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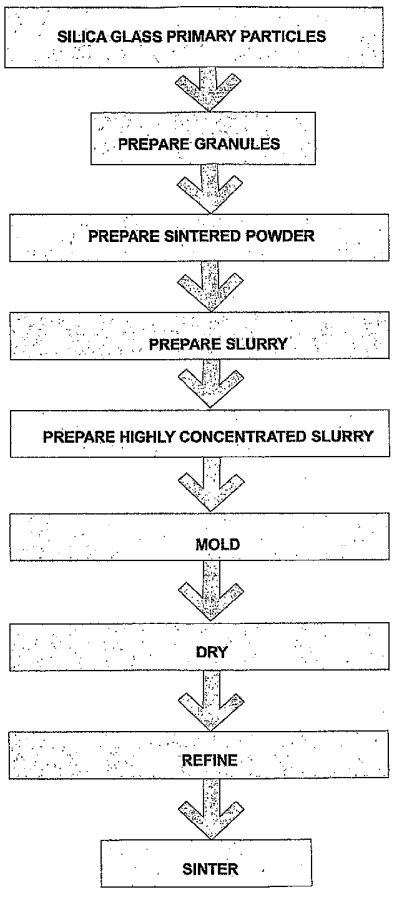
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(54) Title: METHOD FOR THE MANUFACTURE OF A SILICA GLASS PRODUCT



(57) Abstract: The present invention relates to an inexpensive and productive method for the manufacture of a silica glass product of a comparatively complex shape. The above-noted object is achieved by a method for the manufacture of a silica glass product, which comprises: a step in which a sintered silica powder is mixed with water to form a high concentration silica glass slurry of solid component density 70 to 85 mass% which is cast in a mould, then dried, and subjected to a purification process, before undergoing a glass formation process.

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Patent Application

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Method for the Manufacture of a Silica Glass Product

The present invention relates to a method for the manufacture of a silica glass product for use in the fields of, by way of example, the optical instrument, illumination lamp and scientific apparatus industries, processing jigs for semiconductor manufacture, scientific apparatus, and quartz glass crucibles and more particularly relates to the manufacture of a transparent silica glass product of a comparatively complex shape such as a reflector.

Prior art

Conventional methods used for the manufacture of a transparent or non-transparent silica glass product of a comparatively complex shape configured from silica glass include a method for the fused assembly of simple-shaped members based on flame processing, a method for the processing of bulk silica glass employing a mechanical processing technique, and a method of moulding based on the employment of a hot press moulding method. The problems inherent to the above mentioned method of assembly based on fusion include, because almost all the steps associated with the implementation of this method are manually performed, the time that the method requires and the need for a substantial level of expertise to implement the method and, furthermore, the sagging of the end parts of the product and associated loss of external appearance thereof caused by the high level of heat generated during the flame processing. The problems inherent to the mechanical processing technique include, because the silica glass which constitutes a brittle material of high hardness is machined employing a whetstone or the like, the long time required to implement the method along with the frequent chipping and so on of the silica glass producing fragments and, in addition, the high level of input energy

necessitated by the method. The problems inherent to the method of moulding based on the hot press moulding method include, because even quartz glass exhibits a high viscosity of logη 5 or more at 2000°C, the high cost of the device used, the lack of a mould able to withstand a high temperature press in actual practice and, in addition, the need for the mould to be replaced frequently because of the marked wear thereof that occurs employing even commonly used carbon material matter due to a reaction with the silica glass at high temperatures and, furthermore, because of the poor surface state of the product obtained and the fact that, as a result, a significant amount of the product must be machined off, the high manufacturing costs of this method.

A so-called cast moulding method in which a slurry formed by the dispersion of silica glass powder in a solution is introduced into a mould and moulded has been proposed as an inexpensive and productive method for the manufacture of a transparent silica glass product designed to resolve the above-noted problems. Conventional methods for the cast moulding of a silica glass product include, by way of example, as described in JP-A- 53-33965 or JP-A-64-56331. JP-A-64-56331 discloses a method that employs a 10 to 500nm silica fine powder which is mixed with water and dried before being heat processed to form silica glass granules of 0.5 to several 10μm which are then re-dispersed in water to form a slurry which is then cast into a mould and dried. Additionally proposed methods include the method described in JP-A- 08-059222 in which a slurry is produced from silica powder and water in two stages and dried to manufacture silica granules of less than 1mm which are then cast into a mould, and the method described in JP-A-05-124828 in which a slurry is formed by the dispersion of monodispersed particles of uniform grain size in water or an organic solvent to which a binder has been added which is then moulded using a centrifugal casting method. However, the drawback inherent to the method of manufacture of the above mentioned JP-A-64-056331 has its origin in the low viscosity of the slurry that restricts manufacture to products of a simple shape and precludes the manufacture of large products. Drawbacks inherent to the method of manufacture according to JP-A- 53-33965 include its high manufacturing costs because it necessitates the provision of a special device comprising, for example, a means for the rapid high temperature heating or cooling following sintering in order to prevent devitrification of the product. The drawback inherent to the method of manufacture of JP-A-08-059222 has its origin in the addition of the silica powder in each step for the formation of the slurry which inhibits the production of a slurry of

sufficiently high viscosity and, accordingly, low viscosity slurries cause mould leakage which precludes the manufacture of a satisfactory product, or more particularly a silica glass product of a comparatively complex shape. The drawback inherent to the method of manufacture of JP-A-085-124828 has its origin in the use of an organic material as the binder or the like which results in the generation of a large number of impurities and bubbling in the silica glass product and, accordingly, inhibits the manufacture of a transparent silica glass product.

Problems to be Solved by the Invention

An object of the present invention is the provision of an inexpensive and productive method for the manufacture of high purity silica glass product.

