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(71) Applicant(s)
Vesuvius Crucible Company

(72) Inventor(s)
Rancoule, Gilbert

(74) Agent / Attorney
Fisher Adams Kelly, Level 29 12 Creek Street, Brisbane, QLD, 4000

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- (71) Applicant (for all designated States except US): **VESUVIUS CRUCIBLE COMPANY** [US/US]; 103 Foulk Road, Wilmington, DE 19803 (US).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): **RANCOULE, Gilbert** [FR/FR]; 12, rue de Picardie, F-59700 Marcq-en-Baroeul (FR).
- (74) Agent: **DEBLED, Thierry**; Vesuvius Group S.A., Intellectual Property Department, Rue de Douvrain 17, B-7011 Ghlin (BE).
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(54) Title: CRUCIBLE FOR THE TREATMENT OF MOLTEN SILICON

(57) Abstract: The invention relates to a crucible for the treatment of molten silicon comprising a basic body with a bottom surface and lateral walls defining an inner volume. According to the invention, the basic body comprises at least 65% by weight of silicon carbide, from 12 to 30 % by weight of a constituent selected from silicon oxide or nitride. Moreover, the basic body comprises at least one silicon oxide and/or nitride coating, at least on the surfaces defining the inner volume of the crucible contrarily to the state of the art crucibles, such a crucible can be used several times without any visible degradation of its physical integrity.



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Description

[0001] The present invention relates to a crucible for the treatment of molten silicon, to the manufacture of such crucible and to the use of such crucible for treating molten silicon. [0002] Nowadays, the demand for high purity silicon has significantly increased. The applications of high purity silicon in the generation of photovoltaic energy are widely spread. Yet, the successive energetic crisis have strengthened that need.

[0003] The object of the present application is a vessel used for the treatment of molten silicon. Such treatment can consist in the silicon crystallization, either by directional solidification or by drawing of a crystal from a molten bath. The treatment can also consist in a metallurgical treatment intended for the production of very highly pure silicon or one of its alloys. It can thus consist in a metallurgical treatment of alloys or ores aiming at eliminating certain impurities.

[0004] For such kind of applications, it is well known to use crucibles from quartz or based on other materials essentially constituted of silicon dioxide (see for example the document DE-C- 962868). Indeed, since the main constituent of the crucible is silicon under the form of one of its oxides, the contamination risk by other chemical compounds is strongly reduced. The quartz crucibles present however the major drawback of being attacked by molten silicon, with the consequence that the solidifying silicon ingot tends to adhere to the walls of the quartz crucible. Since the quartz and silicon have different coefficients of thermal expansion, very important mechanical stresses can be generated either inside the ingot resulting into crystallization defects, or into the crucible walls resulting into the crucible cracking. Further, the silicon ingot once solidified strongly adheres to the crucible walls and it is practically impossible to extract the ingot without destroying the crucible or at least seriously damaging it.

[0005] The quartz and certain silica derivatives are also known to be subject to crystallographic phase changes during their thermal cycling. These crystallographic phase changes induce very high mechanical stresses within the crucible walls. Further, they can also induce changes of density and, therewith, of thermal conductivity within the wall, leading to problems of losses of homogeneity of the transmission or withdrawal of energy towards or from silicon. So far, this crucial problem has not found a solution likely to be industrially carried out.

[0006] Moreover, at the temperatures of use, quartz is subject to geometrical changes. These geometrical changes are relatively uneasy to manage since the treatment furnace wherein the vessel containing molten silicon stands must heat of a fully controlled way the quantity of silicon being treated. Any deformation of the vessel wall induce a loss of homogeneity of the transmission of withdrawal of energy towards or from silicon which adds to the loss of geometry of the silicon ingot during the crystallization.

[0007] This problem has been partly remedied by reinforcing the external walls of the quartz crucible by carbon plates, more particularly by graphite plates.

[0008] Such carbon plates, and more particularly graphite plates are widely used in all kinds of processes carried out at high temperature due to their excellent resistance to thermal stresses

for quite long periods. For example, graphite crucibles have been used to receive a germanium bath during the carrying over of a process of crystal drawing according to the Czochralski method. So far, it has however not been possible to use such graphite crucibles for the treatment of silicon since, at high temperature, the molten silicon bath attacks the graphite walls and forms silicon carbide, the presence of which being incompatible with the required purity. According to the currently used technique, as indicated hereabove, the different processes of treating silicon at high temperature take place in quartz or other silica based materials crucibles of which the walls have been reinforced with carbon, more particularly graphite, plates.

