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Keller

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[54] **APPARATUS FOR CRUCIBLE-FREE ZONE MELTING OF CRYSTALLINE RODS**

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[30] **Foreign Application Priority Data**

June 10, 1965 Germany ....S 97543

[52] **U.S. Cl.** ....**23/273 SP**, 23/301 SP

[51] **Int. Cl.** **B01j 17/10**

[58] **Field of Search** ....23/273 SP, 301 SP, 273 SP

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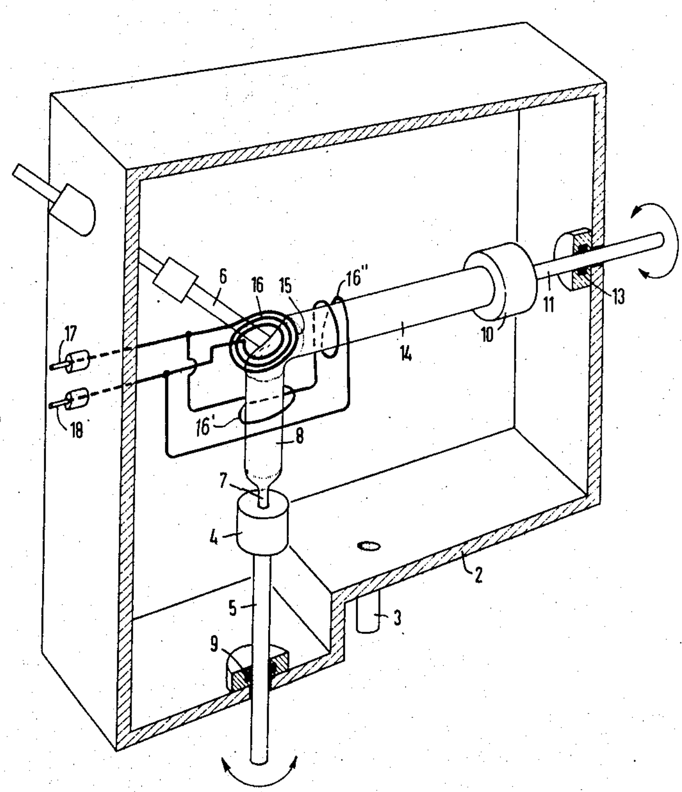
[57] **ABSTRACT**

Apparatus for crucible-free zone melting a rod of crystalline material includes a melting chamber, axially displaceable and rotatable holders for supporting a stock rod to be recrystallized and a recrystallized rod mounted in the melting chamber, the holders having axes extending inclined or transversely to one another, and means for heating the stock rod so as to form a melting zone therein connecting the stock rod with the recrystallized rod.