A further object of the present invention is the provision of a method for the simple manufacture of a high purity silica glass product of a comparatively complex shape.

Means to Solve the Problems

With the foregoing conditions in mind, the inventors of the present invention, as a result of their continuous and committed research, discovered that the present invention, which achieves the above-noted objects, pertains to a method for the manufacture of a silica glass product characterized in that it comprises: a step in which a sintered silica powder is mixed with water to form a high concentration silica glass slurry of solid component density 70 to 85 mass% which is cast in a mould, then dried, and subjected to a purification process, before undergoing a glass formation process.

According to the method of manufacture of the present invention, a silica glass slurry of a solid component density of 70 to 85 mass% is produced by the mixing of silica glass primary particles of 1μm or less manufactured by, by way of example, a sol-gel method employing ethyl silicate, a method for the heat oxidation of waste silicon fine particles, or a method for the hydrolysis of silicon tetrachloride. Irrespective of the method of manufacture, each of the elements of sodium, potassium, lithium, calcium, magnesium, aluminium, iron, titanium, copper, nickel and boron should be contained in the abovementioned silica glass primary particles in an amount of no more than 1ppm. In addition, the water mixed with the silica glass primary particles has an electrical conductivity preferably of less than 10μs.

According to the method of manufacture of the present invention, a silica glass product can be inexpensively and productively manufactured and, in addition, also a transparent silica glass product of a comparatively complex shape can be manufactured by the employment of high purity silica glass primary particles and, without need for the employment of a material containing impurities such as an organic binder, the mixing thereof with water to produce a high concentration slurry which is then cast into a mould for formation into glass.

The sintered silica powder for the high concentration silica glass slurry is manufactured by sintering the material formed by drying and granulizing of a slurry configured from silica glass primary particles and water. This is executed by packing the silica granules into a vessel such as a crucible covered with a quartz glass plate in a packing density of no less than 0.6g/cm^3 and then sintered in an air atmosphere at a temperature between 1220°C and 1250°C. Vibration should be imparted during the packing of the silica glass granules. A non-uniform packing density or a packing density less than the abovementioned packing density value leads to a non-uniform sintered state which inhibits the production of an homogeneous slurry. The moisture content of the granules prior to sintering should be no more than 5 mass% and the grain diameter thereof should be within the range 0.5 to 100μm. The sintering of the slurry increases the skeletal strength of the slurry which, in turn, inhibits fracture and cracking of the moulded body and assists in the smooth implementation of the glass formation process. In addition, when the temperature of sintering exceeds the abovementioned temperature range the silica glass granules fuse to the inner wall of the vessel which lowers the operability as a result of the time required for the removal thereof and, in addition, the silica glass slurry becomes very hard which rubs against the inner wall of the vessel increasing the likelihood of impurities and pollutants and the like mixing with the slurry. On the other hand, if the temperature of sintering is too low the granule skeletal strength drops which leads to an increase in the likelihood of cracking and fracturing of the product.

The mixing of the silica glass sintered power and water to a solid component density of 70 to 85 mass% should be implemented in a rotating tubular vessel. Furthermore, silica glass balls may be introduced therein. The inner wall of the abovementioned rotating tubular vessel should be covered with a high purity polyurethane or silica glass lining to prevent the infiltration of impurities. The rotating speed of the rotating tubular vessel is adjusted between 1 and 100rpm during the operation thereof.

Although the operating time of the abovementioned rotating tubular vessel differs depending on the amount of silica glass sintered powder to be produced, a time period of approximately 1 to 7 days is normally used. In addition, the silica glass balls introduced into the rotating tubular vessel should be no more than 100 mass% of the sintered powder, and silica balls of 20 to 25mm diameter and silica balls of 25 to 35mm diameter should be mixed in a mass ratio of 1:2. If the silica glass balls exceed 100 mass% of the sintered powder, apart from the fact that this is likely to cause damage to the lining layer resulting in the infiltration of impurities, a hardening of the slurry, which should be removed, occurs in the proximity of the silica glass balls.

A silica glass slurry of average grain diameter 6 to 15 µm and solid component density 70 to 85 mass% is produced by the above-noted operation. If the average grain diameter of the abovementioned slurry is less than 6µm the close-packing characteristics of the moulded body following casting will be inadequate, while an average grain diameter in excess of 15µm is undesirable because it causes sedimentation during the formation of the slurry. In addition, a slurry solid component density of less than 70 mass% is undesirable because of the long processing time that it necessitates while, in addition, apart from the fact that a solid component density in excess of 85 mass% necessitates the use of very expensive equipment because of the significant increase in the slurry resistance that it causes which makes the agitation thereof almost impossible, the post-processing thereof is made more difficult because it necessitates the addition of an acid as a pH adjuster.

A preferable method of manufacture of the present invention refers to first produce a slurry of lower silica glass particle concentration, then forming the high concentration slurry. This preferable method comprises: a step in which the sintered silica powder is first mixed with water and then crushed to form a 70 to 78 mass% slurry which is then dried to form a high concentration slurry of silica glass particle concentration of 80 to 85 mass%; a step in which the high concentration slurry is cast in a mould; and a step in which the moulded body is removed from the mould and then dried and subjected to a purification process before undergoing a glass formation process.

