

DESCRIPTION

[Title of Invention]

METHOD FOR PRODUCING POLISHING SLURRY, POLISHING ABRASIVE
5 PARTICLES, POLISHING SLURRY, AND METHOD FOR
MANUFACTURING GLASS SUBSTRATE

[Technical Field]

[0001] The present invention relates to a method for producing a polishing
10 slurry, polishing abrasive particles, a polishing slurry, and a method for
manufacturing a glass substrate.

[Background Art]

[0002] In general, magnetic disks and glass substrates to be used in a
photomask, a mask blank that is a substrate for a photomask, or the like are
15 subjected to polishing using polishing abrasive particles (hereinafter referred to
as cerium-based polishing material) whose main component is cerium oxide
(ceria), and thereafter is subjected to finishing polishing using colloidal silica.
Among these, the cerium-based polishing material includes oxides of rare earth
elements, which are costly, and therefore the cerium-based polishing material
20 is collected after use and is re-used.

For example, the recycling method for re-using the cerium-based
polishing material is performed by removing foreign matter from the used
polishing slurry, thereafter performing solid-liquid separation, drying, firing,
and crushing the solid matter, and furthermore performing filtering. As a
25 conventional method for recycling a polishing material, it is known that an acid
treatment is carried out on the used polishing slurry before the solid-liquid
separation in order to bring the lower polishing rate of the used polishing
material closer to the polishing rate of the unused polishing material (e.g., see
Patent Document 1).

30 [Citation List]

[Patent Literature]

[0003] [PLT1]: JP 2007-276055A

[Summary of Invention]

[Technical Problem]

- 5 [0004] The polishing rate of the cerium-based polishing material is improved through bonding at particle boundaries by firing and thereby increasing the diameter of the particles functioning as the particles during actual polishing. However, it has been found that even if the polishing rate of the polishing material is restored to a level near that of the unused polishing material by
10 recycling using the method disclosed in Patent Document 1, the bonding strength at the particle boundaries is insufficient, and therefore when the polishing material is re-used, it tends to break and become smaller in size, and thus the polishing rate decreases in some cases. Also, it has been found that if the polishing material breaks during use and many decomposed particles are
15 generated, the particle size distribution of the polishing material will become uneven, and the load received by the polishing material with a larger particle diameter will increase, as a result of which the load applied to the glass substrate will increase locally, making it more likely that polishing marks will form on the glass substrate.
- 20 [0005] The present invention aims to provide a method for producing a polishing slurry, polishing abrasive particles, and a polishing slurry, according to which a polishing rate is improved and the formation of marks on a glass substrate can be suppressed. Also, the present invention aims to provide a method for manufacturing a glass substrate using such a polishing slurry and
25 polishing abrasive particles.

[Solution to Problem]

[0006] A first aspect of the invention is a method for producing a polishing slurry including polishing abrasive particles for use in processing for polishing a glass substrate, including:

adding processing in which binders are added to a raw-material slurry including raw-material abrasive particles serving as a raw material for the polishing abrasive particles;

5 drying processing in which the raw-material slurry including the binders is dried to produce a mass of the raw-material abrasive particles including the binders; and

firing processing in which the mass of the raw-material abrasive particles is fired to produce a cluster of the raw-material abrasive particles including the binders.

10 [0007] It is preferable that the binders include silica particles.

[0008] It is preferable that an average particle diameter of the binders is 3 to 20 nm.

[0009] It is preferable that the average particle diameter of the raw-material abrasive particles is 0.3 to 2 μm .

15 [0010] It is preferable that crushing processing in which the cluster of the raw-material abrasive particles is crushed to produce the polishing abrasive particles is further included, and

the average particle diameter of the polishing abrasive particles produced by the crushing processing is 0.5 to 10 μm .

20 [0011] It is preferable that in the adding processing, a binder aggregation suppressing agent for suppressing aggregation of the binders is further added, and

in the drying processing, the binders are dispersed in the mass of the raw-material abrasive particles via the binder aggregation suppressing agent.

25 [0012] It is preferable that in the firing processing, at least a portion of the binder aggregation suppressing agent is eliminated by firing the mass of the raw-material abrasive particles.

[0013] It is preferable that the binder aggregation suppressing agent is a polysaccharide, and it is more preferable that the binder aggregation

suppressing agent is a polysaccharide that dissolves or gels in water due to being heated.

[0014] It is preferable that the firing is performed at a temperature of 800°C or less.

5 [0015] It is preferable that in the drying processing, the raw-material slurry including the binders is dried through spray-drying.

[0016] It is preferable that the raw-material slurry includes ceria particles that were used in processing for polishing a glass substrate.

[0017] Another aspect of the first aspect is polishing abrasive particles to be
10 used in processing for polishing a glass substrate,

wherein in the polishing abrasive particles, silica particles exist as binders between ceria or zirconia particles.

[0018] It is preferable that the average value of the crushing strength of the polishing abrasive particles, which is measured in accordance with JIS R1639-5,
15 is 0.1 to 20 MPa.

[0019] Another aspect of the first aspect is a polishing slurry including the polishing abrasive particles according to the above-described other aspect.

[0020] Another aspect of the first aspect is a method for manufacturing a glass substrate, wherein a surface of a glass substrate is polished using the polishing
20 slurry produced through the method of producing a polishing slurry, the polishing abrasive particles, or the polishing slurry.

[0021] A second aspect of the invention is a method for producing a polishing slurry including polishing abrasive particles for use in processing for polishing a glass substrate, including:

25 adding processing in which a pore-forming agent is added to a raw-material slurry including raw-material abrasive particles serving as a raw material for the polishing abrasive particles;

drying processing in which the raw-material slurry including the pore-forming agent is dried to produce a mass of the raw-material abrasive
30 particles containing the pore-forming agent; and

firing processing in which the mass of the raw-material abrasive particles is fired and the pore-forming agent forms a gap in a portion of the mass of the raw-material abrasive particles due to at least a portion of the pore-forming agent being eliminated.

5 [0022] The pore-forming agent is preferably a polysaccharide, and is more preferably a polysaccharide that dissolves or gels in water due to being heated.

[0023] It is preferable that in the mass of the raw-material abrasive particles, the average particle diameter of the pore-forming agent is 3 to 20 μm .

10 [0024] It is preferable that the average particle diameter of the raw-material abrasive particles is 0.3 to 2 μm .

[0025] Furthermore, it is preferable that crushing processing in which the cluster of the raw-material abrasive particles is crushed to produce the polishing abrasive particles is included, and

15 the average particle diameter of the polishing abrasive particles produced by the crushing processing is 0.5 to 10 μm .

[0026] It is preferable that the raw-material slurry including the pore-forming agent is dried through spray-drying in the drying processing.

[0027] It is preferable that the raw-material slurry includes the ceria particles that were used in the processing for polishing the glass substrate.

20 [0028] It is preferable that in the adding processing, binders to be distributed on surfaces of the raw-material abrasive particles are further added, and

in the drying processing, the binders are dispersed in the mass of the raw-material abrasive particles via the pore-forming agent.

25 [0029] It is preferable that the average value of the crushing strength of the polishing abrasive particles, which is measured in accordance with JIS R1639-5, is 0.1 to 20 MPa.

[0030] Another aspect of the second aspect is a method for manufacturing a glass substrate,

30 wherein a surface of a glass substrate is polished using a polishing slurry produced using the method for producing a polishing slurry.

[Advantageous Effects of the Invention]

[0031] According to the method for producing the polishing slurry of the present invention, the raw-material abrasive particles in the clusters of the raw-material abrasive particles are bonded via binders so that the strength at the particle boundaries is increased, and therefore the polishing abrasive particles produced from the clusters of the raw-material abrasive particles are less likely to break during use. For this reason, a case is suppressed in which marks are formed on a glass substrate due to decomposed particles generated by breaking. Also, due to the polishing abrasive particles being produced from raw-material abrasive particles joined with binders to increase their size, the polishing rate increases, and a high polishing rate can be maintained due to breaking being less likely to occur.

The polishing abrasive particles and polishing slurry of the present invention include ceria or zirconia particles with binders distributed on the surfaces thereof, and thus the polishing abrasive particles are less likely to break compared to polishing abrasive particles with no binders, and a decrease in the polishing rate is suppressed.

According to the method for producing a glass substrate of the present invention, a glass substrate can be polished at a high polishing rate, and a glass substrate with few marks can be obtained.

[Brief Description of Drawings]

[0032] FIG. 1(a) is a diagram showing a mass of raw-material abrasive particles in first and second embodiments. FIG. 1(b) is a diagram showing a cluster of raw-material abrasive particles in the first and second embodiments.

FIG. 2 is a diagram conceptually showing a polishing abrasive particle produced using a method for producing a polishing slurry in the first and second embodiments.

[Description of Embodiments]

[0033] Hereinafter, a method for producing a polishing slurry, polishing abrasive particles, a polishing slurry, and a method for manufacturing a glass substrate of the present invention will be described in detail.

[0034] First Embodiment

5 Method for Producing Polishing Slurry

A first embodiment of the present invention will be described here.

The method for producing a polishing slurry of the first embodiment is a method for producing a polishing slurry including polishing abrasive particles for use in processing for polishing a glass substrate, the method including
10 addition processing, drying processing, and firing processing. In the addition processing, binders are added to a raw-material slurry including raw-material abrasive particles serving as raw materials for the polishing abrasive particles. In the drying processing, the raw-material slurry including the binders is dried to produce masses of raw-material abrasive particles including the binders. In
15 the firing processing, the masses of raw-material abrasive particles are fired, and clusters of raw-material abrasive particles containing the binders are produced.

The raw-material slurry is obtained by dispersing the raw-material abrasive particles using water as the dispersion medium.

20 A mass of raw-material abrasive particles refers to a mass-like substance formed due to multiple raw-material abrasive particles gathering together, and a mass of raw-material abrasive particles includes raw-material abrasive particles, binders, and a binder aggregation suppressing agent that is blended as appropriate. The mass of raw-material abrasive particles has a
25 form in which many raw-material abrasive particles are attached to a moisture-containing binder aggregation suppressing agent so as to cover the surface thereof, and the binders are dispersed between the raw-material abrasive particles, for example.

A cluster of raw-material abrasive particles refers to raw-material
30 abrasive particles bonded together by at least a portion of the binders (e.g., by

the binders melting and solidifying) in a mass of raw-material abrasive particles. A cluster of raw-material abrasive particles includes raw-material abrasive particles and binders. A cluster of raw-material abrasive particles preferably has holes (gaps) that are formed due to at least a portion of the binder aggregation suppressing agent included in the mass of raw-material abrasive particles being eliminated.

Also, a state after the drying processing and before the firing processing can be referred to as a mass of raw material abrasive particles, and a state after the firing processing and before the crushing processing can be referred to as a cluster of raw material abrasive particles.

[0035] Note that there is no particular limitation on the application of the glass substrate, and for example, the glass substrate may be used as a panel for various types of display apparatuses, such as liquid crystal display apparatuses, photomasks or mask blanks, which are substrates for photomasks, and magnetic disks for HDD apparatuses. The processing for polishing the glass substrate is performed by, for example, using a double-side polishing apparatus in the later-described method for manufacturing the glass substrate.

