July 7, 1964 T. H. OREM 3,139,653

APPARATUS FOR THE GROWTH OF PREFERENTIALLY ORIENTED SINGLE CRYSTALS OF METALS

Original Filed Aug. 6, 1959

3 Sheets-Sheet 1

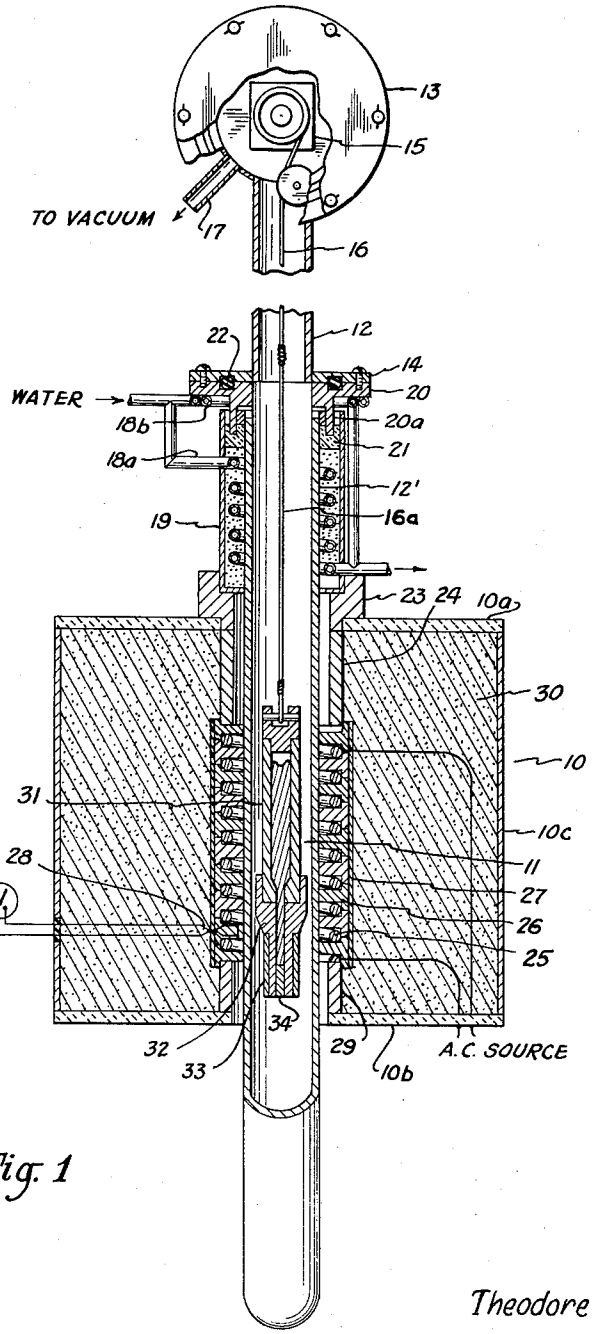


Fig. 1

INVENTOR

Theodore H. Orem

BY David Gobbins
John C. Stahl

ATTORNEYS

July 7, 1964 T. H. OREM 3,139,653

APPARATUS FOR THE GROWTH OF PREFERENTIALLY ORIENTED SINGLE CRYSTALS OF METALS

Original Filed Aug. 6, 1959

3 Sheets-Sheet 2

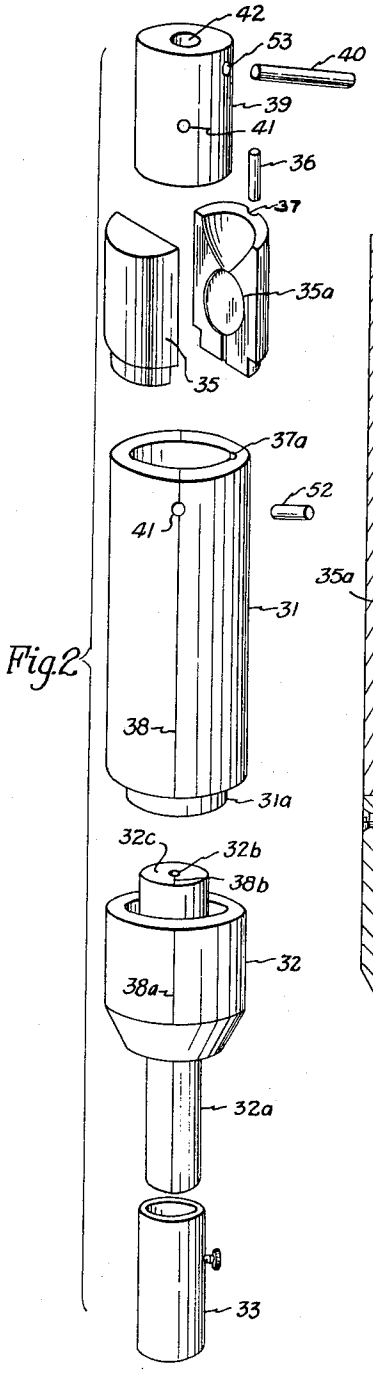


Fig. 2

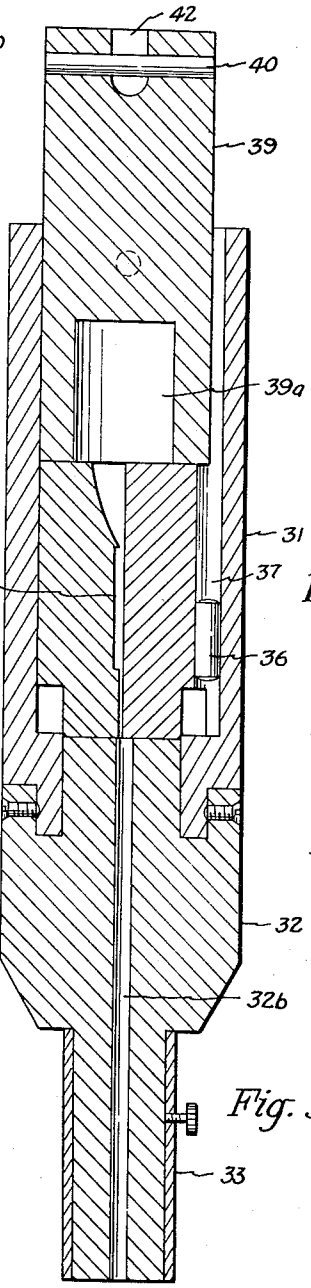


Fig. 3

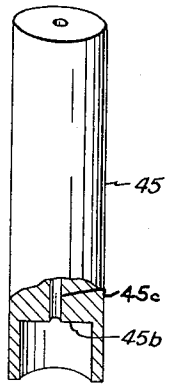


Fig. 4B

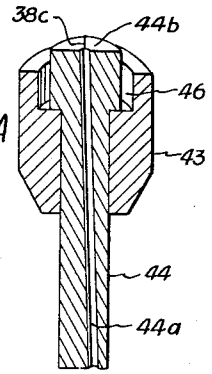


Fig. 4A

INVENTOR

Theodore H. Orem

BY David Cobbins

John C. Stahl

ATTORNEYS

July 7, 1964 T. H. OREM 3,139,653

APPARATUS FOR THE GROWTH OF PREFERENTIALLY ORIENTED SINGLE CRYSTALS OF METALS

Original Filed Aug. 6, 1959 3 Sheets-Sheet 3

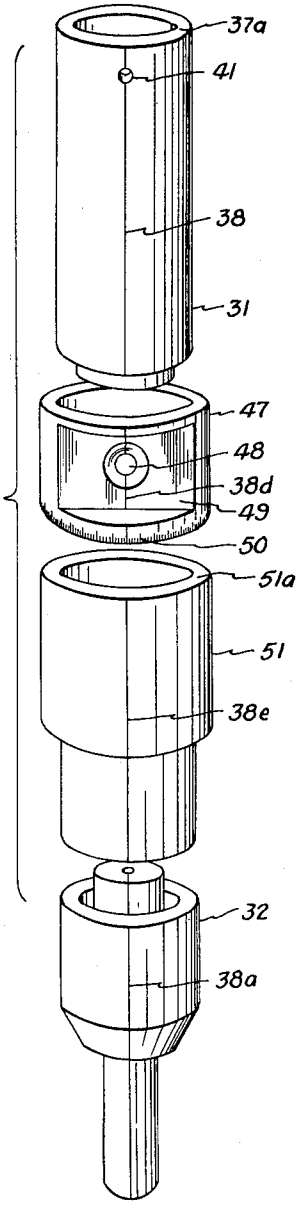


Fig. 5

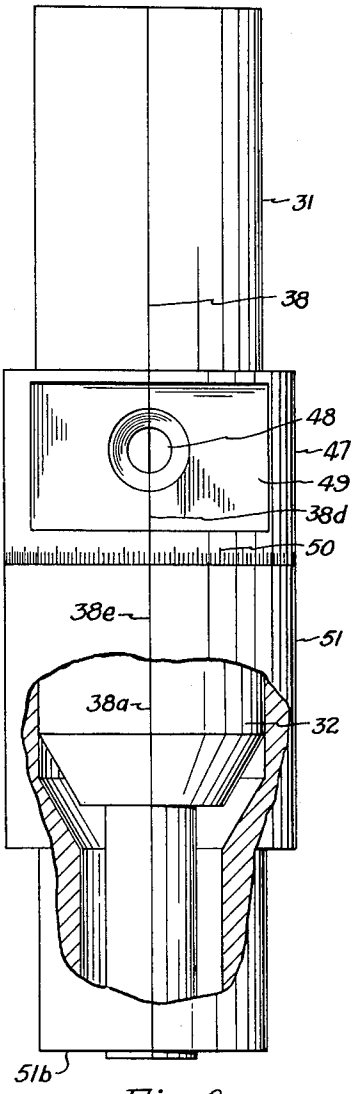


Fig. 6

INVENTOR

Theodore H. Orem

BY David Cobbins
John C. Stahl
ATTORNEYS

United States Patent Office 3,139,653 Patented July 7, 1964

3,139,653

APPARATUS FOR THE GROWTH OF PREFERENTIALLY ORIENTED SINGLE CRYSTALS OF METALS

Theodore H. Orem, Silver Spring, Md., assignor to the United States of America as represented by the Secretary of Commerce

Original application Aug. 6, 1959, Ser. No. 832,127, now Patent No. 3,060,065, dated Oct. 23, 1962. Divided and this application May 10, 1961, Ser. No. 109,233

2 Claims. (Cl. 22—57)