11 Claims, 5 Drawing Figures



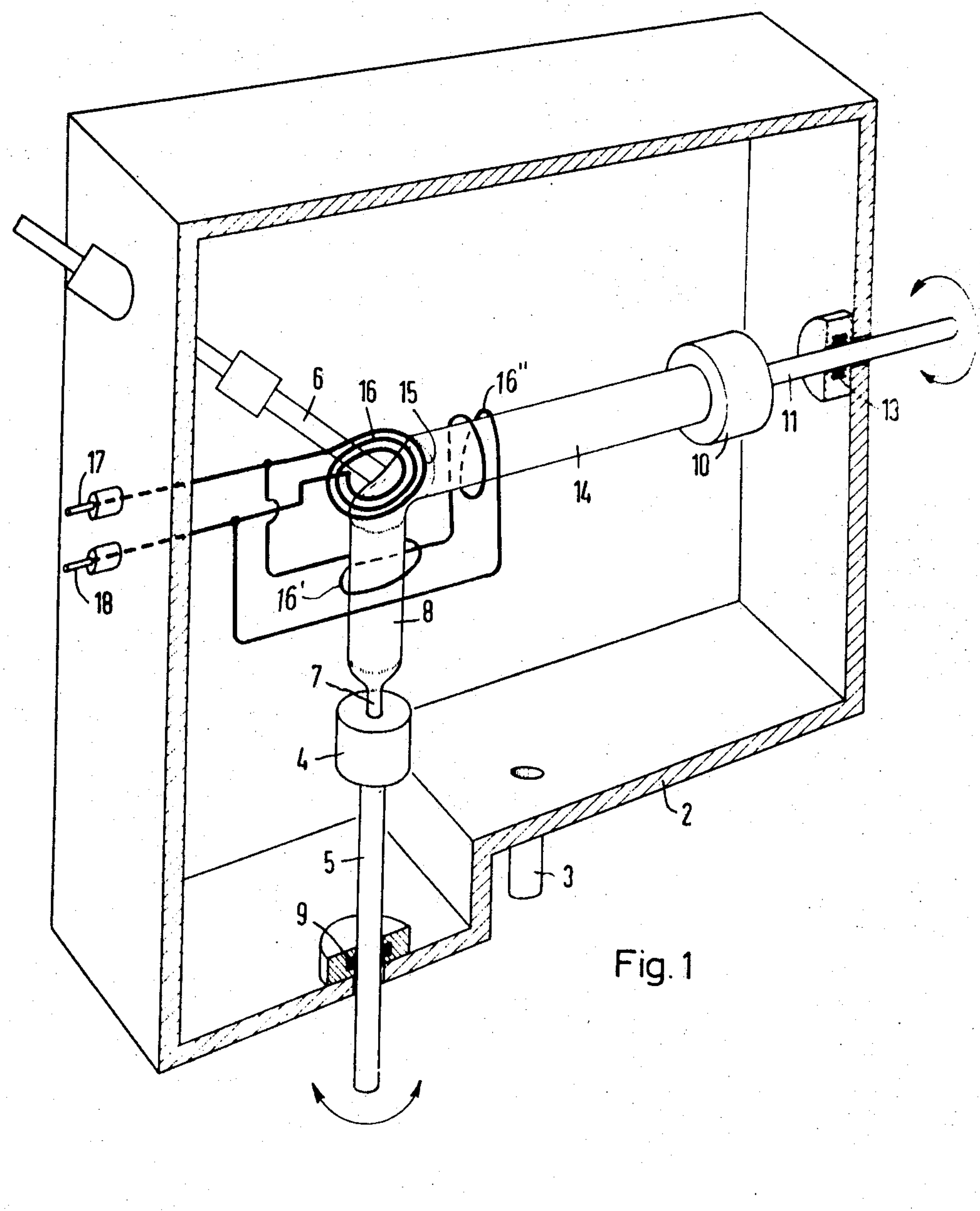
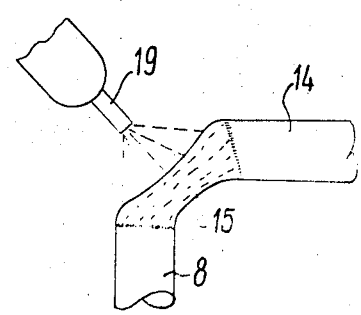