Accordingly, silica glass primary particles of no more than 1µm are introduced together with water into an air inhalable and exhaustible rotating-type tubular vessel

in such a way as to produce a silica glass primary particle concentration of 60 to 70 mass% and, furthermore, silica glass balls of no more than 40 mass% of the silica glass primary particles are also introduced therein and, while the rotating-type tubular vessel is rotated at a speed of 10 to 20 rpm, the system is agitated and dried to produce silica glass granules. A silica glass primary particle concentration of less than 60 mass% is undesirable for the abovementioned agitation because of the resultant increase in processing time, while a concentration thereof in excess of 70 mass% necessitates the use of very expensive equipment because of the significant increase in the slurry resistance that it causes which essentially prevents the agitation thereof and, in addition, which increases the difficulty associated with the post-processing because it necessitates the addition of an acid as a pH adjuster. The mixing of the silica glass balls serves to not only narrow the grain size distribution of the silica glass granules and shorten the operating time in the subsequent steps, but it also serves to reduce the infiltration of impurities and pollutants to a minimum which result from wear of the agitation blade. Whilst the drying of the abovementioned silica glass granules should be based on the blowing of air warmed to between 100°C and 150°C at a rate of 10 to 20m^3/min into the rotating-type tubular vessel, the final moisture content of the slurry should be no more than 5 mass% and the grain size of the silica glass granules should be in the range 0.5 µm to 100µm. A moisture content of the slurry in excess of 5 mass% necessitates the implementation of a separate drying step prior to the sintering step which results in increased costs. In addition, a silica glass granule range in excess of the abovementioned range increases the time required for the production of the slurry and precludes the production of granules of a strength within the abovementioned range. An additional heat processing forming a sintered powder is administered on the above-noted silica glass granules to eliminate the pH effect and impart the appropriate granule skeletal strength thereto. The omission of this heat processing results in a weakening of the granule skeletal strength and, in subsequent steps, the generation of cracks and fractures in the moulded article. The heat processing is implemented in an air atmosphere so as to reduce costs and, at this time, a silica glass vessel such as a crucible is employed and the silica glass granules are packed therein and covered with a quartz glass plate. The silica glass granules must be packed in such a way as to produce an apparent packing density of no less than 0.6 g/cm^3. Notably, vibration should be imparted during the packing. A non-uniform packing density or a packing density less than the above mentioned

packing density value leads to a non-uniform sintered state that inhibits the production of an homogeneous slurry. The temperature of sintering in the air atmosphere should be in the range of 1220°C to 1250°C. When the temperature of sintering exceeds the above mentioned temperature range the silica glass granules fuse to the inner wall of the vessel which, as a result of the time required for the removal thereof, lowers the operability. Furthermore, the silica glass slurry becomes very hard and rubs against the inner wall of the vessel increasing the likelihood of impurities and pollutants and the like mixing with the slurry. On the other hand, if the temperature of sintering is too low the granule skeletal strength drops which leads to an increase in the likelihood of the cracking and fracturing of the product.

The sintered powder produced in the above-noted step is subsequently introduced into a rotating tubular sealed vessel together with water. The abovementioned sintered powder ratio should be 70 to 78 mass%. In addition, to prevent the infiltration of impurities, the inner wall of the abovementioned rotating tubular sealed vessel should be covered with a high purity polyurethane or silica glass lining. The rotating speed of the abovementioned rotating tubular sealed vessel is adjusted between 10 and 100rpm during the operation thereof. Although the operating time of the abovementioned rotating tubular sealed vessel differs depending on the amount of silica glass sintered powder to be produced, a time period of approximately 1 to 7 days is normally used.

If needed to optimise slurry conditions silica glass balls are introduced into the rotating tubular sealed vessel. The amount of silica glass balls should be no more than 100 mass% of the sintered powder, and silica balls of 20 to 25mm diameter and silica balls of 25 to 35mm diameter should be mixed in a mass ratio of 1:2. If the silica glass balls exceed 100 mass% of the sintered powder this is likely to cause damage to the lining layer resulting in the infiltration of impurities.

A slurry of silica glass particle concentration 70 to 78 mass% is produced by the above-noted operation. Because the slurry hardens in proximity of the silica glass balls if they are left in the abovementioned slurry the silica glass balls are removed, after which the slurry is introduced to an open-type rotating vessel that inclines at an angle of 10 to 60° with respect to the centre axis and then heated and dried in a purified atmosphere between room temperature and 50°C forming a slurry of even higher concentration. The drying should be implemented using a gradient in which

the moisture evaporation speed in the abovementioned drying process is no more than 50g/hour per kilogram in the initial stage and no more than 5g/hour in the final stage. If the moisture is removed at a high speed throughout the whole drying process the slurry hardens toward its upper surface region which, as a result, leads to the formation of a non-uniform slurry. In addition, if the moisture is removed slowly it takes a long time to achieve the desired moisture content and a resultant drop in operability occurs. A high concentration slurry in which the silica glass particle concentration in the slurry is 80 to 85 mass% is produced by this drying, and the grain size distribution of the silica glass particles describes, as shown in **FIG. 1**, a peak between 6 µm and 15µm and shoulders between 1µm and 6µm and 15 µm and 40µm. This grain size distribution affords the maintenance of the flowability of the high concentration slurry and the implementation of gravity casting in the mould and, accordingly, the precise manufacture of products of a complex shape. However, when the grain size distribution of the silica glass particles describes a single peak as shown in **FIG. 2**, release from the mould during casting is difficult, fractures and bubbling is generated and, accordingly, production of high purity products is difficult. To reduce the generation of bubbling the rotating speed of the open-type rotating vessel during the above mentioned drying step should be no more than 5rpm. In addition, stress caused by the incline resulting from the use of the above mentioned inclined open-type rotating vessel can be imparted to the high concentration slurry, whereupon the flowabilty of the high concentration slurry and, accordingly, a uniform slurry of high viscosity and in which the flowability is maintained can be produced.

