90.5	95.2	50.9	96.1	95.3
	Ratio of quartz in crystalline silica	92.3	99.2	94.3	90.4	94.8	99.7	96.6	90.0	94.6	90.1	90.7	98.0	90.0	90.0	90.1	92.7	94.1	98.2	91.8	90.2
Circularity and average particle size of silica after heat treatment	b/(b+c+d)*100	0.90	0.91	0.89	0.87	0.88	0.90	0.89	0.89	0.86	0.85	0.87	0.91	0.90	0.92	0.90	0.91	0.89	0.90	0.87	0.87
	Average particle size	32.6	32.4	32.3	32.5	32.4	32.3	32.8	32.8	33.3	33.8	32.5	2.5	2.4	2.4	2.6	2.6	2.6	2.5	2.5	2.3
Am't of impurities of silica after heat treatment	wt% (oxide eq.)																				
	Li	(9 ppm)	(9 ppm)	0.009	(9 ppm)	0.027	0.048	0.048	0.048	0.047	0.048	0.047	(9 ppm)	(9 ppm)	(9 ppm)	(9 ppm)	0.009	0.028	0.048	0.046	0.047
	Ca	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.87	0.88	0.87	0.87	0.87	0.87	0.87	0.87	0.87

[0085]

[Table 2]

Sample no.		Comp. Ex. 1	Comp. Ex. 2	Comp. Ex. 3	Comp. Ex. 4	Comp. Ex. 5	Comp. Ex. 6	Comp. Ex. 7	Comp. Ex. 8	Comp. Ex. 9	Comp. Ex. 10	Comp. Ex. 11	Comp. Ex. 12	Comp. Ex. 13	Comp. Ex. 14	Comp. Ex. 15
Al content		29	30	31	32	33	34	35	36	37	38	39	40	41	42	43
	ppm	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237	1,237
Additive 1	Ca constituent addition	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray	Added at thermal spray
	ppm (oxide eq.)	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80	0.80
Additive 2	Li constituent addition	Not added	Not added	Not added	Not added	Not added	Not added	Not added	Not added	Not added	Not added	Not added	Not added	Not added	Not added	Not added
	Method of addition (oxide eq.)	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Heat treatment	Am't of addition	1100	1350	1100	1100	1350	1350	1100	1350	1350	1250	1250	1250	1250	1250	1250
	Holding time	12	1	12	12	1	1	12	1	1	8	8	8	1	8	1
	Rate of temperature rise	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600
Atmospheric pressure	MPa	196	196	196	196	196	196	147	147	147	118	118	118	118	118	118
Constituent phases Ratio in silica overall	a. amorphous	86.1	4.5	65.8	49.7	4.6	3.8	87.8	4.2	3.5	18.6	16.3	11.8	4.2	34.7	15.5
	b. quartz	11.5	68.2	29.8	41.8	79.1	75.7	10.7	60.4	55.0	62.4	70.7	72.2	77.0	26.6	22.2
	c. cristobalite	2.3	25.8	4.0	7.2	15.0	19.2	1.3	34.1	40.3	18.1	12.2	15.2	17.9	37.3	60.8
	d. tridymite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
	e. other crystals	0.1	1.5	0.4	1.3	1.3	1.3	0.2	1.3	1.2	0.9	0.8	0.8	0.9	1.4	1.5
Ratio of constituent phases	Ratio of crystalline silica in silica overall	13.8	94.0	33.8	49.0	94.1	94.9	12.0	94.5	95.3	80.5	82.9	87.4	94.9	63.9	83.0
	b+c+d															
Circularity and average particle size of silica after heat treatment	Ratio of quartz in crystalline silica	83.3	72.6	88.2	85.3	84.1	79.8	89.2	63.9	57.7	77.5	85.3	82.6	81.1	41.6	26.7
	b/(b+c+d)*100															
	Average particle size	0.91	0.89	0.88	0.86	0.92	0.91	0.89	0.87	0.92	0.89	0.9	0.89	0.88	0.89	0.9
Am't of impurities of silica after heat treatment	wt% (oxide eq.)	26.9	28.9	29.2	30.2	27.4	28.2	28.7	29.7	27.6	27.4	27.9	28.1	28.3	27.9	28.5
	Li	(9 ppm)	(9 ppm)	0.009	0.047	0.009	0.0048	(9 ppm)	0.009	0.046	(9 ppm)	0.009	0.028	0.047	(9 ppm)	0.047
	Ca	0.793	0.790	0.787	0.786	0.795	0.789	0.787	0.786	0.779	0.780	0.769	0.781	0.782	0.781	0.785

[0086]

(Regarding Comparison of Examples and Comparative Examples)

In the examples according to the present invention, in each case, spherical crystalline silica particles having a lithium content of 0.05 mass% or less in oxide equivalent, having a calcium content of 0.10 mass or more and less than 1.0 mass% in oxide equivalent in range, having 50% or more of the overall mass comprised of crystalline silica, and having 90.0% or more of the crystalline silica comprised of quartz were obtained. The particles of the examples according to the present invention had circularities of 0.86 to 0.92. Regarding the average particle size, in the examples of the present invention, three types of amorphous spherical silica with respective average particle sizes of 27.8 μm , 30.2 μm , and 2.20 μm were used as materials. The average particle sizes of the silica particles of the present invention using the materials with the average particle size of 27.8 μm were 27.8 μm to 30.2 μm . Further, the average particle sizes of the silica particles of the present invention using the materials with the average particle size of 30.2 μm were 32.3 μm to 33.8 μm . Still further, the average particle sizes of the silica particles of the present invention using the materials with the average particle size of 2.2 μm were 2.3 μm to 2.6 μm .