Fig. 1

Fig. 1a



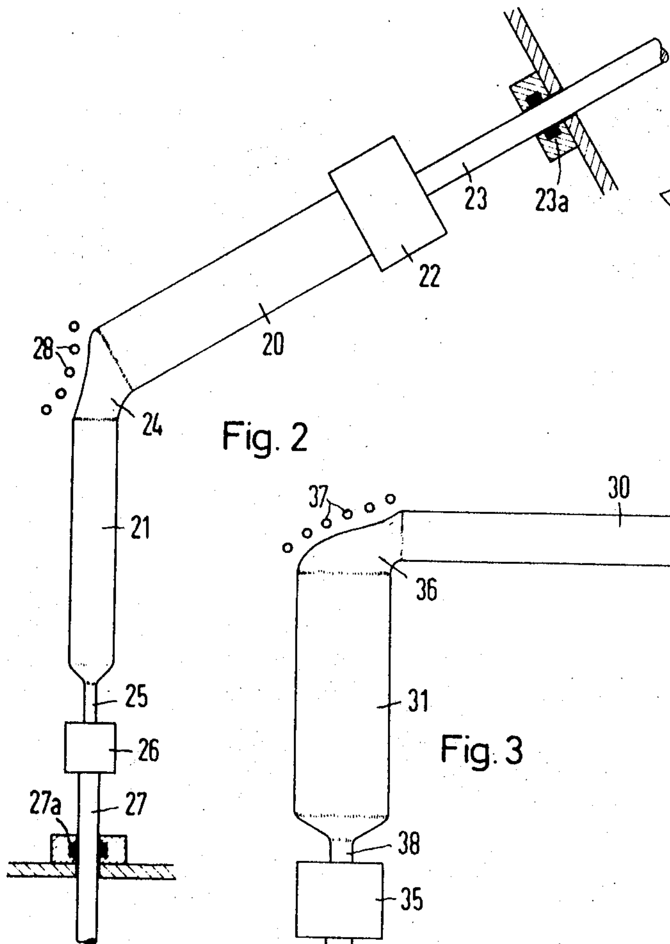


Fig. 2

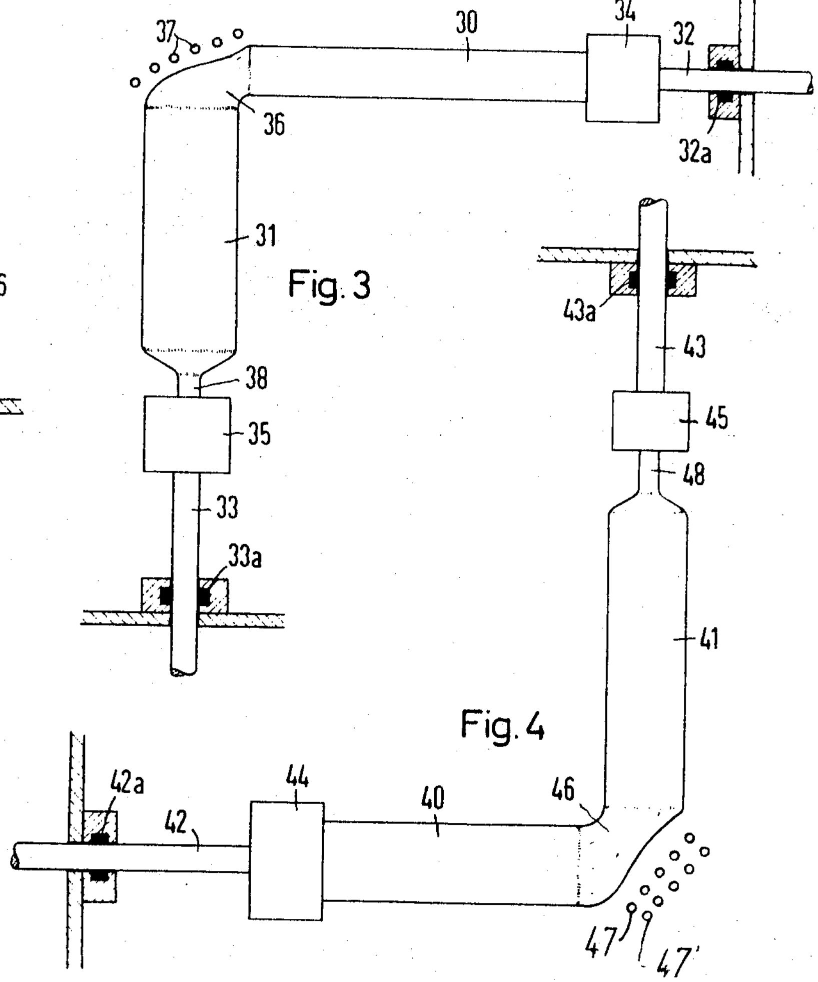


Fig. 3

Fig. 4

APPARATUS FOR CRUCIBLE-FREE ZONE MELTING OF CRYSTALLINE RODS

This is a continuation application of my parent application, Ser. No. 556,157, filed June 8, 1966, now abandoned.

My invention relates to apparatus for crucible-free zone melting of crystalline rods, particularly of semiconductor material.

Apparatus for crucible-free zone melting of semiconductor rods have been known heretofore in which a heating device, for example a flat induction heating coil supplied with high-frequency alternating current, surrounds a vertically disposed rod and produces a melting zone therein. This melting zone is passed through the rod in the longitudinal direction thereof for the purpose of purifying the rod and for producing a monocrystalline structure therein. Methods of altering the rod cross section during a crucible-free zone melting process are also known wherein the rod portions of different cross sections which are connected to one another by the melting zone are disposed vertically.

