United States Patent

DeBie

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[54] PROCESS AND APPARATUS FOR PULLING SINGLE CRYSTALS OF GERMANIUM

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[51] **Int. Cl.** **B01j 17/00,** H01l 7/00

[58] **Field of Search** .....148/1.6; 23/273 SP, 273 V

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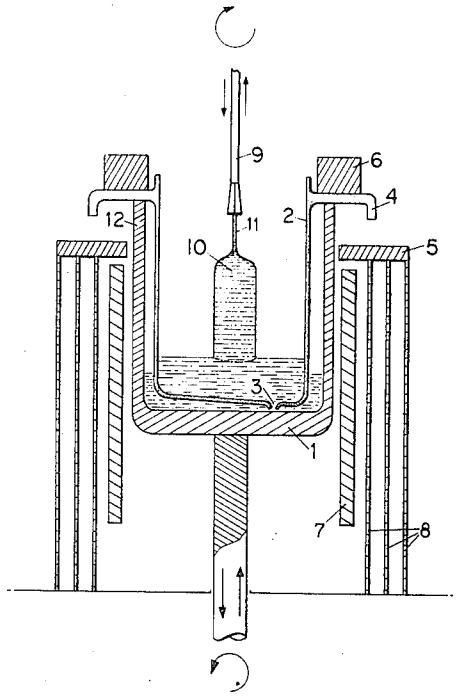
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[57] **ABSTRACT**

A process and apparatus for separating scum from molten metal, particularly germanium, and the pulling of single crystals with the use of outer and inner crucibles. The metal is placed in the outer crucible and there melted. In the inner crucible is weighted with a ballast to ensure its penetration into the molten metal and to avoid its flotation on the molten metal. The outer crucible is then lifted and rotated to segregate the scum from the molten metal and to introduce the metal from the outer to the inner crucible through an orifice provided in the bottom of the inner crucible while the scum remains in the outer crucible. The outer crucible is then lowered to empty the inner crucible and again lifted and rotated to reintroduce scum-free metal from the outer to the inner crucible. The steps are repeated until all traces of the scum are separated from the molten metal, which is followed by growing a single crystal of metal from the scum-free metal in the inner crucible.

