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Method for preparing of ceramic shaped part, apparatus and use thereof.

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The present invention concerns a method for preparing of at least one ceramic shaped part, apparatus for preparing of at least said ceramic shaped part and use thereof.

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Description of prior art:

Regarding ceramic shaped parts, it is a problem today to produce shapes with the requested dimensions, especially large shaped parts, which can be recycled several times. Further, large ceramic shaped parts are required within several fields such as for example preparing of silicon ingots to the solar cell industry.

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Today, when preparing silicon ingots for further production of silicon wafers, shaped parts consisting of silica is used. At high temperatures, which are necessary when preparing silicon for solar cell purposes, shaped parts of silica, so-called silica crucibles, is exposed to temperatures up to 1500 °C. Silica crucibles soften at high temperatures such as 1500 °C. When cooling the silica crucibles to room temperature, crack formation arises which involve no recycling of the crucibles. In several production processes, crucibles which can only be used once, involve a substantial cost.

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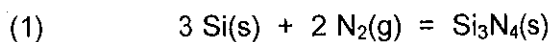
Several known techniques for preparing ceramic shaped parts involve different methods for moulding. In such processes a slicker/dispersion which is an aqueous composition of mainly the preferred powder and a suitable binding agent, is prepared. The slicker/dispersion can also be based on other liquids than water, such as ethanol and other alcohols. The slicker is poured into a casting mould (typical a plaster mould). The liquid of the slicker is extracted in the mould and the mould is dismantled after a while. A green body consisting of powder bounded by the binding agent is achieved. The green body is then prepared in several processes such as drying, removing of the binding agent and nitriding/sintering, before a desired product is achieved. The green body has low strength and thus

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can easily change shape and crack in further processing and handling. This is more critical when larger and more complicated shaped parts are prepared.

Pressure casting is another known technique. The basis is mainly a composition of powder, binding agent and some liquid. The composition is compressed by different methods to the desired shape, a green body. Compression of big and or complicated geometries are very difficult and today not solved technically. The green body possesses the same problems as mentioned above.

The nitriding of silicon to silicon nitride takes place at high temperatures, typical 1150-1400 degrees Celsius, according to the following reaction;



The reaction is strongly exothermic and thus can cause overheated areas and hence the following escalating reaction. In such cases the probability of forming liquid silicon is huge. Liquid silicon will not be converted into silicon nitride, and thus results in a weakening of the material. This is a well known problem when preparing silicon nitride, and is especially difficult to avoid when preparing large shaped parts.

The present invention is intended to solve or at least facilitate the problems identified above. Particularly, an object of the invention is to provide a method well suitable for preparing ceramic shaped parts for use when preparing silicon ingots for the solar cell industry. Further, it is an object of the present invention to provide a method in which said ceramic shaped part can be recycled several times. Problems such as deforming and cracking of the prepared ceramic shaped part are avoided in the present invention. Further, no binding agent or liquid is used in the present invention, and thus there is no need for an extra process step to dry and remove the binding agent. It is also used a shape which equalizes the temperature of the ceramic shaped part during the nitriding process which by that means will minimize the probability of forming liquid silicon. Compared with prior art in the field the present invention represents a method which is simplified, which

is suitable for preparing of large shaped parts, which consist of fewer process steps, which avoid deformation and which is economical favourable.

The present invention provides a method for preparing of at least one ceramic shaped part, wherein

- a cavity is provided between at least one external shape and at least one internal shape,
- a Si-containing powder composition is placed in the cavity,
- the Si-powder composition is heated in a reactive gas atmosphere to a temperature in which a reaction bounded ceramic shaped part is obtained.

Further, it shall be mentioned that at least one of the external shapes are perforated and also at least one of the internal shapes are perforated. Perforated shapes result in a relatively uniform reactive gas atmosphere. Further, the reaction for preparing of the reaction bonded ceramic shaped part will take place quickly on the basis of the perforated shapes which ensure supply of the desired gas atmosphere. The internal shapes according to the invention are separated from each other by inserting of a thermal resistant deformable material in which the thermal resistant deformable material is chosen from graphite felt, graphite wool or graphite bar. The cavity provided between at least the external- and internal shape as mentioned above is coated with a slurry prior to providing the cavity. A foil is applied according to the invention between at least one external shape and said slurry prior to coating with the slurry. Further, a foil is applied between at least one internal shape and said slurry prior to coating with the slurry. A temperature resistant perforated foil is applied prior to coating with the slurry. Said slurry comprises a powder containing silicon nitride of particle size $\leq 100 \mu$, $\leq 80 \mu$, $\leq 60 \mu$, $\leq 40 \mu$, $\leq 20 \mu$, $\leq 10 \mu$, $\leq 5 \mu$ og $\leq 1 \mu$.

