Feb. 21, 1967 J. BURMEISTER ETAL 3,305,485

METHOD AND DEVICE FOR THE MANUFACTURE OF A BAR BY SEGREGATION FROM A MELT

Filed April 16, 1963 2 Sheets-Sheet 1

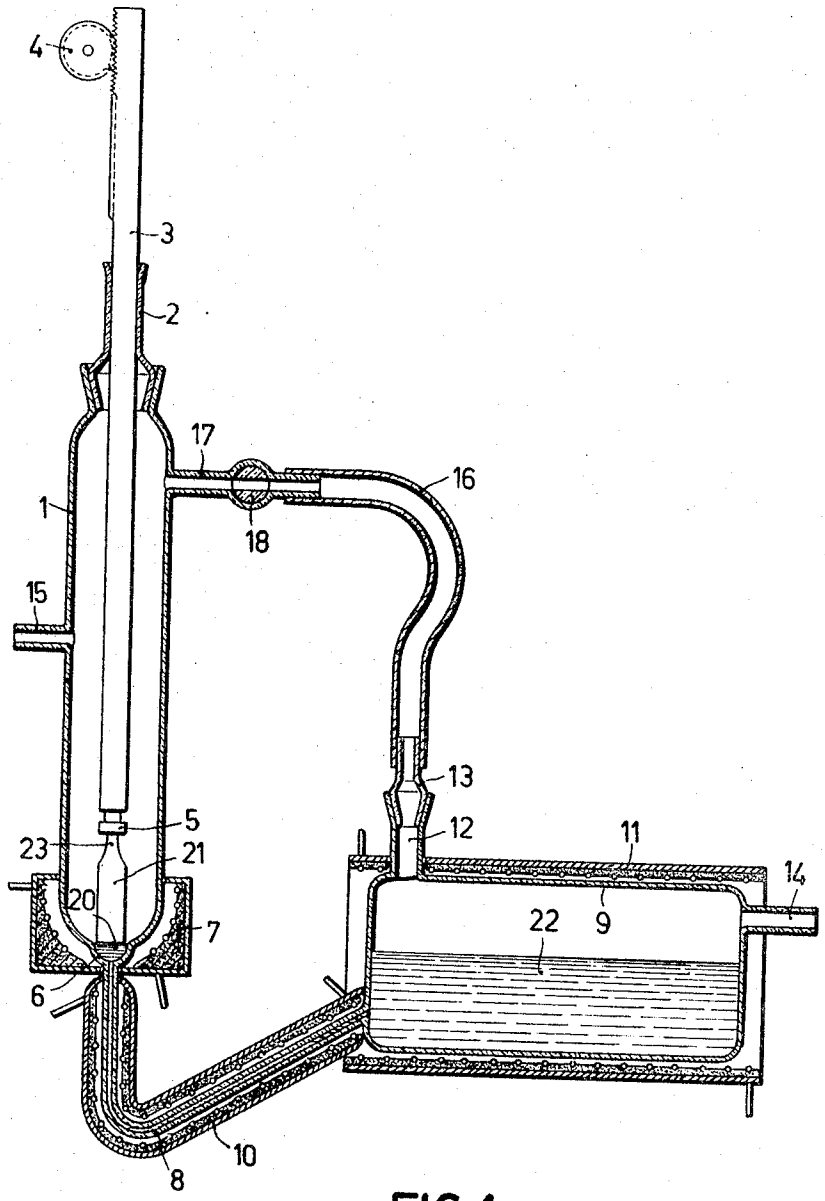

FIG.1

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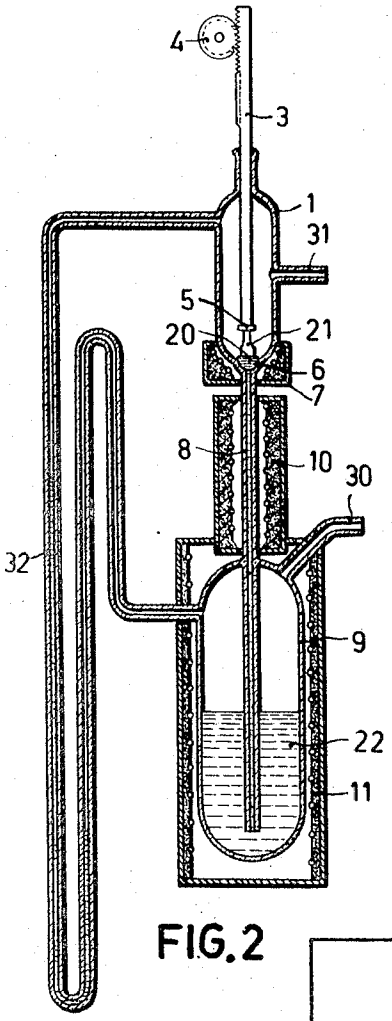