[0009] This technique either is not problem-free. It is indeed well known that the gaseous phases, in the neighboring of the molten silicon bath, influence the formation of an equilibrium between the silicon vapor escaping from the molten silicon bath and the carbon monoxide atmosphere prevailing in the furnace. Reactions are observed as well on carbon or graphite as in the silicon bath, leading to a change of physical and mechanical properties.

[0010] Starting from the same concept consisting of avoiding introducing other constituents than silicon, it has also been proposed in the state of the art to use silicon nitride crucibles. Therefore, document WO-A1-2004/016835 discloses a crucible essentially constituted of silicon nitride. Even though some of the properties of this crucible are satisfactory, its price makes its use currently unrealistic. Further, it has been reported that these crucibles are also sensitive to deformation at high temperature. DE-C-962868 teaches crucibles made from silicon carbide as an alternative to quartz.

[0011] The applicant has thus set as an objective the provision of a vessel for the treatment of molten silicon which would not present the drawbacks observed in the prior art. In particular, it would be desirable that the crucible could be used a certain number of times without any significant degradation of its physical integrity. Moreover, the thermal conductivity properties of the crucible in question should not change in the course of its use; in other words, that the material be not sensitive either to deformation or to crystallographic phase changes. Eventually, it is necessary that the crucible be not a source of silicon pollution.

[0012] The applicant has established that these objectives and others are reached with a crucible according to claim 1 and which is manufactured according to the process of claim 7. Such a crucible comprises thus a basic body with a bottom surface and lateral walls defining an inner volume, mainly constituted (at least 65% by weight of the material) of silicon carbide. It is actually surprising that a crucible for the treatment of

molten silicon could be manufactured from a material mainly constituted of silicon carbide. Indeed, until now, the skilled person has always tried to avoid the presence of silicon carbide which is perceived as a problem in any process for the treatment of molten silicon.

- 5 [0013] On the contrary, the applicant has demonstrated that a crucible comprising a basic body mainly constituted of silicon carbide does not present the drawbacks observed with conventional crucibles. In particular, the fact that the main component of the basic body consists in silicon carbide showing a well defined crystallographic phase which is not subject to phase transition at the temperatures of treatment of the molten
- 10 silicon, permits to suppress the problems of loss of homogeneity of the transfer / withdrawal of energy observed with conventional crucibles.

Further, silicon carbide does not have plastic phases at these temperatures and, therefore, is not subject to deformation.

[0014] Thanks to these excellent properties, such a crucible can be reused a significant number of times while conventional crucibles must be replaced after each use. It is very surprising that the solution to this problem comes precisely from the use of a material which has been considered until now as a source of problems.

[0015] The material forming the crucible basic body further comprises from 12 to 30 % by weight of one or more constituents selected from silicon oxide or nitride. The remainder of the material forming the basic body can comprise up to 13 % by weight of one or several other constituents such as binders (chemical, hydraulic or other), agents regulating the fluidity of the composition before shaping and curing, etc.

[0016] The constituent selected from silicon oxide or nitride can be introduced as such in the composition used to form the basic body or can be introduced under the form of metallic silicon that will be either oxidized or nitrized during the curing of the crucible. The curing conditions (nitriding or oxidizing atmosphere) shall thus be selected according to the desired composition. It will be noted that the silicon oxide can also have an effect on the fluidity of the composition before shaping and curing as well as a binding effect, in particular when this compound is introduced under the form of fumed silica. In such a case, obviously, it is taken into account only once (in the 12 to 30 % by weight of one or more constituents selected from silicon oxide and / or nitride).

[0017] Other viscosity regulating agents can also be introduced in order to modify the hot properties of the crucible. The addition of fine reactive alumina particles (grain size lower or equal to 200 μ m) is particularly advantageous for its effect of modifying the fluidity during its shaping as well as its binding effect after curing.

[0018] Other binders that could be used comprise for example organic resins (leaving a carbonaceous residue after curing), magnesia and calcium aluminate and / or silicate. According to an advantageous embodiment, the bond is generated by the formation *in situ* of a silicon nitride or oxide type bond. Such a bond is easily obtained by regulating the curing conditions of the article and, in particular, the curing atmosphere of the article.

[0019] Further, it has been established that it is necessary to provide the crucible internal walls of a coating of the type silicon nitride as described, for example, in WO-A1-2004053207 or in the European patent application 05447224.6, of the type silicon oxide or of a combination thereof as disclosed for example in the European patent application 05076520 or in the document WO-A1-2005/106084. Generally, an oxide type coating is used for the crystallization of silicon as a monocrystal and of the nitride type for the polycrystalline crystallization of silicon. It will be noted that the coating can be produced during the curing of a raw crucible comprising silicon (for example a curing in nitriding atmosphere will produce a surface coating of silicon nitride while an oxidizing atmosphere curing will produce a surface coating of the silicon oxide type).

