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(71) Applicant (for all designated States except US): **EVONIK
DEGUSSA GMBH** [DE/DE]; Rellinghauser Straße 1-11,
45128 Essen (DE).

(72) Inventors; and

(71) Applicants (for US only): **LANG, Jürgen Erwin**
[DE/DE]; Niddastr.28b, 76229 Karlsruhe (DE).
RAULEDER, Hartwig [DE/DE]; Uhlandweg 51A, 79618
Rheinfelden (DE). **FRINGS, Bodo** [DE/DE]; Grau-
thoffweg 106 b, 33758 Schloss Holte Stukenbrock (DE).
OLEK, Maciej [PL/DE]; Forststraße 20, 63796 Kahl

(DE). **BORCHERS, Georg** [DE/DE]; Kurstraße 2, 61231
Bad Nauheim (DE).

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(54) Title: INSERT FOR A MELTING CRUCIBLE AND MELTING CRUCIBLE COMPRISING SUCH AN INSERT

(57) Abstract: The present invention relates to an insert for a melting crucible, which comprises a silicon dioxide vessel, wherein the silicon dioxide vessel comprises silicon dioxide elements which are joined together and the silicon dioxide elements are joined over their area to at least one graphite element layer.



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INSERT FOR A MELTING CRUCIBLE AND MELTING CRUCIBLE COMPRISING SUCH AN INSERT

The present invention relates to an insert for a melting crucible, which comprises a silicon dioxide vessel, and also a melting crucible comprising at least one such insert.

Melting crucibles for various fields of use are widely known. For the processing of high-melting metals or semimetals, these have to satisfy demanding requirements. In a solidification of silicon, the volume increases, so that a melting crucible suitable for carrying out a directional solidification is subjected to particular stresses.

Depending on their use, inserts for melting crucibles, e.g. composites, in particular composite glasses, have to meet demanding safety requirements and also particular stability requirements in respect of external mechanical forces which can be some kPa. Particularly in the case of metallurgical applications involving compressive stresses of typically at least about 15 kPa (about 1.5 m of water or a load of about 1.5 tonnes/m²) or even up to ten times this value, the mechanical properties of inserts for melting crucibles, e.g. composite safety glass systems, have to meet extremely demanding requirements.

According to existing safety regulations, composite glasses have to withstand, in tests, four times the stresses occurring in practice and thus values of up to 60 tonnes/m² and more. A high mechanical stability can be achieved using hardened glass plates provided by means of thermal treatment (thermally prestressed/hardened or partially prestressed glass) or other known processes.

Glass vessels in which metal melts, in particular silicon melts, can be handled during processing are known. These glass vessels have to be fitted into graphite melting crucibles..

An inexpensive and constructionally simple to obtain insert for a melting crucible for the handling of silicon melts, in particular for the directed solidification of silicon, should be provided.

Furthermore, a insert for a melting crucible which is suitable as vessel for purification of a silicon melt should be provided.

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The insert for a melting crucible and also the melting crucible comprising such a insert should also be able to meet very high purity requirements for the material.

A melting crucible for such a insert to be used according to the invention should also be provided.

- 5 The present invention accordingly provides a insert for a melting crucible, which comprises a silicon dioxide vessel, wherein the silicon dioxide vessel comprises silicon dioxide elements which are joined together by means of a ceramic adhesive and the silicon dioxide elements are joined over their area to at least one graphite element layer; and also a melting crucible comprising at least one such insert. In an
10 embodiment of the present invention the ceramic adhesive comprises an alkoxysilane

This newly developed insert for a melting crucible has been found to be suitable as vessel for purification of a silicon melt.

- 15 The insert for a melting crucible and also the melting crucible comprising such an insert also meets very high purity requirements for the material.

A melting crucible for such an insert to be used according to the invention was also able to be provided.

- Furthermore, an insert to be used according to the invention for a melting crucible for a metal melt, in particular for a silicon melt, is suitable for being able to apply a
20 temperature gradient for the directed solidification of a silicon melt.

- For the purposes of the present invention, individual silicon dioxide elements are various individual building blocks which are composed of silicon dioxide and are suitable for the production of a fused silicon dioxide vessel, where the fused silicon dioxide vessel is a constituent of an insert for a melting crucible. In general, these
25 elements have a tile shape, so that the elements have a low thickness compared to the length and width. The width is defined as the minimum dimension of the silicon dioxide element over the area, where in each case a curvature is included. The

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length is defined here as the maximum dimension of the silicon dioxide element perpendicular to the width. The thickness is the minimum dimension perpendicular to the plane formed by the length and the width.

The length of the silicon dioxide elements can preferably be in the range from 1 to 10^4 mm, preferably from 10 to 1000 mm, particularly preferably from 10 to 250 mm. In a particular embodiment, a silicon dioxide element can preferably have a width of from 1 to 10^4 mm, preferably from 10 to 1000 mm, particularly preferably from 10 to 250 mm.

Furthermore, the ratio of the average length of an individual silicon dioxide element to the average width of an individual silicon dioxide element can be from 1 to 100, preferably from 1 to 3, particularly preferably about 1.

Such individual silicon dioxide elements can, for the purposes of the present invention, have an area of from 1 to 10^8 mm², preferably from 10^2 to 10^6 mm², particularly preferably from 10^2 to 10^3 mm².

The silicon dioxide elements can, in the embodiments according to the invention, have a thickness in the range from 0.1 to 100 mm, preferably from 1 to 50 mm, particularly preferably from 2 to 25 mm.

In a preferred embodiment of the invention, the ratio of the individual area of such a silicon dioxide element to the total volume of the fused silicon dioxide vessel can be from 10^{-10} to 10^{-1} 1/mm, preferably from 10^{-6} to 10^{-2} 1/mm, particularly preferably from 10^{-5} to 10^{-3} 1/mm.

The number of individual silicon dioxide elements required to produce a fused silicon dioxide vessel according to the invention should be from 5 to 20 000, preferably from 10 to 1000.

In a preferred embodiment, the size of the individual elements can overall be guided by the target geometry which can be indicated by the approximate error which is at least produced by the component. This applies, for example, to embodiments having

round or oval subregions of the insert, in which case the components do not correspondingly have to have these round or oval shapes, so that circular sections having annular gaps, joints or the like are obtained. Here, the maximum size of the component can be selected so that this error is not more than 20%, preferably not
5 more than 10%.

The shape of the individual silicon dioxide elements for producing the insert can be identical or different, but a closed vessel has to be obtained. The joints are closed by means of a ceramic adhesive. The silicon dioxide elements can have any shape of a polygon, with the polygon having to have at least three corners preferably at least
10 four corners. The corners can be pointed or rounded, with a pointed shape being preferred if silicon dioxide elements having an identical shape are to be used for producing the vessel.

Furthermore, the individual silicon dioxide elements can have a shape which has both corners and also round shape elements, preferably at least two corners and at
15 least one round shape element, particularly preferably at least three corners and at least two round shape elements.

To form a large-area insert for a melting crucible according to the present invention, it is necessary to join a plurality of silicon dioxide elements according to the invention to produce a silicon dioxide vessel. This can, for example, be effected by means of a
20 right-angled or oblique abutment. Furthermore, the silicon dioxide elements can preferably be configured so that the silicon dioxide elements can be joined particularly simply and reliably, with the type of joining not being critical per se. Thus, the silicon dioxide elements can be provided with a joining system.

In a preferred embodiment of the insert for a melting crucible, the silicon dioxide
25 elements can be joined to one another by means of a tongue-and-groove system.

Furthermore, the silicon dioxide elements can have a shape at the edges which allows an overlapping joint or a tongue and groove joint. Furthermore, knobs and recesses which allow a frictional join can be formed.

In addition, the silicon dioxide elements can have a purity of preferably at least 90%, with the silicon dioxide elements particularly preferably being produced from a high-purity material.

For the purposes of the present invention, a high-purity material is a material whose
5 total metallic impurities are less than 10 000 ppm, preferably less than 1000 ppm. In a particularly preferred embodiment, the contamination with aluminium and boron is less than 20 ppm, that with calcium is less than or equal to 5 ppm, that with iron is less than or equal to 150 ppm, that with magnesium, manganese, chromium and nickel is less than or equal to 25 ppm, that with phosphorus is less than or equal to
10 10 ppm, that with titanium is less than or equal to 5 ppm, that with zinc is less than or equal to 3 ppm and the total contamination with sodium silicate is less than or equal to 5 ppm.

The individual silicon dioxide elements can preferably be obtained from any high-purity silicon dioxide and can be obtained by casting.

15 In a preferred embodiment of the invention, the individual silicon dioxide elements which when joined together form the silicon dioxide vessel of the insert of a melting crucible can be produced from a water-containing SiO_2 composition.