Next, the high concentration slurry of silica glass particle concentration 80 to 85 mass% is cast into a mould - in order to produce products of a complex shape the mould used in the present invention comprises an outer mould and an inner mould. The mould is manufactured as an integrated mould. Although, with consideration to the ease of mould release, the use of a dividable mould of two or more sections is preferred, this is undesirable because of the resultant loss of the external appearance of the product due to the traces where the mould divides that are evident on the product following moulding.

The mould used for casting can also comprise an upper mould and a lower mould. A mould approximately 8 to 12% larger than the size of the desired product is employed. The use of a mould approximately 8 to 12% larger than the desired product allows for the contraction of the slurry that occurs during the formation of the

slurry into glass to be absorbed and, accordingly, affords the manufacture of a product of good precision.

At least the outer mould is configured from a moisture-absorbing material. Examples of the moisture-absorbing materials from which the mould can be configured include ceramics, gypsum and porous resins of which, from the viewpoint of the pore diameter, handling and cost and so on of the mould material, gypsum is preferred. An essentially non-porous material is used for the inner mould. Apart from the worsening of the surface state of the mould that occurs as a result of the presence of pores, a porous inner mould will absorb water and then contract and fracture. An essentially non-porous material such as a metal, plastic or ceramic or the like is used for the inner mould and, because of their manufacturing costs and shorter manufacturing time, as well as their good bulk production characteristics and mould releasability, a rubber elastic body such as silicone rubber should be used for the inner mould. If a material of high hardness is used for the inner mould the slurry fuses thereon and, apart from the resultant increase in the time required for mould release, this results in the generation of fractures in the product and a lowering of the yield thereof. In addition, compressed air discharge outlets should be provided in the outer mould in sections where there is a change in thickness, in sections where there is a large change in shape, and in the fine sections thereof, and an air line should be provided for the feed of compressed air thereto.

Because of the very high viscosity and dilatancy characteristics of the above-noted high concentration slurry a moulded body in which variations in density caused by sedimentation of the silica glass particles can be suppressed, and in which the maximum packing density can be approached, can be produced. Gravity casting is used in the step for the casting of the high concentration slurry into the mould. Gravity casting facilitates the packing of the slurry into the very smallest sections of the mould and, accordingly, affords the manufacture of a hard moulded body of good transfer characteristics which, in turn, affords the production of a silica glass products of good precision and comparatively complex shape. In the conventionally employed pressure casting method, apart from the fact that the moulded body attaches to the inner mould and is difficult to remove therefrom, when the inner mould is configured from a rubber elastic body deformation and changes in the shape of the inner mould occur during heating which results in the generation of fractures in the complex and uneven sections thereof. This phenomenon, which is referred to as the so-called “springback” phenomenon, is generated when the elastic

body, in the removal of pressure from the mould, attempts to restore itself to its original shape.

The moulded body released from the mould is let stand to dry at room temperature with the temperature raised 50°C every 4 hours up to 200°C. At this time, and with cost in mind, the use of an air atmosphere is regarded as adequate. The moulded body obtained is preferably subjected to a purification process - the conditions for which are based on heating to a temperature between 900 to 1200°C in a stream of no more than 0.5L/min of an HCl containing gas. As a result of this purification process impurities are removed from, in particular, the upper surface of the moulded body and, accordingly, this facilitates the production of a product in which the generation of cracks is prevented.

The dried moulded body is heated to a temperature in the range 1400°C to 1800°C for formation into glass, and this heating should be performed in a reduced pressure atmosphere of 10Pa or less between 1200°C to 1400°C while being maintained for 1 to 5 hours subsequent to each 100°C rise in temperature. The maintaining of the temperature in this way reduces the time required for the production of the final silica glass body. In addition, the heating in the 1400 to 1800°C range is performed in an inert gas atmosphere at a pressure of 2×10^5 Pa. Examples of the inert gas able to be employed include He, N_2 and Ar.

FIG. 3 shows a process flow chart of the method for the manufacture of the above-noted silica glass product of the present invention.

The dried and purification processed moulded body can also be then mounted on a carbon carrier coated and/or impregnated with a glasslike carbon carrier and, in an atmosphere between 1500 to 1800°C and more preferably 1700 to 1800°C, it is vacuum sintered and formed into glass. The abovementioned carbon carrier coated and/or impregnated with a glasslike carbon, which constitutes a carrier in which a glasslike carbon is coated and/or impregnated on a carbon carrier by, by way of example, the method described in Carbon No. 51 (1967), is highly purified by a purification process based on the use of a Cl_2 containing gas and, in addition, has a surface roughness Ra of no more than 10μm and, more preferably, no more than 1μm. The coating and/or impregnating of the surface of the carrier with a glasslike carbon produces a silica glass product of high dimensional tolerance and low

surface roughness in which reaction with the silica glass of the carrier is suppressed.

Although a specific description of the present invention is given below based on working examples thereof, the present invention should in no way be regarded as being restricted to these working examples.

Examples

Example 1

130kg of silica glass slurry primary particles of average grain size 100nm obtained by the hydrolysis of silicon tetrachloride were introduced together with 70kg of water of electrical conductivity 5μs into a rotating tubular vessel comprising an inner surface lined with a high purity polyurethane and an intake exhaust air opening, following which 45kg of silica glass balls was introduced thereto and agitated. 1 hour following the initiation of the agitation a stream of air warmed to 130°C and purified by way of a HEPA filter was caused to flow therein at a flow rate of $10m^3$/minute to gradually evaporate the moisture. After approximately 30 hours, silica glass granules of moisture 0.5 mass% and average grain size in the range of 1 to 80μm were obtained.