FIG. 2

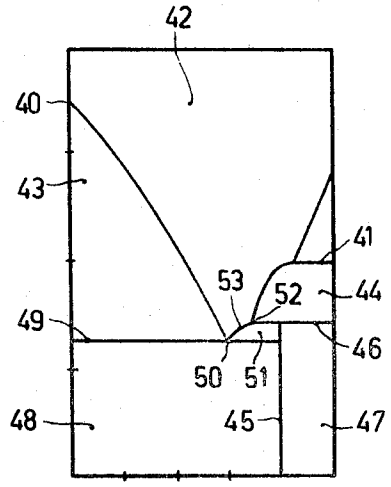

FIG. 3

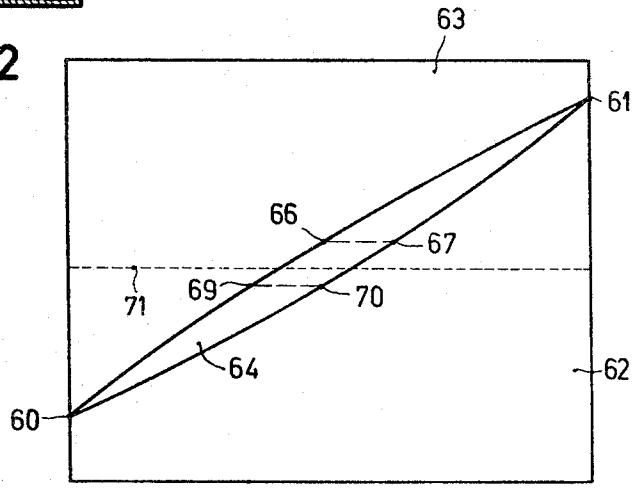

FIG. 4

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METHOD AND DEVICE FOR THE MANUFACTURE OF A BAR BY SEGREGATION FROM A MELT

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10 Claims. (Cl. 252—62.3)

The invention relates to a method of manufacturing a bar having over at least part of its length a substantially homogeneous composition by segregation from an incongruently solidifying melt consisting of at least two constituents, in which during the segregation material of this homogeneous composition is added to the melt. An incongruently solidifying melt is to denote herein a melt from which solid substance is separated out upon cooling, the total composition of which solid substance differs from that of the melt without regard to eventual differences in concentration of any doping substances, usually employed in very small concentrations. Such solid substances in the form of compounds thus possess an incongruent melting point or peritectic point. The composition of the melt differs, for example, from the composition of congruently melting compounds or of melts having a eutectic composition, from which latter melts, upon solidification, solid substance having more than one phase, each having a composition deviating from that of the melt, is separated out. However, in the latter cases, the total composition of said solid substance is equal to that of the melt.

Such a method may be employed for example for the manufacture of semi-conductive bodies, preferably in the form of monocrystals. The term "constituents" does not include herein any desirable doping substances in very low concentrations as used for example for semi-conductors.

In such a known method, a molten zone consisting of such an incongruently solidifying melt was passed through a bar, while the molten zone was heated below the melting point of the solid bar material. It had been suggested to manufacture in this way a bar consisting of gallium arsenide by passing a molten zone containing an excess quantity of gallium through a bar containing approximately equivalent quantities of gallium and arsenic. It had also been proposed to produce in this manner a peritectic compound from a bar containing the constituents in approximately the desired ratio.

With this known method the composition of the melt may vary in an undesirable manner with a variation of the volume of the molten zone and with zone-melting processes it is often difficult to avoid fluctuations of the volume of the melt. Moreover, the volume of such molten zones is comparatively large, so that a rapid, homogeneous mixing of the melt with the material dissolved during the displacement of the zone is rendered more difficult. The solid starting material must furthermore have a composition of optimum homogeneity, which can be realized only with difficulty in many cases.

It has furthermore been proposed to manufacture a bar of gallium arsenide by drawing it from a melt containing an excess quantity of gallium, while during the drawing a further bar containing equivalent quantities of gallium and arsenic is immersed into the melt. Here also the difficulty arises that the bar to be immersed must have a composition of optimum homogeneity. Moreover, the melting surface must be sufficiently large to immerse at the same time a bar into the melt and to draw up a further bar therefrom. Also in this case a rapid homogeneous mixing of the melt is difficult. The speeds

of drawing up one bar and of immersing the other bar and the thickness of the growing bar must be accurately adjusted in order to avoid variation of the melt.

The invention has for its object inter alia to provide a method and a device in which the aforesaid disadvantages are avoided or occur to a reduced extent only. In accordance with the invention, a bar is drawn up from an incongruently solidifying melt contained in a vessel, while during the drawing-up process by means of a narrow tube a melt is fed from a supply container to the vessel, the composition of said melt being substantially equal to the homogeneous composition of the drawn-up bar, use being made of heating means by which the melts in the vessel, in the tube and in the container are heated and by which such a temperature difference is produced between the melt in the container and in the tube on the one hand, and the melt in the vessel on the other hand that separation or segregation of solid substance from the melt in the container and in the tube is avoided. In the supply container a melt of the desired composition can be readily provided and since there is a liquid in the container, the composition is homogeneous. This ensures an addition of material of a homogeneous composition to the melt in the drawing vessel. Since the melts in the container and in the tube can be heated at a higher temperature than the temperature of the melt in the vessel, it is possible to feed a melt to the drawing vessel which could be unstable at the temperature prevailing in the vessel and could solidify at least partly. It is easy to feed liquid material to the vessel in quantities equal to the quantities of material removed from the vessel by the drawing-up process, so that fluctuations of the volume of the melt in the vessel are avoided. The supply may be controlled automatically by employing the principle of communicating vessels, for example with a constant pressure difference between the atmosphere above the melt in the container and the atmosphere above the melt in the vessel. The levels of the melts in the vessel and in the container are preferably maintained equal by using a substantially equal pressure above the two melts. If the surface of the melt in the container is sufficiently large with respect to the diameter of the bar, a bar of adequate length can be drawn up without a marked drop of the level of the melt.