The present invention relates to apparatus for producing metallic monocrystals of a preferred axial orientation and more particularly to apparatus for growing monocrystals of metals with any desired axial orientation and external configuration.

The present invention is a division of application Serial No. 832,127, now U.S. Patent 3,060,065, issued October 23, 1962.

Single crystals of metals are widely used in fundamental research on metals. It is often desirable that single crystals have a definite atomic arrangement, either in their surfaces or in certain crystallographic directions within the specimen. Heretofore, difficulty has been experienced in producing specimens having a preselected crystallographic orientation in combination with a desired external configuration.

The internal structure of a crystal as revealed by X-ray diffraction measurement demonstrates planes which contain relatively large numbers of atoms. It is possible to identify these internal planes by reference to imaginary coordinate axes. These axes define a framework, or lattice, that is fundamental to the description of the crystal structure.

For purposes of explanation throughout the body of the specification the term horizontal plane of atoms will refer to a specific horizontal plane of atoms having the desired axial orientation whereas the term vertical plane of atoms will refer to a specific vertical plane of atoms having the desired vertical axial orientation as determined by conventional X-ray diffraction methods. See Crystals and X-rays by K. Lonsdale, pages 50–80.

To a certain degree monocrystals of a preferred axial orientation may be produced by a method generally known as seeding. This procedure is described in Bridgeman Patent No. 1,793,672, wherein a vertical furnace is employed together with a seed crystal of desired horizontal axial orientation. In this procedure, the seed, a small, single crystal of the same material as the specimen to be produced, is mounted in a position against a polycrystalline specimen. By using a suitable furnace, the heating conditions are then adjusted so that the entire charge, with the exception of a small portion of the seed crystal, becomes molten. By properly controlling the rate of withdrawal of the melt from the hot zone of the furnace, the molten plane is allowed to freeze progressively from the seed and the new single crystal will have a horizontal orientation identical with that of the seed. However, in order to control the direction of the horizontal plane of atoms as in Bridgeman, it is necessary, in the first place, to start with a seed crystal of the desired horizontal axial orientation. The seed may be selected from a large number of single crystal castings of small diameter which has the desired axial orientation. Furthermore, it is to be noted that the crystal produced by this prior art method contains a horizontal plane of atoms parallel to the plane of atoms within the seed crystal only, orientation along a desired or specific vertical plane of atoms within the specimen occurs merely by chance.

