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(54) MANUFACTURE OF SILICON MOULDINGS

(71) We, WACKER-CHEMITRONIC, Gesellschaft für Elektronik-Grundstoffe mbH., a body corporate organised according to the laws of the Federal Republic of Germany, of 8263 Burghausen, Johannes-Hess-Strasse 24, Federal Republic of Germany, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

The present invention relates to a process for the manufacture of silicon mouldings and, more particularly, for the manufacture of rotationally symmetric hollow silicon mouldings, for example hemispherical or calotte-shaped shells.

Silicon has a high infrared transmission and silicon mouldings are therefore used for optical purposes in the infrared region of the spectrum. In order to attain the infrared transmission which is theoretically possible for silicon, however, it is necessary for the silicon mouldings to be of high purity and to be built up of coarsely crystalline columnar crystal areas located mainly perpendicular to the surface of the moulding.

Silicon mouldings can be manufactured by the pyrolytic decomposition of, for example, gaseous silicon tetrachloride with deposition of the silicon so formed onto an appropriately shaped substrate (see, for example, British Patent Specification No. 1 420 388). Silicon mouldings produced in this way do not, however, have an adequate infrared transmission : the desired crystal structure can be obtained only by manufacture of the moulding from a silicon melt.

Polycrystalline silicon rods grown from a melt by the Czochralski crystal-pulling method may have the desired infrared transmission and silicon bodies may be machined from such rods. This method is very expensive, however, because of the labour involved and because of the high loss of silicon.

Silicon mouldings can also be manufactured by melting and resolidifying silicon in an appropriately shaped mould of, for example, graphite, quartz or silicon nitride. The disadvantage of this is that the mould becomes wetted by the silicon with the result that, on cooling, a firm bond forms between the mould and the silicon moulding such that they cannot easily be separated from one another. Moreover, if the thermal expansion coefficients of the mould and of silicon differ appreciably from one another, the mould and/or the moulding may be destroyed on cooling.

Another method of manufacturing silicon mouldings is to melt silicon in a water-cooled copper crucible by means of inductive heating and then slowly to cool the melt. Silicon mouldings manufactured in this way are, however, unsuitable for optical purposes because of contamination of the silicon by the copper.

A process for the manufacture of silicon mouldings suitable for optical purposes has been described in British Patent Specification No. 1 344 382. In that process, silicon is melted, by means of inductive heating, in a cooled mould, the moulding surface of which is covered by a protective layer of sintered quartz wool and/or sintered quartz sand. When all the silicon has been melted, it is cooled by lowering it out of the inductively heated zone. This process is, however, not suitable for the manufacture of large silicon mouldings because the protective layer becomes destroyed through contact with molten silicon during the longer time needed to melt all the silicon.

In order to overcome this problem, British Patent Specification No. 1 445 861 describes a process in which silicon is melted in a vessel separate from that in which it is to be moulded, and the silicon melt is then poured into a mould the moulding surface of which consists of one or more substances selected from graphite, graphite densified by pyrolytic coating within the pores, sintered quartz wool, sintered quartz sand or sintered silicon nitride, the temperature of the mould being such that when the silicon melt contacts the moulding surface a solid layer of silicon immediately forms thereon. When using this process for the manufacture of, for example, hollow silicon mouldings, such as hemispherical or calotte-shaped shells, it is necessary to use a two-part mould, namely a mould consisting of a male part and a female part. The problem can then arise of crystal growth commencing at both the male moulding surface and at the female moulding surface, even when solidification is effected by means of a temperature gradient. The two crystallisation fronts thus formed move toward one another at different rates and impurities and small gas bubbles can become trapped between them, resulting in a reduction in the infrared transmission of the solidified moulding. One of the crystallisation layers may have to be ground off in order to improve the infrared transmission.

The present invention provides a process for the manufacture of a rotationally symmetric hollow silicon moulding, which comprises pouring a silicon melt into a rotationally symmetric hollow mould while the mould is rotating about its vertical axis at a speed within the range of from 50 to 500 rev/min and while the mould is maintained at a temperature within the range of from 500 to 1200°C.