The temperature in the drawing vessel is preferably controlled independently of the temperature in the tube and in the supply container, so that the first-mentioned temperature can be adjusted to a value which is optimum for drawing up the bar without affecting the temperatures in the tube and in the container.

It should be noted that it is known per se to produce homogeneously doped germanium crystals by drawing them up from a germanium melt in a crucible, which floats on a germanium melt in a larger crucible. The first-mentioned, so-called inner crucible has a narrow duct in the bottom, through which during the drawing-up process melt from the larger outer crucible can flow into the inner crucible. In this case we are not concerned with an incongruently solidifying melt, while the materials in the inner crucible and in the outer crucible have substantially the same melting point and the outer crucible and the inner crucible are together heated by heating means surrounding the outer crucible.

Since only a single bar is in contact with the melt, a small volume of the melt may be used, the diameter of the surface of the melt being required to be only slightly larger than the diameter of the bar to be drawn up, while it is possible to have a small height of the level of the melt above the bottom of the crucible e.g. at most not much greater than the bar diameter being grown. Such a small volume of melt has furthermore the advantage

that the temperature thereof can be rapidly adjusted or varied.

The method according to the invention permits of manufacturing homogeneous bars, even in cases in which the compositions of the melt in the vessel and the melt in the container are highly different, for example at least 5 atom percent or mol percent of at least one of the constituents calculated on the total atomic or molecular quantities of the constituents in the melts concerned. Since the melt in the vessel can be adjusted to a lower temperature than the lowest temperature at which the melt in the container is still stable it is not necessary to regard the stability of the melt to be supplied in the adjustment of the temperature suitable for drawing up the bar from the melt vessel.

The invention is particularly suitable for the production of peritectic compounds, i.e. compounds having a peritectic point and which are not stable above a given temperature, at which temperature they decompose into a melt and a solid substance of relatively different compositions. This decomposition temperature may lie far below the lowest temperature at which the melt of corresponding composition is still stable. The temperature range in which the peritectic compound can be separated from the melt may be comparatively low, while the composition of the melt from which the bar is drawn up must be maintained within narrow limits. When using the method according to the invention these conditions can be readily fulfilled.

In order to obtain a peritectic compound, the starting material may consist of a melt in the drawing vessel of approximately the same composition as the peritectic compound itself. During the drawing-up process first material of a different composition is separated out, the composition of the melt changing gradually so that the peritectic compound starts crystallizing out.

A further suitable use of the method according to the invention is the manufacture of a bar consisting of a mixed crystal which has a homogeneous composition over at least part of its length. Such a mixed crystal is separated out from a melt the composition of which may differ considerably from that of the separated material, particularly when the constituents may each have a concentration of more than 5 atomic or molecular percent in the material separated out. The composition of the mixed crystal is furthermore determined by the composition of the melt so that in the present case fluctuations of the last-mentioned composition are undesirable. With the manufacture of a bar consisting of a mixed crystal the melts in the vessel and in the container may also have initially the same compositions, while during the drawing-up process the melt in the vessel changes its composition gradually so that material of substantially the same composition as the melt in the container grows on the bar.

The invention may also be employed for drawing up a material having a comparatively high melting point from a melt of a different composition, from which said material can be separated out at a much lower temperature. If such a material consists of a compound having a readily evaporable constituent the drawing-up process may be carried out at such a low temperature that only a low vapour pressure of this volatile constituent need be adjusted above the melt in the vessel.

The device for drawing up a bar from a melt in carrying out the method according to the invention comprises a vessel for a melt, means for drawing up a bar from such a melt in the vessel, a supply container for a melt separated from the vessel, a narrow, for example, capillary, communication tube for guiding the melt from the container to the vessel, and such means for heating the melt in the vessel, the container and the communication tube that the temperature difference between the melts in the container and in the communication tube and that in the vessel can be controlled, preferably by means of independently adjustable heating means for the melt in the container and in the communication tube on the one hand, and for the melt in the vessel on the other hand.

The container and the vessel are preferably arranged side by side and the spaces for the atmospheres above the melts communicate with each other.

The invention will now be described with reference to the accompanying drawing.

FIG. 1 shows a device for drawing up a bar from a melt in a diagrammatic, vertical sectional view.

FIG. 2 shows a further device for drawing up a bar from a melt in a diagrammatic, vertical sectional view.

FIG. 3 shows partly a phase diagram of two constituents capable of forming a peritectic compound.

FIG. 4 shows a phase diagram of two constituents capable of forming together a continuous series of mixed crystals.

The device shown in FIG. 1 comprises a vertically arranged tube 1 of vitreous quartz, which is connected at its upper end by means of a ground member with a detachable tube 2, through which a cylindrical rod 3 is taken in a movable and gas-tight manner. The rod 3 can be moved vertically with the aid of a mechanism 4 shown diagrammatically and, if necessary, be rotated about its longitudinal axis by a mechanism (not shown). At the lower end of the rod 3 there is arranged a holder 5 for a bar to be drawn up from the melt.