3 Claims, 2 Drawing Figures



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SHEET 1 OF 2

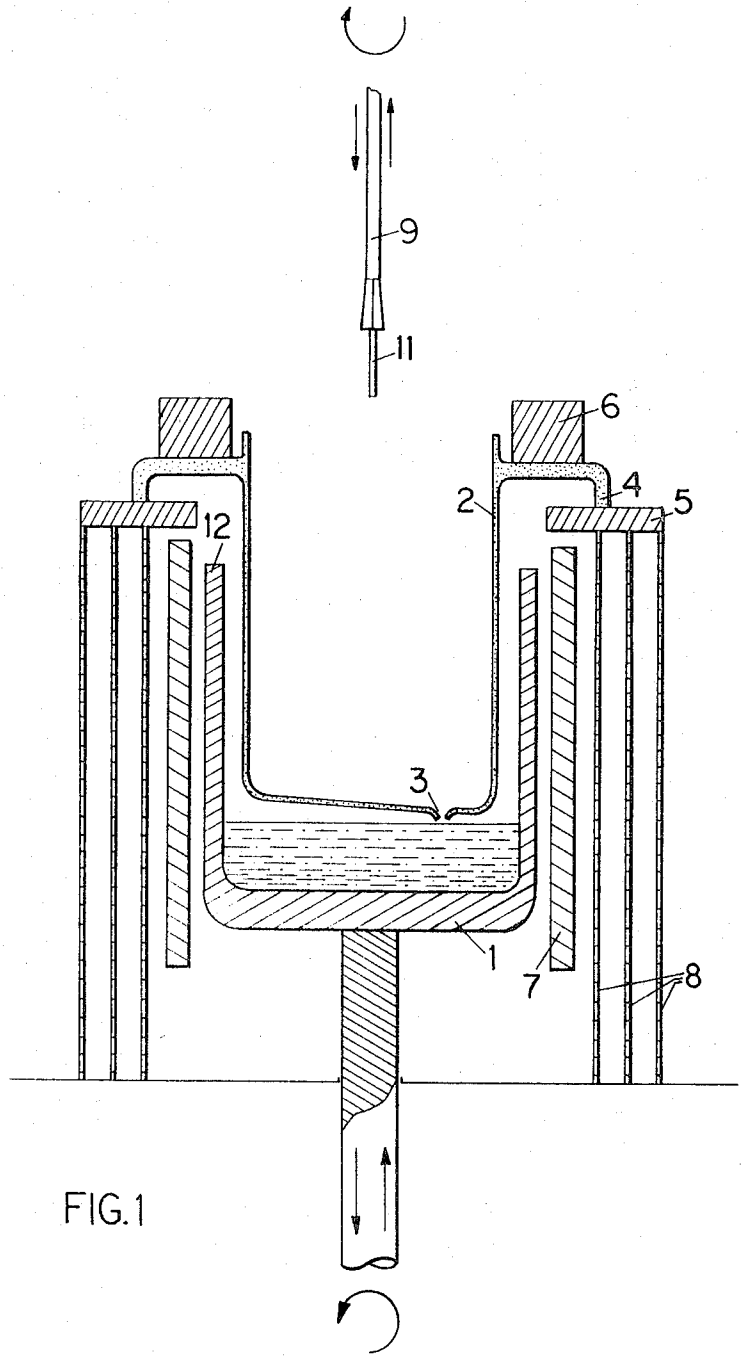


FIG. 1

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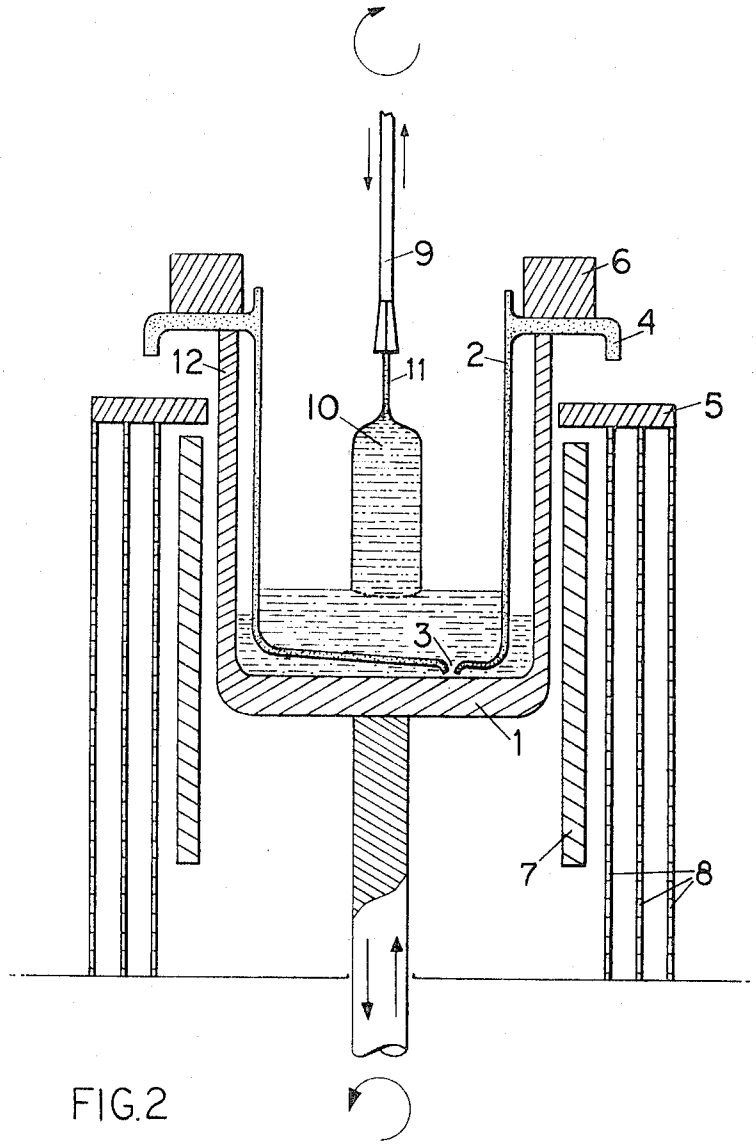


FIG.2

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PROCESS AND APPARATUS FOR PULLING SINGLE CRYSTALS OF GERMANIUM

This invention relates to the process and apparatus for pulling single crystals of metals, more particularly of germanium.

For pulling single crystals by known methods, the charge consisting of a metal element, for instance germanium, silicon, tellurium, or of compounds such as intermetallic compounds, is melted in a cylindrical crucible compatible with the material charge, then a starting crystal called a "seed" is brought into contact with the molten bath and then pulled slowly upwards, the molten material solidifying at the contact with the seed, thus forming a single crystal.

Very often, the molten bath obtained after the melting of the charge may partially be covered by a scum film, formed of solid particles, difficult to identify and to remove.

