April 7, 1970 A. I. BENNETT 3,505,032

HEATER IMMERSED ZONE REFINED MELT

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FIG. 1.

PRIOR ART

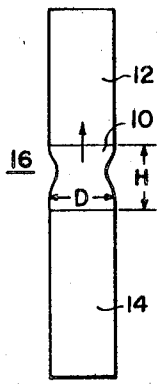


FIG. 2.

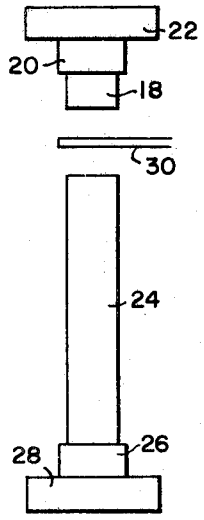


FIG. 3.

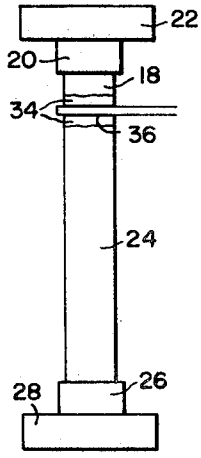
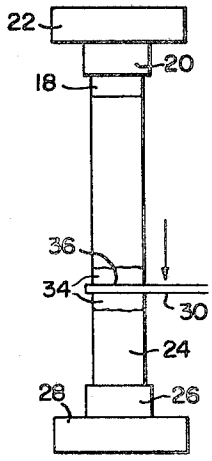


FIG. 4.



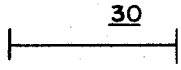


FIG. 5A.

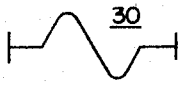


FIG. 5B.

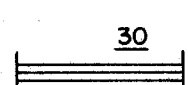


FIG. 5C.

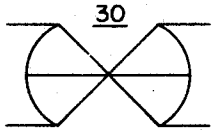


FIG. 5D.

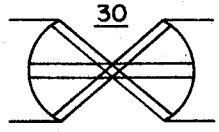


FIG. 5E.

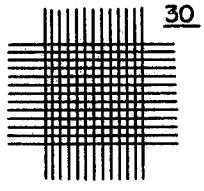


FIG. 5F.

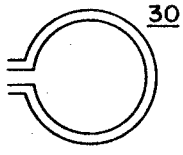


FIG. 5G.

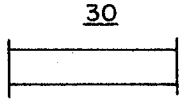


FIG. 5H.

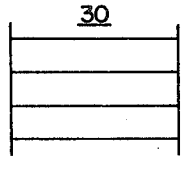


FIG. 5J.

WITNESSES

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HEATER IMMERSED ZONE REFINED MELT

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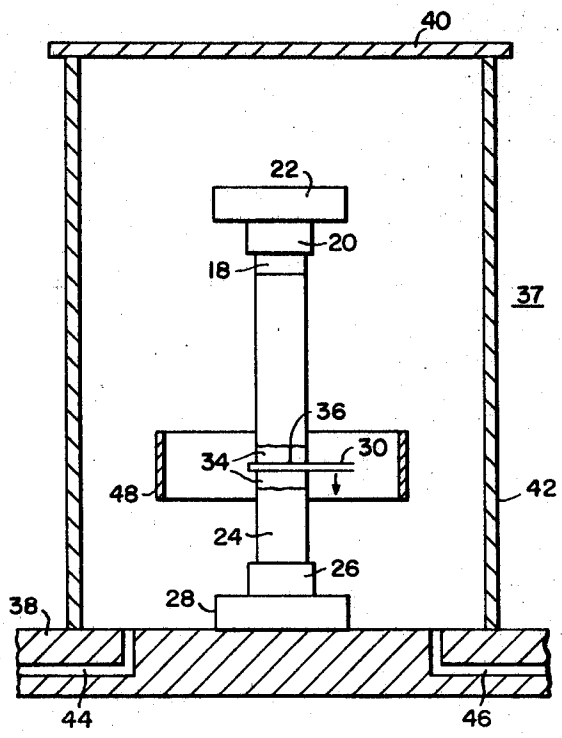


FIG.6.