The above-noted silica glass granules were packed into a plurality of crucibles of diameter 300mm manufactured from silica glass which were covered with a quartz glass plate and let stand in an air atmosphere. A vibrator was employed to vibrate the crucibles during the packing of the silica glass granules so as to produce a packing density of 0.65 g/cm^3. The packed silica glass granules were heat sintered for 10 hours at 1225°C. 100kg of a silica glass sintered powder of average grain diameter in the range 6 to 15μm was introduced together with 33kg of water into a rotating tubular vessel of diameter 500mm and length 500mm lined with a high purity polyurethane, 80kg of silica glass balls were then introduced therein and the rotating tubular vessel was operated for 5 days at a rotating speed of 18rpm to manufacture a slurry of solid component density 75 mass%. The packing of the abovementioned slurry was based on a natural flow through a funnel into the mouth of a dome-shaped casting mould. The slurry was let stand without alteration for 1 hour before compressed air was blown therein through an air-introducing port provided in the upper mould to afford the release of the moulded body. The moulded

body produced was approximately 10% larger than the specification dimensions. The moulded body was let stand at room temperature and the temperature was raised 50°C every 4 hours up to 200°C. Next, a stream of an HCl containing gas was allowed to flow at a rate of 1.5L/min over the dried moulded body which was then heat processed and purified for 3 hours at 1200°C, resulting in the removal therefrom of the small amount of absorbed water.

On the other hand, a furfural-phenol copolycondensed resin solution was immersion-coated and cured on the carbon carrier body which was then heated to a maximum temperature of 1100°C in an argon atmosphere and carbonised to produce a glasslike carbon-impregnated carbon carrier. The glasslike carbon-impregnated carbon carrier was heat processed and purification treated for 10 hours at 900°C in a vessel through which a stream of Cl_2 containing gas was caused to flow at a rate of 1.5L/min.

The purified silica glass moulded body was mounted on the glasslike carbon-impregnated carbon carrier obtained and heated in a vacuum atmosphere to a temperature 1400°C following which, in an N_2 flow, the temperature was raised to 1720°C at a pressure of 1×10^5Pa and maintained for 10 minutes at these conditions producing a silica glass reflector. The silica glass reflector obtained was a high precision reflector of dimensional tolerance 150µm with a surface roughness Ra of 0.03µm. Following the heating of the silica glass reflector to 100°C and immersion in 25°C water no evidence of a resultant fracture was observed.

Example 2

130kg of silica glass slurry primary particles of average grain size 100nm obtained by the hydrolysis of silicon tetrachloride were introduced together with 70kg of water of electrical conductivity 5µs into a rotating tubular vessel comprising an inner surface lined with a high purity polyurethane and an intake exhaust air opening, following which 45kg of silica glass balls was introduced thereto and agitated. 1 hour following the initiation of the agitation a stream of air warmed to 130°C and purified by way of a HEPA filter was caused to flow therein at a flow rate of $10m^3$/minute to gradually evaporate the moisture. After approximately 30 hours, silica glass granules of moisture 0.5 mass% and average grain size in the range of 1 to 80µm were obtained.

The silica glass granules were packed into a plurality of crucibles of diameter 300mm manufactured from silica glass and let stand in an air atmosphere. A vibrator was employed to vibrate the crucibles during the packing of the silica glass granules producing a packing density of 0.65 g/cm^3. The packed silica glass granules were heat sintered for 10 hours at 1225°C. 100kg of the silica glass sintered powder of average grain size in the range of 6 to 15μm was introduced together with 33kg of water into a rotating tubular sealed vessel of diameter 500mm and length 1000mm lined with a high purity polyurethane, 80kg of silica glass balls were then introduced therein and the rotating tubular sealed vessel was operated for 5 days at a rotating speed of 18rpm to manufacture a slurry containing approximately 75 mass% of silica glass particles. The grain size distribution of the silica glass granules was measured employing a laser-analysis grain size distribution meter and, as shown in **FIG. 1**, a peak exists between 6μm and 15μm and shoulders exist between 1 and 6μm and 15 and 40μm. Next, the silica glass balls were removed and the slurry was moved to a open-type rotating vessel where, after further heating in a purified air of 25°C, a high concentration slurry of 82 mass% silica glass particle concentration solid component was produced. The inner side of the open-type rotating vessel was coated with a high purity polyurethane and the centre axis thereof was inclined at 45° to its perpendicular axis. The abovementioned drying was performed to remove the moisture content in a gradient of 40g/hour per kilogram in the initial stage and 4g/hour in the final stage, and the rotating speed of the rotating tubular sealed vessel at this time was 1rpm. Next, the abovementioned high concentration slurry was introduced into a mould for producing a bowl-shaped reflector. The casting involved the mounting of a funnel on a casting opening through which the slurry was let flow naturally and then let stand for an hour before compressed air was blown through an air-introducing port provided in the outer mould to execute the mould release. The moulded body released from the mould was let stand to dry at room temperature and the temperature was raised 50°C every 4 hours up to 200°C. A purification process based on the heat processing for 1 hour at 1200°C in which a 1.5L/min stream of an HCl containing gas was caused to flow on the dried moulded body was implemented. Next, formation into a glass was implemented by heating to a temperature between 1200 and 1400°C in a reduced pressure atmosphere of 10Pa with the temperature maintained for 2 hours at each temperature rise of 100°C, the further heating to 1400 to 1500°C in a inert gas atmosphere of 1 x 10^5

Pa, and then the maintaining of the temperature for 10 minutes at 1500°C. The reflector obtained was transparent and of satisfactory shape.

Example 3

Apart from the employment of a high concentration slurry containing 84 mass% of silica glass granules of example 2 and, in addition, the implementing of casting in the mould while very minute vibrations were imparted, a transparent reflector of satisfactory shape was manufactured in the same way as working example 2.

Example 4

Apart from the change of the glass formation temperature of example 1 to 1500°C, a silica glass reflector was manufactured in the same way as example 1. The surface roughness Ra of the silica glass reflector obtained was 0.8µm.