There is no particular limitation on the polishing abrasive particles, but a cerium-based polishing material or a zirconia-based polishing material having zirconium oxide (zirconia) as a main component is preferably used in light of the fact that a glass substrate can be polished using a chemical action in addition to a mechanical action. The polishing slurry is obtained by dispersing polishing abrasive particles using water as the dispersion medium, and the polishing abrasive particles are used as free abrasive particles in the polishing processing. The polishing slurry may include a component other than polishing abrasive particles and water, such as a phosphoric acid-based dispersing agent, for example. Although there is no limitation on the concentration of the polishing abrasive particles in the polishing slurry, it is 1 to 30 mass%, and preferably 3 to 20 mass%, for example.

[0036] (a) Adding Processing

The raw-material abrasive particles are raw materials for the abrasive particles included in the polishing slurry produced using the method according to the first embodiment, and if the polishing abrasive particles included in the later-described used polishing slurry are to be used as raw-material abrasive particles, raw-material abrasive particles means used abrasive particles. It is preferable that the average particle diameter of the raw-material abrasive particles is 0.3 to 2 μm . By using raw-material abrasive particles with such an average particle diameter, polishing abrasive particles of a size appropriate for performing processing for polishing a glass substrate can be produced. It has been found that raw-material abrasive particles with relatively small average particle diameters (e.g., less than 0.3 to 0.5 μm) among the raw-material abrasive particles in the 0.3 to 2.0 μm range are not likely to be collected through solid-liquid separation, and even if they are collected, those recycled using the conventional method decrease in size, lower the polishing rate, and cause marks to form on the glass substrate in the polishing processing. According to the production method of the first embodiment, polishing abrasive particles having an appropriate hardness (crushing strength) are produced as described below, and therefore the production method of the first embodiment is suitable for producing a polishing slurry using polishing abrasive particles with a relatively small average particle diameter as the raw-material abrasive particles. Note that the raw-material abrasive particles are secondary particles formed by several to several tens of primary particles aggregating, and the average particle diameter of the raw-material abrasive particles means the average particle diameter of the secondary particles. Note that a secondary particle acts as one polishing abrasive particle at a time of actual polishing. Also, in the present specification, the average particle diameter means the median diameter (d_{50}). d_{50} is a particle diameter at which the cumulative particle diameter measured using a laser diffraction/scattering particle size distribution measurement method corresponds to 50% accumulation, starting from a small particle side.

The raw-material slurry may be unused or may be a used polishing slurry. In the present specification, “used” means having been used in processing for polishing a glass substrate at least once. In the case where the polishing slurry is produced using the used polishing slurry, the used polishing
5 abrasive particles can be recycled, and the cost of the polishing slurry can be suppressed. Note that in the present specification, if the used polishing slurry is used as the raw-material slurry, the method for producing the polishing slurry of the present embodiment can be called a method for recycling used polishing slurry, and if the polishing slurry includes a cerium-based polishing
10 material having ceria particles as a main component, it can be called a method for recycling used ceria slurry.

Also, the used polishing slurry used as the raw-material abrasive particles may be recycled using the method for recycling used polishing slurry. In this case, by repeatedly recycling and using the used polishing slurry, the
15 cost of the polishing slurry can be further suppressed.

[0037] The binders can increase the strength of the particle boundaries by melting during the firing processing and joining the raw-material abrasive particles together. Note that the particle boundary refers to the boundary between adjacent raw-material abrasive particles. Accordingly, due to the
20 secondary particle diameter (particle diameter of the particles acting as one polishing abrasive particle at the time of polishing) of the polishing abrasive particles being larger, the polishing rate of the polishing abrasive particles increases, the polishing abrasive particles are less likely to break in the polishing processing, and a high polishing rate can be maintained. On the
25 other hand, if raw-material abrasive particles are joined via the binders, the strength of the particle boundaries is not excessively strong compared to the case where the raw-material abrasive particles are directly joined, and therefore a case is suppressed in which marks are formed on the glass substrate in the polishing processing.

Also, if breaking occurs easily during the polishing processing, the percentage of small particles will increase, and the polishing load will be applied more greatly to the large particles, of which there are relatively few, and therefore polishing marks are more likely to be formed. Accordingly, the formation of polishing marks can be suppressed by joining the abrasive particles with the binders.

On the other hand, since the strength of the particle boundaries is not excessively strong, the clusters of raw-material abrasive particles including the binders can be crushed easily using ultrasonic irradiation or the like, and polishing abrasive particles with a size suitable for polishing processing and a uniform particle size distribution can be obtained. For this reason, there is no need to perform crushing by pulverization or the like, which is costly, and there is no need to perform classification, and therefore the polishing abrasive particles can be produced easily and at a low cost.

[0038] Specifically, binders that are not eliminated in the firing step are used. In this respect, it is preferable that the temperature at which the binders decompose is a temperature greater than the firing temperature in the firing step. Accordingly, the binders are preferably not organic. This is because organic binders will be eliminated in the firing step. The binders are preferably particles composed of a non-organic compound, and among these, particles composed of oxides such as silicon dioxide (silica) and titanium oxide (titania), hydrates thereof, glass such as aluminosilicate glass, and hydroxides such as cerium hydroxide, silicon hydroxide, and zirconia hydroxide are preferable in light of the fact that they have an excellent dispersibility in the raw-material slurry. Among these, silica melts at a relatively low temperature (e.g., 800°C or less) and joins together raw-material abrasive particles, and therefore even if the firing temperature at the time of the firing processing is such a low temperature, the strength of the particle boundaries of the raw-material abrasive particles can be increased. It is thought that silica exists as a hydrate in the slurry, is dehydrated at the time of firing processing

to become silica anhydride, and thereby joins together raw-material abrasive particles. Note that the particle boundary refers to the boundary between adjacent raw-material abrasive particles. Examples of silica include colloidal silica and fumed silica, and colloidal silica is preferably used in light of the fact that it has a more excellent dispersibility. Note that if silica or glass is melted to join together the raw-material abrasive particles, it is thought that a portion thereof forms a vitrified bond.

[0039] It is preferable that the average particle diameter of the binders is 3 to 20 nm. Binders with such an average particle diameter are sufficiently small relative to the raw-material grinding particles, are easily dispersed and arranged between the raw-material grinding particles in the drying processing and the firing processing, and thus favorably function as the binders that join together the raw-material abrasive particles. If the average particle diameter of the binders is less than 3 nm, the joining of the raw-material abrasive particles will be insufficient in some cases, and if the average particle diameter of the binders is greater than 20 nm, the binders will join together and form coarse particles, which can cause polishing marks. The average particle diameter of the binders can be measured using a laser diffraction particle size distribution measurement apparatus.

[0040] The binders are preferably used polishing abrasive particles that were used in the second polishing processing of the later-described method for manufacturing a glass substrate. Since colloidal silica, which is an example of the used polishing abrasive particles, is normally discarded after use, using colloidal silica as the binders eliminates the need for raw material cost, and thus the polishing slurry can be produced at a low cost. Also, since the collected used polishing slurry can be added as-is to the raw-material slurry, excellent productivity is achieved.

The adding amount of the binders is preferably 1 to 10 parts by mass, and more preferably 1 to 5 parts by mass, relative to 100 parts by mass of the raw-material abrasive particles. If it is less than 1 part by mass, the effect of

the binders is not sufficiently obtained and the polishing abrasive particles are more likely to break, as a result of which the polishing rate decreases in some cases. Also, if it is greater than 10 parts by mass, the binders aggregate and form coarse particles, which cause marks to form on the glass substrate. Also, if it is greater than 10 parts by mass, there is a risk that an excessive amount of binders will attach to the surfaces of the ceria polishing abrasive particles, whereby the polishing function exhibited by the abrasive particle surface will decrease, and the polishing rate will decrease. In particular, if the polishing abrasive particles are made of a cerium-based polishing material, it is said that a high polishing rate is achieved by exhibiting the chemical action on the glass substrate, and therefore if a material other than ceria excessively covers the surfaces, the surface area of contact with the substrate to be polished decreases, and the polishing rate decreases.

[0041] In the adding processing, a binder aggregation suppressing agent for suppressing aggregation of the binders is preferably further added. If the binder aggregation suppressing agent exists in the raw-material slurry, aggregation of the binders is suppressed, and the binders are dispersed between the raw-material abrasive particles. In particular, the smaller the particle diameter of silica is, the more easily aggregation occurs in water, resulting in coarse silica particles, which cause marks to form on the glass substrate, in some cases, and therefore such aggregation of the silica particles can be suppressed by adding the binder aggregation suppressing agent. In particular, if the average particle diameter of the silica is 3 to 20 nm, it is preferable to add the binder aggregation suppressing agent.

[0042] The binder aggregation suppressing agent preferably has a high affinity to the binders, and examples of such substances include substances having hydroxyl groups on their surfaces. Specifically, examples thereof include polysaccharides. More preferably, a polysaccharide that dissolves or gels in water due to being heated (hereinafter referred to also as “the above-described polysaccharide” in the present embodiment) is used. Since such a

polysaccharide enters a state of being likely to attach to a binder in the process of being dried in the drying processing, it has a function of suppressing aggregation of the binders while helping the binders to disperse and be arranged between the raw-material abrasive particles. This function is
5 thought to be performed due to water-containing polysaccharides capturing the binders and thus positioning the binders relative to the raw-material abrasive particles.

[0043] Although there is no particular limitation on the temperature at which the above-described polysaccharide dissolves or gels in water, it is preferable
10 that the above-described polysaccharide has dissolved or gelled in water at the drying temperature in the drying processing, for example. Due to the above-described polysaccharide including water in the drying processing, the raw-material abrasive particles are more likely to attach to the surfaces of the polysaccharides. Also, the above-described polysaccharide can easily be
15 eliminated by firing at a relatively low temperature. In this respect, it is preferable that the decomposition temperature of the binder aggregation suppressing agent is 600°C or less, and more preferably 500°C or less. Also, due to at least a portion of the above-described polysaccharide being eliminated in the firing processing, portions existing in the masses of raw-material
20 abrasive particles become pores (gaps) in the clusters of the raw-material abrasive particles, and therefore the clusters of the raw-material abrasive particles can be made porous. In this respect, the binder aggregation suppressing agent can be said to be a pore-forming agent.

[0044] Specifically, starch, glycogen, agarose, pectin, or a combination thereof
25 is preferably used as the above-described polysaccharide. Examples of starch include corn starch, wheat flour, potato starch, and rice starch. There is no limitation on the raw materials of the starch, and cereals such as corn, wheat, rice, potatoes, and sweet potatoes can be used as the raw materials.

[0045] The adding amount of the binder aggregation suppressing agent is
30 preferably 10 to 100 parts by mass, or more preferably 10 to 50 parts by mass

with respect to 100 parts by mass of the raw-material abrasive particles. If the adding amount is less than 10 parts by mass, pores will not be sufficiently formed in the clusters of the raw-material abrasive particles, and crushing will be difficult to perform in some cases. Also, if the adding amount is greater than 100 parts by mass, the effect of the binders will be hindered, the polishing abrasive particles (raw-material abrasive particles) will not become sufficiently large, and the effect of improving the polishing rate through granulation will not be obtained in some cases.

The binder aggregation suppressing agent is added to the raw-material slurry in a state of being dispersed in a solvent such as water, for example.

[0046] Note that in the case of using used polishing slurry as the raw-material abrasive particles, it is preferable to perform filtering, solid-liquid separation, and crushing in advance on the used polishing slurry before the adding processing. In the filtering, large-sized (e.g., 15 μm or more) foreign matter is removed. In the solid-liquid separation, glass components such as glass sludge included in the collected used polishing slurry are removed. In the crushing, solid matter generated in the solid-liquid separation is crushed through ultrasonic irradiation using a homogenizer, for example. In order to easily perform the crushing, a hard caking prevention agent (e.g., a polysaccharide that is not water-soluble) that prevents the solid matter from becoming too hard may be added to the used polishing slurry before the solid-liquid separation.