It is therefore an object of this invention to produce metallic monocrystals of a preferred axial orientation.

A more specific object of this invention is to prepare monocrystals of metals having any desired axial orientation and of any external configuration.

Another object of this invention is to provide means for changing the axial orientation of a seed crystal.

Other uses and advantages of the invention will become apparent upon reference to the specification and drawings in which:

FIG. 1 is a front view, partly in section, of a suitable type of vertical furnace in which metallic monocrystals of this invention may be produced showing the position of the improved crucible employed in connection with this invention;

FIG. 2 is an exploded view of the crucible assembly of this invention showing the relative positions of parts preparatory to assembly;

FIG. 3 is a vertical sectional view of the crucible assembly of FIG. 2;

FIG. 4A is a vertical sectional view of a modified seed receptacle;

FIG. 4B is an isometric view of an aligning mold to be used with the modified seed receptacle of FIG. 4A for modifying the axial orientation of a seed crystal;

FIG. 5 is an exploded isometric view of an aligning fixture employed in connection with this invention preparatory to assembly; and

FIG. 6 is a side elevational view of the assembled aligning fixture of FIG. 5 showing the crucible in position.

Referring to the drawings, there is shown in FIG. 1 a furnace **10**. The complete crucible assembly **11** is lowered through a chamber formed by tubes **12—12'** into the heating zone of the furnace **10**. The upper end of guide tube **12** connects in a conventional manner with a sealed chamber **13**. The lower end of tube **12** is integral with a plate **14**. A constant speed motor **15** is mounted within chamber **13** and is attached by means of a flexible metallic cable **16** and an Inconel extension **16***a* with assembly **11** and controls the rate at which the crucible traverses the furnace. Preferably, a rate of travel of the crucible **11** through the furnace at approximately one-half inch per hour is maintained. A conduit **17** connects the sealed chamber **13** to a vacuum source in order to reduce the pressure within the furnace chamber to approximately 100 microns of mercury absolute.

A cooling coil **18***a* is mounted concentric about the upper portion of tube **12'** and in spaced relation thereto. Coil **18***a* is positioned within a cylindrical jacket **19** and passes through openings in the upper and lower side walls, respectively, of jacket **19**. A mixture of zinc dust and zinc powder bonded with sodium silicate is placed in jacket **19** and tamped between coils **18***a* to conduct heat away from the upper portion of tube **12'**. The inlet of a heat exchanger coil **18***b* connects with coil **18***a* outside of the jacket **19**. The coil **18***b* is spirally wound and passes adjacent the under surface of a collar **20** which is suitably constructed of brass or the like. A projecting member **20***a* on the under surface of collar **20** and integral therewith fits within the upper portion of jacket **19** between the inner wall of said jacket and the outer surface of tube **12'**. Member **20***a* is pressed into a sealant **21** which is deposited within the jacket **19** on the upper surface of the zinc powder-zinc dust conducting material thereby completing a vacuum-tight seal. Water circulating within coils **18***a*–**18***b* prevents reflected heat from the heating zone of the furnace from melting the sealant **21**. As shown in FIG. 1 an O-ring seal **22** positioned in a recessed portion in the lower surface of plate **14** and the upper surface of collar **20** maintains a vacuum-tight seal.

As further shown in FIG. 1, a cylindrical graphite collar **23**, positioned on the top wall **10***a* of the furnace **10**, supports jacket **19**. A recessed portion in the bottom surface of collar **23** fits within and extends to the lower surface of wall **10***a*. A refractory collar **24**, concentric about the mid-portion of tube **12'** and on a common vertical axis with collar **23**, extends from the lower end of collar **23** to the heating zone of the furnace.

A heating coil **25** is provided intermediate of the refractory collar. The materials chosen for heating coil **25** depend upon the temperature gradient required in the furnace, i.e., Kanthal or Nichrome is satisfactory. The windings of coil **25** are separated by ceramic spacers **26** or the like, and a coating of fire clay **27** or other insulating material covers the outer surface of the spacers **26**. A thermocouple indicated diagrammatically at **28** passes through an aperture in the fire clay and into proximity to windings **25** in order to measure and control the temperature of the furnace. Extending from the lower portion of the heating zone of the furnace to the bottom wall **10***b* and in spaced relation around the lower portion of the tube **12'** is a second refractory collar **29**. A granular material **30** such as diatomaceous earth, or the like, insulates the heating elements of the furnace thereby maintaining a constant temperature within the device.