The mentioned Si-containing powder composition according to the present invention is chosen from at least one of the following components: silicon, silicon carbide, silicon nitride. The reactive gas atmosphere contains at least nitrogen. Further, other gas atmospheres or gas compositions can be used when the invention is performed. At least one external shape and at least one internal shape according to the invention comprise a graphite containing material.

Further, the present invention comprises an apparatus for preparing at least one ceramic shaped part comprising:

at least a cavity between at least one external shape and at least one internal shape,

- 5 means for inserting of a Si-containing powder composition,
- means for heating in a reactive gas atmosphere.

Apparatus according to the invention comprises that at least one of the external- and internal shapes are perforated. Further, it is as mentioned desirable to provide
10 apparatus which can be exposed to thermal stress and at the same time maintain the original dimensions and also avoid crack formation. In relation to this it shall further be mentioned that the present invention comprises apparatus as described in the preceding where at least the internal shape possess a thermal expansion coefficient which is higher than the thermal expansion coefficient of a reaction
15 bounded ceramic shaped part, and at least the external shape possess a thermal expansion coefficient lower than of the reaction bounded ceramic shaped part. In the instance in which an internal shape is used with thermal expansion coefficient lower than the reaction bounded ceramic shaped part, shall a thermal resistant deformable material separate at least two internal shapes. The thermal resistant
20 deformable material is chosen from graphite felt, graphite wool or graphite bar.

Further, the present invention comprises use of a cavity provided between at least one external shape and at least one internal shape, wherein a Si-containing powder composition is provided in the cavity previous of heating the powder
25 composition in a reactive gas atmosphere to a temperature in which a ceramic shaped part is prepared. Said cavity is coated with a silicon nitride containing slurry prior to providing the cavity. A foil is used between at least one external shape and said slurry prior to coating with the slurry. Further, a foil is used between at least one internal shape and said slurry prior to coating with the slurry.
30 The foil consists of a temperature resistant perforated foil. The use of the present invention takes place in a gas atmosphere comprising nitrogen or a nitrogen containing gas atmosphere.

Description of the figures.

The shaping of at least one ceramic shaped part depends on the object and the use of the ceramic shaped part. In preparing of silicon ingots to the solar cell industry the shaping will often be in the form of square or rectangular shaped parts. Figure 1 shows a cross-section of composed shape of different parts. In figure 2 a cross-section seen from the side of a square shape is shown. Figure 3 shows a cross-section of a square shape seen from above. Figures 4 and 6 respectively show a circular internal shape and also a circular complete shape seen from above. Figures 5 and 7 shows a cross-section of a circular internal and external shape.

Example 1:

A shape composed of different parts of graphite containing material was used in the example. The shape consisted of an internal shape (A), an external shape (B), a basis plate (bottomplate) (C) and a plate (D) as shown in figure 1. The graphite containing parts was perforated, except the basis plate. The internal shape comprising four relatively similar graphite containing parts were fastened to each other and to the basis plate. Said parts were fastened to each other with suitable fixing devices in the form of i.a. screws. In a distance between the internal shaped parts a thermal resistant deformable material (E) in the form of graphite bar, graphite felt or graphite wool were applied. Perforated graphite foil was applied at the internal graphite containing shapes. The perforations of the foil shall preferably not coincide with the perforations of the graphite containing parts. The external shapes consisted of four relatively similar graphite containing plates. Perforated graphite foil was applied at the external graphite containing shapes. The surfaces coated with graphite foil were further coated with a silicon nitride containing slurry. The slurry dried at room temperature. The external graphite containing shapes was assembled at the basis plate (figure 1). Further, said external graphite containing parts were fastened above the internal shape and to the basis plate. Silicon containing powder, with the preferred size within one or several ranges is as follows: <10 micron, <20 micron, <40 micron, <60 micron, <75 micron, <100 micron, <120 micron, <150 micron, <180 micron, <200 micron, was placed in the provided cavity (figure 1, F) between the internal- and external shape. Further, the