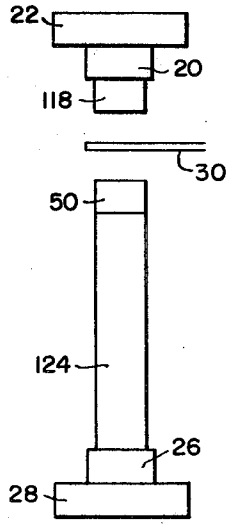
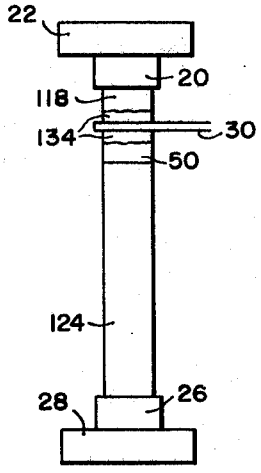


FIG.7.

FIG.8.



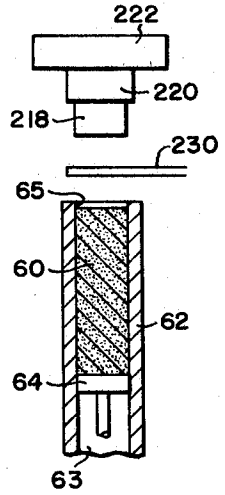


FIG.9.

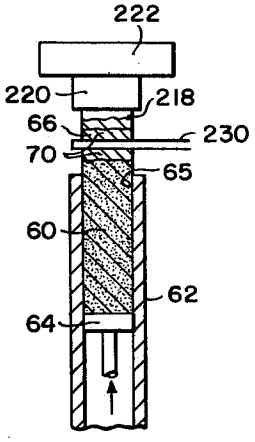


FIG.10.

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3,505,032

HEATER IMMERSED ZONE REFINED MELT

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Filed Nov. 9, 1965, Ser. No. 506,948
Int. Cl. B01j 17/20
U.S. Cl. 23—301 7 Claims

ABSTRACT OF THE DISCLOSURE

This disclosure relates to a process for zone refining a body of material supported vertically by employing a heating means which is in direct physical and thermal contact with a molten zone within the body. The heating means is connected by an electrical conductor directly to an electrical power source.

This invention relates to a new and novel process of zone refining and crystal growth.

An object of the present invention is to provide a new and novel process for zone refining wherein a solid heating means is in direct physical and thermal contact with the molten zone.

Another object of the present invention is to provide a new and novel process for converting a crystalline structure of a member from polycrystalline to a single crystal by zone refining wherein the solid heating means is in direct physical and thermal contact with the molten zone.

A still further object of the present invention is to provide a new and novel process for growing a solid crystalline member from a powder.

Still another object of the present invention is to provide a process for passing a molten zone through a solid crystalline body without restrictive limitations on the diameter of the molten zone or diameter of the crystalline body.

Other objects of this invention will, in part, be obvious, and will, in part, appear hereinafter.

For a better understanding of the nature and objects of this invention, reference should be had to the following detailed description and drawings, in which:

FIGURE 1 is a side view of a rod being zone refined in accordance with the prior art;

FIGS. 2 to 4 are side views of a rod being zone refined in accordance with the teachings of this invention;

FIGS. 5*a* to 5*j* are a series of top views of heater means used in practicing the teachings of this invention;

FIG. 6 is a side view partly in cross-section of a rod being in accordance with the teachings of this invention in a closed chamber;

FIGS. 7 and 8 are side views of a rod being zone refined in accordance with the teachings of this invention; and

FIGS. 9 and 10 illustrate an example of operation in accordance with my invention.

In accordance with the present invention and attainment of the foregoing objects, there is provided a process for passing a molten zone through a solid body of material comprising disposing a heating means in direct physical and thermal contact with the molten zone and passing the molten zone, with the heating means inserted therein, through at least a portion of the body at least once, whereby the molten material flows around the heating means, and thereby the molten zone is relatively short and relatively unlimited laterally.