At the inner end the tube 1 terminates in a melting or drawing vessel 6, which is shaped in the form of a hemisphere having an inner diameter of 8 mms. The vessel is laterally surrounded by a controllable furnace 7, for example a resistance heating furnace. The bottom of the vessel 6 is connected by means of a curved capillary tube 8 of vitreous quartz with a supply container 9. The capillary tube 8 has an inner diameter of 1 mm. and an overall length of 15 cms. The tube 8 is surrounded up to a distance of 15 mms. from the vessel 6 by a controllable furnace 10 comprising a wound resistance wire embedded in an insulating, refractory material. The container 9 consists of a horizontal tube of vitreous quartz, closed at both ends, having an inner diameter of 5 cms. and a length of 8 cms. The container 9 is arranged in a controllable, electric furnace 11. On the side facing the vessel 6 the container communicates near the bottom with the capillary tube 8. The container is furthermore provided with a filling opening 12 having a ground piece for fastening a tube 13. The container 9 is provided on the opposite side with a gas supply tube 14 and the tube 1 with the melting vessel 6 is provided with a gas outlet tube 15. The atmospheres in the container 9 and the tube 1 communicate via the filling opening 12 with the ground piece, the tube 13, a gastight flexible tube 16 and a lateral tube 17 sealed to the tube 1 and having a valve 18.

The container 9 can be filled with a melt so that via the capillary tube 8 the vessel 6 is completely filled. From the melt 20 in the vessel 6 a bar 21 can be drawn up by moving the rod 3 gradually upwardly. Owing to the larger volume of the container 9 the meniscus of the melt 22 in the container from where melt is supplied during the drawing-up process, via the capillary tube to the vessel 6, will practically not drop, so that the volume of the melt in the vessel 6 remains substantially constant or will fall at the most by a very small amount in a gradual manner without undesirable fluctuations.

The temperatures of the melts in the supply container 9, the capillary tube 8 and the melting vessel 6 can be adjusted independently of each other by means of the furnaces 11, 10 and 7 respectively.

The device shown in FIG. 2 is a variant of the device shown in FIG. 1 and corresponding parts are designated by the same reference numerals. The supply container 9 is arranged beneath the melt vessel 6 and the capillary tube 8 extends to below the container 9. The container 9 communicates via a tube 30 with a device for the sup-

ply of gas, while the gas pressure in the container **9** can be regulated. The vertical tube **1** communicates with a gas container of lower pressure via a tube **31**. The tube **1** and the container **9** communicate furthermore with a manometer **32**, by means of which the pressure difference between the atmospheres in the tube **1** and in the container **9** can be checked. This pressure difference can be adjusted during the drawing-up process to such a constant value that a constant level difference between the melt **20** in the vessel **6** and the melt **22** in the container can be obtained, so that during the drawing-up of a bar **21** from the melt **20** the volume of the latter remains substantially constant due to the supply of melt from the container **9**.

The invention will now be described more fully with reference to two embodiments of the method according to the invention in which use is made of the device shown in FIG. 1, and one embodiment of said method in which use is made of the device shown in FIG. 2.

In the first embodiment the manufacture of a bar is described which consists over part of its length of the peritectic compound of thallium sesquitelluride (Tl_2Te_3). Part of the phase diagram of thallium and tellurium is indicated in FIG. 3. This phase diagram is derived from an article of A. Rabenau and collaborators under the title of: "Untersuchungen im System Tellur-Thallium," published in "Zeitschrift für Metallkunde," 51 (1960), No. 5, pages 295–299, particularly page 298, FIG. 7.

In FIG. 3 the temperature is plotted on the ordinate and the percentages of tellurium and thallium are plotted on the abscissa, said percentages varying from 100% of tellurium on the left-hand side to 50 atom percent of thallium and 50 atom percent of tellurium on the right-hand side. Tellurium has a melting point of 452° C., indicated in FIG. 3 by **40**. The compound TlTe is dissociated peritectically at a temperature of 300° C., indicated by the line **41**, while a melt or liquid is formed which is richer in tellurium. The range **42** indicates temperatures and compositions in which a single molten phase is present. The range **43** indicates temperatures and compositions in which a molten phase and solid tellurium are present side by side. The range **44** indicates temperatures and compositions in which side by side a molten phase and solid TlTe occur. The vertical line **45** indicates the composition and temperatures with which solid Tl_2Te_3 may occur as a single phase. With a temperature of 238° C. (see the horizontal line **46**) this compound dissociates peritectically and changes into solid TlTe and a melt containing about 34 atom percent of thallium. The range **47** indicates the temperatures and compositions in which solid Tl_2Te_3 and solid TlTe may occur side by side. The range **48** indicates the temperatures and compositions in which solid Tl_2Te_3 and solid tellurium may exist side by side. With about 224° C., indicated by the horizontal line **49**, the eutectic temperature is found, where melt, solid Tl_2T_3 and solid tellurium may exist side by side. The melt has, with this temperature, a thallium content of about 29 atom percent and is indicated in the phase diagram at **50**. The range **51** indicates the temperatures and compositions with which solid thallium telluride and melt may occur side by side.

From the phase diagram it clearly appears that solid Tl_2Te_3 will not be formed from a thallium-tellurium melt containing 40 atom percent of thallium without the need for further measures, since in the first place solid TlTe will be separated out. Tl_2Te_3 can be separated first indeed from a melt the composition of which is lying between the eutectic composition **50** and the composition **52**, which may be in equilibrium at a temperature of 238° C. with solid Tl_2Te_3 and solid TlTe. The curve **53** indicates the compositions and temperatures of melts being in equilibrium with solid Tl_2Te_3.