It has been found that with the known zone-melting apparatus the melting zone in the rod has a non-uniform temperature distribution. Thus the melt in the vicinity of the surface of the melting zone is hotter than the melt in the interior thereof. Consequently, convection currents appear wherein hot liquid melt rises to the surface of the melting zone out of the region heated by the induction coil to the upper boundary of the melting zone and is there cooled somewhat due to the melting of new material of the rod. The liquid melt then flows into the interior of the melting zone and reaches the lower boundary thereof and rises from there again to the surface at the region of the melting zone which is subjected to heating directly by the induction coil. Therefore cones of solidified crystal material are formed at the upper and the lower boundary surfaces of the melting zone extending to respective apexes in the center thereof. When the melting zone is passed through the rod, the melt surrounding the cones therefore recrystallizes later than the material of the cones, that is, the melt does not recrystallize simultaneously over the entire cross section of the rod. Furthermore, a non-uniform temperature distribution is formed over the cross section of the rod from the material recrystallized out of the melt. Both of the foregoing phenomena can be the reason for the formation of mechanical stresses in the material of the rod while it is in the plastic stage and can thereby be the cause of dislocations and twinning of the crystal in the finally recrystallized material of the rod.

It has furthermore been found that vertically oriented crystalline rods having a diameter exceeding a specific critical value, which is for example about 30 mm. for silicon, cannot easily be subjected to a zone melting process. The surface stresses of the melt in the melting zone and the supporting forces of the electromagnetic field of the induction coil are no longer sufficient for preventing dripping of the melt.

Similar difficulties arise in apparatus wherein a crystalline rod surrounded by an induction coil is subjected to a zone melting process while its cross-sectional area is being simultaneously varied or altered by compression or pulling, i.e. elongation. Also in such case, cones of solidified material are formed in the melting zone and the danger arises that the melt will drip out of the melting zone.

It is accordingly an object of my invention to provide apparatus for crucible-free zone melting of crystalline rods which avoids the aforementioned disadvantages of the known apparatus.

More particularly, it is an object of my invention to provide such apparatus which will afford a zone melting process applied to a crystalline rod that will prevent solidification of the material in the interior of the melting zone as well as dripping of the melt.

With the foregoing and other objects in view I provide apparatus for crucible-free zone melting of crystalline rods in accordance with my invention wherein the crystalline rod which is to be processed is located at an inclination to the recrystallized rod with which it is connected by the melting zone so that a uniformly heated melting zone can be produced.

Further in accordance with my invention, the melting zone can thereby either be supported by the recrystallized rod or by the rod which is to be recrystallized or by a supporting magnetic field produced by one or more induction coils.

In accordance with further and more specific features of my invention, I provide apparatus for crucible-free zone melting of a rod of crystalline material, particularly of semiconductor material, comprising a melting chamber, and axially displaceable and rotatable holders respectively, for a rod which is to be recrystallized and for a recrystallized rod mounted in the melting chamber, the holders having axes which are inclined with respect to one another or disposed transversely to one another rather than axially aligned or substantially axially aligned with one another.

The characteristics of the invention are set forth in the appended claims.

Although the invention is illustrated and described herein as embodied in apparatus for crucible-free zone melting of crystalline rods, it is nevertheless not intended to be limited to the details shown, since various modifications and structural changes may be made therein without departing from the spirit of the invention and within the range and scope of equivalents of the claims.

The construction and method of operation of the invention, however, together with additional objects and advantages thereof will be best understood from the following description of specific embodiments when read in connection with the accompanying drawings, in which:

FIG. 1 is a perspective partly sectional view of apparatus for crucible-free zone melting of a semiconductor rod in accordance with my invention wherein rods of equal diameter are melted in a melting chamber;

FIG. 1*a* is a fragmentary view of FIG. 1 showing a modification thereof;

FIG. 2 is a partly sectional front elevational view of a modified form of the embodiment of FIG. 1, wherein a thin rod is being pulled;

FIG. 3 is another partly sectional front elevational view of a modified form of the embodiment shown in FIG. 1, wherein a thin rod is being compressed into a thick rod; and

FIG. 4 is a further embodiment of the invention shown in FIG. 1, wherein the semiconductor rods are of equal diameter.

Referring now to the drawings and first particularly to FIG. 1 thereof, there is shown a melting chamber 2 which is either evacuated through a suction outlet tube 3 or is filled with a protective gas. A holder 4 mounted at the end of a shaft 5 which is displaceable in the axial direction thereof is so disposed within the melting chamber 2 that a seed crystal 7 secured in the holder 4 and a recrystallized rod 8 which is grown thereon are disposed in a vertical orientation. The shaft 5 is located at the base of the melting chamber 2 and is mounted in a seal 9 of conventional construction provided at an opening in the melting chamber housing. Another holder 10 is mounted at the end of a shaft 11 in the upper portion of the melting chamber 2, the shaft 11 being displaceable in the axial direction thereof and being also mounted in a seal 13 at an opening of the melting chamber housing.