In the conventional zone refining or float zone process, as shown in FIG. 1, a liquid zone **10** is established between two solid segments **12** and **14** respectively of a rod-like member **16** and the zone is passed through the solid

member at least once. The figure shows the zone being passed upward from segment **14** to segment **12**.

The molten zone **10** is formed by employing one or more heating means such as (1) flame, (2) plasma torch, (3) gas conduction from a surrounding heater, (4) radiation, (5) electron bombardment, or (6) induction heating.

These heating methods have proven to be satisfactory inasmuch as they do not normally result in the deliberate introduction of foreign substances into the liquid zone. However, means (1) to (3) inclusive may inadvertently introduce contaminants in the gas stream; means (4) is particularly difficult for low-emissivity materials and further has poor heat transfer efficiency; means (5) requires a vacuum, and means (6) is limited to an electrically conductive melt.

In the prior art process the liquid zone **10** is held in place between the solid segment **12** and solid segment **14** primarily by surface tension of the melt.

The maximum height H of the molten zone is limited by the surface tension and density of the molten material.

The maximum diameter D is limited by the requirement that the bar be melted entirely through without exceeding the maximum height H.

For most materials D cannot exceed H, which in turn for most materials cannot exceed about 0.5 inch.

This limitation is due to the fact that in conventional zone refining the heat is introduced at the external surface of the zone.

Certain benefits may be obtained by applying limiting forces derived from a closely adjacent induction coil, but there are definite limits to the width of rod that can be zone melted.

The teachings of the process and apparatus embodying the present invention will first be explained relative to converting a rod-like member having a polycrystalline structure to single crystal.

With reference to FIG. 2, a single crystal seed **18** is secured in a chuck **20** in a top holder **22** and a rod **24** having a polycrystalline structure is secured in a chuck **26** in a bottom holder **28**. Normally, the seed **18** and rod **24** are of the same material. The rod may if desired be doped with an impurity or impurities which are not in the original seed but which it is desired to have present in the final crystal.

A solid heater means **30** is disposed between the seed **18** and the rod **24**.

With reference to FIG. 3, the solid heater means **30** is energized until its temperature is at least slightly above the melting point of the materials and then the seed **18** and the rod **24** are brought together with the heater means **30** disposed therebetween. This results in a molten zone **34** being formed on each side of the heater means **30**. As will be explained later in detail, the heater is of such geometry that the molten materials join together to form a single zone.

With reference to FIG. 4, there is relative motion between the heater and rod **24**, so that the molten zone **34** passes slowly, downwardly in this case, through the rod **24** in the conventional zone refining manner, except that the heater means **30** is kept at all times in direct physical and thermal contact with the material in the molten zone **34**, whereby the rod is converted from a polycrystalline structure to the single crystalline structure of the seed **18**.

It should be understood of course that the molten zone **34** could be originally established at the bottom of the rod and the molten zone passed upward through the rod.

It should also be understood that the molten zone can be passed through the rod several times.

The process of this invention can be practiced on any material which can be melted without decomposing and will crystallize on freezing, and includes crystalline elec-

trical conductors such for example, as tin, copper, aluminum, silver, and brass; crystalline electrical insulators such for example, as aluminum oxide, calcium fluoride, potassium chloride, calcium fluorophosphate; and crystalline semiconductors such for example as silicon, germanium, Group III-Group V compounds such as, for example, indium antimonide, gallium antimonide and Group II–VI compounds such as, for example, zinc selenide, cadmium sulfide and zinc sulfide.

The heater means **30** comprises an electrically conductive, high melting point material which is essentially nonreactive with the material of rod **24**. Examples of suitable materials include gold, platinum, iridium, silver and silicon carbide and many metallic alloys such as platinum-10% rhodium.

When it is impossible or impractical to use as the heater a material which concurrently is (1) electrically conductive, (2) has a high melting point and (3) is also esentially nonreactive with the material of rod **24**, at least that portion **36** of the heater means **30** which is in actual contact with the molten zone **34** may be coated with an essentially nonreactive metal such, for example, as gold, iridium, platinum, rhodium, molybdenum, rhenium, tantalum and tungsten. A resistance heating element such as nichrome or platinum could be inserted in a tube of such nonreactive metal, with suitable insulation such as magnesia or alumina therein.