Also, after the solid-liquid separation, the remaining liquid, which is a supernatant liquid, may be further subjected to solid-liquid separation, and the resulting solid matter may be crushed and used as the raw-material slurry. Accordingly, by collecting the used polishing abrasive particles with a small average particle diameter (e.g., 0.3 to 2 μm) that were not collected in the first solid-liquid separation and using them as the raw-material abrasive particles, the polishing abrasive particles can be recycled. If the solid-liquid separation is thus performed multiple times, the rate of collecting costly polishing abrasive

particles such as cerium-based polishing material in particular is increased, and the effect of suppressing the cost of the polishing slurry increases. Note that in this case, solid matter with a large average particle diameter (e.g., 0.5 to 5 μm) obtained in the first solid-liquid separation may be separately supplied with water, subsequently crushed, and furthermore subjected to filtering, and thereafter may be used cyclically while processing for polishing the glass substrate is performed, may be stored in a tank for storing the polishing slurry, or may be recycled using the method for producing the polishing slurry according to the present embodiment.

10 [0047] (b) Drying Processing

In the drying processing, the raw-material slurry containing the binders are preferably dried using a spray-drying method. By performing spray-drying, the sizes of the masses of raw-material abrasive particles can be controlled. The spray-drying method is preferable because the average particle diameter can be made smaller in comparison to other methods, and furthermore, variation in the particle diameter can be reduced. Specifically, spray-drying is performed by spraying the raw-material slurry using a known spraying means, such as a rotary disc type, a binary fluid nozzle type, or a pressure nozzle type, supplying the raw-material slurry to a drying chamber of a spray dryer, and performing drying. Conditions such as the type of the spraying means, the nozzle hole diameter, and the pressure for supplying the raw-material slurry are set as needed according to the target sizes of the masses of raw-material abrasive particles. The sizes (average particle diameters) of the masses of raw-material abrasive particles obtained through spray-drying are preferably around 5 to 10 μm , for example. If the average particle diameter is larger than 10 μm , coarse particles will remain after crushing and cause polishing marks in some cases. On the other hand, if the average particle diameter is less than 5 μm , the percentage of small particles will increase and the polishing rate will decrease in some cases. Note that the average particle diameter in this context is a value obtained by obtaining the

major axis lengths of 100 randomly-selected masses of the raw-material abrasive particles in SEM observation and finding the average thereof.

Also, in the case of adding a pore-forming agent to the raw-material slurry that has not been subjected to the spray-drying, the size of the pore-forming agent (average particle diameter of the pore-forming agent) is preferably 3 to 20 μm . Due to the pore-forming agent falling within such a size range, the sizes of the pores in the clusters of the raw-material abrasive particles resulting from firing can be set appropriately, and the sizes of the crushed polishing abrasive particles can be set appropriately (e.g., to an average particle diameter of 0.5 to 10 μm). As for the drying temperature (atmospheric temperature in the drying chamber), the temperature at the entrance to the drying chamber is 150 to 250°C, for example. Note that the drying processing may be performed without heating.

Here, FIG. 1(a) shows a mass of raw-material abrasive particles produced through drying processing. Here, a spherical mass of raw-material abrasive particles produced by drying the raw-material slurry containing the binder aggregation suppressing agent is shown as an example. A mass 10 of the raw-material abrasive particles is formed by many raw-material abrasive particles 3 attaching to a moisture-containing binder aggregation suppressing agent 7 so as to cover the surface thereof, and binders (not shown) are dispersed between the raw-material abrasive particles 3. Note that the mass 10 of the raw-material abrasive particles contains many raw-material abrasive particles 3, but in FIG. 1(a), the boundaries of the many raw-material abrasive particles 3 are not shown, for the sake of convenience.

[0048] (c) Firing Processing

Although there is no limitation on an apparatus for performing firing processing, an example thereof is a muffle furnace. It is preferable that the firing temperature in the firing processing is 800°C or less. The firing temperature is the atmospheric temperature in the space for performing firing. By setting the firing temperature to 800°C or less, the energy cost for producing

the polishing slurry can be reduced. If the firing temperature exceeds 800°C, bonding at the particle boundaries between the raw-material abrasive particles will advance, and the strength at the particle boundaries of the polishing abrasive particles will become excessively high in some cases. Also, the binders will bond together and become coarse particles in some cases. In these cases, marks on the glass substrate are likely to be formed. Also, if the firing temperature exceeds 800°C, the composition of the raw-material abrasive particles will change, increasing the hardness, which causes marks to form on the glass substrate in some cases. Also, the firing temperature in the firing processing is preferably 500°C or more, and more preferably, 600°C or more. If the firing temperature is less than 500°C, the bonding between the raw-material abrasive particles will be insufficient in some cases.

[0049] In the firing processing, if the binder aggregation suppressing agent is added to the raw-material slurry, it is preferable that at least a portion of the binder aggregation suppressing agent is eliminated through firing. Accordingly, the portions at which the binder aggregation suppressing agent was distributed in the masses of raw-material abrasive particles become pores, and porous clusters of raw-material abrasive particles are produced.

Here, FIG. 1(b) shows a cluster of raw-material abrasive particles produced through firing processing. Here, a cluster of raw-material abrasive particles produced by drying and firing the raw-material slurry containing the binder aggregation suppressing agent is shown as an example. A cluster of the raw-material abrasive particles includes pores that are formed due to the binder aggregation suppressing agent being eliminated. Note that the clusters of the raw-material abrasive particles become porous due to having, in addition to the pores shown in the drawing, many minute gaps between the raw-material abrasive particles formed by the binder aggregation suppressing agent distributed between the raw-material abrasive particles surrounding the pores also being eliminated. The size (average particle diameter) of the cluster of the raw-material abrasive particles is preferably around 5 to 10

μm , for example. If the average particle diameter is larger than $10\ \mu\text{m}$, coarse particles will remain after crushing and cause polishing marks in some cases. On the other hand, if the average particle diameter is less than $5\ \mu\text{m}$, the percentage of small particles will increase and the polishing rate will decrease in some cases. Note that the average particle diameter in this context is a value obtained by obtaining the major axis lengths of 100 randomly-selected masses of the raw-material abrasive particles in SEM observation and finding the average thereof. The binders (not shown) in the cluster 20 of the raw-material abrasive particles are melted in the firing processing, and when the binders solidify thereafter, the raw-material abrasive particles 3 are bonded, and thereby the strength at the particle boundaries of the raw-material abrasive particles 3 reaches an appropriate magnitude (e.g., the average value of a later-described crushing strength is 0.1 to 20 MPa). Note that the cluster 20 of the raw-material abrasive particles contains many raw-material abrasive particles 3, but in FIG. 1(b), the boundaries of the many raw-material abrasive particles 3 are not shown, for the sake of convenience. For example, element mapping using an EDX (Energy Dispersive X-ray microanalyzer) can be used to confirm that the binders are disposed between the raw-material abrasive particles 3.

[0050] (d) Crushing Processing

The method for producing the polishing slurry according to the first embodiment preferably further includes crushing processing in which the clusters of the raw-material abrasive particles are crushed to produce polishing abrasive particles. Accordingly, polishing abrasive particles of a size appropriate for polishing processing can be obtained. If pores are formed in the clusters of the raw-material abrasive particles, crushing is even easier to perform.

Crushing is performed by performing ultrasonic irradiation on the clusters of the raw-material abrasive particles using a homogenizer, for example. The frequency of the ultrasound is preferably 16 to 120 kHz. The

crushing may be performed using a means other than a homogenizer. Although there is no particular limitation on the crushing time, it is 1 to 20 minutes, for example.

The crushing is preferably performed such that the average particle diameter of the polishing abrasive particles is 0.5 to 10 μm . The average particle diameter is more preferably 0.5 to 5 μm or 0.7 to 3 μm . Upon performing polishing processing using polishing abrasive particles with such an average particle diameter, polishing can be performed at a high polishing rate, and a case can be suppressed in which marks are formed on the surface of the glass substrate.

The crushing processing may be performed using a milling method in which the particles are physically broken down using a ball mill or the like, but the above-described ultrasonic method is superior in terms of simplicity.

[0051] After the crushing processing, the polishing slurry can be produced by dispersing the polishing abrasive particles in water. At this time, it is preferable that large-sized (e.g., 15 μm or more) particles are removed by performing filtering before the water is supplied. Large-sized particles in this context are portions of clusters of the raw-material abrasive particles that were not crushed to a predetermined size through the crushing processing.

[0052] According to the method for producing the polishing slurry according to the first embodiment, binders are added to a raw-material slurry and the resulting slurry is dried and fired, whereby clusters of raw-material abrasive particles containing binders can be produced. Since the clusters of the raw-material abrasive particles include portions at which raw-material abrasive particles are bonded with binders interposed therebetween, the strength of the particle boundaries is not excessively high compared to a cluster in which raw-material abrasive particles are directly bonded together. For this reason, crushing can be easily performed using ultrasonic irradiation or the like, and polishing abrasive particles that have a size suitable for polishing processing and have a uniform particle size distribution can be obtained.

Thus, according to the method of the first embodiment, since there is no need to perform pulverization or the like, which is costly, and there is no need to perform classification, the polishing abrasive particles can be produced easily and at a low cost. The polishing abrasive particles have an improved polishing rate due to the raw-material abrasive particles being larger. Also, with the polishing abrasive particles produced with the method of the first embodiment, the strength of the particle boundaries is not excessively high due to the raw-material abrasive particles being joined together via binders, and therefore a case is suppressed in which the glass substrate is damaged. On the other hand, with the polishing abrasive particles produced using the method of the first embodiment, the secondary particle diameter is larger due to the raw-material abrasive particles being bonded via binders, and thus the polishing rate can be increased, and due to the strength of the particle boundaries being higher, breaking is less likely to occur in the polishing processing and a high polishing rate can be maintained.

Also, with the polishing abrasive particles produced using the method of the first embodiment, the polishing rate is improved due to the raw-material abrasive particles being joined together via binders to have a greater size, and due to having a suitable strength of the particle boundaries, breaking is less likely to occur during use and a high polishing rate can be maintained.

[0053] Polishing Abrasive Particles and Polishing Slurry

FIG. 2 conceptually shows a polishing abrasive particle 1 according to the first embodiment.

The polishing abrasive particle 1 includes raw-material abrasive particles 3, which include ceria or zirconia particles to be used in the processing for polishing the glass substrate, and binders 5, which are distributed on the surfaces of the raw-material abrasive particles 3. More specifically, the polishing abrasive particle 1 is a polishing abrasive particle to be used in processing for polishing a glass substrate, silica particles existing as the binders 5 between the ceria or zirconia particles.

Note that as shown in FIG. 1, many raw-material abrasive particles 3 are included in the mass 10 of raw-material abrasive particles and the cluster 20 of raw-material abrasive particles.

The raw-material abrasive particles 3 are similar to the cerium-based polishing material or zirconia-based polishing material among the above-described raw-material abrasive particles. The cerium-based polishing material is preferably a mixture of, in addition to ceria, at least one of an oxide of another rare earth element such as lanthanum, praseodymium, and neodymium, and fluorides thereof, in order to achieve a high polishing rate while suppressing a case in which marks are formed on the glass substrate. The zirconia-based polishing material may be a mixture including silicon dioxide in addition to zirconia.

The average particle diameter of the raw-material abrasive particles 3 is 0.3 to 2 μm , for example, and the raw-material abrasive particles 3 are formed due to the aggregation of particles with a primary particle diameter of about 80 to 150 nm, for example.