By using an appropriately shaped mould, the process of the invention may be used for the manufacture of various rotationally symmetric hollow bodies of silicon, for example, calotte-shaped shells, hemispherical shells or hollow cylinders or tubes that are closed at one end.

As the silicon melt is, according to the process of the invention, poured into the rotating hollow mould it is thrown outward and upward against the walls of the mould and solidifies to form a silicon moulding complementary to the shape of the mould. The speed of rotation of the mould is, according to the present process, within the range of from 50 to 500 rev/min but the actual speed used in any given case will depend partly on the type of moulding being manufactured: for example, lower rotational speeds are required in the manufacture of relatively shallow calotte-shaped shells than are required in the manufacture of hemispherical shells or of hollow cylinders or tubes.

The process of the present invention has the advantage that it is not necessary to use a two-part mould: the expensive male part of the mould is dispensed with. Consequently, there is only one crystallisation front and this moves inward from the mould surface, pushing any impurities or small gas bubbles out of the moulding. Moreover, especially when the process is carried out according to the preferred method discussed below, solidification of the silicon on the mould surface commences rapidly and thus there is no wetting of the mould by the molten silicon. The solidified moulding can therefore be released from the mould without difficulty.

The mould used in the process according to the invention - or at least the moulding surface thereof - is preferably of graphite, of graphite densified by pyrolytic coating within the pores, or of silicon nitride. During the process, it is maintained at a temperature within the range of from 500 to 1200°C, preferably from 800 to 1200°C.

In order to obtain mouldings having as uniform a wall thickness as possible, especially when manufacturing shell-shaped mouldings, it is advantageous to pour the silicon melt into the mould in two or more discrete stages, with the rotational speed of the mould in the second and subsequent stages being greater than that in the immediately preceding stage. For example, a hemispherical silicon shell may advantageously be manufactured by carrying out the process in two stages. In the first stage, from 15 to 45% of the total amount of the silicon melt is poured into the mould while it is rotating at a speed of from 60 to 120 rev/min and is preferably maintained at a temperature of from 800 to 1200°C. The silicon melt solidifies very rapidly to form the bottom of the shell, with no wetting of the mould. The remaining 55 to 85% of the silicon melt is then poured into the mould from 60 to 180 sec after the termination of the first stage while the mould is rotating at a speed of from 150 to 200 rev/min and is still maintained at a temperature of from 800 to 1200°C. In this stage, the molten silicon moves upward against the walls of the mould and solidifies to form the desired hemispherical shell, having a marked columnar crystal structure perpendicular to the surface of the shell, and therefore having a good infrared transmission.

One method of carrying out the process of the invention will now be described with reference to the accompanying drawing, which is a diagrammatic longitudinal cross-sectional view through one form of apparatus suitable for carrying out the process.

The upper part of a vertically tubular closed gas-tight vessel 3 (of which, for simplicity, only the side walls are shown) is surrounded by a multicoil induction heater 2. A melting crucible 1 having a pouring lip and made, for example, of translucent fused quartz is pivotally mounted in a crucible holder 4 in the upper part of the vessel 3 and immediately above a quartz funnel 5 fitted within a graphite block 7 which stands on carbon support pillars 6. Immediately below the graphite block 7 is a hollow graphite mould 8 with a hemispherical casting cavity having a radius of, for example, 75 mm, which is supported on a rotatable drive shaft 9 which is a hollow coaxial double tube and serves to supply cooling water to a chamber 10, which is lined with metal for the purposes of good heat conductance, situated in the bottom of the mould 8. Carbon support pillars 11 are provided on which the mould 8 can stand when it is not being supported by the drive shaft 9.

