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(54) Title: GLUE AND COATING FOR REFRACTORY MATERIALS AND CERAMICS

(57) Abstract: The present invention relates to a heat crucible glue or coating for use in connection with refractory materials and ceramics. The glue or coating comprises 25 to 50 weight % silicon powder, 5 to 20 weight % SiC powder, 20 to 60 weight % formaldehyde resin or polyfurfuryl alcohol and 10 to 30 weight % of an organic solvent.

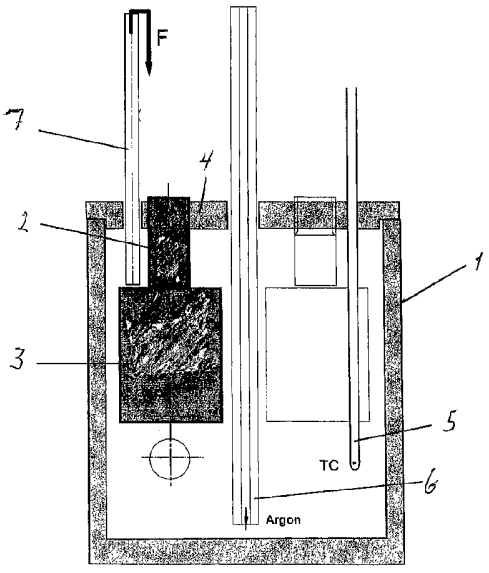

Figure 1

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Title of Invention

Glue and coating for refractory materials and ceramics.

Field of Invention

The present invention relates to a glue and a coating for refractory materials and ceramics, such as carbon materials, silicon nitride, silicon carbide and quartz.

Technical background

It is known a plurality of glues for gluing refractory materials and ceramics such as carbon materials, silicon nitride, silicon carbide and quartz which are to be used at high temperatures. From US patent No. 5,474,849 is is thus known a glue for carbon components. The glue comprises a thermoset polysilagen polymer, 20 to 50 % by weight based on the weight of polymer of a ceramic powder which can be SiC, 10-40 % by weight based on the weight of polymer of Si-powder and 5-15 % by weight based on the weight of polymer of carbon powder.

It has however been found that this type of glue is not suitable for carbon material, silicon nitride, silicon carbide and quartz that is to be used in furnaces, moulds, crucibles or details for such intended to be contact with molten silicon. It is important that glue used in connection with parts does not contaminate the molten silicon which is in contact with the mentioned furnaces, moulds, crucibles or details for such. This is particularly important in connection with treatment of high purity silicon which is to be used for the production of solar cells. It is further important that the glue joints are not wettable by molten silica.

Description of the Invention

By the present invention it is provided a glue and coating which is easy to use, has a good strength at high temperatures, is not wettable by molten silicon and that can be stored for a long time. The glue and coating further has the surprising effect that it looses its strength during cooling from high

temperatures and down to below 1000°C. This effect is particularly useful when the glue is used for gluing together moulds made from separate sheets of for instance silicon nitride, quartz or graphite used for directional solidification of molten silicon. During cooling of silicon a solid phase transformation takes place which results in a volume increase and may cause failure of the moulds. By the use of moulds made from separate sheets glued with the glue according to the present invention the glue will at the temperature where the phase transformation takes place have a low strength and the moulds will therefore crack in the glue layers while the individual sheets not will be damaged. The sheets can therefore be reused for making new moulds.

The present invention thus relates to a heat curable glue or coating for use in connection with carbon materials, silicon nitride, silicon carbide and quartz, which glue or coating consist of 25 to 50 % by weight of silicon powder, 5 to 20 % by weight of silicon carbide powder, 20 to 60 % by weight of fenol formaldehyde resin or polyfurfuryl alcohol and 10 to 30 % by weight of an organic solvent.

According to a preferred embodiment the organic solvent is selected among monoethylene glycol, diethylene glycol and triethylene glycol. The preferred organic solvent is monoethylene glycol.

The solvent is added in an amount sufficient to obtain a suitable viscosity of the glue or coating.

According to a preferred embodiment the glue or coating comprises 35 to 45 % by weight of silicon powder, 8 to 18 % by weight of silicon powder, 25 to 35 % by weight of formaldehyde resin or polyfurfuryl alcohol and 15 to 25 % by weight of organic solvent.

According to another preferred embodiment the glue or coating contains a curing agent in order to lower the polymerization temperature for the formaldehyd resin or the polyfurfuryl alcohol. The curing agent is preferably

hexamine, but aluminium phosphate and acid such as sulfuric acid, para-toluene sulphonic acid (PTS), PTS neutralized with urea and para-toluene sulphonic acid ethyl ester(PTSEE) can also be used.