The binders 5 are similar to the above-described binders. Note that in FIG. 2, the binders 5 are distributed on the surfaces of the raw-material abrasive particles 3, which are the secondary particles, but the binders 5 may be distributed on the surfaces of the primary particles constituting the raw-material abrasive particles 3. The binders 5 preferably cover less than 50% of the surface area of the surfaces of the raw-material abrasive particles 3. If the binders 5 cover 50% or more, the surface of contact between the surfaces of the polishing abrasive particle and the polished substrate decreases in size, and the polishing rate tends to decrease.

[0054] The average value of the crushing strength of the polishing abrasive particles 1, which is measured in accordance with JIS R1639-5, is preferably 0.1 to 20 MPa. Due to the average value of the crushing strength being 0.1 MPa or more, a case is suppressed in which the polishing abrasive particles easily break into smaller sizes in the polishing processing, and thus a decrease

in the polishing rate is suppressed. Note that since there is a large variation in the crushing strength, it is preferable to perform measurement at 20 points or more. From the viewpoint of more reliably suppressing a decrease in the polishing rate, the average value of the crushing strength is more preferably 3 MPa or more. Also, due to the average value of the crushing strength being 20 MPa or less, it is possible to suppress a case in which marks are formed on the surface of the glass substrate in the polishing processing.

The average particle diameter of the polishing abrasive particles 1 is, for example, 0.5 to 10 μm . The number of raw-material abrasive particles 3 included in the polishing abrasive particle 1 is several to around a dozen, for example, although there is no limitation thereto.

[0055] The polishing slurry of the first embodiment includes the polishing abrasive particles 1 and a dispersion medium such as water in which the polishing abrasive particles 1 are dispersed.

The polishing abrasive particles and the polishing slurry of the first embodiment are produced using the above-described method of producing the polishing slurry, for example.

[0056] Second Embodiment

Method for Producing Polishing Slurry

A second embodiment of the present invention will be described next.

The method for producing a polishing slurry of the second embodiment is a method for producing a polishing slurry including polishing abrasive particles for use in processing for polishing a glass substrate, the method including adding processing, drying processing, and firing processing. In the adding processing, a pore-forming agent is added to a raw-material slurry including raw-material abrasive particles serving as raw materials for the polishing abrasive particles. In the drying processing, the raw-material slurry including the pore-forming agent is dried to produce masses of the raw-material abrasive particles containing the pore-forming agent. In the firing processing, at least a portion of the pore-forming agent is eliminated by

firing the masses of abrasive particles, thereby forming holes in the portions of the masses of the raw-material abrasive particles where the pore-forming agent was located.

5 The raw-material slurry is obtained by dispersing the raw-material abrasive particles using water as the dispersion medium.

A mass of raw-material abrasive particles refers to a mass-like substance formed by multiple raw-material abrasive particles gathering together, and a mass of raw-material abrasive particles includes raw-material abrasive particles, a pore-forming agent, and binders that are blended as appropriate. The mass of raw-material abrasive particles has a form in which 10 many raw-material abrasive particles are attached to a moisture-containing pore-forming agent so as to cover the surface thereof. Binders are preferably dispersed between the raw-material abrasive particles.

A cluster of raw-material abrasive particles refers to a substance in 15 which holes (gaps) have been formed due to at least a portion of the pore-forming agent being eliminated in a mass of raw-material abrasive particles. A cluster of raw-material abrasive particles includes raw-material abrasive particles and binders that are blended as appropriate. In a cluster of raw-material abrasive particles, it is preferable that the raw-material abrasive 20 particles are joined together by the binders (e.g., by the binders melting and solidifying).

Also, a state after the drying processing and before the firing processing can be referred to as a mass of raw-material abrasive particles, and a state after the firing processing and before the crushing processing can be referred to 25 as a cluster of raw-material abrasive particles.

[0057] The polishing rate of the cerium-based polishing material is improved by performing bonding at particle boundaries through firing to increase the size of the particles functioning as the particles at a time of actual polishing. However, the polishing materials that increased in size due to the firing are 30 generally pulverized in order to be adjusted to a size appropriate for the

polishing processing. However, pulverization of the polishing material is costly and inconvenient. Also, when pulverization is performed, the particle size distribution of the polishing material is likely to become non-uniform, and therefore there arises a need to perform classification after pulverization, which is also costly and inconvenient. For this reason, the second embodiment aims to provide a method for easily producing a polishing slurry with an improved polishing rate, at a low cost. Also, the second embodiment aims to provide a method for producing a glass substrate using such a polishing slurry.

According to the method for producing a polishing slurry of the second embodiment, clusters of raw-material abrasive particles are produced in which holes (gaps) are formed by using the pore-forming agent, and which are easily crushed. For this reason, the clusters of the raw-material abrasive particles can be crushed using a simple method, and the polishing slurry can be produced simply and at a low cost. Also, with the polishing abrasive particles, the raw-material abrasive particles are made larger through drying and firing, and therefore the polishing rate is improved. Also, according to the method for producing a glass substrate of the second embodiment, a glass substrate can be polished at a high polishing rate.

[0058] Note that there is no particular limitation on the application of the glass substrate, and for example, the glass substrate may be used in a panel for various types of display apparatuses, such as liquid crystal display apparatuses, photomasks or mask blanks, which are substrates for photomasks, and magnetic disks for HDD apparatuses. The processing for polishing the glass substrate is performed by, for example, using a double-sided polishing apparatus in the later-described method for manufacturing the glass substrate.

There is no particular limitation on the polishing abrasive particles, but a cerium-based polishing material or a zirconia-based polishing material having zirconium oxide (zirconia) as a main component is preferably used in light of the fact that a glass substrate can be polished using a chemical action in addition to a mechanical action. The polishing slurry is obtained by

dispersing polishing abrasive particles using water as the dispersion medium, and the polishing abrasive particles are used as free abrasive particles in the polishing processing. The polishing slurry may include a component other than polishing abrasive particles and water, such as a phosphoric acid-based dispersing agent, for example. Although there is no particular limitation on the concentration of the polishing abrasive particles in the polishing slurry, it is 1 to 30 mass%, and preferably 3 to 20 mass%, for example.

[0059] (a) Adding Processing

The raw-material abrasive particles are raw materials for the polishing abrasive particles included in the polishing slurry produced using the method according to the second embodiment, and if a later-described used polishing slurry is to be used as raw-material abrasive particles, raw-material abrasive particles means used polishing abrasive particles. It is preferable that the average particle diameter of the raw-material abrasive particles is 0.3 to 2 μm .

By using raw-material abrasive particles with such an average particle diameter, polishing abrasive particles with a size appropriate for performing polishing processing on a glass substrate can be produced. It has been found that raw-material abrasive particles with a relatively small average particle diameter (e.g., less than 0.3 to 0.5 μm) among the raw-material abrasive particles in the 0.3 to 2.0 μm range are not likely to be collected through solid-liquid separation, and even if they are collected, those recycled using the conventional method decrease in size, lower the polishing rate, and cause marks to form on the glass substrate in the polishing processing. According to the production method of the second embodiment, polishing abrasive particles having an appropriate hardness (crushing strength) are produced as described below, and therefore the production method of the second embodiment is suitable for producing a polishing slurry using polishing abrasive particles with a relatively small average particle diameter as the raw-material abrasive particles. Note that the raw-material abrasive particles are secondary particles formed by several to several tens of primary particles aggregating,

and the average particle diameter of the raw-material abrasive particles means the average particle diameter of the secondary particles. Note that a secondary particle acts as one polishing abrasive particle at a time of actual polishing. Also, in the present specification, the average particle diameter means the median diameter (d50). d50 is a particle diameter at which the cumulative particle diameter measured using a laser diffraction/scattering particle size distribution measurement method corresponds to 50% accumulation, starting from a small particle side.

The raw-material abrasive particles may be unused or may be a used polishing slurry. In the present specification, “used” means having been used in processing for polishing a glass substrate at least once. In the case where the polishing slurry is produced using the used polishing slurry, the used polishing abrasive particles can be recycled, and the cost of the polishing slurry can be suppressed. Note that in the present specification, if the used polishing slurry is used as the raw-material slurry, the method for producing the polishing slurry of the present embodiment can be called a method for recycling used polishing slurry, and if the polishing slurry includes a cerium-based polishing material having ceria particles as a main component, it can be called a method for recycling used ceria slurry.

Also, the used polishing slurry used as the raw-material abrasive particles may be recycled using the method for recycling used polishing slurry. In this case, by repeatedly recycling and using the used polishing slurry, the cost of the polishing slurry can be further suppressed.

[0060] The pore-forming agent is preferably an organic compound having a hydroxyl group on its surface, a polysaccharide can be given as an example of such a substance, and preferably, a polysaccharide (hereinafter referred to also as “the above-described polysaccharide” in the present embodiment) that dissolves or gels in water by being heated can be given as an example thereof. The raw-material abrasive particles can attach to the surface of the above-described polysaccharide when the above-described polysaccharide

includes water in the drying processing, and in the firing processing, at least a portion of the polysaccharide is eliminated through firing, and portions of the polysaccharide located in the mass of the raw-material abrasive particles become pores in the clusters of the raw-material abrasive particles, and therefore porous clusters of the raw-material abrasive particles can be produced. Although there is no limitation on the temperature at which the above-described polysaccharide dissolves or gels in water, it is preferable that the above-described polysaccharide has dissolved or gelled in water at the drying temperature in the drying processing, for example. The decomposition temperature of the pore-forming agent is preferably 600°C or less, or more preferably 500°C or less, in light of the fact that the pore-forming agent is easily eliminated by firing at a relatively low temperature.

Also, since the above-described polysaccharide enters a state of being likely to attach to later-described binders in the process of being dried in the drying processing if the binders are added to the raw-material slurry, it has a function of suppressing aggregation of the binders while helping the binders to disperse and be arranged between the raw-material abrasive particles. This function is thought to be performed due to the water-containing polysaccharides capturing the binders and thus positioning the binders relative to the raw-material abrasive particles. In this respect, the pore-forming agent can be said to be a binder aggregation suppressing agent.

[0061] Specifically, starch, glycogen, agarose, pectin, or a combination thereof is preferably used as the above-described polysaccharide. Examples of starch include corn starch, wheat flour, potato starch, and rice starch. There is no limitation on the raw materials of the starch, and cereals such as corn, wheat, rice, potatoes, and sweet potatoes can be used as the raw materials.

[0062] The adding amount of the pore-forming agent is preferably 10 to 100 parts by mass, or more preferably 10 to 50 parts by mass with respect to 100 parts by mass of the raw-material abrasive particles. If the adding amount is less than 10 parts by mass, pores will not be sufficiently formed in the clusters

of the raw-material abrasive particles, and crushing will be difficult to perform in some cases. Also, if the adding amount is greater than 100 parts by mass, the effect of the binders will be hindered, the polishing abrasive particles (raw-material abrasive particles) will not become sufficiently large, and the effect of improving the polishing rate through granulation is not obtained in some cases.

The pore-forming agent is added to the raw-material slurry in a state of being dispersed in a solvent such as water, for example.