The process required for this type of production of SiO_2 elements comprises production of a water-containing SiO_2 composition, solidification of the water-
20 containing SiO_2 composition and drying of the solidified SiO_2 composition, with the water-containing SiO_2 composition being self-organizing.

The term “ SiO_2 composition” refers to a composition which comprises SiO_2 together with various proportions of free and/or bound water, with the degree of condensation of the silicon dioxide not being critical per se for this composition. Accordingly, the
25 term “ SiO_2 composition” also encompasses compounds having SiOH groups, which can usually also be referred to as polysilicic acids.

The term “self-organizing” indicates that a water-containing SiO_2 composition suitable for the present silicon dioxide vessel can be reversibly converted from a solidified

state into a flowable state. Here, it is preferred that no permanent phase separation occurs to any great extent, so that the water is, viewed macroscopically, distributed essentially uniformly in the SiO₂ phase. However, in this context it can be pointed out that when viewed microscopically, two phases are of course present. For the purposes of the present invention, a flowable state means that the water-containing SiO₂ composition has a viscosity of preferably not more than 30 Pas, preferably not more than 20 Pas and particularly preferably not more than 7 Pas, measured immediately after production of the composition (about 2 minutes after sampling) by means of a rotational rheometer at about 23°C and a shear rate in the range from 1 to 200 [1/s]. At a shear rate of 10 [1/s], input is carried out over a period of about 3 minutes. The viscosity is then about 5 Pas, determined by means of a Rheostress viscosity measuring instrument from Thermo Haake using the bladed rotational body 22 (diameter 22 mm, 5 blades) having a measuring range from 1 to 2.2 10⁶ Pas. At a shear rate of 1 [1/s] and otherwise the same setting, a viscosity of 25 Pas is measured.

The water-containing SiO₂ composition has a solidified state at an initial viscosity of preferably at least 30 Pas, particularly preferably at least 100 Pas. This value is determined by using the viscosity value given by the rheometer 1 second after starting of the bladed rotational body of the rotational rheometer at about 23°C and a shear rate of 10 [1/s].

A solidified, water-containing SiO₂ composition for shaping can preferably be liquefied again by action of shear forces. For this purpose, it is possible to use conventional processes and apparatuses with which a person skilled in the art will be familiar, for example mixers, stirrers or mills having an appropriate tool geometry, for the input of shear forces. Preferred apparatuses include, inter alia, intensive mixers (Eirich), continuous mixers or cylindrical layer mixers, for example from Lödige; stirred vessels having mixing elements which preferably have an inclined blade or a toothed disc; and also mills, in particular colloid mills, or other rotor-stator systems which utilize annular gaps of differing width and differing speed of rotation. Further suitable apparatuses are ultrasound-based apparatuses and tools, in particular

ultrasonic probes and preferably ultrasound sources which have a curved transducer, by means of which shear forces can be introduced particularly simply and in a defined manner into the SiO_2 -water composition, leading to liquefaction of the latter. A particularly advantageous aspect here is that no particular abrasion of a tool occurs. This ultrasound arrangement is preferably operated in the nonlinear range. The apparatus used for liquefaction of the water-containing SiO_2 composition is generally dependent on the shear force required for liquefaction. Advantages can, inter alia, be achieved by an apparatus whose shearing velocity (reported as circumferential velocity of the tool) is in the range from 0.01 to 50 m/s, in particular in the range from 0.1 to 20 m/s and particularly preferably in the range from 1 to 10 m/s. These values can in the case of ultrasonic liquefaction reach the vicinity of the speed of sound. The time over which shearing is carried out can, depending on the shearing velocity in a continuous process, preferably be in the range from 0.01 to 90 minutes, particularly preferably in the range from 0.1 to 30 minutes.

To solidify the water-containing SiO_2 composition, it can preferably be left to stand for at least 0.1 minute, preferably at least 2 minutes, in particular 20 minutes and particularly preferably at least 1 hour. The expression "allow to stand" in this context preferably means that the composition is not subjected to any shear forces.

Furthermore, solidification can be effected or accelerated by, for example, input of energy, preferably heating or addition of additives. Additives can be all crosslinkers with which those skilled in the art are familiar, for example silanes, in particular functional silanes and here, without restricting the invention, for example TEOS ($\text{Si}(\text{OC}_2\text{H}_5)_4$; tetraethoxysilane) which is advantageously available inexpensively in very high purity. Additives can also be materials which bring about an increase in the pH, for example to values which are preferably in the range from 2.5 to 6.5, particularly preferably from 2.5 to 4, for example alkaline compounds, with preference being given to using aqueous ammonia which is preferably added after pouring into a mould.

A preferred solidified, water-containing SiO_2 composition can have a water content in the range from 2 to 98% by weight, in particular from 20 to 85% by weight, preferably

from 30 to 75% by weight and particularly preferably from 40 to 65% by weight. The water content of a flowable SiO₂ composition can be in the same ranges.

In a particular embodiment, an SiO₂ composition having a relatively low water content can be mixed with an SiO₂ composition which has a higher water content in order to
5 achieve the abovementioned water content. The SiO₂ compositions used for this purpose do not necessarily have to be self-organizing, but can individually have this property.

Furthermore, a solidified, water-containing SiO₂ composition is preferably characterized by a pH of less than 5.0, preferably less than 4.0, in particular less than
10 3.5, more preferably less than 3.0, particularly preferably less than 2.5.

Advantages can be achieved, in particular, by means of a solidified, water-containing SiO₂ composition having a pH of greater than 0, preferably greater than 0.5 and particularly preferably greater than 1.0. The pH of the solidified, water-containing SiO₂ composition can be determined by liquefaction of the composition and
15 determination on the resulting flowable SiO₂ composition. Here, it is possible to use conventional measurement methods, for example those which are suitable for determining the H⁺ ion concentration.

The SiO₂ compositions can, for example, be poured into a mould using moulds which can have any suitable geometry and, in one variant, preferably consist of textile-like
20 wovens or meshes which consist of and/or are produced from high-temperature-resistant, pure polymers (silicone, PTFE, POM, PEEK), ceramic (SiC, Si₃N₄), carbon fibres, graphite in all its modifications, metal fibres having a suitable high-purity coating and/or fused silica and/or in combination with glass fibres and/or carbon fibres. In a particularly preferred embodiment, the moulds are segmented, which
25 allows particularly simple removal from the mould.

The high permeability of water vapour and/or liquid water through the woven fabric considerably improves the dry behaviour of the moulding. The textile behaviour of the mould also surprisingly has the property of making stress-free shrinkage of the cast moulding during the drying process possible, which allows particularly simple

removal from the mould without fracture.

The self-organizing SiO₂ compositions which are suitable for carrying out the present invention can, according to a preferred aspect, have a very high purity. A preferred pure silicon dioxide is characterized in that it has a content, measured by means of ICP-MS and sample preparation known to those skilled in the art, of:

- a. aluminium less than or equal to 100 ppm or preferably in the range from 10 ppm to 0.0001 ppm;
- b. boron from < 10 ppm to 0.0001 ppm;
- c. calcium less than 6 ppm, preferably in the range from 2 ppm to 0.0001 ppm;
- 10 d. iron less than or equal to 50 ppm, preferably in the range from 10 ppm to 0.0001 ppm;
- e. nickel less than or equal to 10 ppm, preferably in the range from 5 ppm to 0.0001 ppm;
- f. phosphorus from < 10 ppm to 0.0001 ppm;
- 15 g. titanium less than or equal to 10 ppm, preferably from ≤ 1 ppm to 0.0001 ppm;
- h. zinc less than or equal to 6 ppm, preferably from ≤ 1 ppm to 0.0001 ppm;
- i. tin less than or equal to 20 ppm, preferably from ≤ 3 ppm to 0.0001 ppm.

A preferred high-purity silicon dioxide is characterized in that the sum of the abovementioned impurities (a-i) is less than 1000 ppm, preferably less than 100 ppm, particularly preferably less than 10 ppm, very particularly preferably less than 5 ppm, especially preferably in the range from 0.5 to 4.9 ppm and very especially preferably in the range from 0.9 to 3.9 ppm, where a purity in the region of the detection limit can be sought for each element, in particular the metallic elements. The figures in ppm are by weight.

25 The determination of impurities is carried out by means of ICP-MS/OES (inductively

coupled plasma-mass spectrometry/optical electron spectrometry) and AAS (atomic absorption spectroscopy).

A water-containing SiO_2 composition which can be used according to the invention can, for example, be obtained from a silicate-containing solution, for example a water glass, by means of a precipitation reaction.