A stock rod 14 of crystalline material, particularly semiconductor material such as silicon, is secured in the holder 10 and is located perpendicularly to a rod 8 of recrystallized material with which it is connected by a melting zone 15. A heating device such as an electrically heated radiating member or induction coil 16 is located on one side at the exterior of the bend or knee formed by the intersection of the axes of the rod holders 4 and 10 which coincide respectively with those of the rods 8 and 14. As shown in the illustrated embodiment of FIG. 1, the induction coil 16 is of the flat type, its windings being advantageously disposed in one plane which is, for example, inclined at an angle of about 45° with respect to the axes of the rod 14 and of the recrystallizing rod 8 and which is disposed perpendicularly to a plane in which the axes 14 and 8 are located. The induction coil 16, which is secured in sealed inlets 17 and 18 in the melting chamber wall, consists of hollow wire which is traversible by a cooling fluid and which is supplied with high-frequency alternating current through the leads located at the inlets 17 and 18.

The heating device can also be in the form of an electrically heating ring which radiates or emits heat rays and which surrounds the melting zone 15. Especially for the purpose of achieving better coupling and thereby a greater efficiency, the heating device can be in the form of a flat or cylindrical induction coil whose windings surround the melting zone 15. The cylindrical induction coil can be shaped in the form of a bend or knee. When a flat induction coil is used for surrounding the melting zone 15, the windings thereof can lie in a plane which is perpendicular to the plane in which the rods 8 and 14 are disposed. Furthermore, an electron gun 19, as shown in FIG. 1*a*, can be used as the heating device, the electron beam being directed onto the melting zone 15. In addition, the melting zone 15 can be heated by an electric arc.

At the beginning of the zone melting process, the stock rod 14, which can consist of polycrystalline silicon, for example, is first placed in rotation. It is then displaced in the axial direction thereof so that its free end extends within the region or range of heating by the induction coil 16 where it is melted. A monocrystalline seed 7, which can have a smaller diameter than that of the stock rod 14 and which is secured in holder 4 and can be previously placed in rotation, is thereupon displaced in the axial direction thereof towards the molten end of the stock rod 14 and is fused therewith. This can occur in such a manner that the axes of the stock rod 14 and the seed 7 or the recrystallized portion 8 grown on the seed either intersect or are spaced from one another always at the same distance during the entire zone melting process. The shaft 11 with the stock rod 14 are subsequently displaced towards the melting zone 15, whereas the shaft 5 with the seed 7 and the recrystallizing rod 8 growing thereon are displaced away from the melting zone. If the recrystallized rod 8, which is essentially monocrystalline, is to have the same diameter as the stock rod 14, these displacements, i.e. that of the rods 8 and 14, must take place at the same speed. Impurities present in the stock rod 14 are kept away from the recrystallized rod 8 and finally accumulate at the end of the stock rod 14 that is gripped in the holder 10.

The melting zone 15, whose volume is essentially smaller than the melting zones in apparatus of this general type used heretofore, is uniformly heated under the action of induction coil 16 and is supported by a monocrystalline seed 7 or the recrystallized rod portion 8 so that no solid material is formed in the interior of the melting zone 15 and no portion of the melt drips out of the melting zone 15.

It can be advantageous to after-heat the end of the recrystallized rod, i.e. the rod 8 in FIG. 1, which is connected with the melting zone 15, with the aid of an additional device, for example a heat-radiating ring or an induction coil 16′ which surrounds this end of the recrystallized rod. By the foregoing means, the axial temperature gradient in the recrystallized rod and consequently also the radial temperature gradient are reduced. Therefore, the mechanical stresses in the material recrystallizing from the melting zone 15, which is still in a plastic state, are also kept as small as possible, so that the number of dislocations in the crystallized rod are minimized. In order thereby to maintain the smallest possible melting zone 15, it can be advantageous to preheat the end of the stock rod, i.e. the rod 14 in FIG. 1, connected to the melting zone 15 with the aid of an additional heating device, such as for example an electrically heated ring which emits heat radiation or an induction coil 16″ which surrounds this end of the stock rod.

