METHOD FOR TREATING MATERIALS HAVING A HIGH SURFACE TENSION IN THE MOLTEN STATE IN A CRUCIBLE

Filed Nov. 18, 1957

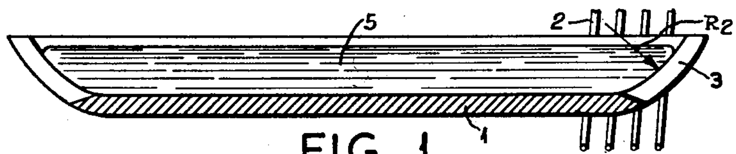


FIG. 1

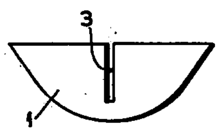


FIG.2

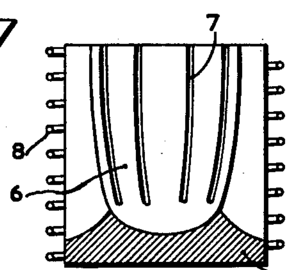


FIG 3

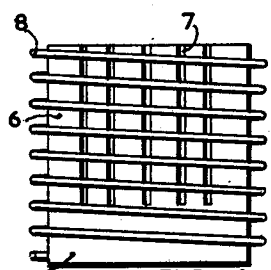


FIG.4

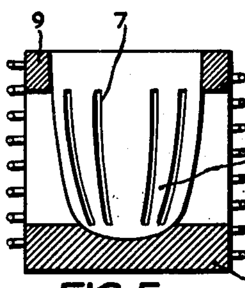


FIG.5

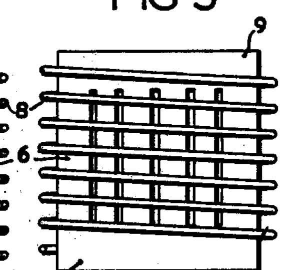


FIG.6

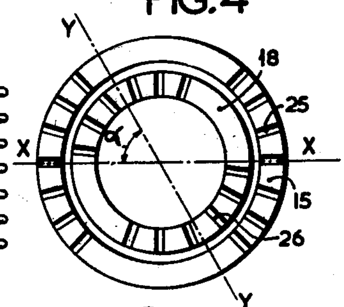


FIG.8

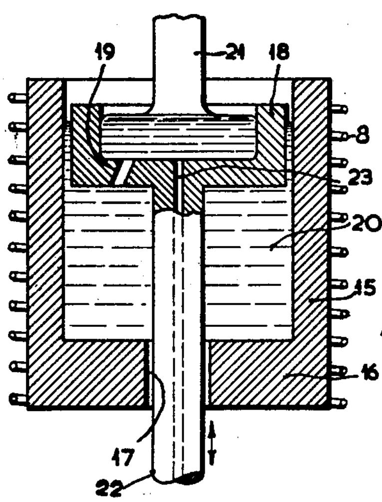


FIG.7

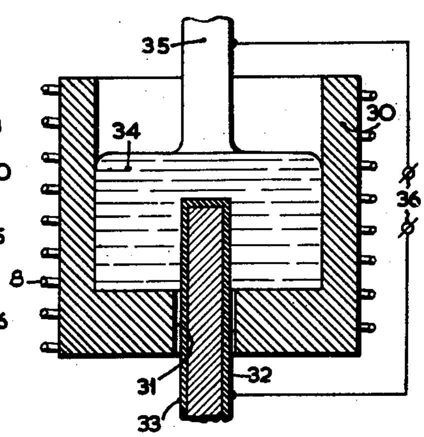


FIG.9

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## METHOD FOR TREATING MATERIALS HAVING A HIGH SURFACE TENSION IN THE MOLTEN STATE IN A CRUCIBLE

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This invention relates to methods and devices for treating materials having a high surface tension in a molten state in a crucible. The term "materials having a high surface tension" is used herein to denote materials, the surface tension of which in a molten state is so high that they do not wet the crucible. However, the invention relates particularly to the treatment in a crucible of semi-conductive elements, such as germanium and silicon, and compounds such as indium antimonide, cadmium telluride and the like. The treatment of such substances frequently gives rise to difficulties of widely different origin. A few of these difficulties will be discussed hereinafter.

Frequently, the substances are melted in crucibles made of graphite, which are arranged in a high-frequency electromagnetic field. Although usually the electrical conductivity of the graphite is utilized, the conductivity of the crucibles sometimes prevents the melt from being satisfactorily agitated.

In other cases, it is also desirable for the crucible to be heated, however, there may arise the difficulty of uneven heating.

A completely different problem is involved when certain parts in the crucible have to be controlled and this control for some reason cannot be effected at the open upper end of the crucible.