A preferred precipitation of a silicon oxide dissolved in an aqueous phase, in particular a completely dissolved silicon oxide, is preferably carried out by means of an acidifying agent. After reaction of the silicon oxide dissolved in the aqueous phase with the acidifying agent, where the silicon oxide dissolved in an aqueous phase is preferably added to the acidifying agent, a precipitation suspension is obtained.

An important process feature is control of the pH of the silicon dioxide and of the reaction media in which the silicon dioxide is present during the various process steps of the preparation of silicon dioxide.

According to this preferred aspect, the initial charge and the precipitation suspension into which the silicon dioxide dissolved in an aqueous phase, in particular the water glass, is added, preferably added dropwise, always has to have an acid reaction. For the purposes of the present invention, acidic means a pH of below 6.5, in particular below 5.0, preferably below 3.5, particularly preferably below 2.5, and according to the invention from < 2.0 to < 0.5 . Control of the pH so that the pH does not fluctuate excessively in order to obtain reproducible precipitation suspensions can be sought. If a constant or largely constant pH is sought, the pH should display a variation of plus/minus 1.0, in particular plus/minus 0.5, preferably plus/minus 0.2.

In an especially preferred embodiment of the present invention, the pH of the initial charge and of the precipitation suspension is always kept below 2, preferably below 1, particularly preferably below 0.5. Furthermore, preference is given to the acid always being present in a significant excess over the alkali metal silicate solution in order to make a pH of less than 2 of the precipitation suspension possible at any time.

Particular preference is given to a precipitation process for preparing purified silicon oxide, in particular high-purity silicon dioxide, which comprises the following steps

- a. preparation of an initial charge of an acidifying agent having a pH of less than 2, preferably less than 1.5, particularly preferably less than 1, very particularly preferably less than 0.5;
- b. provision of a silicate solution, where, in particular, the viscosity for preparing the silicon oxide purified by precipitation can advantageously be set in particular viscosity ranges, with preference being given, in particular, to a viscosity of from 0.001 to 1000 Pas, where, depending on the way the process is carried out, this viscosity range can, as indicated below, be widened further due to further process parameters;
- c. addition of the silicate solution from step b. to the initial charge from step a. in such a way that the pH of the precipitation suspension obtained always remains at a value of less than 2, preferably less than 1.5, particularly preferably less than 1 and very particularly preferably less than 0.5; and
- d. isolation and washing of the silicon dioxide obtained, where the washing medium has a pH of less than 2, preferably less than 1.5, particularly preferably less than 1 and very particularly preferably less than 0.5.

Depending on the pH of the washing medium used, the SiO₂ composition can be washed to a higher pH by means of water. Here, the SiO₂ composition can also be washed to pH values above the abovementioned values and subsequently reduced by addition of acid. Accordingly, the silicon dioxide obtained can preferably be washed with water so as to reduce the pH of the SiO₂ composition obtained to a value which is preferably in the range from 0 to 7.5 and/or the conductivity of the washing suspension to a value of less than or equal to 100 µS/cm, preferably less than or equal to 10 µS/cm and more preferably less than or equal to 5 µS/cm.

In a first particularly preferred variant of this process, preference is given to a precipitation process for preparing purified silicon oxide, in particular high-purity silicon dioxide, which is carried out using silicate solutions of low to medium viscosity, so that step b. can be modified as follows:

- 5 b. provision of a silicate solution having a viscosity of from 0.001 to 0.2 Pas

In a second particularly preferred variant of this process, preference can be given to a precipitation process for preparing purified silicon oxide, in particular high-purity silicon dioxide, which is carried out using silicate solutions having a high or very high
10 viscosity, so that step b. can be modified as follows:

- b. provision of a silicate solution having a viscosity of from 0.2 to 10 000 Pas

In the various variants of the process presented above, an initial charge of an acidifying agent or an acidifying agent and water is prepared in the precipitation
15 vessel in step a. The water is preferably distilled or deionized water.

In all variants of the present process, not only the particularly preferred embodiments described in detail above, it is possible to use organic or inorganic acids, preferably mineral acids, particularly preferably hydrochloric acid, phosphoric acid, nitric acid, sulphuric acid, chlorosulphonic acid, sulphuryl chloride, perchloric acid, formic acid
20 and/or acetic acid in concentrated or dilute form or mixtures of the abovementioned acids as acidifying agent. Particular preference is given to the abovementioned inorganic acids. Very particular preference is given to using hydrochloric acid, preferably from 2 to 14 N, particularly preferably from 2 to 12 N, very particularly preferably from 2 to 10 N, especially preferably from 2 to 7 N and very especially
25 preferably from 3 to 6 N, phosphoric acid, preferably from 2 to 59 N, particularly preferably from 2 to 50 N, very particularly preferably from 3 to 40 N, especially preferably from 3 to 30 N and very especially preferably from 4 to 20 N, nitric acid, preferably from 1 to 24 N, particularly preferably from 1 to 20 N, very particularly preferably from 1 to 15 N, especially preferably from 2 to 10 N, sulphuric acid,

preferably from 1 to 37 N, particularly preferably from 1 to 30 N, very particularly preferably from 2 to 20 N, especially preferably from 2 to 10 N. Very particular preference is given to using concentrated sulphuric acid.

The acidifying agents can be used in a purity which is usually referred to as
5 "technical grade". It will be clear to a person skilled in the art that ideally no impurities which do not remain dissolved in the aqueous phase of the precipitation suspension should be introduced into the process via the dilute or undiluted acidifying agents or mixtures of acidifying agents used. In any case, the acidifying agents should not have any impurities which would precipitate with the silicon oxide in the acidic precipitation,
10 unless they could be kept in the precipitation suspension by means of added complexing agents or by control of the pH or be washed out by means of the later washing media.

The acidifying agent utilized for the precipitation can be the same as that which is, for example, also used in step d. for washing the filter cake.

15 In a preferred variant of this process, a peroxide which produces a yellow/orange colour with titanium(IV) ions under acidic conditions is added in addition to the acidifying agent to the initial charge in step a. This is particularly preferably hydrogen peroxide or potassium peroxodisulphate. The yellow/orange coloration of the reaction solution enables the degree of purification during the washing step d. to be monitored
20 very well.

Particular preference is given to the variants in which the peroxide is added in step a. or b. since in this case it can exercise a further function in addition to the indicator function. Without wishing to be tied to a particular theory, it can be assumed that some, in particular carbon-containing, impurities are oxidized by reaction with the
25 peroxide and removed from the reaction solution. Other impurities are brought by oxidation into a form which is better soluble and can thus be washed out more readily. The precipitation process of the invention thus has the advantage that no calcination step has to be carried out, although this is naturally optionally possible.

In all variants of the process of the invention, an aqueous silicate solution, particularly

preferably an alkali metal silicate and/or alkaline earth metal silicate solution, very particularly preferably a water glass, can preferably be used as silicon oxide dissolved in an aqueous phase. Such solutions can be procured commercially, prepared by liquefaction of solid silicates, prepared from silicon dioxide and sodium carbonate or prepared directly from silicon dioxide and sodium hydroxide and water at elevated temperature, for example by the hydrothermal process. The hydrothermal process can be preferred over the sodium carbonate process because it can lead to cleaner precipitated silicon dioxides. A disadvantage of the hydrothermal process is the limited range of obtainable moduli, for example the modulus of SiO_2 to Na_2O is up to 2, while preferred moduli are from 3 to 4; in addition, the water glasses generally have to be concentrated after the hydrothermal process before precipitation. The preparation of water glass is generally known per se to those skilled in the art.

In an alternative, an alkali metal water glass, in particular sodium water glass or potassium water glass, is optionally filtered and subsequently, if necessary, concentrated. The filtration of the water glass or of the aqueous solution of dissolved silicates for separating off solid, undissolved constituents can be carried out by methods known per se to those skilled in the art and using apparatuses known to those skilled in the art.

The silicate solution used preferably has a modulus, i.e. weight ratio of metal oxide to silicon dioxide, of from 1.5 to 4.5, preferably from 1.7 to 4.2, particularly preferably from 2 to 4.0.

The use of ion exchangers for purifying the silicate solutions and/or acidifying agents before the precipitation is not necessary, but can prove to be advantageous depending on the quality of the aqueous silicate solutions. An alkaline silicate solution can therefore also be pretreated as described in WO 2007/106860 in order to minimize the boron and/or phosphorus content beforehand. For this purpose, the alkali metal silicate solution (aqueous phase in which silicon oxide is dissolved) can be treated with a transition metal, calcium or magnesium, a molybdenum salt or an ion exchanger modified with molybdate salts in order to minimize the phosphorus

content. Before the precipitation according to the process of WO 2007/106860, the alkali metal silicate solution can be subjected to the precipitation according to the invention in an acid medium, preferably at a pH of less than 2. However, the process of the invention is preferably carried out using acidifying agents and silicate solutions which have not been treated by means of ion exchangers before the precipitation.