The crucible, as is apparent from FIGS. 2 and 3, comprises a lower seed receptacle **32**, an intermediate crucible housing **31**, a segmented mold **35** and a riser **39**.

The lower shouldered portion **31***a* of crucible housing **31** is machined to seat on the upper portion of seed receptacle **32**. The seed receptacle is provided with a vertical seed receiving chamber **32***b* which traverses the length of receptacle **32**. An extension **32***a* of the receptacle (FIG. 2) provides a contact surface for a cooling sleeve **33**.

The interior of crucible housing **31** is machined to slidably receive the segmented mold **35**. The mold may be internally machined to provide a casting matrix **35***a* of any desired geometric configuration. In the particular implementation shown in FIG. 2 a crystal of substantially disc-shaped configuration will be formed.

In order to secure the necessary crystallographic orientation as will be described, mold **35** is provided with a notch **37** which registers with a similar notch **37***a* in crucible housing **31**. The notch **37***a* is positioned with respect to an indicia mark **38** inscribed on housing **31**. The mold **35** is securely fixed in a position determined by the notches **37—37***a* by means of a key **36** as is clearly shown in FIG. 3.

Seed holder **32** is similarly provided with indicia marks **38***a* and **38***b* which are aligned with indicia mark **38**. The mark **38***b* serves to initially position the seed within the seed receptacle. As will be described, each seed is provided with a reference mark, the position of which is obtained from X-ray diffraction patterns.

The riser **39** is applied over the mold **35** to complete the assembly and is fastened in place by a pin **52** which traverses a bore **41** provided in the housing **31** and riser **39**, respectively.

In order to permit raising and lowering of the crucible assembly through the vertical furnace as will be described, the riser **39** is provided with a recess **42**, a bore **53**, and pin **40** to permit attachment of the operating cable **16** forming part of the furnace mechanism as shown in FIG. 1.

It will be noted from the assembled view of FIG. 3 that the orientation of the above-described elements of the crucible results in the upper end of seed receptacle **32** abutting the lower surface of mold **35** in a manner such that the seed receiving chamber **32***b* is continuous with the matrix **35***a* of the mold **35**. The upper portion of the mold **35** in turn registers with a chamber **39***a* in the riser **39** to permit expansion of the specimen melt.

The mold **35** is fixedly positioned within the crucible housing **31**. A charge of metal is placed within the casting matrix **35***a* of mold **35**, the chamber **32***b* is suitably

plugged, and the metal is melted in any conventional manner to form a polycrystalline specimen having an external configuration corresponding to that of the matrix. A seed crystal of the desired axial orientation or as produced by the method and apparatus hereinafter to be discussed in connection with FIGS. 4A—4B, 5 and 6 of the drawings, respectively, is inserted within the (unplugged) seed receiving chamber **32***b*. The referred-to reference mark on the seed crystal is positioned with respect to mark **38***b* on surface **32***c* of receptacle **32**; the upper surface of the seed is then ground even with surface **32***c* in a conventional manner thereby insuring that the seed crystal and surface **32***c* are in a horizontal plane. The seed receptacle **32** is then joined to the crucible **31** so that the ground surface of the seed crystal abuts the lower end of the specimen in the matrix of the mold. To insure that the lower portion of the cast specimen within matrix **35***a* abuts the seed crystal within chamber **32***b*, a plug **34** (see FIG. 1) may be applied against the lower portion of the seed crystal within chamber **32***b*.

The correct furnace temperature to permit just partial melting of the seed is obtained by trial and error or by surveying the furnace to obtain the correct temperature for a specified location of the assembly in the furnace. Seeds of undesirable axial orientation may be used in the determination of the correct furnace temperature, because, until this temperature is established for a fixed position of the assembly in the furnace, there is a possibility that the entire seed might be melted. This temperature can usually be established after a few trial runs. Once this temperature has been fixed, the same percentage of seed can be melted on each successive run, provided the assembly is placed in the same relative position in the furnace on each successive run.

It will be clear then that the specimen and the seed crystal with the exception of the portion surrounded by the cooling sleeve will be in a liquid phase. The lowering rate of the complete crucible assembly is then adjusted to permit all the heat of crystallization to be conducted away in the direction of the solidified portion of the seed. The solid/liquid interface is then maintained planar and horizontal. If lowering is too rapid, cooling may occur from the sides producing spurious crystal growth and a polycrystalline ingot.