Such particles act as nucleating centers and may introduce twins and lineages into the growing crystal and impede the production of high physical quality single crystals. The harmful interaction of the scum particles increases as the diameter of the required crystals becomes larger, for instance greater than 40 to 50 mm.

The invention is more particularly useful for pulling germanium single crystals such as used for gamma-ray radiation detectors where crystals of high physical perfection and increasing diameter are required.

Known methods for scum elimination consist of introducing into the molten charge a "cold finger" to which the scum particles will float and adhere, or in utilizing a floating crucible which may be emptied by lifting or lowering it by means of a central supporting rod which passes through the bottom of the crucible containing the molten charge.

It is also known that by depositing upon the charge, before melting, an inner crucible with a small opening in the bottom, it is possible to obtain from time to time a scum-free bath, the scum being retained between the walls of the inner and outer crucible, when the inner crucible floating upon he charge is being filled with liquid material as the melting proceeds.

The above-described technique may now and then lead to success, but very often the scum particles enter the inner crucible together with the molten metal without any possibility to repeat the process from the start.

To overcome this inconvenience, frequently the inner crucible has been provided with a rod enabling by repeated vertical displacements of the inner crucible to obtain a scum-free melt.

This arrangement however has several drawbacks.

It is indeed difficult during the successive displacements to maintain the inner crucible constantly well centered relatively to the outer crucible and to avoid wedging of the inner crucible into the outer crucible.

The present invention relates to a process avoiding the above drawbacks.

The invention consists in a process for the separation of scum from molten germanium and subsequent pulling of large germanium single crystals, with the use of a double crucible (outer and inner crucible) in which germanium pieces are introduced in the outer crucible and are subjected to melting, then lifting and simultaneously rotating the outer crucible to introduce molten scum-free metal from the outer into the inner crucible through an orifice provided in the bottom of the latter crucible while the scum particles remain in the outer crucible, repeating the same operation until all traces of scum have been completely separated from the surface of the molten metal, and pulling in a manner known "per se," such as the well-known Czochralski technique, a large germanium single crystal, while weighting the inner crucible with ballast to ensure its penetration into the molten metal and avoid its flotation on the molten metal.

The invention also consists in an apparatus for the separation of scum from a molten metal with a view to pulling single crystals from the latter metal, comprising an outer crucible made of a substance resisting to the reaction of the said molten metal, an inner crucible which is inert and noncontaminating to the molten metal which is placed inside the outer crucible, an orifice provided at the bottom of the inner crucible for allowing metal contained in the outer crucible to enter the inner crucible, supporting means for the outer crucible allowing lifting, lowering and rotating the outer crucible, means for heating the outer crucible, means for supporting the inner crucible, suspension means fixed to the inner crucible permitting the latter to bear upon the said supporting means when the outer crucible move downwards and permitting the inner crucible to be lifted to rotate together with the outer crucible when the upper border of the outer crucible comes into contact with the said suspension means, means for weighting the inner crucible resting upon the said suspension means, to facilitate penetration of the inner crucibles into the molten metal.

The apparatus, in one form of carrying it into effect, has been shown in the accompanying drawings.

FIG. 1 is a longitudinal section of the apparatus according to the invention, and

FIG. 2 is a longitudinal section of the apparatus in another position.

Referring to the drawings, the melting operation of the impure material is carried out in an outer crucible 1 made preferably of graphite when germanium is treated.

A second crucible 2, the bottom of which has an orifice 3, is adapted to be introduced into the crucible 1. This second crucible is preferably made of quartz.

The dimensions of the crucibles 1 and 2 are not critical and depend essentially on the size of the oven used for pulling a single crystal 10 (FIG. 2). The inner crucible 2 must move easily inside the outer crucible 1 without contact with the latter.

The orifice 3 serves to fill and empty the inner crucible 2. The diameter of the orifice and its position are not critical; however the removal of the scum is carried out more efficiently when the orifice is situated in an excentric position, preferably at a distance from the center representing the fourth part of the diameter; moreover, the bottom of the crucible is preferably inclined to insure a complete emptying of he crucible when it is raised from the molten bath.

The inner crucible is provided with a few side hooks 4 (at least three) which rest alternately upon a fixed support 5 and upon an upper border 12 of the outer crucible 1 according to the position of the outer crucible. A counterweight 6 is placed upon the said hooks 4 in order to maintain them upon the support 5 to avoid a floating of the inner crucible 2 when it is introduced into the molten bath. The counterweight 6 thus facilitates the filling of the inner crucible and may also serve as a heat shield to control the cooling of the upper part of the crystal 10 (FIG. 2).