In a specific embodiment, a silicate solution can be pretreated by the process of EP 0 504 467 B1 as silica sol before the actual acidic precipitation according to the invention. The silica sol which can be obtained by the processes disclosed in EP 0 504 467 B1 is preferably, after a treatment corresponding to the process of EP 0 504 467 B1, redissolved completely and subsequently subjected to an acidic precipitation according to the invention in order to obtain purified silicon oxide according to the invention.

The silicate solution before the acidic precipitation preferably has a silicon dioxide content of at least about 10% by weight or higher.

A silicate solution, in particular a sodium water glass, whose viscosity is from 0.001 to 1000 Pas, preferably from 0.002 to 500 Pas, in particular from 0.01 to 300 Pas, especially preferably from 0.04 to 100 Pas (at room temperature, 20°C) can preferably be used for the acidic precipitation. The viscosity of the silicate solution can preferably be measured at a shear rate of 10 1/s, with the temperature preferably being 20°C.

In step b. and/or c. of the first preferred variant of the precipitation process, a silicate solution having a viscosity of from 0.001 to 0.2 Pas, preferably from 0.002 to 0.19 Pas, in particular from 0.01 to 0.18 Pas and especially preferably from 0.04 to 0.16 Pas and very especially preferably from 0.05 to 0.15 Pas, is provided. The viscosity of the silicate solution can preferably be measured at a shear rate of 10 1/s, with the temperature preferably being 20°C. Mixtures of a plurality of silicate solutions can also be used.

In step b and/or c of the second preferred variant of the precipitation process, a silicate solution having a viscosity of from 0.2 to 1000 Pas, preferably from 0.3 to

700 Pas, in particular from 0.4 to 600 Pas, especially preferably from 0.4 to 100 Pas, very especially preferably from 0.4 to 10 Pas and very particularly preferably from 0.5 to 5 Pas, is provided. The viscosity of the silicate solution can preferably be measured at a shear rate of 10 1/s, with the temperature preferably being 20°C.

- 5 In step c. of the main aspect and of the two preferred variants of the precipitation process, the silicate solution from step b. is added to the initial charge and the silicon dioxide is thus precipitated. Here, it has to be ensured that the acidifying agent is always present in excess. The addition of the silicate solution is carried out in such a way that the pH of the reaction solution is always below 2, preferably below 1.5,
10 particularly preferably below 1, very particularly preferably below 0.5 and especially preferably from 0.01 to 0.5. If necessary, further acidifying agent can be added. The temperature of the reaction solution is maintained at from 20 to 95°C, preferably from 30 to 90°C, particularly preferably from 40 to 80°C, by heating or cooling of the precipitation vessel during the addition of the silicate solution.
- 15 Particularly readily filterable precipitates are obtained when the silicate solution enters the initial charge and/or precipitation suspension in droplet form. In a preferred embodiment, care is therefore taken to ensure that the silicate solution enters the initial charge and/or precipitation suspension in droplet form. This can be achieved, for example, by the silicate solution being introduced into the initial charge by
20 addition in drops. Metering apparatuses located outside the initial charge/precipitation suspension and/or dipping into the initial charge/precipitation suspension can be used for this purpose.

- In the first particularly preferred variant, i.e. the process using low-viscosity water glass, it has been found to be particularly advantageous for the initial
25 charge/precipitation suspension to be set into motion, e.g. by stirring or pump circulation, in such a way that the flow velocity measured in a region bounded by the half radius of the precipitation vessel $\pm$ 5 cm and the surface of the reaction solution to 10 cm below the reaction surface is from 0.001 to 10 m/s, preferably from 0.005 to 8 m/s, particularly preferably from 0.01 to 5 m/s, very particularly preferably from 0.01

to 4 m/s, especially preferably from 0.01 to 2 m/s and very especially preferably from 0.01 to 1 m/s.

This effect can be increased further by combination of an optimized flow velocity with an introduction of the silicate solution ideally in drops, so that in an embodiment of the precipitation process, the silicate solution is introduced in droplet form into an initial charge/precipitation suspension at a flow velocity measured in a region d bounded by the half radius of the precipitation vessel $\pm$ 5 cm and the surface of the reaction solution to 10 cm below the reaction surface of from 0.001 to 10 m/s, preferably from 0.005 to 8 m/s, particularly preferably from 0.01 to 5 m/s, very particularly preferably from 0.01 to 4 m/s, specially preferably from 0.01 to 2 m/s and very especially preferably from 0.01 to 1 m/s. In this way it is also possible to produce silicon dioxide particles which can be filtered very readily. In contrast, very fine particles which are very difficult to filter are formed in processes in which there is a high flow velocity in the initial charge/precipitation suspension.

In the second preferred embodiment of the precipitation process, i.e. when using high-viscosity water glass, particularly pure and readily filterable precipitates are likewise formed by addition of the silicate solution in the form of drops. Without being tied to a particular theory, it can be assumed that the high viscosity of the silicate solution together with the pH results in a readily filterable precipitate being formed after step c. and in no impurities or only a very small amount of impurities being incorporated in internal voids of the silicon dioxide particles since the droplet shape of the silicate solution introduced in drops is largely maintained due to the high viscosity and the droplets are not finely dispersed before the gelling/crystallization commences at the surface of the drop. The alkali metal silicate and/or alkaline earth metal silicate solutions defined in more detail above can preferably be used as silicate solution, with preference being given to using an alkali metal silicate solution, particularly preferably sodium silicate (water glass) and/or potassium silicate solution. Mixtures of a plurality of silicate solutions can also be used. Alkali metal silicate solutions have the advantage that the alkali metal ions can easily be separated off by washing. The viscosity can, for example, be set by concentration of commercial

silicate solutions or by dissolution of the silicates in water.

As indicated above, the filterability of the particles can be improved by means of suitable selection of the viscosity of the silicate solution and/or the stirring speed, since particles having a specific form are obtained. Preference is therefore given to
5 purified silicon oxide particles, in particular silicon dioxide particles, which preferably have an external diameter of from 0.1 to 10 mm, particularly preferably from 0.3 to 9 mm and very particularly preferably from 2 to 8 mm. In a first specific embodiment of the present invention, these silicon dioxide particles have a ring shape, i.e. have a
10 "hole" in the middle and are thus comparable in terms of their shape to a miniature torus, hereinafter also referred to as "donut". The ring-shaped particles can have a largely round shape but also a rather oval shape.

In a second specific embodiment of the present precipitation process, these silicon dioxide particles have a shape comparable to a "mushroom head" or a "jellyfish", i.e. instead of the hole of the above-described "donut"-shaped particles, there is a
15 preferably thin, i.e. thinner than the ring-shaped part, layer of silicon dioxide which is curved to one side and spans the inner opening of the "ring" in the middle of the basic ring-shaped structure. If these particles were to be placed on the ground with the curved side downward and looked at from vertically above, the particles would correspond to a dish having a curved bottom, a rather massive, i.e. thick, upper
20 margin and a somewhat thinner bottom in the region of the curvature.

The silicon dioxide obtained after precipitation is separated off from the remaining constituents of the precipitation suspension. This can, depending on the filterability of the precipitate, be carried out by conventional filtration techniques known to those skilled in the art, e.g. filter presses or rotary filters. In the case of precipitates which
25 are difficult to filter, the separation can also be effected by means of centrifugation and/or decantation of the liquid constituents of the precipitation suspension.

After the supernatant liquid has been separated off, the precipitate is washed, ensuring by means of a suitable washing medium that the pH of the washing medium during washing and thus also that of the purified silicon oxide, in particular silicon

dioxide, is less than 2, preferably less than 1.5, particularly preferably less than 1, very particularly preferably 0.5 and especially preferably from 0.01 to 0.5.

As washing medium, preference is given to using aqueous solutions of organic and/or inorganic water-soluble acids, e.g. the abovementioned acids or fumaric acid, oxalic acid, formic acid, acetic acid or other organic acids known to those skilled in the art which themselves do not contribute to contamination of the purified silicon oxide when they cannot be removed completely by means of high-purity water. In general, all organic water-soluble acids, in particular those consisting of the elements C, H and O, are therefore preferred both as acidifying medium and in the washing medium because they themselves do not contribute to contamination of the following reduction step. The acidifying agents or mixtures thereof used in step a. and c. is preferably used in dilute or undiluted form.