Example 5

Apart from the additional drying of the slurry of solid component density 75 mass% of example 1 in a 25°C atmosphere to form a slurry of solid component density 83 mass%, a silica glass reflector was manufactured in the same way as example 1. The silica glass reflector obtained in this way was transparent and described a satisfactory shape.

Comparative Example 1

Apart from omission of the purification process of the silica glass moulded body of example 1, a silica glass reflector was manufactured in the same way as example 1. Cracks were observed in the silica glass reflector obtained and bending was evident in the product produced.

Comparative Example 2

Apart from the use of an anisotropic graphite carrier (manufactured by Toyo Tanso Co., Ltd.) instead of the glasslike carbon-impregnated carbon carrier of example 1, a silica glass reflector was manufactured in the same way as example 1. Reaction with the carbon carrier was observed in the silica glass reflector produced and cracks were evident therein.

Comparative Example 3

130kg of silica glass slurry primary particles of average grain size 3μm obtained by the heat oxidation of waste silicon fine particles were introduced together with 70kg of water of electrical conductivity 5μs into a rotating tubular vessel comprising an inner surface lined with a high purity polyurethane and an intake exhaust air opening, following which 45kg of silica glass balls was further introduced thereto and agitated. 1 hour following the initiation of the agitation a stream of air warmed to 130°C was caused to flow therein at a flowrate 10 m^3/minute to gradually evaporate the moisture content. After approximately 30 hours silica glass granules of moisture content 1 mass% and grain size in the range 1 to 100μm were obtained. 120kg of the silica glass granules were packed into a plurality of crucibles of diameter 300mm under vibration. The packing density of the silica glass granules was 0.6g/cm^3. The crucibles in which the silica glass granules were packed were let stand in an air atmosphere and heated. The heat processing was maintained at conditions of 1300°C for 10 hours. Next, 100kg of the silica glass sintered powder obtained, 33kg of ion-exchanged water, and 80kg of silica glass balls were introduced into a rotating tubular sealed vessel lined with a high purity polyurethane of diameter 500mm and length 1000mm, and the rotating tubular sealable vessel was operated for 5 days at a rotating speed of 18rpm to manufacture a slurry containing approximately 75 mass% of silica glass particles. The grain size distribution of the silica glass particles described a single peak as shown in **FIG. 2.** The slurry obtained was heated in air to 25°C in an open-type rotating vessel to form a high concentration slurry of an 83 mass% solid component silica glass particle concentration. The abovementioned removal of moisture was implemented in a gradient of 40g/ hour per kilogram in the initial stage and 4g/hour in the final stage. In addition, the rotating speed of the open-type rotating vessel at this time was 1rpm.

Next, the high concentration slurry was introduced into a mould for producing a bowl-shaped reflector. Gypsum was employed as the material of the outer mould and, after 1 hour, mould release was executed employing a 4kg/cm^2 compressed air. The high concentration slurry was firmly attached to the mould and, accordingly, mould release was difficult. A large number of cracks appeared in the product as a result of its forceful release from the mould.

Comparative Example 4

Apart from the change of the high concentration slurry solid component to 75 mass%, a reflector was manufactured in the same way as example 2. The high concentration slurry was firmly attached to the mould and, accordingly, mould release was difficult. A large number of cracks were observed in the product subsequent to the drying of the slurry and formation into glass.

Effect of the Invention

The method of manufacture of the present invention affords the inexpensive and productive manufacture of a silica glass product of a comparatively complex shape used in the fields of, by way of example, the optical instrument, illumination lamp and scientific apparatus industries, processing jigs for semiconductor manufacture, scientific apparatus, and quartz glass crucibles and, accordingly, the method of manufacture of the present invention carries significant industrial value.

Brief Description of the Drawings

FIG. 1 shows the grain size distribution of the silica glass particles of a high concentration slurry of the present invention;

FIG. 2 shows the grain size distribution of the silica glass particles of a high concentration slurry of a comparative example;

FIG. 3 is a process flow chart of the present invention.

Claims

1. Method for the manufacture of a silica glass product, characterized in that it comprises: a step in which a sintered silica powder is mixed with water to form a high concentration silica glass slurry of solid component density 70 to 85 mass% which is cast in a mould, then dried, and subjected to a purification process, before undergoing a glass formation process.

2. Method for the manufacture of the silica glass article according to Claim 1, characterized in that the silica glass solid component consists of a silica glass sintered powder produced by the sintering of silica glass granules formed by mixing of silica glass primary particles of no more than 1µm with water and drying and granulization of said.

3. Method for the manufacture of the silica glass product according to Claim 2, characterized by that the silica glass granules show a moisture concentration of no more than 5 mass% and a granule grain size in the range of 0.5 µm to 100µm.

4. Method for the manufacture of the silica glass product according to Claim 2 to Claim 3, characterized in that the silica glass granules are packed into a vessel manufactured from quartz glass in a packing density of no less than 0.6 g/cm^3 and sinter processed in an air atmosphere at a temperature between 1220°C and 1250°C.

5. Method for the manufacture of the silica glass product according to any of Claim 1 to Claim 4, characterized in that the grain size of the silica glass primary particles forming the sintered silica powder is preferably in the range between 10 nm and 500nm.

6. Method for the manufacture of the silica glass product according to Claim 1, characterized in that the grain size of the sintered silica powder forming the solid component of the silica slurry is preferably in the range between 6 µm and 15 µm.

7. Method for the manufacture of the silica glass article according to Claim 1, characterized in that a silica glass slurry of solid component density of 70 to 85 mass% is manufactured in a rotating tubular vessel rotated at a rotating speed of 1 to 100 rpm of which the inner side is coated with a high purity polyurethane or silica glass.