The glue or coating according to the present invention is in liquid state at room temperature and can be stored for a long time.

When using the glue or coating not containing curing agent, the organic solvent will be volatilized at 150 to 290°C and polymerization of formaldehyde resin and polyfurfuryl alcohol will take place within a temperature range between 250°C to 400°C whereby a solid structure is being formed. If a curing agent is added the polymerization process will start at lower temperature.

During further heating it will at about 700°C remain a carbon structure consisting of the remains of the formaldehyde resin or polyfurfuryl alchohol. The strength of the glue will in this temperature range be higher than 20 MPa. By further temperature increase a reaction will take place between the carbon structure and the silicon powder in the glue and with continued heating to a temperature above 1413°C the Si powder will melt and react with carbon to SiC. If the temperature increase is slow, the reaction between Si powder and carbon will, however, take place in solid state.

When using the glue for gluing of carbon lids for smelting crucibles the glue according to the invention has shown to create a seal against contact with molten silicon. During cooling of the smelting crucible after having been used for smelting of silicon the strength of the glue disappears and the parts glued together can be released from each other without resistance. The glue according to the invention thus maintains its strength as long as the glued parts are kept at high temperature.

Test with use of the coating in graphite moulds for solidification of molten silicon has shown that the coating provides a layer which fills pores and

cavities and totally seals against penetration of silicon into the walls of the graphite mould.

After cooling of the silicon and removal of the silicon ingot the remains of the coating could be brushed away as a dust-like powder and the mould could again be coated with the coating according to the invention.

The glue according to the invention can also be used for gluing moulds for use in directional solidification of silicon where the moulds consists of a bottom sheet and side sheets that are glued together. The glue seals cavities and surface roughness in the sheets and the requirement to the surface finish of the sheets can thus be lowered. After solidification and cooling the glue will as mentioned above loose its strength and the sheets can thus be used for making a new mould. The sheets that are glued can be made of carbon material such as prebaked carbon sheets or graphite sheets, silicon nitride sheets or quartz sheets.

Short description of the Drawing

Figure 1 shows a set-up for testing of strength of graphite parts glued with glue according to the invention.

Detailed description of Invention

Example

Figure 1 shows a set-up for testing of the strength of glue for graphite parts glued with glue according to the invention. The glue had the following composition:

38 weight % silicon powder, 12 weight % silicon carbide powder, 28 weight % formaldehyde resin, 18 % monoethylene glycol and 4 weight % hexamin.

On figure 1 there is schematically shown a graphite crucible 1 placed in an induction furnace (not shown). Three samples were prepared consisting of an upper graphite cylinder 2 having a diameter of 24 mm being glued to a lower graphite cylinder 3 by means of the glue according to the invention. The cylinder 3 has a greater diameter than the graphite cylinder 2. The three glued samples were screwed to the lower side of lid 4 for the crucible 1. The temperature in the crucible was measured by means of a thermocouple and the atmosphere in the crucible was kept inert by addition of argon via a pipe 6. A ceramic rod 7 was inserted through the lid 4 in order to exert a force to the part 3 of the samples. The ceramic rod 7 was connected to a feather-weight of 20 kg.

The crucible was heated according to the following program:

20-1000°C: 20 minutes
1000-1600°C: 60 minutes
Holding time at 1600°C: 60 minutes
Cooling from 1600°C to 1000°C: 60 minutes
The furnace was thereafter shut-off and the samples were slowly cooled to room temperature.

The samples1-3 was loaded with a force of 20 kg at different temperatures and different times. The results are shown in Table I.

Table 1

Temperature °C	Time from start minutes	Sample 1 kg	Sample 2 kg	Sample 3 kg
1350	35	>20		
1500	50	>20		
1600	60	12		
1600	120		>20	>20
1350	145		18	>20
1000	180			>20
Room temp				No strength

The results shown in Table 1 show that Sample 1 which was loaded with a weight of 20 kg during the heating period had a good strength up to 1600°C.

Sample 2 was loaded with a weight of 20 kg after having been kept at 1600°C for 60 minutes and had a good strength at that temperature. Also after been cooled to 1350°C Sample 2 showed a good strength.

Sample 3 was loaded with a weight of 20 kg after having been kept at 1600°C for 60 minutes and during cooling to 1350°C and during further cooling to 1000°C. The results show that the strength of the glue was very good at these temperatures. By further cooling to room temperature the part 3 of Sample 3 fell off the upper part 2 of the Sample.

The results from these examples show that the glue according to the invention has a very good strength during heating to 1600°C and maintains it strength

during cooling to a temperature below 1000°C, while the strength thereafter is reduced.