If the material of rod **24** is itself an electrically conductive material it may be necessary or desirable to coat the heater means **30** if the heater means is carrying current or at least that portion **36** which is in actual contact with the molten zone **34** with an electrically insulating material so that electrical current flowing through the heater means **30** is not conducted into the rod **24**.

Such an electrically insulating material applied as a coating to means **30** should be (1) nonreactive with the material of the rod **24**, and (2) be a reasonably good thermal conductor. Examples of such materials include quartz, magnesium oxide, aluminum oxide (Al_2O_3), glass and glass-ceramic materials.

The insulating material does not have to be a solid at the operating temperature if it is highly viscous at the temperature of molten zone, such for example as quartz used for melting copper.

The shape of the heater means **30** is variable, and should have a geometry to allow the molten zone to pass by or through it. With reference to FIG. 5, there are shown nine (A to J) possible configurations, which the heater means **30** can take when it is an electrical conductor.

The heater means can be a single electrically conductive wire as shown in either A or B, a plurality of electrically conductive wires as shown in C to G inclusive or one or more bars or strips of an electrically conductive material as shown in H and J.

In each case, an electrical current is passed through the conductor or conductors, the molten zone being formed by the resultant resistance heating effect.

While the preferred technique is to use an electrical heater means other means may be employed. For example, the heater means having any one of the shapes shown in FIG. 5, or any other suitable shape, can be hollow and a heated fluid passed therethrough to effect the melting and formation of the molten zone.

In still another modification, the heater means can be a solid body contained partially or wholly within the molten zone and heated by inducting heating, radiation or electron bombardment. A solid metal sphere is an especially suitable heating means when heating is to be effected by one of those latter methods.

The process of this invention may be carried out in the ambient or it may be carried out in an enclosed controlled environment or in a vacuum. This atmosphere depends on the material comprising the rod, seed and the heater.

For example, if any one or all of the materials are affected by oxygen or if there is a preferred atmosphere for doping or alloying the process will be carried out in a suitable controlled gaseous environment.

The use of an enclosed environment will also in some cases substantially decrease the possibility of unduly convention cooling of the molten zone.

With reference to FIG. 6, there is shown the apparatus of FIG. 4 enclosed in a suitable enclosure or chamber **36**.

The chamber **36** comprises a base **38**, a top **40** and side walls **42**. The chamber **36** may be comprised of any high temperature material. Preferably, at least the side walls **42** are of quartz or some other transparent material such for example as silica glass for visibility.

The base **38** contains a conduit **44** and, if necessary, a vent **46** so that a protective atmosphere may be introduced into the chamber **36**, and if necessary by utilizing vent **46** the protective atmosphere may be circulated through the chamber **36**.

A heat shield **48** may be employed to eliminate or at least to substantialy decrease convection or radiation cooling.

The heat shield **48** may be movable in a vertical direction so as to always be disposed about the molten zone **32** or it may extend the length of the rod. The heat shield may also be heated by an auxiliary means if desired.

If the seed **18** is short, that is, its length is less than five times its diameter, it may be necessary to preheat the chuck or to have a heater means connected to the chuck to which the seed is attached, chuck **20** in FIG. 1, to prevent or at least substantially decrease heat losses by conduction to the chuck.

The process of this invention is useful in zone refining materials which have extremely high melting points and which do not readily lend themselves to standard zone refining techniques.

With reference to FIG. 7, there is shown a seed **118** disposed in the chuck **20** and holder **22** of FIG. 2. A rod **124** of the same material as the seed **118** is disposed in the chuck **26** and holder **28** of FIG. 2. Heater means **30** is disposed between the seed **118** and rod **124**.

Disposed on the rod **124** between the rod **124** and the heater means **30** is a body **50** of a flux which is capable of dissolving or alloying with the material of rod **124** which thereby lowers the melting point of the material of the molten zone.

With reference to FIG. 8, the heater means **30** is energized and the seed **118** and the rod **124**, with the body **50** of flux disposed thereon, are brought together with the heater means **30** disposed therebetween. This results in a molten zone **134** being formed on each side of the heater means **30**.