[0063] In the adding processing, it is preferable to further add binders to be distributed on the surfaces of the raw-material abrasive particles. The binder can increase the strength of the particle boundaries by dissolving during the firing processing and joining together raw-material abrasive particles. Note that the particle boundary refers to the boundary between adjacent raw-material abrasive particles. Accordingly, due to the secondary particle diameter (particle diameter of a particle acting as one polishing abrasive particle at the time of polishing) of the polishing abrasive particles being larger, the polishing rate of the polishing abrasive particles increases, the polishing abrasive particles are less likely to break in the polishing processing, and a high polishing rate can be maintained. On the other hand, if raw-material abrasive particles are joined via binders, the strength of the particle boundary is not excessively high compared to the case where the raw-material abrasive particles are directly joined, and therefore a case is suppressed in which marks are formed on the glass substrate in the polishing processing.

Also, if breaking occurs easily during the polishing processing, the percentage of small particles will increase, and the polishing load will be applied more greatly to the large particles, of which there are relatively few, and therefore polishing marks are more likely to be formed. Accordingly, the formation of polishing marks can be suppressed by joining the abrasive particles using the binders.

On the other hand, since the strength of the particle boundaries is not excessively high, the clusters of raw-material abrasive particles including the binder can be crushed easily using ultrasonic irradiation or the like, and polishing abrasive particles with a size suitable for polishing processing and a uniform particle size distribution can be obtained. For this reason, there is no need to perform crushing by pulverization or the like, which is costly, and there is no need to perform classification, and therefore the polishing abrasive particles can be produced easily and at a low cost.

[0064] Specifically, binders that are not eliminated in the firing step are used.

In this respect, it is preferable that the temperature at which the binders decompose is a temperature exceeding the firing temperature in the firing step. Accordingly, the binders are preferably not organic. This is because organic binders will be eliminated in the firing step. The binders are preferably particles composed of a non-organic compound, and among these, particles composed of oxides such as silicon dioxide (silica) and titanium oxide (titania), hydrates thereof, glass such as aluminosilicate glass, and hydroxides such as cerium hydroxide, silicon hydroxide, and zirconia hydroxide are preferable in light of the fact that they have excellent dispersibility in the raw-material slurry. Among these, silica melts at a relatively low temperature (e.g., 800°C or less) and joins together raw-material abrasive particles, and therefore even if the firing temperature at the time of the firing processing is such a low temperature, the strength of the particle boundaries of the raw-material abrasive particles can be increased. It is thought that silica exists as a hydrate in the slurry, is dehydrated at the time of firing processing to become silica anhydride, and thereby joins together raw-material abrasive particles. Examples of silica include colloidal silica, fumed silica, and the like, and colloidal silica is preferably used in light of the fact that it has a more excellent dispersibility. Note that if silica or glass is melted to join together the raw-material abrasive particles, it is thought that a portion thereof forms a vitrified bond.

[0065] The binders have a property of being likely to aggregate, but due to the presence of the pore-forming agent in the raw-material slurry, aggregation of the binders is suppressed, and the binders are likely to be dispersed between the raw-material abrasive particles. In particular, silica is likely to aggregate in water, and becomes coarse silica particles, which cause marks to form on the glass substrate in some cases, but due to the pore-forming agent being added, this kind of aggregation of silica particles can be suppressed.

[0066] It is preferable that the average particle diameter of the binders is 3 to 20 nm. Binders with such an average particle diameter are sufficiently small relative to the raw-material abrasive particles, are easily dispersed and arranged between raw-material abrasive particles in the drying processing and the firing processing, and thus favorably function as the binders that join together the raw-material abrasive particles. If the average particle diameter of the binders is less than 3 nm, the joining of the raw-material abrasive particles will be insufficient in some cases, and if the average particle diameter of the binders is greater than 20 nm, the binders will join together and form coarse particles, which can cause polishing marks. The average particle diameter of the binders can be measured using a laser diffraction particle size distribution measurement apparatus.

[0067] The binders are preferably used polishing abrasive particles that were used in the second polishing processing of the later-described method for manufacturing a glass substrate. Since colloidal silica, which is an example of the used polishing abrasive particles, is normally discarded after use, using colloidal silica as the binders eliminates the need for raw material cost, and thus the polishing slurry can be produced at a low cost. Also, since the collected used polishing slurry can be added as-is to the raw-material slurry, excellent productivity is achieved.

The adding amount of the binders is preferably 1 to 10 parts by mass, and more preferably 1 to 5 parts by mass, relative to 100 parts by mass of the raw-material abrasive particles. If it is less than 1 part per mass, the effect of

the binders is not sufficiently obtained and the polishing abrasive particles break more easily, as a result of which the polishing rate decreases in some cases. Also, if it is greater than 10 parts by mass, the binders aggregate, generating coarse particles, which cause marks to form on the glass substrate.

5 Also, if it is greater than 10 parts by mass, there is a risk that an excessive amount of binders will attach to the surface of the ceria polishing abrasive particles, whereby the polishing function exhibited by the abrasive particle surface will decrease, and the polishing rate will decrease. In particular, if the polishing abrasive particles are cerium-based polishing materials, it is said
10 that a high polishing rate is achieved by exhibiting the chemical action on the glass substrate, and therefore if a substance other than ceria excessively covers the surface, the surface area of contact with the substrate to be polished decreases, and the polishing rate decreases.

[0068] Note that in the case of using used polishing slurry as the raw-material
15 abrasive particles, it is preferable to perform filtering, solid-liquid separation, and crushing in advance on the used polishing slurry before the adding processing. In the filtering, large-sized (e.g., 15 μm or more) foreign matter is removed. In the solid-liquid separation, glass components such as glass sludge included in the collected used polishing slurry are removed. In the
20 crushing, solid matter generated in the solid-liquid separation due to ultrasonic irradiation using a homogenizer are crushed. In order to easily perform the crushing, a hard caking prevention agent (e.g., a polysaccharide that is not water-soluble) that prevents the solid matter from becoming too hard may be added to the used polishing slurry before the solid-liquid separation.

25 Also, after the solid-liquid separation, the remaining liquid, which is a supernatant liquid, may be further subjected to solid-liquid separation, and the resulting solid matter may be crushed and used as the raw-material slurry. Accordingly, by collecting the used polishing abrasive particles with a small average particle diameter (e.g., 0.3 to 2 μm) that were not collected in the first
30 solid-liquid separation and using them as the raw-material abrasive particles,

the polishing abrasive particles can be recycled. If the solid-liquid separation is thus performed multiple times, the rate of collecting costly polishing abrasive particles such as cerium-based polishing material in particular is increased, and the effect of suppressing the cost of the polishing slurry increases. Note
5 that in this case, solid matter with a large average particle diameter (e.g., 0.5 to 5 μm) obtained in the first solid-liquid separation may be separately supplied with water, subsequently crushed, and furthermore subjected to filtering, and thereafter may be used cyclically while processing for polishing the glass substrate is performed, may be stored in a tank for storing the polishing slurry,
10 or may be recycled using the method for producing the polishing slurry according to the present embodiment.

[0069] (b) Drying processing

In the drying processing, the raw-material slurry containing the pore-forming agent is preferably dried using a spray-drying method. By
15 performing spray-drying, the sizes of the masses of raw-material abrasive particles can be controlled. The spray-drying method is preferable because the average particle diameter can be made smaller in comparison to other methods, and furthermore, variation in the particle diameter can be reduced. Specifically, spray-drying is performed by spraying using a known spraying
20 means, such as a rotary disc type, a binary fluid nozzle type, or a pressure nozzle type, whereby drying is performed by supplying the sprayed material to a drying chamber of a spray dryer. Conditions such as the type of the spraying means, the nozzle hole diameter, and the pressure for supplying the raw-material slurry are set as appropriate according to the target sizes of the
25 masses of raw-material abrasive particles. The sizes (average particle diameter) of the masses of raw-material abrasive particles obtained through spray-drying are preferably around 5 to 10 μm , for example. If the average particle diameter is larger than 10 μm , coarse particles will remain after crushing and cause polishing marks in some cases. On the other hand, if the
30 average particle diameter is less than 5 μm , the percentage of small particles

will increase and the polishing rate will decrease in some cases. Note that the average particle diameter in this context is a value obtained by obtaining the major axis lengths of 100 randomly-selected masses of the raw-material abrasive particles in SEM observation and finding the average thereof.

Also, in the case of adding a pore-forming agent to the raw-material slurry that has not been subjected to the spray-drying, the size of the pore-forming agent (average particle diameter of the pore-forming agent) is preferably 3 to 20 μm . Due to the pore-forming agent falling within such a size range, the sizes of the pores in the clusters of the raw-material abrasive particles resulting from firing can be set appropriately, and the sizes of the crushed polishing abrasive particles can be set appropriately (e.g., to an average particle diameter of 0.5 to 10 μm). As for the drying temperature (atmospheric temperature in the drying chamber), the temperature at the entrance to the drying chamber is 150 to 250°C, for example. Note that the drying processing may be performed without heating.

Here, FIG. 1(a) shows a mass of raw-material abrasive particles produced through drying processing. Here, a spherical mass of raw-material abrasive particles produced by drying the raw-material slurry containing the binders is shown as an example. A mass 10 of the raw-material abrasive particles is formed by many raw-material abrasive particles 3 attaching to a moisture-containing pore-forming agent 7 so as to cover the surface thereof, and binders (not shown) are dispersed between the raw-material abrasive particles 3. Note that the masses 10 of the raw-material abrasive particles contain many raw-material abrasive particles 3, but in FIG. 1(a), the boundaries of the many raw-material abrasive particles 3 are not shown, for the sake of convenience.

[0070] (c) Firing Processing

Although there is no limitation on an apparatus for performing firing processing, an example thereof is a muffle furnace. It is preferable that the firing temperature in the firing processing is 800°C or less. The firing

temperature is the atmospheric temperature in the space for performing firing. By setting the firing temperature to 800°C or less, the energy cost for producing the polishing slurry can be reduced. If the firing temperature exceeds 800°C, bonding at the particle boundaries between the raw-material abrasive particles will advance, and the strength at the particle boundaries of the polishing abrasive particles will become excessively high in some cases. Also, the binders will bond together and become coarse particles in some cases. In these cases, marks on the glass substrate are likely to be formed. Also, if the firing temperature exceeds 800°C, the composition of the raw-material abrasive particles will change, increasing the hardness, which causes marks to form on the glass substrate in some cases. Also, the firing temperature in the firing processing is preferably 500°C or more, and more preferably, 600°C or more. If the firing temperature is less than 500°C, the bonding between the raw-material abrasive particles will be insufficient in some cases.

[0071] In the firing processing, if the pore-forming agent is added to the raw-material slurry, it is preferable that at least a portion of the pore-forming agent is eliminated through firing. Accordingly, the portions at which the pore-forming agent was distributed in the masses of raw-material abrasive particles become pores, and porous clusters of raw-material abrasive particles are produced.

Here, FIG. 1(b) shows a cluster of raw-material abrasive particles produced through firing processing. Here, a cluster of raw-material abrasive particles produced by drying and firing the raw-material slurry containing the binders is shown as an example. A cluster of the raw-material abrasive particles includes pores that are formed due to the pore-forming agent being eliminated. Note that the clusters of the raw-material abrasive particles become porous due to having, in addition to the pores shown in the drawing, many minute gaps between the raw-material abrasive particles formed by the binder aggregation suppressing agent distributed between the raw-material abrasive particles surrounding the pores being eliminated. The size

(average particle diameter) of the cluster 20 of the raw-material abrasive particles is preferably a size of around 5 to 10 μm , for example. If the average particle diameter is larger than 10 μm , coarse particles will remain after crushing and cause polishing marks in some cases. On the other hand, if the average particle diameter is less than 5 μm , the percentage of small particles will increase and the polishing rate will decrease in some cases. Note that the average particle diameter in this context is a value obtained by obtaining the major axis lengths of 100 randomly-selected masses of the raw-material abrasive particles in SEM observation and finding the average thereof. The binders (not shown) in the cluster 20 of the raw-material abrasive particles are melted in the firing processing, and when the binders solidify thereafter, the raw-material abrasive particles 3 are joined together, and thereby the strength at the particle boundaries of the raw-material abrasive particles 3 reaches an appropriate magnitude (e.g., the average value of a later-described crushing strength is 0.1 to 20 MPa). Note that the cluster 20 of the raw-material abrasive particles contains many raw-material abrasive particles 3, but in FIG. 1(b), the boundaries of the many raw-material abrasive particles 3 are not shown, for the sake of convenience. For example, element mapping using an EDX (Energy Dispersive X-ray microanalyzer) can be used to confirm that the binders are disposed between the raw-material abrasive particles 3.