When from a melt, the composition of which is lying between the compositions which correspond to the points

50 and **52**, a bar is drawn up, the drawn material may consist of solid Tl_2Te_3. However, owing to the difference in composition of the material crystallized out and the melt the tellurium content in the residual melt will increase gradually until the eutectic composition **50** is reached, at which no longer only solid Tl_2Te_3 but a mixture of solid Tl_2Te_3 and solid tellurium will be separated out. By adding, during the drawing-up process, to the melt such a quantity of material consisting of thallium and tellurium in approximately the molecular ratio of 2:3, that the volume of the melt remains substantially constant, the composition of the melt may be maintained so that during the drawing-up process only solid Tl_2Te_3 grows on the bar.

The starting material may also be a melt the composition of which corresponds to Tl_2Te_3, from which a rod is drawn while adding a mixture of thallium and tellurium in the ratio of 2:3 in such quantities that the volume of the melt remains substantially constant. In this case in the first place also solid TlTe will be separated out so that the tellurium content of the melt will increase gradually until the composition **52** of the melt is attained, after which solid Tl_2Te_3 is separated out.

From FIG. 3 it appears that it is necessary for the separation of Tl_2Te_3 to maintain the composition of the melt between narrow limits, i.e. between approximately 29 and 34 atom percent of thallium (points **50** and **52**). To this end it is necessary for material added to the melt to vary as little as possible in its composition, while the addition of said material must be carried out so that the volume of the melt is practically not varied. To this end the method according to the invention is particularly suitable. The embodiment hereinafter describes the manufacture of a bar consisting of Tl_2Te_3 over part of its length.

Example I

In the device shown in FIG. 1 the container **9** is filled through the opening **12** with 600 gms. of a mixture of 40 atom percent of thallium and 60 atom percent of tellurium. Then the filling opening **12** is closed by means of the ground piece connected with the tube **13**. Through the tube **14** pure hydrogen is guided through the apparatus with a speed of 1 litre an hour, the valve **18** being open. The hydrogen is conducted away via the tube **15**. Thus the atmosphere in the container and in the tube **1** is replaced by pure hydrogen. Then the material in the supply container is heated by means of the furnace **11**, siad material being thus melted. The temperature is adjusted to approximately 320° C. The furnace **10** surrounding the capillary tube **8** is also adjusted to a temperature of about 320° C. Then with the aid of the furnace the vessel **6** is heated at about 300° C. The molten material of the container **22** flows through the capillary tube **8** towards the vessel **6** until the meniscus of the melt in the vessel **6** is at the same level as the melt in the container **9**, the vessel being thus filled almost completely with melt. To the bar holder **5** is previously attached a bar-shaped seed of TlTe. It is dipped into the melt **20** and drawn up gradually by means of the rod **3**, the furnace **7** being continuously regulated so that material grows on the seed **23** until a bar diameter of 7 mms. is reached, which diameter is then maintained. In this first phase of drawing solid TlTe grows on the seed over a length of about 2 cms., the composition of the melt changing gradually and becoming gradually richer in tellurium. Since continuously new melt is fed from the container **9**, the volume of the melt in the vessel **6** remains substantially constant. The speed of drawing is 3 mms. an hour. The temperature of the melt **20** is gradually lowered to below 250° C. At this temperature a melt of thallium and tellurium in an atomic ratio of 2:3 is no longer stable. The composition of the melt in the vessel **6** has changed gradually so that with this temperature it is stable. After approximately

2 cms. have been drawn up, the composition of said melt has changed so that solid Tl_2Te_3 grows on the bar. Since continuously molten Tl_2Te_3 is supplied, the composition of the melt **20** is substantially no longer varied. After the bar **21** has grown to a length of about 8 cms. it is withdrawn from the melt so rapidly that the connection between the bar and the melt is interrupted. Then the furnaces are switched off, so that the melts in the container, the capillary tube and the vessel solidify. After cooling to room temperature the bar **21** is removed from the apparatus. When the bar is removed from the melt and the part last solidified and the first two centimetres of the bar have been removed, there is left a bar consisting completely of semi-conductive material of the formula Tl_2Te_3.

In the preceding embodiment the starting material in the vessel was a melt of thallium and tellurium in an atomic ratio of 2:3. Of course, the process may start directly from a composition in the vessel **6**, from which solid Tl_2Te_3 is directly separated out. Use may then be made of a Tl_2Te_3 seed, preferably in the form of a monocrystal. Such a process may be carried out for example after the process described in the preceding example in which the vessel **6** contains already the material of the desired composition. Into the container **9** the material supplied to the vessel **6** can again be introduced.

It should be noted that during the drawing-up process the volume of the melt **22** in the container diminishes gradually, it is true, the levels of the melts in the container and hence also in the vessel **6** thus also dropping gradually, but with a view to the large melt surface in the container this drop is so slight that the reduction of volume in the crucible **6** is not of a nature such that the composition of the melt **20** reaches the eutectic composition. The consequence of the small gradual reduction in volume may also be compensated for by using slightly varied composition in the container, in this case a slightly higher thallium concentration. The very slight reduction in volume may in this case even have the favourable effect that the composition of the melt will not stick to the value indicated at **52** in FIG. 3, which might give rise to the separation of a small quantity of TlTe in the solid state. The composition of the melt shifts gradually along the line **53**, the formation of the bar being terminated before the composition can have reached the point **50**.