The washing medium can if necessary also comprise a mixture of water and organic solvents. Advantageous solvents are high-purity alcohols, such as methanol or ethanol. Possible esterification does not interfere in the subsequent reduction to silicon.

The aqueous phase preferably does not contain any organic solvents such as alcohols and/or any organic, polymeric materials.

In the process of the invention, it is usually not necessary to add chelating agents to the precipitation suspension or during the purification. The present invention nevertheless also encompasses processes in which a complexing agent for metals, e.g. EDTA, is added to the precipitation suspension or to a washing medium in order to stabilize acid-soluble metal complexes.

A peroxide can also be added for colour marking, as "indicator" of undesirable metal impurities. For example, hydroperoxide can be added to the precipitation suspension or the washing medium in order to show up titanium impurities present by development of a colour. Marking can generally also be carried out by means of other organic complexing agents which themselves do not interfere in the subsequent reduction process. These are generally all complexing agents based on

the elements C, H and O, and the element N can advantageously also be present in the complexing agent, for example to form silicon nitride which advantageously decomposes again in the later process.

5 Washing is continued until the silicon dioxide has the desired purity. This can, for example, be recognized by the washing suspension containing a peroxide and no longer showing a visible yellow colour.

Further information on the precipitation and washing of SiO_2 is given in the document WO 2010/037694.

10 The silicon dioxide which has been washed and purified in this way is preferably washed further with distilled water or deionized water until the pH of the silicon dioxide obtained is in the range from 0 to 7.5 and/or the conductivity of the washing suspension is less than or equal to 100 $\mu\text{S}/\text{cm}$, preferably less than or equal to 10 $\mu\text{S}/\text{cm}$ and more preferably less than or equal to 5 $\mu\text{S}/\text{cm}$. The pH here can particularly preferably be in the range from 0 to 4.0, more preferably from 0.2 to 3.5,
15 in particular from 0.5 to 3.0 and particularly preferably from 1.0 to 2.5. A washing medium containing an organic acid can also be used here. In this way, it is possible to ensure that any interfering acid radicals adhering to the silicon dioxide are sufficiently well removed.

20 The silicon dioxide can be separated off by means of conventional measures which are adequately known to those skilled in the art, e.g. filtration, decantation, centrifugation and/or sedimentation, with the proviso that the degree of contamination of the purified silicon oxide precipitated under acid conditions does not deteriorate again as a result of these measures.

25 In the case of precipitates which are difficult to filter, it can be advantageous to carry out washing by passing the washing medium from below through the precipitate in a fine-meshed sieve basket.

The purified silicon dioxide which has been obtained in this way, in particular high-purity silicon dioxide, can be dried and processed further in order to bring the self-

organizing SiO₂ composition to the preferred proportions of water indicated below. Drying can be carried out by means of all methods and apparatuses known to those skilled in the art, e.g. belt dryers, tray dryers, drum dryers, etc.

5 It is possible to obtain an SiO₂ element of any shape in a particularly simple and economical way by means of the process of the invention. For this purpose, a flowable water-containing SiO₂ composition can be poured into a mould.

The flowable water-containing SiO₂ composition can be introduced into and distributed in a mould having the desired dimensions in any way. For example, the introduction can be effected manually or by machine using portioning devices. The
10 filled mould can be subjected to vibration in order to achieve rapid and uniform distribution of the water-containing SiO₂ composition in the mould.

The casting moulds to be used for producing the elements are not subject to any particular requirements, but their use should not introduce any impurities into the SiO₂ element. For example, suitable casting moulds can be produced from high-
15 temperature-resistant, pure polymers (silicone, PTFE, POM, PEEK), ceramic (SiC, Si₃N₄), graphite in all its modifications, metal having a suitable high-purity coating and/or fused silica. In a particularly preferred embodiment, the moulds are segmented, which allows particularly simple removal from the mould.

Instead of the solid moulds, the moulds can, in a preferred embodiment, be made of
20 open materials such as textile-like wovens or meshes which consist of and/or are produced from high-temperature-resistant, pure polymers (silicone, PTFE, POM, PEEK), ceramic (SiC, Si₃N₄), carbon fibres, graphite in all its modifications, metal fibres having a suitable high-purity coating and/or fused silica and/or in a composite with glass fibres and/or carbon fibres. In a further particularly preferred embodiment,
25 the moulds are segmented which allows particularly suitable removal from the mould by taking the mould apart. Elastic heat-resistant materials (for example similar to nylon stockings) here allow, in particular, a continuous mode of operation.

The high permeability of water vapour and/or liquid water through the woven fabric considerably improves the drying behaviour of the moulding. Furthermore, the textile

behaviour of the mould surprisingly has the properties that, for example in the case of a tube-like mould, stress-free shrinkage of the cast moulding during the drying process is possible, which allows particularly simple removal from the mould without fracture.

- 5 After shaping, the solidified, water-containing SiO_2 composition is stabilized by means of an alkaline additive and/or by drying. For this purpose, the filled casting mould can, without or after addition of additives, be transferred to a dryer which is heated, for example, electrically, by means of hot air, hot steam, IR radiation, microwaves or combinations of these heating methods. Conventional apparatuses
10 such as belt dryers, tray dryers, drum dryers which dry continuously or batchwise can be used here.

The SiO_2 elements can advantageously be dried to a water content which allows damage-free removal from the casting moulds. Accordingly, drying can be carried out in the casting mould to a water content of less than 60% by weight, in particular less
15 than 50% by weight and particularly preferably less than 40% by weight.

Drying to a water content below the abovementioned values can particularly preferably be effected after removal of the SiO_2 element from the mould, with the abovementioned dryers being able to be used.

Advantages are displayed by, inter alia, SiO_2 elements which after drying have a
20 water content in the range from 0.0001 to 50% by weight, preferably from 0.0005 to 50% by weight, in particular from 0.001 to 10% by weight and particularly preferably from 0.005 to 5% by weight, measured by means of the thermogravimetric method (IR moisture measuring instrument) which is generally known to those skilled in the art.

25 Drying of the solidified, water-containing SiO_2 composition are carried out at a temperature in the range from 50°C to 350°C, preferably from 80 to 300°C, in particular from 90 to 250°C and particularly preferably from 100 to 200°C, under normal conditions (i.e. at atmospheric pressure).

The pressure at which drying is carried out can be within a wide range and drying can be carried out at subatmospheric pressure or superatmospheric pressure. For economic reasons, drying at ambient or atmospheric pressure (from 950 to 1050 mbar) can be preferred.

- 5 To increase the hardness of the dried SiO_2 element, it can be thermally densified or sintered. This can, for example, be carried out batchwise in conventional industrial furnaces, for example shaft furnaces, or microwave sintering furnaces, or continuously in, for example, push-through furnaces or shaft furnaces.

10 The thermal densification or sintering can be carried out at a temperature in the range from 400 to 1700°C, in particular from 500 to 1500°C, preferably from 600 to 1200°C and particularly preferably from 700 to 1100°C.

The duration of thermal densification or sintering is dependent on the temperature, the desired density and optionally the desired hardness of the SiO_2 element. The thermal densification or sintering can preferably be carried out for a time of 5 hours,
15 preferably 2 hours, particularly preferably 1 hour.

The dried and/or sintered SiO_2 elements having the above-described typical dimensions can, for example, have a compressive strength (reported as fracture force) of at least 10 N/cm², preferably more than 20 N/cm², with sintered SiO_2 elements in particular being able to display compressive strength values of at least
20 50 or even at least 150 N/cm², in each case measured by means of compressive tests on an apparatus for compressive strength testing.

In a particular embodiment, the SiO_2 element can preferably have a density of at least 0.7 g/cm³, preferably a density of at least 1 g/cm³, particularly preferably at least 1.4 g/cm³. In the case of high-temperature sintering, a density of as high as 2.65
25 (fused silica density) can be achieved.

The silicon dioxide elements are joined to one another by means of a ceramic adhesive.

It can be preferred that the ceramic adhesive comprises a silicon compound which

can be hydrolysed to SiO_2 . Without restricting the generality, specific examples of such silicon compounds are SiCl_4 , HSiCl_3 , $\text{Si}(\text{OCH}_3)_4$, $\text{Si}(\text{OOCCH}_3)_4$ and $\text{Si}(\text{OC}_2\text{H}_5)_4$. The compounds mentioned can be used individually or as a mixture. Preferred silicon compounds include, in particular, alkoxysilanes, particularly preferably tetraalkoxy-

5 silanes, with tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) being particularly preferred.