The flux, melted by the heater means **30**, progressively dissolves the material of the rod **124** and the molten zone **134** is passed through the rod **124** in the manner described above and as shown in FIG. 4. The flux will stay predominantly in the molten zone. Here again the molten zone may be passed in either direction through the rod. The process can be employed to either purify the rod material, convert it to single crystal or both.

During the aforementioned process there may be an appreciable loss of flux from the molten zone due to evaporation or to incorporation in the grown rod. In order to maintain the amount of flux substantially constant in the molten zone, the loss of flux may be compensated by a uniform distribution of flux within rod **124**.

The table below sets forth a sample of materials which can be zone refined employing the flux technique of this invention and a suitable flux for each material. Temperature A indicates the melting point of the material alone and temperature B indicates the temperature at which zone refining can be carried out using the flux.

TABLE

Material	Temperature A, ° C.	Flux	Temperature B, ° C.
ThO_2	3,300	$PbO+PbF_2$	≈1,200
ThO_2	3,300	$Bi_2O_3+PbF_2$	1,250
ThO_2	3,300	$LiWO_4$	1,300
SiC		Si	1,400
$Y_3Fe_5O_{12}$	2,300	$BaO \cdot O \cdot 6B_2O_3$	1,100
$BaTiO_3$	1,680	$2TiO_2 \cdot BaO$	1,390
Al_2O_3	2,050	$PbO+PbF_2+B_2O_3$	1,250

In still another modification of the present invention and with reference to FIG. **9**, a charge **60** of a material to be grown in rod form from a powder is charged as a powder into a cylindrical member **62** of a nonreactive material as for example quartz. The cylindrical member **62** has a bottom opening **63** and a top opening **65**. A piston **64** is disposed in the bottom opening **63** of the cylindrical member **62** in such a way as to push the powder charge **60** in an upward direction through the cylinder member **62** and out of the opening **65** at the top of the cylindrical member **62**.

A seed **218** disposed in a chuck **220** and a holder **222** is disposed immediately above the cylindrical member **62**.

A heater means **230** is disposed between the top **65** of the cylindrical member **62** and the seed **218**.

With reference to FIG. 10, the piston **64** is activated whereby the powdered charge **60** of material is pushed through the cylinder exiting from the cylindrical member **62** at the top opening **65**. The heater means **230** is energized and the seed **218** is brought into contact with the heater means. A molten zone **70** is formed on both sides of the heater means **230**.

The molten zone **70** consists of a portion of the seed **218** in a molten state and a portion of the powder charge **60** in a molten state. The seed is withdrawn in an upwardly direction corresponding to the speed of the piston **64** whereby the powdered charge **60** of material is grown as a solid member and as a prolongation of the seed **218**.

In the process of this invention the heat is introduced in a controlled manner, either uniformly or non-uniform, for example, hotter at the exterior to compensate for radiation losses, throughout a cross section of the molten zone.

The introduction of the heat throughout a cross section, rather than at the outer-surface as in conventional zone refining, permits a short zone to be maintained even in a large diameter rod, thus permitting the zone refining and crystal growth of rods or tubes of large lateral dimensions and shaped without the H and D limitations of the conventional zone refining processes.

The introduction of heat throughout the cross-section in a controlled manner permits control of the shape of the interface between the liquid zone and the grown solid member. In particular, the distribution of heat may be so chosen as to make the interface nearly planar, a condition generally desirable in crystal growth.

In addition to providing a method of zone refining large diameter rods the presence of a molten zone of uniform thickness indicates horizontal plane isotherms and thus implies uniform thermal gradients in the solid. This results in minimum thermal strains in the resultant rod.

The following examples are illustrative of a practice of this invention.

EXAMPLE I

Apparatus of the kind shown in FIG. 2 was used to grow a polycrystalline rod of potassium chloride.

The seed was a piece of polycrystalline potassium chloride ¼ inch in diameter and two inches long.

The rod was a piece of sintered granular potassium chloride. The rod was ¼ inch in diameter and three inches long.