The present invention is based on recognition of the fact that in melting materials having a high surface tension the crucible can be provided with apertures, for example slits, disposed below the level of the molten material, provided that these slits do not exceed certain dimensions.

The method in accordance with the invention is characterized in that use is made of a crucible which, below the level of the material, is provided with at least one aperture of such maximum dimensions that the pressure produced by the surface tension of the material exceeds the hydrostatic pressure. The term "hydrostatic pressure" is used to denote not only the pressure produced by gravity, but also that produced by other causes, for example by centrifugal forces.

In order that the invention may readily be carried out, some embodiments thereof will now be described, by way of example, with reference to the accompanying diagrammatic drawings, in which:

FIG. 1 is a longitudinal sectional view of a crucible for purifying semi-conductive materials,

FIG. 2 is a front elevation of this crucible,

FIG. 3 is a vertical sectional view, and

FIG. 4 is an elevation of a crucible for drawing crystals,

FIGURES 5 and 6 are a vertical sectional view and an elevation, respectively, of another device for drawing crystals,

FIG. 7 is a vertical sectional view of a device for drawing crystals,

FIG. 8 is a plan view of another embodiment of such a device,

FIG. 9 shows still a further modification.

FIG. 1 shows a crucible 1 made of graphite, which is particularly suited for use in the methods known as "zone levelling" and "zone refining," in which the crucible is



heated by means of a high-frequency induction coil 2 shown diagrammatically. This method is described in United States Patent No. 2,739,088 by W. G. Pfann.

When the coil surrounds the end of the crucible, assuming the latter to be normally closed by a transverse wall, more heat will be generated in this end than in the centre part of the crucible, since at the end the cross-sectional area of the graphite exceeds that of the remainder. According to the invention, the end part of the crucible is provided with a saw-cut 3 which may extend to the bottom of the crucible.

This is based on the following theory.

According to Laplace the pressure produced by the surface tension of the molten material generally is

$$\frac{\gamma}{g}\left(\frac{1}{R_1}+\frac{1}{R_2}\right) \text{ gms./cm.}^2$$

where $\gamma$ is the surface tension in dynes/cm., $g$ is the acceleration due to gravity in cm./sec.$^2$, and $R_1$ and $R_2$ are the radii of curvature of the surface of the liquid in two directions at right angles to each other in centimeters (see Am. Inst. of Physics Handbook).

When the crucible is made of graphite and the molten material is germanium, $\gamma$ can be assumed to be substantially equal to 500 dynes/cm. When the slit is ½ mm. wide, it can be assumed that $R_1=\frac{1}{40}$ cm., being half of the width of the slit, and $R_2=\infty$. Further assuming $g$ to be 1000 cm./sec.$^2$, the upward pressure in the slit will be 20 gms./cm.$^2$. The specific gravity of germanium is about 5.3; consequently, such a slit which materially suppresses the occurrence of excessive induction currents can be made to a depth of

$$\frac{20}{5.3}\approx 4 \text{ cms.}$$

below the germanium surface 5 before the melt flows away through the slit.

This depth is amply sufficient for many applications.

A similar problem, which can be simply solved by the use of the invention, occurs in drawing crystals from a melt. In this method, a specific embodiment of which is described, for example, in United States Patent No. 2,683,676 by J. B. Little and G. K. Teal, a crucible made from a conductive material, for example graphite, is heated by an induction coil coaxially arranged about the entire crucible. The melt itself is strongly screened or shielded from the electromagnetic field by the crucible wall and consequently it is heated substantially by conduction and convection only. Thus, the melt cannot be agitated as would be possible if the high-frequency field were to act directly upon the melt, for example, in a crucible made from insulating material, for example, quartz. However, crucibles made from such a material cannot be used satisfactorily for melting materials which, at room temperature, have a resistance such as to prevent a current, which is sufficiently large to produce melting, from being induced in these materials at this temperature.

According to the invention, use can be made of a crucible which may have the construction shown in FIGURES 3 and 4 or 5 and 6.

The crucible shown in FIG. 3 comprises a bottom 5 and a wall 6. The latter is provided with a number of saw-cuts or slots 7 which extend to the bottom. The crucible is surrounded by a coil 8.

It will be appreciated that the screening effect of this crucible is materially less than that of the known crucible having solid walls.

Thus, the action of the field upon the melt itself is increased. At the beginning of the heating process, when the contents of the crucible are still cold, their resistance will be very high in the case of a semi-conductive material. At this stage, heating is effected by the heat produced in the crucible itself. A modification of this construction is shown in FIGURES 5 and 6. In this embodiment, the saw-cuts 7 terminate slightly below the upper rim of the crucible, so that a continuous ring 9 is produced which strengthens the crucible.