silicon containing powder was compacted by vibration. Silicon containing powder in the size ranges as described above were in the end placed in the upper area of said cavity. The powder was further compacted by vibration and mechanical compaction. The shapes mounted rigidly were in this example turned around 180 degrees as shown in figure 1. Further the basis plate was disassembled. The shapes mounted rigidly were placed in a furnace with nitrogen atmosphere. The furnace was quickly heated up to 1100-1200°C, and further slowly heated to 1400-1500°C during 40-60 hours. The shapes mounted were then cooled down to room temperature. The whole furnace cycle (i.e. heating, preparing of at least one ceramic shaped part and cooling down) took place in a time interval of 60-90 hours with starting point in cold mounted shapes, via shapes heated to 1400-1500°C, to in the end cooled/cold mounted shapes. Said mentioned shapes was taken out of the furnace after cooling down. The external- and internal graphite containing shapes were disassembled, and a reaction bounded silicon nitride shaped part/ceramic shaped part with the same dimension as the cavity between the external- and internal graphite containing shapes were provided. Possible remaning slurry from the graphite containing shapes at the ceramic shaped part can in a simple manner be removed with dry ice blasting (tørrisblåsing) or mechanical rubbing /finishing. The graphite containing parts was cleaned with a cleaning cloth and were then ready for re-use.

Example 2:

In example 2 the same procedure as in example 1 was used with exception of the powder composition. In this example, a powder composition comprising silicon (70 weight%, <150 micron) and silicon carbide (30 weight%, <150 micron) was used. After disassembling of the graphitic parts, a nitride bounded silicon carbide-shaped part was provided.

Example 3:

In example 3 the method as described in example 1 was used with the exception of the powder composition. In the present example a powder composition comprising silicon (70 weight%, <150 micron) and silicon nitride (30 weight%, <10 micron)

were chosen. After disassembling of the graphite containing parts, a nitride bounded silicon nitride-shaped part was provided.

s In the previous preferred embodiments of the invention have been described it will be obvious for person skilled in the art that other embodiments including the concepts can be used. These and other examples according to the invention illustrated above are only shown as examples and the scope of the invention is described in the following claims.

Claims

- 5 1. Method for preparing of at least one ceramic mould part of reaction bonded silicon nitride characterised in that,
- a cavity is provided between at least one external mould and at least one internal mould,
 - 10 - at least one of the external and/or internal mould is perforated,
 - a Si-containing powder composition is placed in the cavity,
 - the Si-containing powder composition is heated in a reactive gas atmosphere to a temperature in which a reaction bonded silicon nitride mould part is obtained.
- 15 2. Method according to claim 1, wherein at least two internal moulds are separated from each other by inserting a thermal resistant deformable material.
3. Method according to claim 1 or 2, wherein a thermal resistant deformable material is chosen from at least one of the following: graphite felt, graphite wool,
- 20 graphite bar.
4. Method according to claim 1, wherein a temperature resistant perforated foil is applied to at least one external mould and coated with a silicon nitride slurry.
- 25 5. Method according to claim 1, wherein a temperature resistant perforated foil is applied to at least one internal mould and coated with a silicon nitride slurry.
6. Method according to claim 4 or 5, wherein the slurry comprises a powder containing silicon nitride of particle size $\leq 100 \mu\text{m}$.
- 30 7. Method according to claim 1, wherein the Si-containing powder composition is chosen from at least one of the following components: silicon, silicon carbide, silicon nitride.

8. Method according to claim 1, wherein the reactive gas atmosphere contains at least nitrogen.

5 9. Method according to the claims 1, 4 and 5, wherein at least one external mould and at least one internal mould comprise a graphite containing material.

10. Apparatus for preparing at least one ceramic mould part made of reaction bonded silicon nitride comprising:

10 at least a cavity between at least one external mould and at least one internal mould;

at least one of the external or internal moulds are perforated;

means for inserting of a Si-containing powder composition;

means for heating in a reactive gas atmosphere.

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11. Apparatus according to claim 10, wherein the at least one internal mould has a thermal expansion coefficient higher than the thermal expansion coefficient of a reaction bonded silicon nitride ceramic mould part, and the at least one external mould has a thermal expansion coefficient lower than of the reaction bonded
20 silicon nitride ceramic mould part.

12. Apparatus according to claim 11 or 10, wherein at least a thermal resistant deformable material separates at least two internal moulds.

25 13. Apparatus according to claim 10, wherein the thermal resistant deformable material is chosen from graphite felt, graphite wool or graphite bar.

14. Use of a cavity provided between at least one external mould and at least one internal mould, wherein at least one of the external or internal mould is perforated,
30 and wherein a Si-containing powder composition is provided in the cavity previous of heating the powder composition in a reactive gas atmosphere to a temperature in which a ceramic mould part of reaction bonded silicon nitride is prepared.

15. Use according to claim 14, of a slurry comprising a powder containing silicon nitride.

16. Use according to claim 14, of a gas atmosphere comprising nitrogen.