As a further development of the apparatus for crucible-free zone melting in accordance with my invention, holders for several stock rods can be provided. These stock rods can consist at least in part of another material than that of the stock rod 14 and monocrystalline seed 7 and can be so located in the melting chamber 2 that they are connected with a side of the knee-shaped melting zone 15 and can be displaced onto the melting zone with different adjustable heating velocity. It is thereby possible to supply an adjustable quantity of foreign material to the melting zone 15 so that the foreign material is essentially uniformly concentrated over a cross-sectional area of the crystallized rod 8, the level of concentration being dependent upon the velocity with which the stock rods are displaced onto the melting zone 15. Thus, in the embodiment of the apparatus shown in FIG. 1, an additional stock rod 6 can be provided consisting of a substance such as antimony, for example, with the aforementioned stock rod 14 of semiconductor material such as silicon, whereby the recrystallized rod 8 is doped with the antimony, for example, in order to produce a specific electrical extrinsic conductivity. It can also be noted that the additional stock rods 6 can be selected from the same material as the stock rod 14 which can contain doping substance. The holder for the additional stock rod 6 can be advantageously mounted on a different shaft, as shown in FIG. 1, which is displaceable rotatably and in the axial direction thereof and mounted in a sealed passage through the melting chamber wall.

In FIG. 2 there is shown a crystalline stock rod 20, for example of semiconductor material, located above a vertically disposed recrystallized rod 21, inclined at an obtuse angle with respect to the latter and secured in a holder 22. The holder 22 is similar to the holder 10 of the embodiment shown in FIG. 1 and located in the upper portion of an only partly illustrated melting chamber at the end of a shaft 23 which is mounted in a seal 23*a* at an opening in the melting chamber wall. The shaft 23 is rotatable and movable in the axial direction thereof. The stock rod 20 and the recrystallized rod 21, which has a smaller diameter than the stock rod 20, are connected to one another by a knee-shaped melting zone 24. The recrystallizing rod 21 is grown on a monocrystalline seed 25 which is secured in a holder 26. The holder 26 is also similar to the holder 4 in the embodiment of FIG. 1 and is located at the bottom of the melting chamber secured to the end of a shaft 27 mounted in a seal 27a of an opening in the wall of the partly illustrated melting chamber. The shaft 27 is rotatable and displaceable in the axial direction thereof. A heating device is located on the outside of the knee-shaped melting zone 24 and can consist of an electrically heated radiating body which, in the illustrated embodiment of FIG. 2, consists of an induction coil 28 having a substantially conical construction for better accommodating it to, and uniformly heating, the melting zone 24.

The zone-melting process carried out with the embodiment of FIG. 2 is initiated in a similar manner as for the embodiment of FIG. 1, and the monocrystalline seed 25 secured in the holder 26 is fused with the stock rod 20 secured in the holder 22. This can occur when the axes of the stock rod 20 and of the seed 25, or the recrystallized rod 21, either intersect or are located always at the same distance from one another during the entire zone melting process. Both holders are previously placed in rotation. After formation of the melting zone 24, the rod 20 is displaced towards the melting zone 24 and the monocrystalline seed 25 below the formation of the crystallized rod 20 is displaced away from the melting zone 24. The displacement of the recrystallized rod 21 can take place at a greater speed than the displacement of the stock rod 20 so that the recrystallized rod 21 has a smaller diameter than that of the stock rod 20. Also in the embodiment of FIG. 2, the melting zone 24 can be supported by the recrystallized rod 21 and can be furthermore uniformly heated so that no solidified material is located therein.

In the embodiment of the invention shown in FIG. 3, the stock rod 30 has a smaller diameter than the recrystallized rod 31. The stock rod 30 is secured in a holder 34 which is similar to the holder 10 of the embodiment in FIG. 1 and is located in the upper portion of a partly illustrated melting chamber and secured to the end of a shaft 32 which is mounted in a seal 32a of an opening formed in the melting chamber wall. The shaft 32 is rotatable and displaceable in the axial direction thereof. The stock rod 30 is located perpendicularly to a vertically recrystallized rod 31 and is connected therewith by a melting zone 36. The recrystallized rod 31 is grown on a seed 38 which is secured in the holder **35**. The holder **35** is located, as in the embodiment of FIG. **1**, at the base of the melting chamber mounted on the end of the shaft **33** which is in turn mounted in a seal **33a** in an inlet opening in the melting chamber wall and is rotatable and displaceable in the axial direction thereof.