8. Method for the manufacture of the silica glass product according to Claim 1, characterized in that it comprises:
a step in which the sintered silica powder is first mixed with water and then crushed to form a 70 to 78 mass% slurry which is then dried to form a high concentration slurry of silica glass particle concentration of 80 to 85 mass%;
a step in which the high concentration slurry is cast in a mould;
and a step in which the moulded body is removed from the mould and then dried and subjected to a purification process before undergoing a glass formation process.

9. Method for the manufacture of the silica glass product according to Claim 8, characterized in that, silica glass balls are added to the mixture of sintered silica powder and water, then the resultant mixture is crushed to thereby prepare the 70 to 78 mass% slurry, and thereafter, the silica glass balls are removed from the thus prepared slurry, and, subsequently, the resultant slurry is dried.

10. Method for the manufacture of the silica glass product according to Claim 8 or Claim 9, characterized in that the above-noted drying is implemented in a purified atmosphere between room temperature and 50°C in a gradient in which the initial stage moisture evaporation speed per kilogram is no more than 50g/hr and the final stage moisture evaporation speed is no more than 5g/hr to form a final stage silica glass particle concentration in the slurry of 80 to 85 mass%.

11. Method for the manufacture of the silica glass product according to any of Claim 8 to Claim 10, characterized in that the grain size distribution of the silica glass particles within the high concentration slurry describes a peak between 6 μm and 15μm with shoulders formed between 1 μm and 6μm and 15 μm and 40μm.

12. Method for the manufacture of the transparent silica glass product according to Claim 1 or Claim 8, characterized in that the casting of step is implemented by means of gravity casting.

13. Method for the manufacture of the silica glass product according to Claim 12, characterized in that vibration is imparted during the gravity casting.

14. Method for the manufacture of the silica glass product according to any of Claim 1 to Claim 13, characterized in that the mould is configured from an integrated outer mould and inner mould, the outer mould being configured from gypsum and the inner mould being configured from a bubble-free rubber elastic body

15. Method for the manufacture of the silica glass product according to any of Claim 1 to Claim 14, characterized in that the purification process before undergoing the glass formation process is based on heating to a temperature of 900°C to 1200°C in a vessel through which a stream of HCl containing gas is caused to flow at a rate of no less than 0.5L/min.

16. Method for the manufacture of the silica glass product according to any of Claim 1 to 15, characterized in that the glass formation process is implemented in a reduced pressure atmosphere of no more than 10Pa at temperatures up to 1400°C, and is implemented in an inert gas atmosphere of pressure no more than 2 x 10^5Pa at temperatures between 1400°C and 1800°C.

17. Method for the manufacture of a silica glass product according to any of Claim 1 to 16, characterized in that after molding and drying the silica product is formed during the glass formation process under a high temperature heat onto a carbon carrier coated and/or impregnated with a glasslike carbon.

18. Method for the manufacture of the silica glass article according to Claim 17, characterized in that the glass formation process is implemented in a reduced pressure atmosphere of no more than 10Pa at temperatures between 1500°C and 1800°C.

19. Method for the manufacture of the silica glass article according to Claim 17 or Claim 18, characterized in that the carbon carrier coated and/or impregnated with the glasslike carbon constitutes a carbon carrier subjected to a purification process based on heating to a temperature between 900°Cto 1200°C in a vessel in which a stream of Cl_2 containing gas is caused to flow at a flow rate of 1L/min.

20. Method for the manufacture of the silica glass article according to any of Claim 17 to Claim 19, characterized in that the surface roughness of the carbon carrier coated and/or impregnated with the glasslike carbon is no more than 10µm.