When the melt has reached the composition **52**, a very slight reduction in volume may be produced. To this end at the beginning of the drawing-up process the valve **18** in the device shown in FIG. 1 can be moved into an oblique position such that the flow of hydrogen, when passing through the valve **18**, meets such a resistance that a small increase in pressure in the container **9** with respect to the atmosphere in the tube **1** is obtained, so that the level of the melt **20** rises slightly with respect to that of the melt **22**. When during the drawing-up process the melt **20** reaches the composition **52**, the valve **18** can be reopened completely, so that the volume of the melt **20** is again slightly reduced. During the further drawing-up of the bar the composition of the melt **20** has slightly increased its tellurium content, so that any separation of TlTe is avoided.

In a further example, a method of manufacturing a bar consisting of a mixed crystal of bismuth telluride (Bi_2Te_3) and antimony telluride (Sb_2Te_3) is described. Such mixed crystals are semi-conductive and may be employed in Peltier cooling devices. The two components may form an uninterrupted sequence of mixed crystals, as is indicated in the phase diagram of FIG. 4. In this phase diagram the temperature is plotted on the ordinate and the composition in parts by weight of antimony telluride is plotted on the abscissa. The left-hand end of the abscissa corresponds to pure Bi_2Te_3 and the right-hand end to pure Sb_2Te_3. The point **60** indicates the melting temperature of bismuth telluride (586° C.) and the point **61** the melting temperature of antimony telluride (616° C.). The range **62** indicates temperatures and compositions in which a single phase of mixed crystals may occur, whereas the range **63** indicates temperatures and compositions in which a single molten phase may occur. The range **64** indicates temperatures and compositions in which melt and mixed crystal are in a state of equilibrium with each other.

In order to obtain a mixed crystal of homogeneous composition during the drawingup process the melt from which the mixed crystal is drawn up must have a constant composition deviating from the material to be drawn up. Also in this case it is desirable to replenish the volume of the melt by materials of the same composition as the homogeneous material to be drawn up. A satisfactory mixing of the melt, a constant volume of the melt and an addition of material of constant composition are also desired in this case. Since the content of, for example, antimony telluride of the material to be drawn up may differ considerably from the equilibrium content of the antimony telluride in the melt with which the solid material concerned can be in equilibrium, in general at least 5 atom percent, it is important also in this case to add to the melt homogeneous material of substantially the same composition as the material to be drawn up in the form of a melt, while using the method according to the invention, an example of which will be described hereinafter.

Example II

In the device shown in FIG. 1 the container **9** is filled with 600 gms. of a mixture of equal parts by weight of antimony telluride (Sb_2Te_3) and bismuth telluride (Bi_2Te_3). As in Example I hydrogen is passed through the container **9** and the tube **1** and with the aid of the furnaces **11**, **10** and **7** the mixture is melted and via the capillary tube **8** it is fed to the vessel **6**. The temperature in the container is maintained at 610° C. as well as in the capillary tube **8**. To the bar holder **5** is attached a seed crystal for example of antimony telluride. By moving down the lower end of the seed crystal it is dipped into the melt in the vessel **6** and drawn up therefrom at a rate of 4 mms. an hour. The temperature of the melt in the vessel **6** is adjusted by controlling the furnace **7** so that a bar grows on the seed crystal with a diameter of 7 mms. First material grows on the seed, which material has an antimony telluride content of 60% by weight. FIG. 4 indicates a composition **66** of the melt of 50% by weight of Sb_2Te_3 and of the mixed crystal composition **67** being in equilibrium therewith, the melt thus becoming gradually richer in bismuth telluride, so that also the composition of the crystallizing material becomes gradually richer in bismuth telluride until the crystallizing material contains about 50% by weight of antimony telluride, corresponding to about 56 atom percent, after which the composition becomes homogeneous at this value. The melt in the vessel **6** then has an antimony telluride content of about 37% by weight, corresponding to about 43 atom percent. The compositions of the melt concerned and the mixed crystal are indicated in FIG. 4 by the points **69** and **70** respectively. The temperature of this melt may be gradually reduced to about 600° C., indicated in FIG. 4 by the broken line **71**, i.e. a temperature at which a melt of equal parts by weight of the two constituents is not stable. The temperature of the melt in the capillary tube and in the container remains, however, at 610° C., at which temperature no solid substance can be separated out.

After the bar has grown to a length of about 8 cms., the contact between the melt in the vessel **6** and the bar is interrupted, after which it is cooled and removed from the tube **1**. The bar consists of a monocrystal which apart from the seed and approximately the first two centimetres grown to the seed and furthermore the solidified drop sticking to the bar when removed from the melt, has a

substantially homogeneous composition and consists of 50% by weight of bismuth telluride and 50% by weight of antimony telluride.

It is also possible in this case to use such a composition from the start in the vessel **6**, from which directly the desired composition can be separated out, for example by processing the melt of the vessel **6** left after the preceding process. The vessel **6** may, as an alternative, be provided previously with such a quantity of bismuth telluride that after the supply of molten material from the container **9** the desired composition of the melt is obtained.

In the preceding examples use is made of the principle of communicating vessels in order to obtain the same level of melts in the container **9** and in the vessel **6**. However, in principle, a level difference may be maintained by using a pressure difference between the atmosphere above the two melts, for example by using the device shown in FIG. 2.