The heater means was a single strand of 8 mil diameter platinum wire connected in a series circuit relationship with a 6 volt filament transformer and a variable voltage transformer.

As shown in FIG. 3, the seed and rod were brought together with the energized heater means disposed therebetween.

Ten watts of power were required to form a molten zone ¼ inch in height and ¼ inch in diameter.

After the molten zone was established it was first moved in a downwardly direction through the rod at a rate of ½ inch per hour. The molten zone was then passed upwardly through the rod at the same rate.

The resultant zone refined rod was polycrystalline and uniformly transparent.

EXAMPLE II

Apparatus of the kind shown in FIG. 2 was again used to grow a polycrystalline rod of potassium chloride.

The seed was a piece of polycrystalline potassium chloride ¼ inch in diameter and approximately two inches long.

The rod was a piece of sintered granular potassium chloride ⅜ inch in diameter and three inches long.

The heater means was an 8 mil diameter platinum wire ½ inch long and having the configuration shown in FIG. 5B. The platinum wire was soldered to a copper wire which in turn was connected in a series circuit relationship with a 6 volt filament transformer and a variable voltage transformer.

As shown in FIG. 3, the seed and the rod were brought together with the energized heater means disposed therebetween.

Approximately 10 watts of power were required to form a molten zone ¼ inch in height and ¼ inch in diameter.

After the molten zone was established it was first moved in a downwardly direction through the rod at the rate varying from ½ inch to three inches per hour through the length of the rod.

The molten zone was then moved upwardly through the length of the rod at a rate of varying from ½ inch to three inches per hour.

The boundaries of the molten zone were observed and found to be substantially planar.

The resultant zone refined rod was polycrystalline and uniformly transparent.

EXAMPLE III

Apparatus of the type shown in FIG. 2 was used to grow a single crystal rod of potassium chloride.

The seed was a piece of single crystal potassium chloride ¼ inch in diameter and one inch long. The seed was disposed in the chuck with the 100 axis in a vertical position.

The rod was a piece of granular potassium chloride ⅜ inch in diameter and three inches long.

The heater means consisted of three platinum wires of eight mil diameter intersecting at an angle of 60°.

As shown in FIG. 3 the seed and rod were brought together with the energized heater means disposed therebetween. Ten watts of power were required to form the molten zone. After the molten zone was established it was first moved in a downwardly direction through the length of the rod at a rate of 2 inches per hour. The molten zone was then moved upwardly through the length of the rod at the same rate.

The resultant zone refined homogeneous crystalline rod was single crystal.

EXAMPLE IV

Apparatus of the kind shown in FIG .9 was used to grow a rod of apatite $Ca_5(PO_4)_3F$.

The seed was a piece of sintered rod shaped apatite 3/16 inch in diameter and ¾ of an inch long. The seed was mounted in the chuck as shown in FIG. 9. A ⅛ inch inside diameter silica tube was filled with apatite

powder and the powder compacted to a density of approximately 1/3 to 1/4 theoretical density.

A sapphire rod was positioned at the bottom of the silica tube to serve as a piston. The heater means consisted of three strands of seven mil diameter iridium wire intersecting at 60° angles at the center. As shown in FIG. 10 the seed and powder material were brought together with the energized heater means disposed therebetween.

The compacted powedered apatite in the silica tube was pushed upwardly out of the tube by the sapphire rod piston at a rate of approximately one inch per hour. One hundred watts of power was required to form a molten zone approximately 1/8 inch in height and 1/8 inch in diameter between and including the portion of the seed and a portion of the compacted powder.

The procedure was continued until a rod having a diameter of 1/8 inch was grown to a length of 1/2 inch.

The rod so grown was transparent and presumed to be polycrystalline.

EXAMPLE V

The procedure of Example IV was repeated except that a single crystal seed consisting of a piece of hexagonal rod having a diameter of about 30 mils and a length of approximately 1/4 inch was employed. The powdered apatite charge was pushed from the silica tube at a rate of 3/4 inch per hour and a single crystal rod 1/2 inch in length was grown.

EXAMPLE VI

Apparatus of the kind shown in FIG. 2 was used to grow an apatite rod of polycrystalline material. The seed was a piece of sintered apatite rod 3/16 inch in diameter and one inch long.