Fig. 1

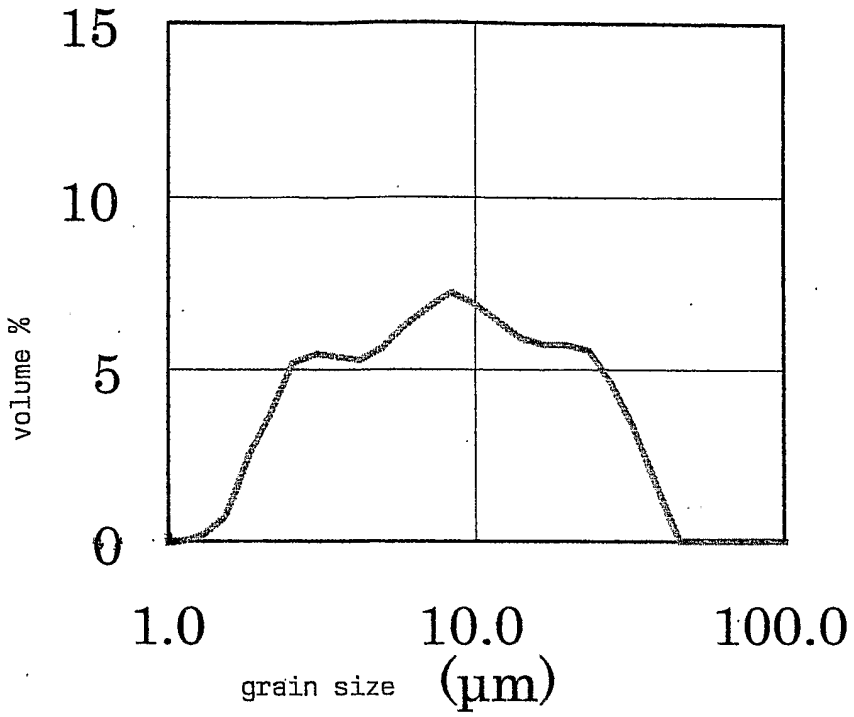
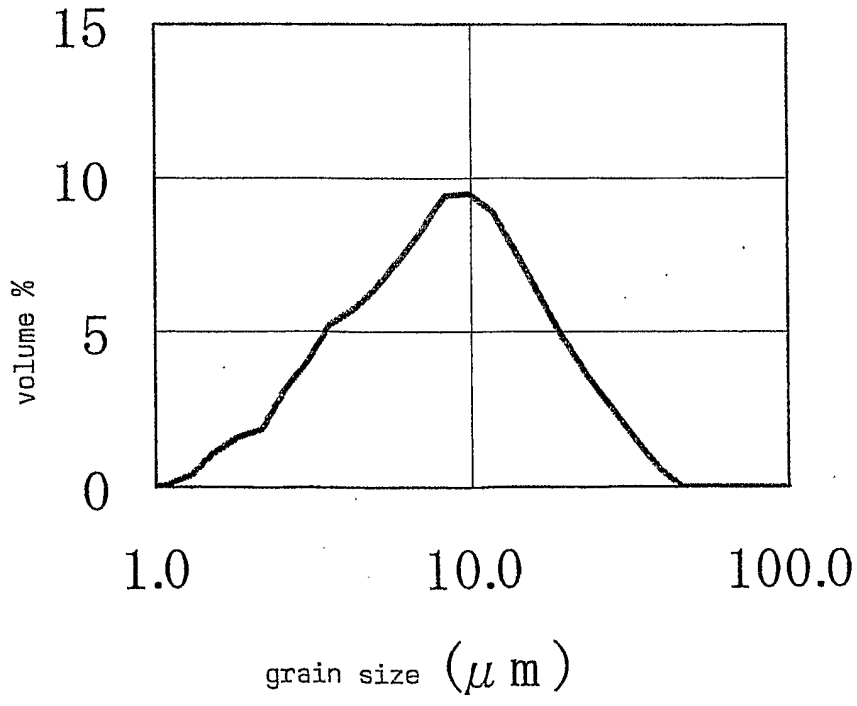
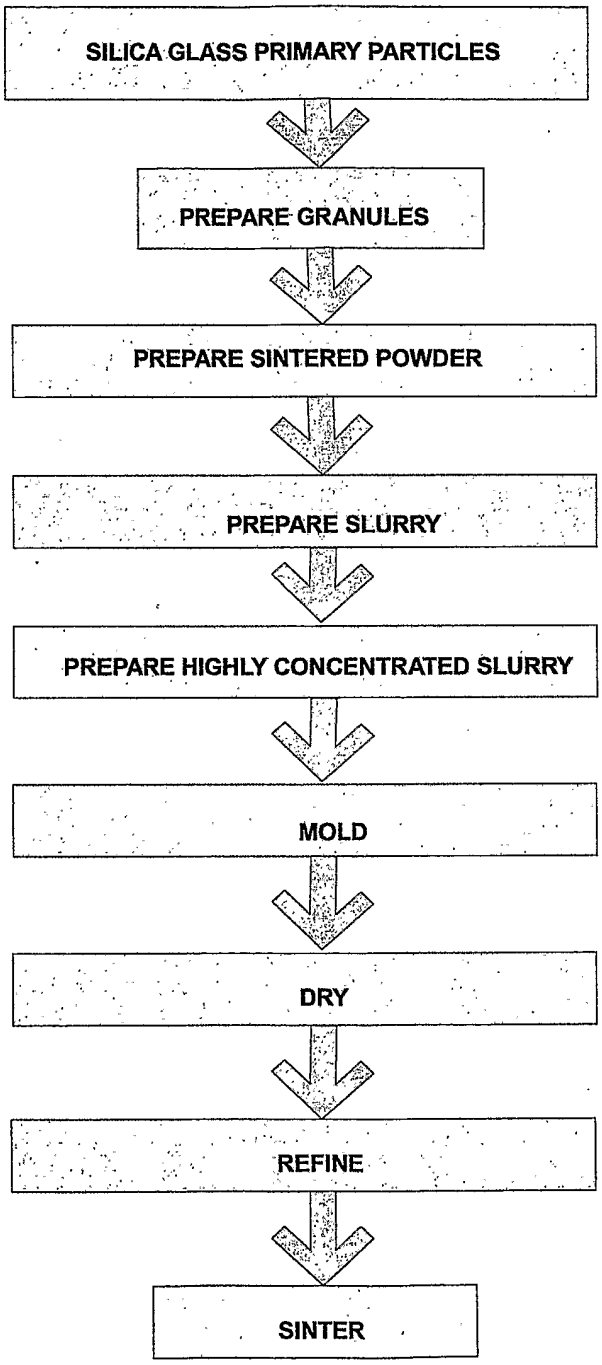


Fig. 2



comparative example

Fig. 3


SILICA GLASS PRIMARY PARTICLES
PREPARE GRANULES
PREPARE SINTERED POWDER
PREPARE SLURRY
PREPARE HIGHLY CONCENTRATED SLURRY
MOLD
DRY
REFINE
SINTER

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/001671

A. CLASSIFICATION OF SUBJECT MATTER
INV. C03B19/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C03B C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 355 587 B1 (LOXLEY TED A ET AL) 12 March 2002 (2002-03-12) example 1	1-20
X	PATENT ABSTRACTS OF JAPAN vol. 014, no. 034 (C-679), 23 January 1990 (1990-01-23) & JP 01 270531 A (NITTO CHEM IND CO LTD), 27 October 1989 (1989-10-27) abstract	1
A	GB 1 058 618 A (DEUTSCHE GOLD-UND SILBER-SCHEIDEANSTALT VORMALS ROESSLER) 15 February 1967 (1967-02-15) claims 1,3	2-4

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
6 June 2006	13/06/2006

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Creux, S

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2006/001671

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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