[0087]

(Regarding Heat Treatment Temperature)

Comparing Example 1 to Example 20 and Comparative Example 1 to Comparative Example 9, it is learned that it is first when using a material having a lithium content of 0.05 mass% or less in oxide equivalent and having a calcium content of 0.10 mass or more and less than 1.0 mass% in oxide equivalent and the isotropic pressure of the atmospheric gas becomes 125 MPa to 196 MPa and the heat treatment temperature becomes 1125°C to 1300°C or less that 50% or more of the whole becomes crystalline silica and 90% or more of the crystalline silica is comprised of quartz.

[0088]

(Regarding Types of Amorphous Spherical Silica Material)

Comparing Example 21 to Example 31 and Comparative Example 16, Comparative Example 17, and Comparative Example 19 to Comparative Example 22 (using amorphous spherical silica with average particle size of 30.2 μm as materials) and further comparing Example 32 to Example 40 and Comparative Example 23, Comparative Example 24, and Comparative Example 26 to Comparative Example 29 (using amorphous spherical silica with average particle size 2.20 μm as materials), it is learned that even when using materials with different average particle sizes such as a lithium content of 0.05 mass% or less in oxide equivalent and a calcium content of 0.10 mass or more and less than 1.0 mass% in oxide equivalent, it is first when the isotropic pressure of the atmospheric gas becomes 125 MPa or more and the heat treatment temperature becomes 1125°C to 1300°C or less that 50% or more of the whole becomes crystalline silica and 90% or more of the crystalline silica is comprised of quartz.

[0089]

(Regarding Isotropic Pressure of Atmospheric Gas)

Comparing Example 3, Example 7, Example 12, Example 17 to Example 20, and Comparative Example 10 to Comparative Example 15, it is learned that even if the heat treatment holding temperature is the same 1250°C, it is first when the isotropic pressure of the atmospheric gas becomes 125 MPa or more that 50% or more of the whole becomes crystalline silica and 90% or more of the crystalline silica is comprised of quartz. It is learned that if the isotropic pressure of the atmosphere becomes less than 125 MPa, the appearance of cristobalite increases and the ratio of quartz in the crystalline silica falls below 90%. It is learned that the isotropic pressure of the atmosphere has to be 125 MPa or more and the heat treatment temperature has to be from 125°C to 1300°C or less.

Further, comparing Example 21 to Example 31 and Comparative Example 18 (using amorphous spherical silica with average particle size of 30.2 μm as materials) and Example 32 to Example 40 and Comparative Example 25 (using amorphous spherical silica with average particle size of 2.20 μm as materials), it is learned that even when using materials with a lithium content of less than 0.05 mass% in oxide equivalent, a calcium content of 0.10 mass or more and less than 1.0 mass% in oxide equivalent, and different average particle sizes, if the isotropic pressure of the atmosphere becomes less than 125 MPa, the appearance of cristobalite increases and the ratio of quartz in the crystalline silica falls below 90%. It is learned that the isotropic pressure of the atmospheric gas has to be 125 MPa or more and the heat treatment temperature has to be from 1125°C to 1300°C or less.

CLAIMS

[Claim 1]

Spherical crystalline silica particles having a circularity of 0.80 or more, having an average
5 particle size (D50) of 1.0 μm or more and 100.0 μm or less, containing lithium in 0.05 mass% or
less in oxide equivalent, containing calcium in 0.10 to less than 1.00 mass% in oxide equivalent,
having 50.0% or more of the whole comprised of crystalline silica, and having 90.0% or more of
the crystalline silica comprised of quartz.

[Claim 2]

The spherical crystalline silica particles according to claim 1, containing lithium in 0.02
mass% or less in oxide equivalent.

[Claim 3]

The spherical crystalline silica particles according to claim 1 or 2, wherein cristobalite
15 comprises 5.0% or less of the whole.

[Claim 4]

The spherical crystalline silica particles according to any one of claims 1 to 3, containing
20 aluminum in 90 to 9000 ppm.

[Claim 5]

The spherical crystalline silica particles according to any one of claims 1 to 4, wherein the
average particle size (D50) is 10.0 μm or more.

[Claim 6]

A method of producing spherical crystalline silica particles comprising
a powder material preparing step of mixing a calcium material with spherical amorphous silica
particles or mixing in a calcium material and lithium compound particles to obtain a powder
30 material and

a heat treatment step of heat treating the powder material obtained in the powder material
preparing step at a temperature of 1125°C or more and 1300°C or less and a pressure of 125 MPa
or more using a hot isostatic pressing apparatus for 1 hour or more to form spherical crystalline
silica particles, wherein

35 the ratios of mixture of the calcium material or the calcium material and lithium compound
particles in the powder material preparing step are adjusted to make the calcium be present in 0.10
to 1.00 mass% in oxide equivalent and the lithium be present in 0.05 mass% or less in oxide

equivalent in the spherical crystalline silica particles formed in the heat treatment.

[Claim 7]

5 A resin composite composition comprising a resin in which are contained spherical crystalline silica particles according to any one of claims 1 to 5.

[Claim 8]

A resin composite comprised of the resin composite composition according to claim 7 which has been cured.

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