The third embodiment shows the manner in which the invention can be used by controlling an object disposed in the crucible.

By a known method, crystals can be drawn from a comparatively small crucible, referred to as the inner crucible, which is arranged in a larger crucible, the outer crucible; the contents of the two crucibles communicate through a small aperture in the inner crucible. This method is described in British patent specification 754,-767. In carrying out this method in practice, the difficulty arises that the inner crucible tends to float on the melt. It is difficult to find a material having a higher specific gravity than the melt, while depressing the inner crucible from above is complicated and gives rise to symmetry disturbances in the proximity of the plane of solidification of the crystal, which result in dislocations.

The device shown in FIG. 7 uses an outer crucible 15 having a bottom 16 provided with a bore 17. An inner crucible 18 fits within the outer crucible with a small amount of clearance. Through a duct 19, the melt 20 flows from the outer crucible to the inner crucible as a crystal 21 is withdrawn therefrom. The advantage accruing from the use of the inner crucible 18 consists in that the properties of the said crystal can be modified by changing the composition of the contents of this inner crucible without the materially larger contents of the other crucible having to be influenced. Diffusion through the duct 19 is negligible. In order to prevent the crucible 18 from floating on the melt 20, the inner crucible is provided with a handle 22 which passes through the bore 17 with some clearance. This handle can be raised and lowered by a device (not shown) acting upon its lower end, as is indicated by arrows. Here also the surface tension prevents the melt from flowing away through the narrow slit between the handle 22 and the bore 17.

A further application of the invention, which is independent of the use of a separate inner crucible and consequently can be used in other devices also, is likewise shown in FIG. 7.

In many cases, for example in drawing crystals, it is desirable for certain substances, which are referred to as active impurities, to be added to the melt. They are usually added from above, but this may give rise to difficulty, for example owing to the presence of the withdrawn crystal.

According to the invention, the bottom of the crucible is provided with a small aperture through which the impurity can be supplied. Thus, the handle 22 is provided with a narrow duct 23 of so small a diameter that the melt does not flow through this duct. The active impurity, however, can be introduced as a pill or a thin wire into the melt through the duct 23 by means of a rod.

Assuming that the depth of the germanium in the inner crucible 18 should be 5 cm., the pressure at the upper end of the duct 23 would be $5 \times 5.3 = 26.5$ gms./cm.$^2$.

In this case $R_1 - R_2$ = half the diameter of the duct. Consequently

$$\frac{\gamma}{g} \cdot \left(\frac{1}{R} + \frac{1}{R}\right) = 26.5$$

or

$$\frac{500}{1000} \cdot \frac{2}{R} = 26.5 \qquad R \approx 0.3 \text{ mm.}$$

In this case, the diameter of the duct should be smaller than 0.6 mm.

Obviously, many alternative embodiments are comprised within the scope of the invention.



In same cases, it may be desirable for the temperature of the melt to be rapidly varied, especially in the proximity of the withdrawn crystal. The above-described device permits of these rapid variations by providing the upper rim of the outer crucible 15 with a number of slits 25 which are concentrated at two opposite portions thereof, as is shown in FIG. 8. The plane of symmetry is designated X—X. Similarly, a number of slits 26 are provided in the inner crucible 18. The plane of symmetry thereof is designated Y—Y. By rotating the inner crucible about its vertical axis and varying the angle $\alpha$ between the planes X—X and Y—Y, the inductive coupling of the inner crucible to a high-frequency coil arranged without the outer crucible can be varied. This results in a variation of the temperature of the inner crucible. This variation may, for example, be used to produce a local modification of the properties of the withdrawn crystal, more particularly of its conductivity type.

This variation of the temperature of the inner crucible may also be ensured by providing slits in the outer crucible only and varying the strength or the direction of the high-frequency field.

The final example relates to the case where an electric current must be passed through the melt. This may be desirable for a variety of reasons, for example also for modifying the properties of a crystal drawn from the melt. In this process, it may be necessary or desirable for a conductor to be passed through the bottom or the wall of the crucible. Such a conductor can be sealed in or can be secured in the crucible by sealing material, but this frequently gives rise to difficulty.

By using the method in accordance with the invention, such a conductor can be arranged freely in an aperture provided in the bottom of the wall of a crucible, provided that the dimensions of the slit produced do not exceed the above-mentioned limits.

Such a device in accordance with the invention is shown in FIG. 9. It comprises a crucible 30 made of a refractory material, for example quartz, graphite, aluminum oxide or beryllium oxide, and having an aperture 31 in its bottom.