The present invention also provides means for modifying available seed crystals having a known horizontal axial orientation to a preferred, predetermined horizontal axial orientation. In other words, should it be desired to provide a seed crystal having a specific desired horizontal axial orientation for use in connection with the crucible assembly of FIGS. 2 and 3, a seed crystal having a horizontal axial orientation that is close to the desired preferred horizontal axial orientation is selected and the special seed receptacle of FIG. 4A is employed to modify the horibontal axial orientation of the seed crystal to produce a seed crystal of the exact desired horizontal axial orientation.

The modified seed receptacle of FIG. 4A comprises a cylindrical yoke **43** and a replaceable seed receptacle **44**. As illustrated, the longitudinal axis of the cavity **44***a* in which the seed crystal is to be positioned is canted with respect to the vertical longitudinal axis of the receptacle **44**. The angle of the cavity axis may be drilled or otherwise provided at any angle with respect to the longitudinal axis of the receptacle to permit a change in the orientation of the selected seed crystal to that of the desired orientation. Preferably a maximum angle of about 5° has proven sufficient.

Using the modified seed receptacle of FIG. 4A, a seed crystal of any approximate horizontal axial orientation may be used to prepare a seed crystal of exact preferred horizontal axial orientation. If the deviation of any seed crystal is 5° or less from the horizontal axial orientation desired, as determined by X-ray diffraction studies, the longitudinal axis of cavity **44***a* of seed receptacle **44** is

made to the specific angle (with respect to the longitudinal axis of the receptacle) required to complement the horizontal axial orientation of the seed crystal placed within the cavity 44*a* to produce a seed crystal of the exact desired horizontal axial orientation. For example, if a specimen is to be produced wherein the desired angle of the horizontal plane of atoms is 42° 35′ with respect to a horizontal reference plane of atoms and a seed crystal having this desired horizontal plane of atoms at an angle of 38° 45′ with respect to the same horizontal reference plane is available, the longitudinal axis of cavity 44*a* of the modified seed receptacle of FIG. 4A will be made at an angle of 3° 50′ with respect to the longitudinal axis of the receptacle 44. The modified seed receptacle of FIG. 4A may then be substituted for receptacle 32 of FIGS. 2 and 3 of the drawings. It will be clear that a number of receptacles 44 each having a different inclination of the angle of the cavity 44*a* is provided.

If the angular deviation between the selected seed crystal and the preferred orientation of the horizontal plane of atoms desired in the seed crystal to be produced exceeds 5°, however, then it is necessary to employ the additional seed mold 45 of FIG. 4B in conjunction with the modified receptacle of FIG. 4A to produce an intermediate seed crystal having the desired horizontal plane of atoms.

The outer wall of cylindrical mold 45 is inserted within an annular recessed portion 46 of the modified seed receptacle of FIG. 4A, the top surface 44*b* of receptacle 44 abutting the lower surface of 45*b* of mold 45. The orientation of the horizontal plane of atoms of the selected seed crystal is determined by conventional X-ray diffraction methods. The angular difference between the measured orientation of the selected seed crystal and the preferred orientation to be produced within the newly-formed crystal is then calculated, and divided into any suitable number of increments such that the angle for any single increment does not exceed 5° (the maximum angular inclination in view of the diameter of receptacle 44). The axis of cavity 44*a* in which the selected seed crystal is inserted is then made, as by drilling, at an angle with respect to the longitudinal axis of receptacle 44 corresponding to such increment.

In utilizing the seed crystal apparatus of FIGS. 4A–4B of the drawings, a charge of metal is placed into cavity 45*c* of the mold 45 and melted to form a polycrystalline ingot. The selected seed crystal of the same metal as that placed into cavity 45*c*, is then inserted within cavity 44*a* of the modified seed receptacle of FIG. 4A, the top of the seed crystal is ground so that its surface is in the same plane as the bottom surface 45*b* of seed mold 45. The cylindrical seed mold 45 and modified seed receptacle 44 are then joined together and lowered into the furnace of FIG. 1 so that the entire charge, with the exception of a small portion of the seed crystal, becomes molten. Upon cooling, the angle between the horizontal plane of atoms within the newly-formed seed crystal within mold 45 and the axis of said seed crystal will vary from the corresponding orientation of the selected seed crystal by an angle equal to the angle of the axis of chamber 44*a* with respect to the longitudinal axis of receptacle 44. As the last step in the incremental method of changing the axial orientation of a seed crystal, or, as previously described in connection with changes of 5° or less, a seed receptacle having a cavity of the exact inclination may be drilled or a replaceable receptacle having the desired angle of inclination may be selected. A reference mark is scribed on the upper surface of the seed crystal to position the seed crystal with respect to mark 38*c* on surface 44*b* of receptacle 44 during each step of this reorienting procedure.