The ceramic adhesive used particularly preferably comprises a composition comprising silicon dioxide, at least one silicon compound which can be hydrolysed to SiO_2 , preferably a tetraalkoxysilane, in particular TEOS, and at least one curing

10 catalyst, preferably H_2O_2 , H_2SO_4 or HNO_3 . The silicon dioxide can preferably be particulate, with the diameter of these particles preferably being in the range from 0.001 to 100 μm , particularly preferably in the range from 0.005 to 10 μm and especially preferably in the range from 0.01 to 1 μm , measured by means of laser light scattering.

15 In a preferred embodiment, the ceramic adhesive used can comprise tetraethoxysilane, preferably TEOS and silicon dioxide based on a self-organizing water-containing SiO_2 composition.

Furthermore, according to the invention, the ceramic adhesive can preferably have a thermal stability greater than or equal to 1000°C, preferably greater than or equal to

20 1200°C, particularly preferably greater than or equal to 1400°C.

It can also be provided for the ceramic adhesive to have a purity of greater than or equal to 75%, preferably greater than or equal to 90%, particularly preferably greater than or equal to 99.9%.

Ceramic adhesives which can be used according to the invention and are preferably

25 based on SiO_2 are commercially available, for example from Polytec PT GmbH.

An insert according to the invention comprises at least one graphite element layer in addition to the above-described SiO_2 elements which preferably form a glass vessel. This layer is joined over its area to the silicon dioxide elements. Accordingly, the area

defined by the length and width of the silicon dioxide elements is directly or indirectly in contact with at least one graphite element layer. This can be effected mechanically or by means of a bonding layer. The term "graphite element layer" means that the insert has at least one layer-like element which is composed essentially of graphite.

- 5 In a preferred embodiment, the graphite element layer is impermeable or liquid-tight so that small amounts of liquid silicon cannot penetrate through this layer. Layers having a high impermeability will hereinafter also be referred to as foils, with a plurality of foils being able to be joined to one another by adhesive bonding.

Preferred embodiments of the graphite element layer are described in the document
10 US 7,708,827 B2.

Graphite can be produced as block material by hot isostatic pressing and can be worked by cutting machining. It is available as high-purity material, for example from SGL Carbon, and has mechanical and chemical properties which are particularly well-suited to achieving the present object, i.e. good thermal stability and especially
15 no damaging influence on the purity of the silicon ultimately produced.

Furthermore, it can be provided that the graphite element layer is flexible in the sense of the claims when it can (starting from a flat shape) in the same way take on the curved shape of walls which typically occur in an insert for a melting crucible for metal melts, in particular for silicon melts, owing to its flexibility. Preferred
20 embodiments of such a graphite element layer survive such conformation to the shape owing to their flexibility without troublesome cracks or fractures occurring.

A graphite element layer to be used according to the invention can also advantageously be in the form of a self-supporting woven fabric, in other words as a weave of carbon fibres. The flexible graphite element layer can alternatively consist
25 of a combination of woven fabric and impermeable layer, as a result of which the advantages of a foil can be combined with those of a woven fabric. A foil is, compared to a woven fabric, advantageously impermeable to oxygen, nitrogen or liquid silicon. However, compared to a woven fabric, carbon layers can become detached relatively easily from a foil, which is a disadvantage. A graphite foil

reinforced by means of a weave of carbon fibres has firstly the mechanical stability necessary for the use and secondly the necessary impermeability.

In addition, the graphite element layer can have a thickness in the range from 0.1 to 50 mm, preferably from 0.5 to 1 mm, particularly preferably about 1 mm.

- 5 In an alternative embodiment of the invention, the thickness of the graphite element layer is less than or equal to 5 mm, preferably less than or equal to 3 mm, particularly preferably less than or equal to 1.5 mm.

Furthermore, the graphite element layer can have at least one functionalized surface.

In addition, the graphite element layer can have a multilayer structure.

- 10 In a preferred embodiment of the invention, the multilayer structure of the graphite element layer is formed by foil strips, with the foil strips having an angle relative to one another in the range from 45 to 135°, preferably from 60 to 120°, particularly preferably from 75 to 105°.

- In a preferred embodiment of the invention, the foil strips can be self-supporting,
15 flexible foil strips of a graphite element layer.

The foil strips to be used according to the invention for the graphite element layer can also preferably have an overall density of the graphite of from 0.1 to 2 g/cm³, preferably from 0.5 to 1.5 g/cm³, particularly preferably from 0.7 to 1.3 g/cm³.

- Furthermore, the foil strips to be used according to the invention for the graphite
20 element layer can, according to the invention, preferably have an ash value of from 0.15 to 4%, preferably from 0.5 to 1.5%, particularly preferably from 0.7 to 1.2%.

In addition, the foil strips to be used according to the invention for the graphite element layer can preferably have a thermal stability of from 0 to 2000°C, preferably from 0 to 1700°C, particularly preferably from 200 to 1000°C.

- 25 Furthermore, the foil strips to be used according to the invention for the graphite element layer can preferably have a specific heat capacity of from 0.2 to 2 kJ/(kg*K),

preferably from 0.5 to 1 kJ/(kg*K), particularly preferably from 0.6 to 0.8 kJ/(kg*K).

The foil strips to be used according to the invention for the graphite element layer can also preferably have a coefficient of thermal expansion parallel to the layer of from 0.2 to $2 \cdot 10^{-6}/K$, preferably from 0.5 to $1.5 \cdot 10^{-6}/K$, particularly preferably from 0.8 to $1.2 \cdot 10^{-6}/K$.

Furthermore, the foil strips to be used according to the invention for the graphite element layer can preferably have a coefficient of thermal expansion perpendicular to the layer of from 10 to $60 \cdot 10^{-6}/K$, preferably from 20 to $40 \cdot 10^{-6}/K$, particularly preferably from 25 to $35 \cdot 10^{-6}/K$.

The foil strips to be used according to the invention for the graphite element layer can also preferably have a Shore hardness of from 10 to 60, preferably from 20 to 40, particularly preferably from 25 to 35.

In addition, the foil strips to be used according to the invention for the graphite element layer can preferably have a chloride content of less than or equal to 30 ppm, preferably less than or equal to 10 ppm, particularly preferably less than or equal to 7 ppm.

Furthermore, a bonding layer can be arranged between the silicon dioxide elements and the graphite element layer. The bonding layer can, for example, be formed by the abovementioned ceramic adhesives, with preferred ceramic adhesives containing a composition comprising silicon dioxide, at least one silicon compound which can be hydrolysed to SiO_2 , preferably a tetraalkoxysilane, in particular TEOS, and at least one curing catalyst, preferably H_2O_2 , H_2SO_4 or HNO_3 . The silicon dioxide can preferably be particulate, with the diameter of these particles preferably being in the range from 0.001 μm to 10 μm , particularly preferably in the range from 0.01 μm to 0.5 μm , measured by means of laser light scattering.

Such a bonding layer to be used according to the invention can have a thickness in the range from 1 μm to 4 mm, preferably 0.1 mm to 1.5 mm, particularly preferably from 0.5 mm to 1.2 mm.

The inside of the silicon dioxide vessel of the insert for a melting crucible which comes into contact with the SiO₂-containing materials can be coated at least in regions with one or more materials.

Furthermore, the silicon dioxide vessel can comprise a coating of silicon nitride (Si₃N₄) on the inside.

Here, the silicon nitride (Si₃N₄) coating can have a thickness in the range from 1 µm to 5 mm, preferably from 10 µm to 1 mm, particularly preferably from 100 to 500 µm.

Furthermore, the silicon dioxide vessel can, in a preferred embodiment, comprise at least two layers of silicon dioxide elements between which at least one graphite element layer is arranged. In a particular embodiment, a bonding layer can be arranged in each case between the graphite element layer and the two silicon dioxide element layers.

Furthermore, a melting crucible comprising at least one such insert to be used according to the invention is provided. Here, the melting crucible can be configured so that the insert forms an integral constituent.

Here, the melting crucible can preferably comprise a graphite crucible into which the present insert is fitted.

The shape of the insert or of the melting crucible can be adapted to various requirements, with the melting crucible being able to assume the shape of a cylinder or a cuboid.

A process for producing such a insert to be used according to the invention for a melting crucible comprises the following process steps:

- a) production of individual silicon dioxide elements;
- b) use of the individual silicon dioxide elements produced in step a) for providing a silicon dioxide vessel by joining these individual silicon dioxide elements by means of a ceramic adhesive;

- c) joining this silicon dioxide vessel comprising a plurality of joined individual silicon dioxide elements over its area to at least one graphite element layer.

In addition, a further layer of silicon dioxide elements can be applied to the graphite element layer on the outside of the silicon dioxide vessel in a process step d).

- 5 The process for producing an insert comprising a silicon dioxide vessel is preferably concluded by a heat treatment step regardless of whether a process step d) is provided.