As in the embodiments of FIGS. **1** and **2**, the monocrystalline seed **38** of the embodiment shown in FIG. **3** is fused with the free end of the stock rod **30**. This is achieved when the axes of the stock rod **30** and of the seed **38**, or the recrystallized rod portion **31**, either intersect or are always spaced the same distance from one another during the entire melting process. Seed **38** and stock rod **30** are previously set in rotation. After the formation of the knee-shaped melting zone **36**, the stock rod **30** is displaced towards the melting zone **36**, while the recrystallized rod **31** is displaced away from the melting zone **36** at a slow speed. The heating device, which can be an electrically heated radiating body, located opposite the melting zone **36**, consists of an induction coil **37** in the embodiment of FIG. **3**. Since the knee-shaped melting zone **36** in the embodiment of FIG. **3** has a relatively large outer side, it is advantageous to provide the induction coil **37** located opposite that outer side with a correspondingly greater number of windings lying in a plane located perpendicularly to a plane in which these rods **30** and **31** are disposed. Also in the embodiment of FIG. **3**, uniform heating of the melting zone **36** and support thereof by the recrystallized rod **31** are ensured.

In the embodiment of FIG. **4**, the holders for the stock rod **40** and the recrystallized rod **41** are both located in the upper portion of a partly illustrated melting chamber. The stock rod **40** and the recrystallized rod **41** can have the same or different diameters. The holder for the stock rods **40** is located at the end of a shaft **42** which is mounted in a seal **42a** at an inlet through the melting chamber wall and is rotatable and displaceable in the axial direction thereof. The stock rod **40** is located perpendicularly to the vertical recrystallized rod **41** and is connected therewith by the knee-shaped melting zone **46**. The recrystallized rod **41** is grown on the seed crystal **48** which is secured in the holder **45**. The holder **45** is located at the end of the shaft **43** which is mounted in the upper portion of the melting chamber in a seal **43*a*** at a passage through the wall of the melting chamber and is rotatable and displaceable in the axial direction thereof.

As in the embodiments of FIGS. **1** to **3**, the monocrystalline seed **48** in the embodiment of FIG. **4** is fused with the free end of the stock rod **40**. This can occur when the axes of the stock rod **40** and the seed **48**, or the subsequently recrystallized rod **41**, either intersect or are always spaced the same distance from one another during the entire zone melting process. The seed **48** and the stock rod **40** are placed in rotation beforehand. After the formation of the knee-shaped melting zone **46**, the stock rod **40** is displaced towards the melting zone **46** while the recrystallized rod **41** is displaced away from the melting zone **46** either at the same or different speed. The heating device, such as an electrically heated radiating body, which is located opposite the outer side of the knee-shaped melting zone **46**, consists of an induction coil **47** in the embodiment of FIG. **4**. The windings of this induction coil **47** are disposed in a plane perpendicular to a plane in which both rods **40** and **41** are disposed, and the electromagnetic field emanating therefrom has a supporting effect upon the liquefied material of the melting zone **46**. Additional supporting coils for the melting zone **46**, such as the coil **47'**, can also be provided. This is particularly advantageous if the heating device is an electrically heated radiating body.

In the embodiment of FIG. **4**, uniform heating and supporting of the melting zone **46** is also ensured. Since the recrystallized rod **41** in the embodiment of FIG. **4** is located in a suspended position, there is therefore no danger that liquefied material from the melting zone **46** will flow outwardly over the edge of the recrystallized rod **41** and will there grow spirally with the formation of crystal dislocations. Furthermore, a specific automatic stabilization of the location of the axis of the recrystallized rod **41** will occur because the pull of gravity exerted on the melt drives the rod axis repeatedly back in the direction to the rotational axis of the rod **41**. Thus, the formation of swings or pulsations, especially in the melting zone **46** which are damaging to the monocrystalline growth are thereby prevented.

The holders of the embodiment shown in FIG. **4** can also be so disposed that the stock rod **40** and the recrystallized rod **41** are inclined so that they meet at a point, i.e. a sharp angle or at an obtuse angle.