[0072] (d) Crushing Processing

The method for producing a polishing slurry according to the present embodiment preferably further includes crushing processing in which the clusters of the raw-material abrasive particles are crushed to produce polishing abrasive particles. Accordingly, polishing abrasive particles of a size appropriate for polishing processing can be obtained. If pores are formed in the clusters of the raw-material abrasive particles, crushing is even easier to perform.

Crushing is performed by performing ultrasonic irradiation on the clusters of the raw-material abrasive particles using a homogenizer, for

example. The frequency of the ultrasound is preferably 16 to 120 kHz. The crushing may be performed using a means other than a homogenizer. Although there is no particular limitation on the crushing time, it is 1 to 20 minutes, for example.

5 The crushing is preferably performed such that the average particle diameter of the polishing abrasive particles is 0.5 to 10 μm . The average particle diameter is more preferably 0.5 to 5 μm or 0.7 to 3 μm . Upon performing polishing processing using polishing abrasive particles with such an average particle diameter, polishing can be performed at a high polishing rate,
10 and a case can be suppressed in which marks are formed on the surface of the glass substrate.

The crushing processing may be performed using a milling method in which the particles are physically broken down using a ball mill or the like, but the above-described ultrasonic method is superior in terms of simplicity.

15 [0073] After the crushing processing, the polishing slurry can be produced by dispersing the polishing abrasive particles in water. At this time, it is preferable that large-sized (e.g., 15 μm or more) particles are removed by performing filtering before the water is supplied. Large-sized particles in this context are portions of clusters of the raw-material abrasive particles that were
20 not crushed to a predetermined size through the crushing processing.

[0074] According to the method for producing a polishing slurry of the present embodiment, the pore-forming agent is added to the raw-material slurry and the resulting slurry is dried and fired, whereby porous clusters of the raw-material abrasive particles, in which holes are formed, can be produced.

25 With such clusters of raw-material abrasive particles, crushing can be performed easily using ultrasonic irradiation or the like, and polishing abrasive particles having a size suitable for polishing processing and a uniform particle size distribution can be obtained. Thus, according to the method of the present embodiment, since there is no need to perform pulverization or the like,
30 which is costly, and there is no need to perform classification, the polishing

abrasive particles can be produced simply and at a low cost. The polishing abrasive particles have an improved polishing rate due to the raw-material abrasive particles being larger.

[0075] Polishing Abrasive Particles and Polishing Slurry

5 FIG. 2 conceptually shows a polishing abrasive particle 1 produced using the above-described method.

Here, a case in which raw-material abrasive particles 3 are cerium-based polishing materials or zirconia-based polishing materials will be described as an example.

10 The polishing abrasive particle 1 includes raw-material abrasive particles 3, which include ceria or zirconia particles to be used in the processing for polishing the glass substrate, and binders 5, which are distributed on the surfaces of the raw-material abrasive particles 3. More specifically, the polishing abrasive particle 1 is a polishing abrasive particle to be used in
15 processing for polishing a glass substrate, silica particles existing as the binders 5 between the ceria or zirconia particles.

Note that as shown in FIG. 1, many raw-material abrasive particles 3 are included in the mass 10 of raw-material abrasive particles and the cluster 20 of raw-material abrasive particles.

20 The cerium-based polishing material used in the raw-material abrasive particles 3 is preferably a mixture including, in addition to ceria, at least one of an oxide of another rare earth element such as lanthanum, praseodymium, and neodymium, fluorides thereof, and the like, in order to achieve a high polishing rate while suppressing a case in which marks are formed on the glass substrate.
25 The zirconia-based polishing material may be a mixture including silicon dioxide in addition to zirconia.

30 The average particle diameter of the raw-material abrasive particles 3 is 0.3 to 2 μm , for example, and the raw-material abrasive particles 3 are formed due to the aggregation of particles with a primary particle diameter of about 80 to 150 nm, for example.

Note that in FIG. 2, the binders 5 are distributed on the surfaces of the raw-material abrasive particles 3, which are the secondary particles, but the binders 5 may be distributed on the surfaces of the primary particles constituting the raw-material abrasive particles 3. The binders 5 preferably cover less than 50% of the surface area of the surfaces of the raw-material abrasive particles 3. If the binders 5 cover 50% or more, the surface of contact between the surfaces of the polishing abrasive particle and the polished substrate decreases in size, and the polishing rate tends to decrease.

[0076] The average value of the crushing strength of the polishing abrasive particles 1, which is measured in accordance with JIS R1639-5, is preferably 0.1 to 20 MPa. Due to the crushing strength being 0.1 MPa or more, a case is suppressed in which the polishing abrasive particles easily break into smaller sizes in the polishing processing, and thus a decrease in the polishing rate is suppressed. Note that since there is a large variation in the crushing strength, it is preferable to perform measurement at 20 points or more. From the viewpoint of more reliably suppressing a decrease in the polishing rate, the average value of the crushing strength is more preferably 3 MPa or more. Also, due to the average value of the crushing strength being 20 MPa or less, it is possible to suppress a case in which marks are formed on the surface of the glass substrate in the polishing processing.

The average particle diameter of the polishing abrasive particles 1 is, for example, 0.5 to 10 μm . The number of raw-material abrasive particles 3 included in the polishing abrasive particle 1 is several to around a dozen, for example, although there is no limitation thereto.

[0077] The polishing slurry includes the polishing abrasive particles 1 and a dispersion medium such as water in which the polishing abrasive particles 1 are dispersed.

[0078] Method for Manufacturing Glass Substrate

Next, a method for manufacturing a glass substrate according to the present embodiment will be described.

Here, a case of manufacturing a glass substrate to be used in a magnetic disk will be described as an example.

In the manufacturing method according to the present embodiment, the surface of a glass substrate is polished using the polishing slurry described in the first and second embodiments above. In other words, the manufacturing method of the present embodiment is a method in which the polishing slurries described in the first and second embodiments can both be used.

[0079] To describe an overview of the manufacturing method according to the present embodiment, first, molding processing for forming a plate-shaped glass blank having a pair of main surfaces is performed. The glass blank is a raw material for a magnetic-disk glass substrate. Next, rough grinding processing is performed on the glass blank. Thereafter, a glass substrate is formed by performing shaping processing on the glass blank, and edge surface polishing processing is furthermore performed thereon. Thereafter, precision grinding processing using fixed abrasive particles is performed on the glass substrate. Thereafter, first polishing processing and second polishing processing are performed on the glass substrate. Note that in the present embodiment, the processing is performed in the above-described flow, but there is no limitation to the above-described flow and the types of processing, and the above-described processing can be omitted as appropriate according to need. Hereinafter, the above-mentioned processes will be described.

[0080] (a) Processing for Molding a Glass Blank

In the molding processing, molding is performed using press molding, for example. With press molding, a disk-shaped glass blank can be obtained. The glass blank may be manufactured using a known molding method such as downdrawing, redrawing, or fusion, instead of press molding. By performing later-described shaping processing as appropriate on the plate-shaped glass blanks produced using these methods, a disk-shaped glass substrate, which is the basis for a magnetic-disk glass substrate, is obtained.

[0081] (b) Rough Grinding Processing

Next, rough grinding processing is performed. In the rough grinding processing, the above-described glass blank is subjected to grinding of both main surfaces of the glass blank while being held in a carrier (not shown) of a known double-side grinding apparatus. Specifically, the glass blank is held in a holding hole provided in the carrier and held between an upper surface plate and a lower surface plate, and both main surfaces of the glass substrate are ground by moving the glass substrate and the surface plates relative to one another by moving one or both of the upper surface plate and the lower surface plate while a grinding liquid including a grinding agent is supplied. Free grinding particles are used as the grinding agent, for example. In the rough grinding processing, the glass blank is ground such that a target plate thickness and a target flatness of the main surface are approximately reached. Note that the rough grinding processing is performed according to the dimensional accuracy or surface roughness of the molded glass blank, but can be omitted as appropriate.

[0082] (c) Shaping Processing

Next, shaping processing is performed. In the shaping processing, a circular hole is formed in the glass blank using a known machining method, and thus a disk-shaped glass substrate having a circular hole is obtained. Thereafter, the edge surfaces of the glass substrate are chamfered. Chamfering is performed on both the inner circumferential edge surface and the outer circumferential edge surface of the glass substrate. By performing chamfering, side wall surfaces that intersect the main surfaces and chamfered surfaces (intermediate surfaces) connecting the side wall surfaces and the main surfaces are formed on the edge surfaces of the glass substrate.

[0083] (d) Edge Surface Polishing Processing

Next, the edge surface polishing processing for the glass substrate is performed. In the edge surface polishing processing, polishing is performed by supplying a polishing liquid including free abrasive particles between polishing brushes and the edge surfaces of the glass substrate, and moving the polishing

brushes and the glass substrate relative to each other in the thickness direction of the glass substrate. With the edge surface polishing processing, the inner circumferential edge surface and the outer circumferential edge surface of the glass substrate are polished to mirror surfaces.

5 [0084] (e) Precision Grinding Processing

Next, precision grinding processing is performed on the main surfaces of the glass substrate. In the precision grinding processing, a double-side grinding apparatus in which fixed abrasive particles are attached to surface plates is used to grind the main surfaces of the glass substrate. Specifically,
 10 both main surfaces of the glass substrate are ground in a manner approximately similar to that of the rough grinding processing, except that grinding is performed using fixed abrasive particles instead of the above-described free abrasive particles.

[0085] (f) First Polishing Processing

15 Next, first polishing processing is performed on the main surfaces of the glass substrate. In the first polishing processing, the glass substrate is held in a carrier and both main surfaces of the glass substrate are polished using a known double-side polishing apparatus. In the first polishing processing, polishing is performed by using free abrasive particles and bringing polishing
 20 pads attached to the surface plates into contact with the main surfaces of the glass substrate. During the first polishing processing, the slurry including the free abrasive particles is supplied between the glass substrate and the polishing pads via tubes (not shown) from a supply tank (not shown) of the double-side polishing apparatus. The slurry is preferably used cyclically.
 25 The polishing slurry described in the embodiments above is used as the slurry including the free abrasive particles. For example, a cerium-based polishing material or a zirconia-based polishing material is used as the free abrasive particles.

The following conditions can be given as examples of preferable
 30 conditions in the first polishing processing.

- Polishing abrasive particle concentration: 1 to 20 wt%
- Load of the upper surface plate and the lower surface plate of the double-side polishing apparatus on the glass substrate: 50 to 200 g/cm²
- Polishing time: 10 to 120 minutes

5 Suede-type polishing pads are preferable since the formation of minute marks can be prevented. From the viewpoint of improving the polishing rate and reducing minute marks, the hardness of the polishing pads preferably have an Asker C hardness of 60 to 90.