The joining of the individual elements, as provided for in step b), can be carried out using a ceramic adhesive. The curing of this ceramic adhesive is dependent on the
10 composition thereof and is generally known. This curing can be carried out before or after the joining of the vessel obtained over its area to a graphite element layer. Depending on the embodiment, a sintering step can be carried out in order to increase the strength of the bond between the ceramic adhesive and the silicon dioxide elements and/or the graphite element layer. For this purpose, the glass
15 vessel with or without graphite element layer can be heated to a temperature in the range from 500 to 1800°C, preferably in the range from 1000 to 1500°C, for a time of at least 12 hours, preferably at least 24 hours.

Preferred embodiments of the present invention are illustrated by way of example below with the aid of figures. The figures show:

- 20 Fig. 1: a schematic structure of one embodiment of an insert for a melting crucible according to the present invention;

Fig. 2: a schematic cross section through an embodiment of an insert according to the invention;

- Fig. 3: a schematic cross section through a preferred embodiment of an insert
25 according to the present invention;

Fig. 4: various embodiments for joining individual, different silicon dioxide elements to produce a silicon dioxide vessel.

Figure 1 shows an embodiment of a silicon dioxide vessel 1 to be used according to the invention, which has been or is being built up from a plurality of individual, different silicon dioxide elements 2. Here, Figure 1a schematically shows a cylindrical silicon dioxide vessel for use according to the invention for a melting crucible and
5 Figure 1b shows a cuboidal silicon dioxide vessel for this purpose.

Figure 2 depicts a cross section through an embodiment of an insert 3 according to the invention which comprises three individual layers of material: a first layer of silicon dioxide elements 4, a bonding layer 5 and a graphite element layer 6. The silicon dioxide elements 4 are adhesively bonded to one another.

10 Figure 3 depicts a cross section through a preferred embodiment of an insert 3' according to the invention which is made of five individual layers of material 4, 5, 6, 7 and 8. Compared to the embodiment in Figure 2, two additional layers of material, namely a second bonding layer 7 and a second layer of silicon dioxide elements 8, has been used, with this embodiment likewise comprising a first layer of silicon
15 dioxide elements 4, a bonding layer 5 and a graphite element layer 6. The silicon dioxide elements 4 and 8 are adhesively bonded to one another.

In these embodiments, both the first and second layers of silicon dioxide elements 4 and 8 have a greater thickness than the graphite element layer 6.

Figure 4 shows different possible ways of joining individual different silicon dioxide
20 elements to form a silicon dioxide vessel according to the invention; in Figure 4A, a first silicon dioxide element 9 is joined by means of a straight butt joint to a second silicon dioxide element 10, with ceramic adhesive 11 being able to be used to strengthen the joint.

Figure 4B depicts an oblique butt joint between a first silicon dioxide element 9' and
25 a second silicon dioxide element 10', with ceramic adhesive 11 being able to be used to strengthen the joint.

Figure 4C depicts joining of the silicon dioxide elements 9'' and 10'' by means of a tongue-and-groove joint, with one edge of the silicon dioxide element 9'' being

provided with a tongue element 12 while a further edge of the silicon dioxide element 10'' is provided with a groove element 13. A ceramic adhesive 11 can additionally be introduced into the joint.

5 An overlap is depicted in Figure 4D. The respective edges of the silicon dioxide elements 9''' and 10''' have a step-like structure, with the projection 14 of a silicon dioxide element 9''' being fitted into the recess 15 of the next silicon dioxide element 10'''. In addition, a ceramic adhesive 11 can be introduced into the joint.

10 An insert to be used according to the invention and a melting crucible comprising such an insert can preferably be provided for a process for purifying a metal melt, in particular a silicon melt.

Such a purification process can be combined with further processes for purifying silicon. Particularly preferred embodiments are known from, inter alia, the thesis "Silicon for Solar Cells" by Anne-Karin Søliland at the Norwegian University of Science and Technology, October 2004, IMT report 2004:65, and the document
15 DE 38 02 531 A1.

The further steps and details of processes for producing metallic silicon are disclosed, inter alia, in WO 2010/037694. In this process, SiO₂ is reduced by carbon in an electric arc furnace to give metallic silicon. A shaped SiO₂ body in combination with a carbon source is usually used as starting material.

20 The insert which can be used according to the invention for a melt crucible thus makes possible an inexpensive and constructionally simple solution to the problem of providing a specific insert for a melting crucible which is suitable, in particular, for the directional solidification of silicon melts in the production of high-purity silicon.

The insert according to the invention for a melt crucible and also a melt crucible
25 comprising at least one such insert are defined by the characterizing features of the accompanying claims.

List of reference numerals

	1	Silicon dioxide vessel
	2	Individual silicon dioxide elements
5	3	Insert
	4	First layer of silicon dioxide elements
	5	First bonding layer
	6	Graphite element layer
	7	Second bonding layer
10	8	Second layer of silicon dioxide elements
	9, 9', 9'', 9'''	First silicon dioxide element
	10, 10', 10'', 10'''	Second silicon dioxide element
	11	Ceramic adhesive
	12	Tongue element
15	13	Groove element
	14	Projection of a first silicon dioxide element
	15	Recess of a second silicon dioxide element

Claims

1. Insert for a melting crucible, which comprises a silicon dioxide vessel, wherein the silicon dioxide vessel comprises silicon dioxide elements which are joined together by means of a ceramic adhesive and the silicon dioxide elements are joined over their area to at least one graphite element layer.
5
2. Insert according to Claim 1, wherein the ceramic adhesive comprises an alkoxysilane.
3. Insert according to Claims 1 or 2, wherein the silicon dioxide vessel comprises at least two layers of silicon dioxide elements between which at least one
10 graphite element layer is arranged.
4. Insert according to any of Claims 1 to 3, wherein the silicon dioxide vessel comprises a coating of silicon nitride (Si_3N_4) on the inside.
5. Insert according to Claim 4, wherein the coating of silicon nitride (Si_3N_4) has a thickness in the range from 1 μm to 5 mm.
- 15 6. Insert according to at least one of the preceding claims, wherein the silicon dioxide elements have a thickness in the range from 0.1 to 100 mm.
7. Insert according to at least one of the preceding claims, wherein the silicon dioxide elements are inserted into one another by means of a tongue-and-groove system.
- 20 8. Insert according to at least one of the preceding claims, wherein a bonding layer is arranged between the silicon dioxide elements and the graphite element layer.
9. Insert according to Claim 8, wherein the bonding layer has a thickness in the range from 1 μm to 4 mm.
- 25 10. Insert according to at least one of the preceding claims, wherein the graphite element layer has a thickness in the range from 0.1 to 50 mm.

- 34 -

11. Insert according to at least one of the preceding claims, wherein the graphite element layer has a multilayer structure.
12. Insert according to Claim 11, wherein the multilayer structure of the graphite element layer is formed by foil strips, with the foil strips having an angle to one another in the range from 45 to 135°.
13. Insert according to at least one of the preceding claims, wherein the silicon dioxide elements have a purity of at least 90%.
- 14 . Melting crucible comprising at least one insert according to at least one of the preceding Claims 1 to 13.

1/3

Figure 1a

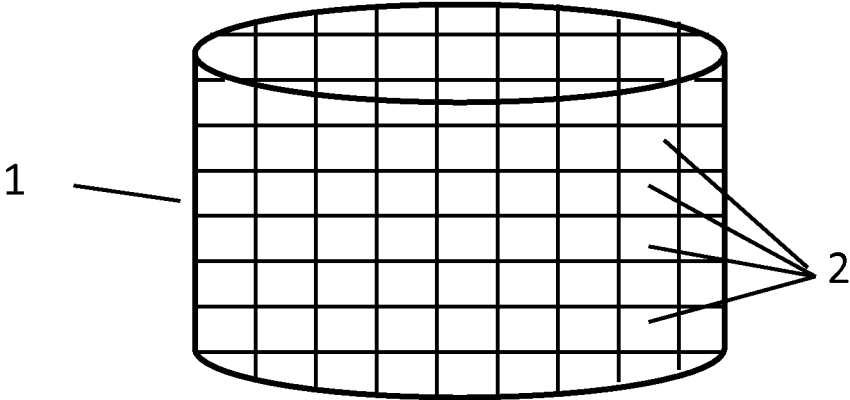
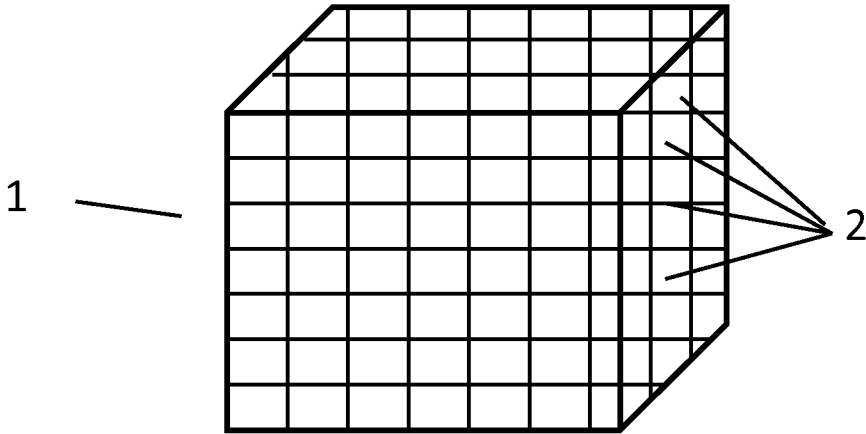