A conductive rod, which is supported in a manner not shown in the figure, is passed through this aperture. This rod may, for example, comprise a core 32 of tungsten which is coated with a layer of carbon or graphite 33. This coating is provided because the surface tension of molten metals and molten semi-conductive materials is higher with respect to carbon than with respect to tungsten, so that the melt is less likely to flow away.

From a melt 34, a crystal 35 is drawn. In this drawing process, a source of electric current 36 can be connected to the rod 32, 33 and to the crystal 35, as is shown diagrammatically.

It should be noted that the coating of the core 32 may alternatively consist of an insulating material, for example quartz. In this event, the upper end of the core is not coated.

What is claimed is:

1. A method of operating on semiconductive materials having high surface tension when molten, comprising melting said semiconductive material in a crucible whose wall portions have an aperture extending completely therethrough whose dimensions establish a given upward pressure at the aperture due to the melt's surface tension, maintaining the level of said melt below that height above the aperture at which the melt's hydrostatic pressure at the aperture equals the said given upward pressure thereby preventing the melt from flowing out through the aperture, and introducing into the melt via the said aperture an active, conductivity-determining impurity for influencing a condition of the melt.

2. A method of operating on semiconductive materials having high surface tension when molten, comprising melting said semiconductive material in a conductive

crucible whose wall portions contain plural slots extending completely therethrough whose dimensions establish a given upward pressure at the slots due to the melt's surface tension, maintaining the level of said melt below that height above the slots at which the melt's hydrostatic pressure at the slots equals the said given upward pressure hereby preventing the melt from flowing out through the slots, and introducing into the melt from outside the walls by way of the slots high-frequency energy to maintain the material in the molten condition and agitate same.

3. A method of operating on semiconductive materials having high surface tension when molten, comprising melting said semiconductive material by means of high-frequency energy in an elongated conductive crucible having side and bottom wall portions and an end wall portion with an aperture extending completely therethrough whose dimensions establish a given upward pressure at the aperture due to the melt's surface tension, and maintaining the level of said melt below that height above the aperture at which the melt's hydrostatic pressure at the aperture equals the said given upward pressure thereby preventing the melt from flowing out through the aperture, said aperture reducing the heat generated by the high-frequency energy in the end wall portion of the crucible.

4. A method of operating on semiconductive materials having high surface tension when molten, comprising providing a crucible having an opening in a bottom wall portion and providing a movable member in said crucible and traversing said opening and spaced from the wall portions surrounding the opening by a given clearance aperture allowing movement thereof, melting semiconductive material in the crucible, said given clearance aperture having dimensions establishing a given upward pressure due to the melt's surface tension thereat, maintaining the level of said melt below that height above the said given clearance aperture at which the melt's hydrostatic pressure thereat equals the said given upward pressure thereby preventing the melting from flowing out through the clearance aperture, growing a crystal from the melt in the crucible, and moving the member in the crucible while the crystal is growing to maintain a condition of the melt and control the growing crystal.

5. A method of operating on semiconductive materials having high surface tension when molten, comprising providing a first outer crucible having an opening in a bottom wall portion, providing a second inner crucible, with an aperture in its wall, within the outer crucible, and providing support means for said inner crucible traversing said



opening and spaced from the wall portions surrounding the opening by a given clearance aperture allowing movement of the support means, melting semiconductive material in both crucibles, said given clearance aperture having dimensions establishing a given upward pressure due to the melt's surface tension thereat, maintaining the level of said melt below that height above the said given clearance aperture at which the melt's hydrostatic pressure thereat equals the said given upward pressure thereby preventing the melt from flowing out through the clearance aperture, said aperture in the inner crucible wall allowing melt to flow between the crucibles, growing a crystal from the melt in the inner crucible, and moving the support means and inner crucible relative to the outer crucible to maintain the melt level in the inner crucible.

6. A method of operating on semiconductive materials having high surface tension when molten, comprising providing a first outer conductive crucible, providing a second inner conductive crucible within the outer crucible, said outer and inner crucibles each having a plurality of vertical slits in wall portions thereof, melting semiconductive material in both crucibles by means of externally-applied high-freqency energy, said slits in both crucibles having dimensions establishing a given upward pressure due to the melt's surface tenson thereat, maintaining the level of said melt in both crucibles below that height above the slits at which the melt's hydrostatic pressure thereat equals the said given upward pressure thereby preventing the melt from flowing out through the slits, and growing a crystal from the melt in the inner crucible, said slits allowing high-frequency energy to interact directly with the melt.

7. A method as set forth in claim 6 wherein the slits in each crucible are arranged in two groups lying in diametrically opposed wall portions, and the first and second crucibles are rotated relative to one another.


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