[0086] In the first polishing processing, for example, cracks or warping
 10 remaining on the main surfaces are removed if grinding was performed using fixed abrasive particles, or minute surface unevenness forming on the main surfaces due to crystallization processing is removed. By adjusting a machining allowance as appropriate, the shape of the edge portions of the main surfaces can be prevented from being recessed or protruding excessively, and
 15 the surface roughness of the main surfaces, for example, the arithmetic mean roughness Ra, can be reduced. Also, since the polishing slurry used in the first polishing processing has polishing abrasive particles that are not likely to break, a case in which the polishing abrasive particles decrease in size and the polishing rate lowers is suppressed. Also, since the polishing abrasive
 20 particles are not excessively hard, a case in which marks are formed on the main surfaces of the glass substrate is suppressed.

[0087] Note that after the first polishing processing, the polishing slurry may be collected and furthermore recycled using the method for producing the polishing slurry according to the above-described embodiment, or in other
 25 words, a method for recycling used polishing slurry, and the recycled polishing slurry may be furthermore used in processing for polishing another glass substrate.

[0088] (g) Second Polishing (Mirror-Surface Polishing) Processing

Next, the second polishing processing is performed. The second
 30 polishing processing is for mirror-polishing the main surfaces. In the second

polishing processing, a double-side polishing apparatus and polishing method similar to those used in the first polishing processing may be used, but it is preferable that the size of the polishing abrasive particles is smaller than that in the first polishing processing. Accordingly, the roughness of the main surfaces can be reduced while preventing a case in which the shapes of the edge portions of the main surfaces are recessed or protrude excessively. After the second polishing processing, the glass substrate in the carrier is taken out of the double-side polishing apparatus and cleaned. The free abrasive particles used in the second polishing processing are colloidal silica, for example. Note that the used polishing slurry used in the second polishing processing can be collected and added to the raw-material slurry in the adding processing in the method for producing the polishing slurry according to the above-described embodiments.

[0089] Working Examples

(1) Working Examples Relating to First Embodiment

The following test was performed in order to confirm the effect of the first embodiment of the present invention. Specifically, the used polishing slurry serving as the raw-material abrasive particles was recycled under various different conditions as shown in Table 1, the crushing strength of the recycled polishing abrasive particles (samples 1 to 5) was measured, the polishing rate when performing polishing processing was measured, and the degree of the formation of marks on the glass substrate was evaluated.

[0090] The used polishing slurry was recycled by performing the following processes 1 to 7 in sequence. A slurry containing an unused cerium-based polishing material with an average particle diameter D50 of 1.0 μm was used to perform the first polishing processing of the above-described embodiment once, and the slurry was collected and used as the used polishing slurry. The average particle diameter D50 of the collected cerium-based polishing material was 0.7 μm . The first polishing processing was performed using a double-side

polishing apparatus under the same conditions as the conditions of the later-described first polishing processing.

[0091] Process 1: Foreign matter removal processing

Foreign matter such as polishing pad waste, mixed-in particles
 5 coarsened by drying in the polishing processing, and glass chips was removed from the used polishing slurry through filtering. The size of the particles and the like to be removed was set to 15 μm or more.

[0092] Process 2: Solid-liquid separation processing

After Process 1, the used polishing slurry was subjected to solid-liquid
 10 separation using a centrifuge at 800G for 20 minutes, and the supernatant liquid was collected. Then, the supernatant liquid was subjected to solid-liquid separation using a centrifuge at 800G for 1 hour, and the solid matter was collected.

[0093] Process 3: Crushing processing

15 Water was added to the solid matter obtained with the second instance of solid-liquid separation in Process 2, such that the concentration of the solid matter was 10 to 30 wt%, and the solid matter was crushed by performing ultrasonic irradiation at a frequency of 20 kHz using a homogenizer. Note that the time for the crushing processing was not fixed, and the crushing
 20 processing was performed until the solid matter was sufficiently crushed.

Process 4: Granulation/drying processing

The raw-material slurry was produced by adding the water to the crushed solid matter such that the concentration of the solid matter was 10 to 30 wt%, and the binders and binder aggregation suppressing agent were added
 25 in accordance with Table 1. The binders were added by adding the used polishing slurry including the used colloidal silica (having an average particle diameter of 3 to 20 nm in the used state). Corn starch and wheat flour were used as the binder aggregation suppressing agents.

Next, a parallel-flow spray dryer was used to spray-dry the
 30 raw-material slurry, whereby particles were formed and masses of the

raw-material abrasive particles were produced. The parallel-flow spray dryer is an apparatus that sprays the slurry in a drying chamber and simultaneously blows hot air thereon so as to dry the slurry. A rotary-disc spraying means was used as the spraying means. The spraying conditions were that the diameter of the rotary disc (atomizer) was 50 mm, the rotary disc rotation rate was 20000 rotations/minute, the ejection amount was 30 mL/minute, the temperature at the entrance to the drying chamber (temperature at the rotating disk position) was 150°C, and the temperature at the exit was 50°C.

Process 5: Firing processing

The masses of raw-material abrasive particles were placed in crucibles and fired for 2 hours at the temperatures shown in Table 1 in a muffle furnace, and clusters of the raw-material abrasive particles were produced.

Process 6: Crushing processing

The clusters of raw-material abrasive particles fired at 800°C or less were subjected to ultrasonic irradiation at a frequency of 20 kHz using a homogenizer, the solid matter was crushed, and the polishing abrasive particles were thus produced. On the other hand, clusters of the raw-material abrasive particles fired at a temperature exceeding 800°C were subjected to pulverization for four hours using a ball mill.

Process 7: Coarse particle removal processing

Coarse particles of 15 μm or more that were mixed into the polishing abrasive particles were removed through filtering.

[0094] Measurement of Crushing Strength

The crushing strength of the polishing abrasive particles of each Sample obtained through Process 7 was measured in accordance with JIS R1639-5. The results are shown in Table 1. Table 1 shows a crushing strength for n (n=20 or more) samples extracted randomly from each Sample as a range of measurement values and an average value.

[0095] Polishing Rate, Evaluation of Degree of Formation of Marks

Polishing slurries were produced by dispersing the polishing abrasive particles of the samples in water, and the first polishing processing of the above-described embodiment was performed on the glass substrates under the following conditions, using the produced polishing slurries and using a double-side polishing apparatus 400 used in the first polishing processing disclosed in JP 2012-133882A as a double-side polishing apparatus including a planetary gear mechanism. Note that suede-type polishing pads made of polyurethane foam were used on the surfaces of the upper and lower surface plates. Also, the slurry discharged from the surface plates after polishing was used cyclically such that the slurry returned once again to the polishing apparatus.

- Polishing abrasive particle concentration: 10 wt%
- Load of upper surface plate and lower surface plate on glass substrate: 100 g/cm²
- Polishing time: 60 minutes

2.5-inch aluminosilicate glass was used in the glass substrate. The number of glass plates polished in one instance of polishing processing was 100.

After the first polishing processing was performed, the glass substrates were cleaned and dried, and thereafter the polishing rate was calculated based on the difference in the weights of the glass substrates before and after polishing. Also, the number of scratches and pits on both surfaces of each glass substrate was counted using a laser-type surface examination apparatus, and an evaluation of “A” was given if the number was less than 20 per surface, an evaluation of “B” was given if the number was greater than or equal to 20 per surface and less than 100 per surface, and an evaluation of “C” was given if the number was greater than or equal to 100 per surface. If the evaluation was “A” or “B”, the formation of marks on the glass was suppressed. The polishing rates were indicated using relative values, with sample 4 being set to 100%. The results are shown in Table 1.

[0096] In Table 1, the mixing ratios indicate mixing ratios (parts by mass) of three components, namely the raw-material abrasive particles, the binders, and the binder aggregation suppressing agent.

[Table 1]

Sample No.	Binders	Binder aggregation suppressing agent	Mixing ratio	Firing temperature (°C)	Crushing strength (Average value) MPa	Polishing rate	Degree of mark formation (after one batch)
1	None	None	100:0:0	600	0.1 to 2 (1)	70	A
2	None	None	100:0:0	1300	100 or more (100 or more)	110	C
3	Included	None	100:3:0	600	0.1 to 20 (13)	110	B
4	Included	Corn starch	100:3:30	600	0.1 to 20 (10)	100	A
5	Included	Wheat flour	100:3:30	600	0.1 to 20 (9)	100	A

5 [0097] As shown in Table 1, regarding the polishing abrasive particles of Samples 1 and 2, which were recycled without adding binders, it was found that in Sample 1, which was fired at a temperature of 800°C or less, no marks on the glass substrates were formed, but the crushing strength was small and the polishing rate was low. Also, it was found that in Sample 2, which was
 10 fired at a temperature exceeding 800°C, the crushing strength was large and the polishing rate was high, but many marks on the glass substrates were formed.

On the other hand, it was found that the polishing abrasive particles of Samples 3 to 5, which were recycled with binders added, had crushing
 15 strengths within a range of 0.1 to 20 MPa and had high polishing rates, and the formation of marks on the glass substrates was suppressed. In particular, it was found that the polishing abrasive particles of Samples 4 and 5, in which binder aggregation suppressing agents were added, had about the same crushing strength as Sample 3, but had sufficiently high polishing rates and
 20 marks on the glass substrates were not formed.

Note that when the clusters of the raw-material abrasive particles of Samples 4 and 5, to which binder aggregation suppressing agents were added,

were observed with a microscope, it was confirmed that pores that were approximately equal in size to the added binder aggregation suppressing agent existed. Also, upon performing element mapping by EDX, it was confirmed that the binders were disposed on the surfaces of the polishing abrasive particles of Samples 3 to 5, to which the binders were added.

[0098] Firing temperature dependence

In order to study the effect of the firing temperature, the used slurry was recycled under the same conditions as those of Sample 3, except that the firing temperature was changed to 800°C and 1000°C (Samples 6 and 7). As a result, in Sample 6, the average value of the crushing strength was 14 MPa, the relative value of the polishing rate was 112, and the degree of the formation of marks was rank B. On the other hand, in Sample 7, the average value of the crushing strength was 53 MPa, the relative value of the polishing rate was 112, and the degree of the formation of marks was rank B. Note that upon comparing the degrees of the formation of marks in detail, Sample 3 had 31 per surface, whereas Sample 7 had 87 per surface. In other words, it was found that differences occurred within rank B as well due to the firing temperature.

[0099] Continuous Polishing Test

The above-described first polishing processing was performed continuously on five batches (500 processed substrates) using the recycled slurries of Samples 1 and 3 to 5, and thereafter the degrees of the formation of marks was evaluated. Upon doing so, Sample 1 became rank C, and the other samples were the same as the ranks shown in Table 1. It is inferred that this is because the recycled slurry of Sample 1 had a low crushing strength, and therefore broke down due to the polishing processing, and the small particles increased in number.

[0100] (2) Working Examples Relating to Second Embodiment

The following test was performed in order to confirm the effect of the second embodiment of the present invention. Specifically, the used polishing slurry serving as the raw-material abrasive particles was recycled under the

various different conditions shown in Tables 2 and 3, and regarding the recycled polishing abrasive particles (Samples 11 to 13, 12A, and 13A), the amount of time needed for crushing in the Samples 11, 12A, and 13A was measured, and regarding Samples 11 to 13, the crushing strengths were measured, and furthermore, the polishing rates at the time of performing polishing processing were measured. Also, the degrees of formation of marks formed on the glass substrates were evaluated for Samples 11 to 13.