Figure 1b



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Figure 2

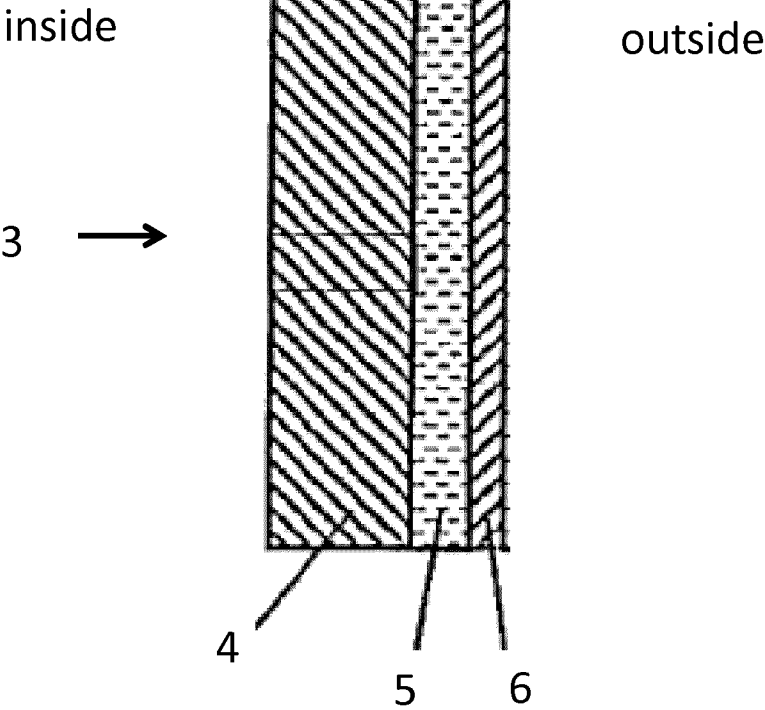
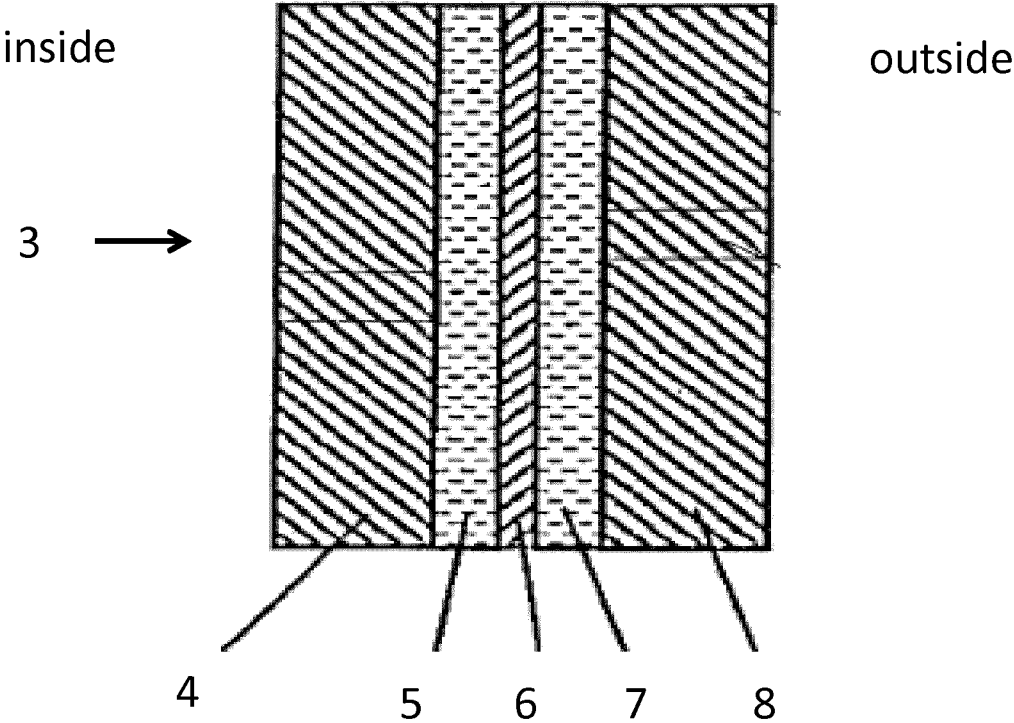
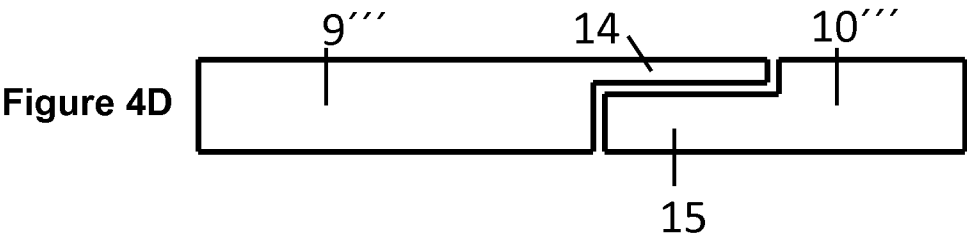
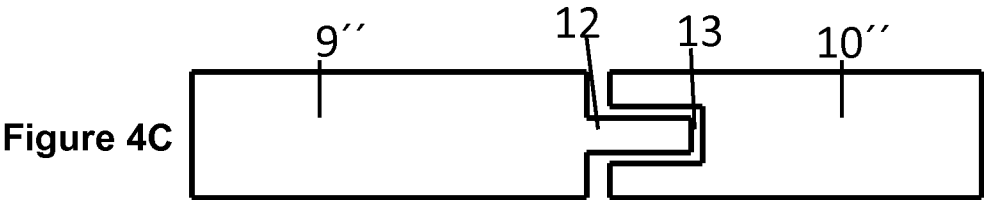
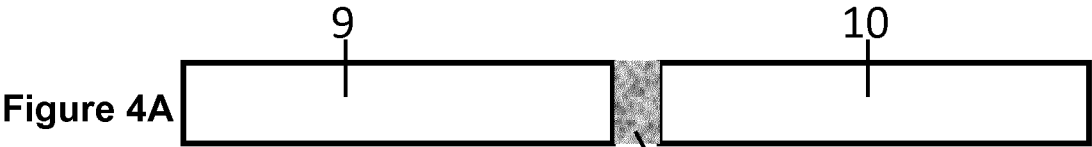


Figure 3





INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/052419

A. CLASSIFICATION OF SUBJECT MATTER
INV. C30B35/00 C30B29/06 C30B11/00 C30B15/10 C01B33/037
ADD.

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)
C30B C01B

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 practicable, search terms used)

EPO-Internal, INSPEC, IBM-TDB, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/037065 A1 (WAGNER ROLF [DE] ET AL) 16 February 2012 (2012-02-16) the whole document	1-14
X	US 2011/180229 A1 (PHILLIPS RICHARD J [US] ET AL) 28 July 2011 (2011-07-28) the whole document	1-14
A	FR 2 804 131 A1 (LORRAINE CARBONE [FR]) 27 July 2001 (2001-07-27) the whole document	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

15 April 2013

Date of mailing of the international search report

23/04/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Brisson, Olivier

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/052419

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2012037065	A1	16-02-2012	CN 102388169 A 21-03-2012
			DE 102009015236 A1 14-10-2010
			EP 2414566 A1 08-02-2012
			JP 2012522710 A 27-09-2012
			US 2012037065 A1 16-02-2012
			WO 2010112259 A1 07-10-2010

US 2011180229	A1	28-07-2011	CN 102741462 A 17-10-2012
			EP 2529043 A1 05-12-2012
			KR 20120128643 A 27-11-2012
			TW 201202491 A 16-01-2012
			US 2011180229 A1 28-07-2011
			WO 2011092659 A1 04-08-2011

FR 2804131	A1	27-07-2001	NONE