In the case of heating by means of electric heating element 7, use is made as a fixed support of vertical screens 8 and of horizontal screens 5 which surround the heating element 7.

The heating may be effected by other means, for instance by induction; since in the latter case the vertical heat shields 8 are no longer required, the annular support 5 is fixed by separate means (not shown in the drawings), for instance to the frame of the apparatus.

The size of the crucibles 1 and 2, the position of the hooks 4 and of the supports 5 are chosen in accordance with the quantity of metal treated so that:

1. The inner crucible shall rest by its hooks upon the fixed support and shall remain completely empty (since it is situated above the level of molten bath) when the outer crucible is in a low position (position of melting).
2. The bottom of the inner crucible shall be at a few millimeters from the bottom of the outer crucible when the outer crucible is in a high position (position of pulling) (FIG. 2). When the inner crucible becomes detached from its fixed support, it rests with its hooks upon the upper border 12 so that when the crystal is pulled by pulling means 9, the two crucibles rotate together. The inner crucible is driven by a movement of rotation of the

outer crucible, the mechanism of rotation of which, known "per se," has not been shown. The pulling of the crystal is then effected in a known manner by placing a seed **11** into contact with the molten bath.

The process is as follows:

The metal to be melted is placed inside the outer crucible (in a low position) (FIG. **1**). The melting is effected inside the outer crucible and the molten charge is collected inside the outer crucible. The scum floats on the surface, either at the center, or at the borders of the outer crucible. The orifice provided in the bottom of the inner crucible is therefore advantageously placed excentrically. By lifting the outer crucible, by means known "per se," not illustrated the molten metal passes into the inner crucible.

When the outer crucible is in a high position or pulling position (FIG. **2**) the inner crucible becomes filled with metal free from scum, the latter accumulating in the free space between the two crucibles. If necessary, the operation is repeated by lowering and lifting the outer crucible until a surface of molten bath free from scum is obtained.

It is not necessary during the pulling of a crystal, completely to empty the molten bath. Indeed, after the pulling of the crystal has been ended the outer crucible is placed in its low position. The inner crucible is completely emptied and there is no danger of breaking the quartz crucible during cooling.

What is claimed is:

1. Process for the separation of scum from molten germanium and subsequent pulling of large single crystals by means of a seed, with the use of an outer crucible and an inner crucible disposed within said outer crucible, in which germanium pieces are introduced in the outer crucible and are there subjected to melting, comprising utilizing a weighting of said inner crucible with ballast to ensure its penetration into said molten germanium and to avoid its flotation on said molten germanium, then lifting and simultaneously rotating the outer crucible to segregate said scum from said molten germanium and to introduce molten scum-free germanium from the outer crucible into the inner crucible through at least one orifice provided in the bottom of the latter crucible while the scum particles remain in the outer crucible, lowering said outer crucible and thus emptying said inner crucible, again lifting and simultaneously rotating said outer crucible to reintroduce molten scum-free germanium from said outer crucible into said inner crucible while the scum particles remain in said outer crucible, repeating the operation of lowering, lifting and rotating said outer crucible until all traces of the scum have been completely separated from the surface of the molten germanium in said inner crucible and pulling a single crystal of germanium upwardly from said scum-free germanium in said inner crucible.

2. Apparatus for the separation of scum from a molten metal and for pulling single crystals from the molten scum-free metal, comprising an outer crucible made of a substance resistant to reaction with said molten metal, an inner crucible placed concentrically inside and spaced from said outer crucible, said inner crucible being made of a substance which is inert and noncontaminating to the molten metal said inner crucible having an orifice situated in the bottom portion thereof allowing metal contained in said outer crucible to enter said inner crucible, supporting means to said outer crucible for lifting, lowering and rotating of said outer crucible, means for heating the outer crucible, means for supporting said inner crucible laterally above said outer crucible, said means including a horizontal member located on the top of said apparatus, suspension means fixed to the inner crucible having at least one hook-shaped appendage permitting said inner crucible to bear upon said horizontal member when said outer crucible is lowered and permitting said inner crucible to be lifted from said horizontal member to rotate together with said outer crucible when the upper part of said outer crucible raises said suspension means from said horizontal means, and means for weighting said inner crucible having a weight resting upon said suspension means to facilitate penetration of said inner crucible into the molten metal which is present during the operation of said apparatus.

3. Apparatus as claimed in claim **2**, in which the orifice provided in the bottom of the inner crucible is eccentrically situated and the bottom of the inner crucible is inclined toward said orifice.

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