[0020] According to the invention, the basic body is bonded. As indicated above, the binder

can be a hydraulic binder (for example calcium silicate or aluminate) forming thereby a cement like composition, of a chemical binder (for example magnesium silicate) or of a cement-free type binder (for example gels, orthosilicates, etc.) or also a bond produced by reactive binding (carbon bond, nitriding curing, etc.).

- 5 **[0021]** Advantageously, the silicon carbide will be used according to a well defined granulometric distribution. In particular, it is preferable that the coarser grains fraction be constituted of silicon carbide so as to provide a silicon carbide matrix constituted of coarse grains wherein finer grains of silicon nitride or oxide will be present. The majority of silicon carbide will thus be preferably constituted of grains having a particle size larger than 200 μm
- 10 while the silicon oxide, the silicon nitride and/or the metallic silicon grains will preferably be introduced under the form of grains having a particle size lower than 10 μm .

- [0022]** The following examples illustrate several embodiments of the invention. In the following Table I, several examples of materials according to the invention constituting the basic body of crucibles for the treatment of molten silica are provided. In this Table, the first column indicates
- 15 the nature of the constituents, columns 2 to 13 indicate the weight percentages of the different constituents. The examples A1, A2, C1, C2, E1 and E2 illustrate several variants of hydraulic binders. Examples A to F illustrate different variants of chemical or reactive binding.

- [0023]** Crucibles have been prepared from these materials and their internal walls have been coated with a silicon nitride or oxide type coating. Crystallization of the same quantity of silicon
- 20 has been performed in each of these crucibles. It has been observed thereby that none of these crucibles had been damaged during the silicon crystallization so that they could be immediately reused in a further crystallization operation without requiring any repairing step.

TABLE I

[illegible]

Claims.

1. Crucible for the treatment of molten silicon comprising a basic body with a bottom surface and lateral walls defining an inner volume, the basic body comprising
 - at least 65% by weight of silicon carbide;
- 5 - from 12 to 30 % by weight of a constituent selected from silicon oxide or nitride, the basic body further comprising at least one silicon oxide and/or nitride coating, at least on the surfaces defining the inner volume of the crucible.
2. Crucible according to claim 1, **wherein** the basic body further comprises up to 13% by weight of one (or more) other constituent(s) selected from carbon, magnesium oxide
- 10 aluminum oxide, calcium silicate and/or aluminate.
3. Crucible according to claim 1 or 2, **wherein** a silicon oxide layer is present between the surface coating and the wall of the surfaces defining the inner volume of the crucible.
4. Crucible according to any one of the claims 1 to 3, **wherein** a silicon oxide layer is present at the surface of the basic body walls, on the side opposite to the side defining
- 15 the inner volume.
5. Crucible according to any one of the claims 1 to 4, **wherein** at least 50% by weight of the silicon carbide grains have a particle size larger than 200 μm .
6. Crucible according to any one of the claims 1 to 5, **wherein** the silicon oxide or nitride grains have a particle size lower than 10 μm .
- 20 7. Process for the manufacture of a crucible for the treatment of molten silicon comprising a basic body with a bottom surface and lateral walls defining an inner volume, the basic body comprising at least 65% by weight of silicon carbide, from 12 to 30 % by weight of a constituent selected from silicon oxide or nitride and further comprising at least one silicon oxide and/or nitride coating, at least on the surfaces defining the inner volume of
- 25 the crucible comprising the following steps:
 - a) shaping of the basic body with a bottom surface and lateral walls defining an inner volume;
 - b) drying of the basic body;
 - c) curing of the basic body; and
 - 30 d) formation of a silicon oxide and/or nitride coating at least on the surfaces defining the inner volume of the crucible.
8. Process according to claim 7, **wherein** steps c) and d) are carried out simultaneously by curing the basic body in an oxidizing or nitriding atmosphere.
9. Process according to claim 7, **wherein** step d) of formation of the coating comprises
- 35 applying the coating before the step of curing the basic body.
10. Use of a crucible comprising a basic body with a bottom surface and lateral walls

defining an inner volume, the basic body comprising at least 65% by weight of silicon carbide, from 12 to 30 % by weight of a constituent selected from silicon oxide or nitride and further comprising at least one silicon oxide and/or nitride coating, at least on the surfaces defining the inner volume of the crucible, for treating molten silicon.