Claims

1. Heat curable glue or coating for use in connection with refractory materials and ceramics, c h a r a c t e r i z e d i n that the glue or coating comprises 25 to 50 % by weight of silicon powder, 5 to 20 % by weight of silicon carbide powder, 20 to 60 % by weight of fenol formaldehyde resin or polyfurfuryl alcohol and 10 to 30 % by weight of an organic solvent.

2. Glue or coating according to claim 1, c h a r a c t e r i z e d i n that the organic solvent is selected among monoethylene glycol, diethylene glycol and triethylene glycol.

3. Glue or coating according to claim 1, c h a r a c t e r i z e d i n that glue or coating comprises 35 to 45 % by weight of silicon powder, 8 to 18 % by weight of silicon powder, 25 to 35 % by weight of formaldehyde resin or polyfufuryl alcohol and 15 to 25 % by weight of organic solvent.

4. Glue or coating according to claim 1-3, c h a r a c t e r i z e d i n that the glue or coating contains a curing agent in order to lower the polymerization temperature for the formaldehyde resin or the polyfurfuryl alcohol.

5. Glue or coating according to claim 4, c h a r a c t e r i z e d i n that the curing agent is selected among hexamine, aluminium phosphate or an acid.

6. Glue or coating according to claim 5, c h a r a c t e r i z e d i n that the acid is selected among sulfuric acid, para-toulene sulphonic acid neutralized with urea and para-toulene sulphonic acid etyl ester.

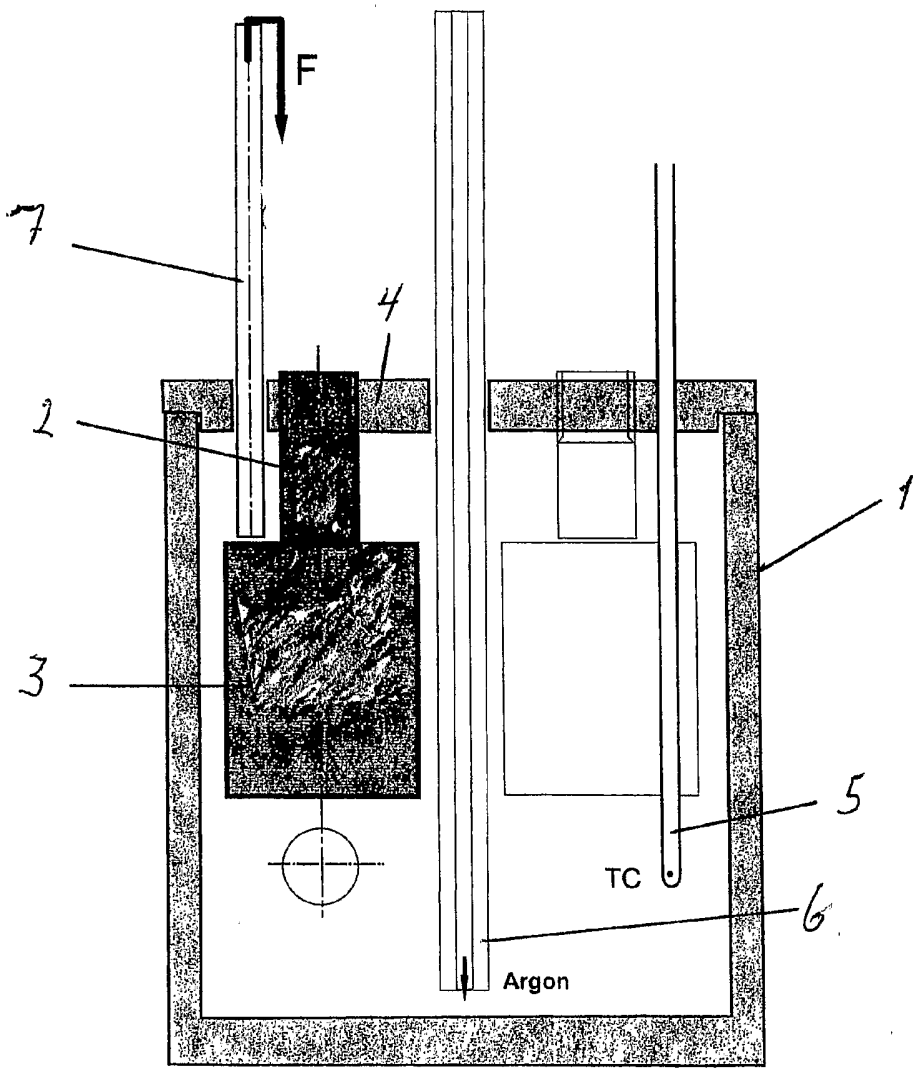

Figure 1