The rod was a piece of sintered apatite 3/16 inch in diameter and one inch long. The heater means was an iridium strip 1/8 inch wide and one mil thick. The heater means was connected in a series circuit relationship with a six volt filament transformer and a variable voltage transformer.

As shown in FIG. 3 the seed and rod were brought together with the energized heater means disposed therebetween. One hundred watts of power were required to form a molten zone between the seed and the rod.

After the molten zone was established it was first moved in an upward direction at a rate of one inch per minute and then passed downwardly through the length of the rod at the same rate.

The resultant zone refined homogeneous rod was polycrystalline.

EXAMPLE VII

Apparatus of the kind shown in FIG. 2 was used to grow a single crystal rod of apatite having a chemical formula $Ca_5(PO_4)_3F$.

The seed was a piece of single crystal hexagonal apatite 1/4 inch long and 1/2 millimeter in diameter. The seed was so mounted in the chuck that the hexagonal axis was parallel to the axis of the seed.

The rod was a sintered rod of apatite 1/8 inch in diameter and two inches long. The heater means employed was that shown in FIG. 5F and was comprised of seven mil diameter iridium wire connected in a series circuit relationship with a six volt filament transformer and a variable voltage transformer.

As shown in FIG. 3 the seed and rod were brought together with the energized heater means disposed therebetween.

One hundred watts of power were required to form a molten zone 1/8 inch in height and 1/8 inch in diameter.

After the molten zone was established it was moved in a downwardly direction through the rod at a rate varying from 3/8 inch per hour to one inch per hour.

The resultant zone refined homogeneous crystalline rod was found to be single crystal.

EXAMPLE VIII

The procedure of Example IV was repeated except that the powder disposed in the silica tube was apatite doped with manganese carbonate $MnCO_3$. 1/10% of the calcium atoms of the apatite were replaced with manganese.

The seed employed was single crystal apatite .04 inch in diameter and .2 inch long. The resultant product was a single crystal rod 3/32 inch in diameter and one inch long.

The examples set forth in the immediately above are equally applicable to the treatment of semiconductor material such as silicon, germanium, Group III-Group V elements and Group II-Group VI elements.

The process of this invention can be used to zone refine rods or members of larger size than can be processed by the prior art zone refining techniques.

The process finds particular usefulness in the preparation of laser rods, rods of semiconductor materials and other electronic components.

The fact that a single crystal body can be grown directly from a powder charge makes this process particularly valuable in the fabrication of electronic components.

Since certain changes in carrying out the above process and in the product embodying the invention may be made without departing from its scope it is intended that the accompanying description and drawings be interpreted as illustrative and not limiting.

I claim as my invention:

1. A process for zone refining an elongated body of material comprising:

(1) supporting the elongated body of material vertically only by its end portions,

(2) forming a molten zone within the body,

(3) maintaining said molten zone within the body by employing a heating means in direct physical and thermal contact with the molten zone, said heating means being connected directly to an electrical power source by an electrical conductor and being heated by the passage of an electrical current flowing from said power source to said heater through said conductor,

(4) and causing relative movement of the molten zone with the heating means inserted therein, through at least a portion of the body at least once.

2. The process of claim **1**, wherein the heating means comprises at least one aperture through which the molten material in the molten zone passes therethrough.

3. The process of claim **1** comprising the steps of (1) disposing a heating means between a seed and a body to be zone refined, (2) energizing the heating means, (3) bring the seed and body together with the heating means disposed therebetween, whereby a molten zone is formed on both sides of the heater means, and (4) passing the molten zone, with the heater means inserted therein through at least a portion of the body at least once.

4. The process of claim **3**, wherein a quantity of flux is disposed on that end of the body which is brought into contact with the seed and heater means.

5. The process of claim **4**, wherein a quantity of flux is uniformly dispersed throughout the body.

6. The process of claim **1**, wherein the heater means comprises at least one transversely elongated member around which the molten material in the molten zones passes during the movement of the molten zone.

7. The process of claim **1** in which the material to be zone refined is a non-electrically conductive material.

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