A further embodiment of the apparatus shown in FIGS. **2** to **4** can include, as for the embodiment shown in FIG. **1**, one or more additional holders for additional stock rods. These additional stock rods can consist of foreign material and can be so disposed in the apparatus that they can be connected with a side of the knee-shaped melting zone **24**, **36** or **46**, and be displaceable with adjustable speed toward the respective melting zone. As in the embodiment of FIG. **1**, one can thereby maintain a uniform optionally adjustable concentration of the foreign material over the cross section of the rod in the recrystallized rods **21**, **31** or **41**. It can, however, also be noted that additional stock rods of the same material as the stock rods **20**, **30**, **40** proper can be selected. The holder for an additional stock rod can advantageously be secured to a particular shaft which is mounted in a seal formed in the melting chamber wall, and is rotatable and displaceable in the axial direction thereof.

In the embodiments of FIGS. **2** to **4** it can also be advantageous, as in the embodiment of FIG. **1**, for the heating device to be in the form of an electrically heated ring emitting heat radiation which surrounds the respective melting zone or which consists of a flat or cylindrical high-frequency coil whose windings surround the respective melting zone. Particularly for producing a recrystallized rod with a larger diameter than that of the stock rod, for example in an embodiment such as that of FIG. **3**, a flat high-frequency coil surrounding the melting zone can be suitable since it ensures the fact that only a very slight radial temperature gradient is formed and therewith practically infinitesimal mechanical stresses in the plastic material thereof and few dislocations in the recrystallized rod. An electron gun can also be employed as in the melting device in the embodiments of FIGS. **2** to **4**. The melting zones can also be heated by an electric arc.

Furthermore, it can also be advantageous for the embodiments of FIGS. **2** to **4** to after-heat the respective recrystallized rod and to preheat the respective stock rod with similar means as aforementioned with regard to the embodiment of FIG. **1**.

It is also possible, in the embodiments of FIGS. **1** to **4**, to secure the stock rods proper in the holders **4**, **26**, **35** and **45** respectively, while the monocrystalline seeds or the recrystallized rods growing thereon are carried by the holders **10**, **22**, **34** and **44** respectively. The holders **4**, **26**, **35** and **45** are then displaced toward the melting zone, while the holders **10**, **22**, **34** and **44** are displaced away from the melting zone.

I claim:

1 Apparatus for crucible-free zone melting a rod of crystalline material, comprising a melting chamber, axially displaceable and rotatable holders for mounting the rods in said melting chamber said holders being respectively fixable only to an end of a stock rod to be recrystallized and a recrystallized rod, said holders having axes extending transversely to one another and means for heating the stock rod so as to form a melting zone therein having a substantially uniform temperature distribution connecting the stock rod with the recrystallized rod, whereby solidification of material in the interior of the zone is prevented.

2. Apparatus according to claim **1**, wherein the axis of said recrystallized rod holder extends substantially vertically and said recrystallized rod holder is located at the bottom of said chamber, and said holder for the stock rod to be recrystallized is located in an upper part of said chamber.

3. Apparatus according to claim **1**, wherein the axis of the holder for the stock rod to be recrystallized extends substantially vertically and said stock rod holder is located at the bottom of said chamber, and said holder for the recrystallized rod is located in an upper part of said chamber.

4. Apparatus according to claim 1, wherein the holders for the stock rod to be recrystallized and for the recrystallized rod are both located in an upper part of said melting chamber.

5. Apparatus according to claim 1, including at least one additional holder for a stock rod adjustable at varying feeding rate.

6. Apparatus according to claim 1, wherein said melting zone is in the form of a bend at substantially the intersection of said inclined axes and said heating means is located adjacent the outer side of said bend.

7. Apparatus according to claim 1, wherein said heating means comprises a flat-wound induction coil having its windings disposed in one plane, said induction coil being adapted to be energized with high-frequency alternating current.

8. Apparatus according to claim 1, wherein said heating means comprises a substantially conically shaped induction coil adapted to be energized with high-frequency alternating current.

9. Apparatus according to claim 1, including at least one additional supporting coil for supporting said melting zone, said supporting coil being adapted to be energized with a high-frequency current.

10. Apparatus according to claim 1, including means for preheating the stock rod and after-heating the recrystallized rod.

11. Apparatus according to claim 1, wherein said heating means comprises an electron gun.

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