[0101] The used polishing slurry was recycled by performing the following Processes 1 to 7 in sequence. A slurry containing an unused cerium-based polishing material with an average particle diameter D50 of 1.0 μm was used to perform the first polishing processing of the above-described embodiment once, and the slurry was collected and used as the used polishing slurry. The average particle diameter D50 of the collected cerium-based polishing material was 0.7 μm . The first polishing processing was performed using a double-side polishing apparatus under the same conditions as the conditions of the later-described first polishing processing.

[0102] Process 1: Foreign matter removal processing

Foreign matter such as polishing pad waste, mixed-in particles coarsened by drying in the polishing processing, and glass chips was removed from the used polishing slurry through filtering. The size of the particles and the like to be removed was set to 15 μm or more.

[0103] Process 2: Solid-liquid separation processing

After Process 1, the used polishing slurry was subjected to solid-liquid separation using a centrifuge at 800G for 20 minutes, and the supernatant liquid was collected. Then, the supernatant liquid was subjected to solid-liquid separation using a centrifuge at 800G for 1 hour, and the solid matter was collected.

[0104] Process 3: Crushing processing

Water was added to the solid matter obtained with the second instance of solid-liquid separation in Process 2, such that the concentration of the solid

matter was 10 to 30 wt%, and the solid matter was crushed by performing ultrasonic irradiation at a frequency of 20 kHz using a homogenizer. Note that the time for the crushing processing was not fixed, and the crushing processing was performed until the solid matter was sufficiently crushed.

5 Process 4: Granulation/drying processing

The raw-material slurry was produced by adding the water to the crushed solid matter such that the concentration of the solid matter was 10 to 30 wt%, and the pore-forming agents and binders were added in accordance with Tables 2 and 3. The binders were added by adding the used polishing
10 slurry including the used colloidal silica (having an average particle diameter of 3 to 20 nm in the used state). Corn starch and wheat flour were used as the pore-forming agents.

Next, a parallel-flow spray dryer was used to spray-dry the raw-material slurry, whereby particles were formed and masses of the
15 raw-material abrasive particles were produced. The parallel-flow spray dryer is an apparatus that sprays the slurry in a drying chamber and simultaneously blows hot air thereon so as to dry the slurry. A rotary-disc spraying means was used as the spraying means. The spraying conditions were that the diameter of the rotary disc (atomizer) was 50 mm, the rotary disc rotation rate
20 was 20000 rotations/minute, the ejection amount was 30 mL/minute, the temperature at the entrance to the drying chamber (temperature at the rotating disk position) was 150°C, and the temperature at the exit was 50°C.

Process 5: Firing processing

The masses of raw-material abrasive particles were placed in crucibles
25 and fired for 2 hours at 600°C in a muffle furnace, and clusters of the raw-material abrasive particles were produced.

Process 6: Crushing processing

The clusters of raw-material abrasive particles were subjected to ultrasonic irradiation at a frequency of 20 kHz using a homogenizer, the solid
30 matter was crushed, and the polishing abrasive particles were thus produced.

Process 7: Coarse particle removal processing

Coarse particles of 15 μm or more that were mixed into the polishing abrasive particles were removed through filtering.

[0105] Measurement of Crushing Strength

5 The crushing strength of the polishing abrasive particles of each Sample obtained through Process 7 was measured in accordance with JIS R1639-5. The results are shown in Table 3. Table 3 shows a crushing strength for n (n=20 or more) samples extracted randomly from each Sample as a range of measurement values and an average value.

10 [0106] Polishing Rate, Evaluation of Degree of Formation of Marks

Polishing slurries were produced by dispersing the polishing abrasive particles of the samples in water, and the first polishing processing of the above-described embodiment was performed on the glass substrates under the following conditions, using the produced polishing slurries and using a
15 double-side polishing apparatus 400 used in the first polishing processing disclosed in JP 2012-133882A as a double-side polishing apparatus including a planetary gear mechanism. Note that suede-type polishing pads made of polyurethane foam were used on the surfaces of the upper and lower surface plates. Also, the slurry discharged from the surface plates after polishing was
20 used cyclically such that the slurry returned once again to the polishing apparatus.

· Polishing abrasive particle concentration: 10 wt%

· Load of upper surface plate and lower surface plate on glass substrate: 100 g/cm²

25 · Polishing time: 60 minutes

2.5-inch aluminosilicate glass was used in the glass substrate. The number of glass plates polished in one instance of polishing processing was 100.

After the first polishing processing was performed, the glass substrates were cleaned and dried, and thereafter the polishing rate was calculated based
30 on the difference in the weights of the glass substrates before and after

polishing. Also, the number of scratches and pits on both surfaces of each glass substrate was counted using a laser-type surface examination apparatus, and an evaluation of “A” was given if the number was less than 20 per surface, an evaluation of “B” was given if the number was greater than or equal to 20 per surface and less than 100 per surface, and an evaluation of “C” was given if the number was greater than or equal to 100 per surface. If the evaluation was “A” or “B”, the formation of marks on the glass was suppressed. The polishing rate is indicated using a relative value using Sample 12 as 100%. The results are shown in Table 3.

In Tables 2 and 3, the mixing ratios express the mixing ratios (parts by mass) of three components, namely the raw-material abrasive particles, the pore-forming agent, and the binders.

[0107] [Table 2]

Sample No.	Pore-forming agent	Binder	Mixing ratio	Amount of time (minutes) needed for crushing
11	None	None	100:0:0	60
12A	Corn starch	None	100:30:0	5
13A	Wheat flour	None	100:30:0	5

[0108] Sample 11, which was recycled without adding the pore-forming agent, took 60 minutes to sufficiently crush in the above-described Process 6. With this, sufficient crushing is not possible in a relatively short amount of time, and polishing abrasive particles of a size appropriate for polishing processing cannot be obtained.

[0109] Firing temperature dependence

In order to study the effect of the firing temperature, the used slurry was recycled under the same conditions as those of Samples 11, 12A, and 13A except that the firing temperature was changed to 500°C and 800°C, and when the amounts of time needed for crushing were evaluated similarly to the above description, the same results were obtained.

[0110] [Table 3]

Sample No.	Pore-forming agent	Binder	Mixing ratio	Crushing strength (MPa)	Polishing rate	Degree of mark formation (after one batch)
11	None	None	100:0:0	0.1 to 2 (1)	70	A
12	Corn starch	Included	100:30:3	0.1 to 20 (10)	100	A
13	Wheat flour	Included	100:30:3	0.1 to 20 (9)	100	A

[0111] As shown in Table 3, it was found that Samples 12 and 13, which were recycled with the pore-forming agent added, both had crushing strengths within a range of 0.1 to 20 MPa and had high polishing rates. Also, it was found that in Samples 12 and 13, marks on the glass substrate were hardly formed at all, regardless of the fact that Samples 12 and 13 had been recycled with binders added.

Note that upon observing the clusters of the raw-material abrasive particles of Samples 12 and 13 with a microscope, it was confirmed that pores approximately equal in size to the added pore-forming agents were present. Also, upon performing element mapping by EDX, it was confirmed that the binders were disposed on the surfaces of the polishing abrasive particles of Samples 12 and 13, to which the binders were added.

[0112] A method for producing a polishing slurry, polishing abrasive particles, a polishing slurry, and a method for manufacturing a glass substrate of the present invention have been described in detail above, the present invention is not limited to the above-described embodiments, and various improvements and modifications are possible without departing from the gist of the present invention.

[Descriptions of Reference Numerals]

[0113] 1 Polishing abrasive particles

3 Raw-material abrasive particle (abrasive particle)

5 Binder

7 Binder aggregation suppressing agent (pore-forming agent)

9	Pore
10	Mass of raw-material abrasive particles
20	Cluster of raw-material abrasive particles

CLAIMS

1. A method for producing a polishing slurry including polishing abrasive particles for use in processing for polishing a glass substrate, comprising:
 - 5 adding processing in which binders are added to a raw-material slurry including raw-material abrasive particles serving as a raw material for the polishing abrasive particles;
 - drying processing in which the raw-material slurry including the binders is dried to produce a mass of the raw-material abrasive particles
 - 10 including the binders; and
 - firing processing in which the mass of the raw-material abrasive particles is fired to produce a cluster of the raw-material abrasive particles including the binders.
- 15 2. The method for producing a polishing slurry according to claim 1, wherein the binders include silica particles.
3. The method for producing a polishing slurry according to claim 1 or 2, wherein an average particle diameter of the binders is 3 to 20 nm.
- 20 4. The method for producing a polishing slurry according to any one of claims 1 to 3, further comprising crushing processing in which the cluster of the raw-material abrasive particles is crushed to produce the polishing abrasive particles,
- 25 wherein the average particle diameter of the polishing abrasive particles produced by the crushing processing is 0.5 to 10 μm .
5. The method for producing a polishing slurry according to any one of claims 1 to 4, wherein in the adding processing, a binder aggregation

suppressing agent for suppressing aggregation of the binders is further added,
and

in the drying processing, the binders are dispersed in the mass of the
raw-material abrasive particles via the binder aggregation suppressing agent.

5

6. The method for producing a polishing slurry according to claim 5,
wherein in the firing processing, at least a portion of the binder aggregation
suppressing agent is eliminated by firing the mass of the raw-material abrasive
particles.

10

7. The method for producing a polishing slurry according to claim 5 or 6,
wherein the binder aggregation suppressing agent is a polysaccharide.

8. The method for producing a polishing slurry according to any one of
15 claims 1 to 7, wherein the firing is performed at a temperature of 800°C or less.

9. The method for producing a polishing slurry according to any one of
claims 1 to 8, wherein in the drying processing, the raw-material slurry
including the binders is dried through spray-drying.

20

10. The method for producing a polishing slurry according to any one of
claims 1 to 9, wherein the raw-material slurry includes ceria particles that
were used in processing for polishing a glass substrate.

25 11. Polishing abrasive particles to be used in processing for polishing a
glass substrate, wherein in the polishing abrasive particles, silica particles
exist as binders between ceria or zirconia particles.

12. A polishing slurry including the polishing abrasive particles according
30 to claim 11.

13. A method for manufacturing a glass substrate, wherein a surface of a glass substrate is polished using the polishing slurry produced through the method of producing a polishing slurry according to any one of claims 1 to 10, the polishing abrasive particles according to claim 11, or the polishing slurry according to claim 12.

14. A method for producing a polishing slurry including polishing abrasive particles for use in processing for polishing a glass substrate, comprising:

adding processing in which a pore-forming agent is added to a raw-material slurry including raw-material abrasive particles serving as a raw material for the polishing abrasive particles;

drying processing in which the raw-material slurry including the pore-forming agent is dried to produce a mass of the raw-material abrasive particles containing the pore-forming agent; and

firing processing in which the mass of the raw-material abrasive particles is fired and the pore-forming agent forms a gap in a portion of the mass of the raw-material abrasive particles due to at least a portion of the pore-forming agent being eliminated.

15. The method for producing a polishing slurry according to claim 14, wherein in the mass of the raw-material abrasive particles, the average particle diameter of the pore-forming agent is 3 to 20 μm .

16. The method for producing a polishing slurry according to claim 14 or 15, wherein

in the adding processing, binders to be distributed on surfaces of the raw-material abrasive particles are further added, and

in the drying processing, the binders are dispersed in the mass of the raw-material abrasive particles via the pore-forming agent.

17. A method for manufacturing a glass substrate, wherein a surface of a glass substrate is polished using a polishing slurry produced using the method for producing a polishing slurry according to any one of claims 14 to 16.