Example III

In the device shown in FIG. 2 the container **9** is filled for about three quarters of its height with grains of indiumarsenide and an amount of arsenic grains, sufficient to cause, when entirely evaporated, an arsenic vapor pressure of ⅓ atm. in the space of said vessel not occupied by indiumarsenide. To the bar holder **5** is previously attached a seed crystal of indiumarsenide. Some pieces of indium are put into the vessel **6**. The apparatus is then exhausted by means of tube **30** and filled with pure nitrogen at atmospheric pressure by means of tube **31**. Then a current of pure nitrogen is flown through the apparatus from tube **31** to tube **30** cleaning the apparatus from atmospheric impurities. Then the indium in the vessel **6** is melted by means of furnace **7**, while applying an excess gas pressure in the container **9** by means of the tube **30** such that the molten indium just does not enter the capillary tube **8**, and adjusting said pressure such that no gas bubbles are passing the molten indium. The indium then is cooled down and the solid indium closes the opening of the capillary. To the vessel **6** is further added an amount of indiumarsenide such that the vessel contains a total amount of indium and indiumarsenide such that the atomic amounts of arsenic comprises about 25% of the total atomic amount of indium in the vessel **6**. A previously calculated pressure difference is exerted by means of tubes **30** and **31** and controlled by means of manometer **32** such that, when melting the indiumarsenide in the container **9** and the indium-indiumarsenide mixture in the vessel **6** in which due to the excess arsenic in the vessel **9** a vapor pressure of ⅓ atm. is added to the nitrogen pressure in the vessel **9**, a gradual flow of melt from the container **9** will enter the vessel **6** through the capillary tube **8** just sufficient to replace the material withdrawn from the crucible **6** during crystal pulling.

The tubes **30** and **31** and the tubes leading to the manometer **32** then are sealed by melting, after which the furnace **11** is put into place, the furnaces **7** and **10** having been present at the places as designated before. A fourth furnace, not shown, was placed around the tube **1** on top of the furnace **7**.

By means of furnace **11** the indiumarsenide in the container **9** is melted, the excess arsenic being evaporated setting up an arsenic pressure of ⅓ atm. sufficient to prevent evaporation of arsenic from the molten indiumarsenide. The temperature in the container **9** is adjusted to about 1000° C., the melting temperature of indiumarsenide being 956° C.

The furnace (not shown) on top of the furnace **7**, surrounding the tube **1** is heated to a temperature of 450° C. Then the furnace **7** is heated to a temperature of 800° C. such that a homogeneous melt of the indium-indiumarsenide mixture is formed. Molten indiumarsenide enters the capillary tube **8** due to the pressure difference between the gases in the container **9** and the tube **1**. The indiumarsenide rising in the capillary tube **8** solidifies, however, above the furnace **11**.

From the melt **20** some arsenic will evaporate. Then by means of the furnace **10** the capillary tube **8** is heated gradually to 956° C. at which molten indiumarsenide will further rise in the capillary **8** and enter the vessel **6**. This may be observed by gas bubbles through the melt **20** in the vessel, followed by a rise of the melt level, at which moment the furnace **10** is quickly cooled down so that the molten indiumarsenide quickly solidifies in the capillary tube. The small amount of indiumarsenide added to the melt **20** in the vessel **6** is sufficient to compensate the loss of arsenic from the melt **20** due to evaporation, the vapor pressure of the arsenic in the vessel **1** being then about 0.01 atm.

By lowering the rod **3** the seed crystal **21** contacts the melt **20**. The furnace **10** is then heated to 1000° C. and by moving the rod **3** upwards the crystal **21** is grown. The speed of the upward movement of the rod is adjusted such that the level of the melt **20** remains at a constant height, the temperature of the furnace **7** being adjusted such that the diameter of the grown crystal **21** is slightly less than the diameter of the upper surface of the melt **20**. A single crystal of indiumarsenide is grown in this manner. When a sufficient length of the crystal has been grown, the pulling rate of the rod **3** is increased such that the contact between the crystal **21** and the melt **20** is broken. Meanwhile the furnace **10** is put out of action, after which the other furnaces are cooled down.

It should be noted that FIGURES 1 and 2 do not show, for the sake of clarity, the means for measuring the temperatures of the furnaces and the means for measuring the temperatures of the melts. These means may be constructed in known manner for example with the aid of thermo-elements and control-resistors or control-transformers for regulating the current intensity across the heating helix of the furnaces. The heating of the melt **20** can better be adjusted so that the drawn-up bar has a given thickness.

It should furthermore be noted that with the method according to the invention the volume of the melt in the vessel **6** may be chosen very small, so that a homogeneous mixing of the melt is readily achieved. Moreover, with the aid of the furnace **7** the temperature of the melt in the vessel **6**, which has a small volume, can be rapidly adjusted or varied.

We may remark that the present method is also suitable in preparing other crystals than referred to in the examples, for instance in preparing mixed crystals of silicon and germanium of a given uniform composition or single crystals of other compounds of the type $A^{III}B^{V}$ such as galliumarsenide and indium phosphide.

The apparatus used according to the invention may be used in preparing peritectic compounds of other composition than Tl_2Te_3 and may be used in the search of phase diagrams of different alloys in which it is supposed that peritectic compounds exist. The preparation of such compounds will aid to a better knowledge of phase diagrams of alloys which is specially important in metallurgical technics. We may refer to the book of Hansen et al., "Constitution of Binary Alloys" (McGraw-Hill Book Co., Inc., New York), second edition, 1958, from which many examples may be deduced of peritectic compounds, the existence of which is not quite certain. Examples are the compounds Cu_2Sb, Tl_2Se_3, Cu_5As_2 and Mg_3Ag (see pages 624, 1191, 161 and 31, resp. of the above book of Hansen). When the peritectic compound exists, but is unstable at room temperature, such as supposed for Tl_2Se_3 and Cu_5As_2, this may be confirmed by the method according to the invention, in which a rod may be prepared showing a homogeneous distribution of the components according to a given formula, but in more than one solid phase, instead of one phase.