When carrying out the process for the manufacture of a hemispherical shell, solid pure silicon is placed in the crucible 1 and the vessel 3 is closed and either evacuated or filled with an inert gas, the pressure of which is generally unimportant and may be, say, 200 torr or may be much higher. The silicon is then melted, and heated to a temperature advantageously within the range of from 1420 to 1600°C, preferably from 1430 to 1480°C, by means of the induction heater 2. The graphite block 7 is also inductively heated to the same temperature to avoid any danger of the silicon solidifying in the funnel 5. The crucible 1 is then tilted so that from 15 to 45 % of the total amount of the silicon melt is poured into the funnel 5 and thus into the mould 8, while it is being rotated by means of the drive shaft 9 at a speed of from 60 to 120 rev/min and while it is maintained at a temperature of from 800 to 1200°C. The mould 8 is heated by radiation from the graphite block 7 and its temperature is regulated by adjusting the pressure of the cooling water being pumped through the drive shaft 9 into the chamber 10. From 60 to 180 sec later the rotational speed of the mould is increased to from 150 to 200 rev/min and the remainder of the silicon melt is poured in. When the silicon has all solidified, the rotation of the mould and the induction heating are ceased but water-cooling of the mould is continued for a while. When the mould has cooled somewhat, water-cooling is ceased and the mould is lowered onto the support pillars 11 and the entire apparatus is allowed to cool slowly and uniformly to room temperature. The silicon moulding can then be removed from the mould 8.

The following worked example was carried out to illustrate the process of the invention. The apparatus used was as shown in the drawing and the procedure was as described immediately above.

750 g of pure silicon in discrete pieces were placed in the crucible, whereupon the vessel was closed and filled with argon under a pressure of 200 torr. The melt and the funnel were heated to a temperature of about 1450°C and then about 25 % of the melt was poured through the funnel into the mould while it was rotated at a speed of about 100 rev/min and maintained at a temperature of about 900°C. At this relatively low rotational speed, the melt moved about half-way up the wall of the mould and solidified very rapidly without wetting the mould. About 90 sec later, the rotational speed of the mould was increased to about 180 rev/min and the remainder of the melt was poured in. At this higher rotational speed, the melt moved up the wall of the mould almost to the top and solidified. The temperature gradient caused by the mould being heated from above and cooled from below ensured that the desired crystalline structure necessary for good infrared transmission formed on solidification. After about 180 sec, rotation of the mould and heating were ceased but cooling was continued until the temperature of the mould had fallen to about 600°C. The mould was then lowered onto the support pillars and the entire apparatus was allowed to cool to room temperature. The resulting silicon moulding, which was about 50 mm high and about 8 mm thick, was removed from the mould and its upper edge and inner face were briefly ground smooth. It had an infrared transmission of more than 50 %. Etching of the moulding showed it to have a columnar structure of monocrystalline zones that had grown radially inward from the surface of the mould.

WHAT WE CLAIM IS:-

1. A process for the manufacture of a rotationally symmetric hollow silicon moulding, which comprises pouring a silicon melt into a rotationally symmetric hollow mould while the mould is rotating about its vertical axis at a speed within the range of from 50 to 500 rev/min and while the mould is maintained at a temperature within the range of from 500 to 1200°C.

2. A process as claimed in claim 1, wherein the mould is maintained at a temperature within the range of from 800 to 1200°C.

3. A process as claimed in claim 1 or claim 2, wherein the melt is poured into the mould in two or more discrete stages, with the rotational speed of the mould in the second and subsequent stages being greater than that in the immediately preceding stage.

4. A process as claimed in claim 3, wherein the process is carried out in two discrete stages with from 15 to 45 % of the total amount of the melt being poured in in the first stage and the remainder of the melt being poured in in the second stage.

5. A process as claimed in claim 4, wherein the mould is rotated at a speed

within the range of from 60 to 120 rev/min during the first stage and at a speed within the range of from 150 to 200 rev/min during the second stage.

6. A process as claimed in claim 4 or claim 5, wherein the second stage is commenced from 60 to 180 sec after the termination of the first stage.

7. A process as claimed in claim 1, carried out in an apparatus substantially as described herein with reference to, and as shown in, the accompanying drawing.

8. A process as claimed in claim 1, carried out substantially as described herein with reference to the accompanying drawing.

9. A process as claimed in claim 1, carried out substantially as described in the example herein.

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*