It may further be mentioned that the method according

to the invention is specially suitable for preparing semiconductor mixed crystals for use in thermo-electric devices such as Peltier-cooling devices. Such materials normally have a low heat-conductivity. In pulling crystals of such materials it is difficult to conduct the heat away from the solid-liquid interface. The temperature of the melt, therefore, may not be raised substantially above the temperature at said interface. As the material to be added to the melt may not be entirely liquid due to a different composition, said material could not be added in the molten state to the said melt according to known methods very well, whereas the method according to the invention enables such an addition.

What is claimed is:

1. A method of manufacturing by growing a bar of crystalline material having a substantially homogeneous composition over at least a part of its length from an incongruently solidifying melt containing at least two constituents, the total composition of said material substantially differing from that of the melt aside from differences in dopant concentrations, comprising providing a vessel for holding a small quantity of a melt and a separate container for holding a large quantity of a melt and a narrow tube connecting the container and the vessel and allowing melt to flow therethrough, providing in said vessel a melt whose composition differs from the substantially homogeneous composition to be grown, drawing a bar upwards from said vessel melt while heating said vessel melt at a temperature at which the bar composition solidifying is of said substantially homogeneous composition desired, and during the drawing of the bar, supplying additional melt from the container through the narrow tube to the vessel while heating the container melt and the narrow tube melt at a temperature higher than that of the vessel and at which segregation of a solid from the container and narrow tube melts is prevented, the composition of the melt in said container being substantially the same as that of the composition desired.

2. A method as set forth in claim 1 wherein the atmosphere pressure above the melt in the container and the atmosphere pressure above the melt in the vessel are maintained the same to maintain the levels of the melts substantially the same.

3. A method as set forth in claim 1 wherein the compositions of the vessel and container melts differ by at least 5% of at least one of the constituents.

4. A method as set forth in claim 1 wherein the desired composition is a compound having a readily volatile constituent as one constituent, the vessel melt contains the other constituent in a quantity in excess of that contained in the growing bar, and the atmosphere above the container melt contains a higher pressure of the said one constitutent than the atmosphere above the vessel melt.

5. A method of manufacturing by growing a bar of crystalline material having a substantially homogeneous composition of a compound having a peritectic point over at least a part of its length from an incongruently solidifying melt containing at least two constituents, the total composition of said compound substantially differing from that of the melt aside from differences in dopant concentrations, comprising providing a vessel for holding a small quantity of a melt whose diameter is approximately the same as that of the bar to be grown and a container for holding a much larger quantity of a melt and a narrow tube connecting the container and the vessel and allowing melt to flow therethrough, providing in said vessel a melt whose composition differs from the compound to be grown, establishing a melt throughout said entire container, drawing a bar upwards from said vessel melt while heating said vessel melt at a temperature at which the bar composition solidifying is of said substantially homogeneous composition desired, and during the drawing of the bar, supplying additional melt from the container through the narrow tube to the vessel to substantially maintain the melt level therein while separately heating the container melt and the narrow tube melt at a temperature higher than that of the vessel and at which segregation of a solid from the container and narrower tube melts is prevented, the composition of melt in said container being substantially the same as that of the growing bar.

6. A method as set forth in claim 5 wherein the compound is Tl_2Te_3.

7. A method as set forth in claim 5 wherein, during an earlier part of the method, the vessel melt and the container melt are of substantially the same composition, but after the bar begins growing, the vessel melt composition slowly changes until it substantially differs from that of the container melt, and during this earlier part, the temperature of the vessel melt is gradually reduced.

8. A method of manufacturing by growing a bar of crystalline material having a substantially homogeneous composition of a mixed crystal over at least a part of its length from an incongruently solidifying melt containing at least two constituents, the total composition of said material substantially differing from that of the melt aside from differences in dopant concentrations, comprising providing a vessel for holding a small quantity of a melt whose diameter is approximately the same as that of the bar to be grown and a separate container for holding a large quantity of a melt and a narrow tube connecting the container and the vessel and allowing melt to flow therethrough, providing in said vessel a melt whose composition differs from the mixed crystal to be grown, establishing a melt throughout said entire container, drawing a bar upwards from said vessel melt while heating said vessel melt at a temperature at which the bar composition solidifying is of said substantially homogeneous composition desired, and during the drawing of the bar, supplying additional melt from the container through the narrow tube to the vessel while separately heating the container melt and the narrow tube melt at a temperature higher than that of the vessel and at which segregation of a solid from the container and narrow tube melts is prevented, the composition of the melt in said container being substantially the same as that of the composition desired.

9. A method as set forth in claim 8 wherein the mixed crystal is composed of Sb_2Te_3 and BiB_2Te_3.

10. A method as set forth in claim 8 wherein at the beginning of the drawing of the bar, the vessel and container melts are of substantially the same composition as that of the mixed crystal to be obtained, but after the bar has been growing, the composition of the vessel melt changes until it substantially differs from that of the container.

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