There is shown in FIGS. 5 and 6 a preferred embodiment of the aligning fixture whereby a preferred vertical plane of atoms may be obtained. Corresponding elements are designated by the same reference characters in FIGS. 2, 3, 5, and 6. Preliminary to mounting the crucible assembly in the furnace, the segmented mold 35 is inserted within housing 31 in the manner previously described in connection with FIGS. 2 and 3 of the drawings. The longitudinal axis or parting plane of mold 35 is then aligned with reference mark 38. The housing 31 is slidably inserted within the cavity of an alignment fixture 47. Fixture 47 is preferably of hollow cylindrical form and constructed of brass or the like. An alignment window 48 in the center of a cut-out portion 49 permits alignment of the reference mark 38 on the crucible 31 inserted within alignment fixture 47 with mark 38*d* scribed on fixture 47, as best seen in FIG. 6 of the drawings. Angular divisions 50 are scribed on the lower peripheral edge of fixture 47 using the reference mark 38*e* as an index.

As shown in the cut-away portion of FIG. 6 of the drawings, seed receptacle 32 fits within a stepped yoke 51, preferably constructed of brass or the like. The upper surface 51*a* of yoke 51 abuts the lower surface of the aligning fixture 47 when the housing 31 and seed receptacle 32 are attached. The reference mark 38 on housing 31 aligns with the marks 38*a*, 38*d*, and 38*e* on the seed receptacle 32, alignment fixture 47 and stepped yoke 51, respectively, as best seen in FIG. 6. As aforementioned, the axis or parting plane of mold 35 is aligned with reference mark 38. The bottom portion of the extension 32*a* extends slightly below the lower surface 51*b* of yoke 51 as shown in FIG. 6 of the drawings.

By means of Laue back-reflection patterns, such as are well known in the art, the vertical planes of atoms within a particular seed crystal are determined, and an alignment mark is scribed on the seed crystal corresponding to a reference vertical plane of atoms. At the same time a corresponding mark is placed on the back-reflection pattern. The angle that a desired vertical plane of atoms makes with respect to the reference vertical plane of atoms is then determined by aligning said reflection pattern (which is an X-ray photograph) with the index mark on a conventional Greninger chart (see "Structure of Metals," 2d ed. by C. S. Barrett).

With reference marks aligned on members 31, 35, 32, 47, and 51, respectively, as best seen in FIG. 6 of the drawings, the yoke 51 is rotated in a direction and at an angle equal to the difference between the reference vertical plane of atoms and the desired, predetermined vertical plane of the atoms as shown on the back reflection pattern. The angular deviation is measured by aligning the reference mark 38*e* scribed on yoke 51 with the computed deviation as measured by angular divisions 50 on the lower peripheral edge of fixture 47. The vertical axis or parting plane of the mold 35 and the crystal to be formed therein now corresponds to the desired, predetermined vertical plane of atoms.

The alignment fixture 47 and yoke 51 are then removed from the housing 31 and seed receptacle 32, respectively. The riser 39 and cooling sleeve 33 are attached in the manner heretofore described in connection with FIG. 2 of the drawings and the apparatus is ready for lowering into the furnace.

It will be apparent that the embodiments shown are only exemplary and that various modifications can be made in construction and arrangement within the scope of invention as defined in the appended claims.

What is claimed is:

1. In combination, a vertical furnace, a vertical mold having a matrix for a specimen, a vertical seed receptacle having a cylindrical cavity the longitudinal axis of which is canted a small amount not more than about five degrees from the vertical, means for holding said vertical mold and said vertical seed receptacle in vertical alignment, a passageway connecting said matrix and said cylindrical cavity together, and means for moving said vertically-aligned mold and seed receptacle through said vertical furnace so as to grow a monocrystalline specimen from a seed in said seed receptacle.

2. The combination set forth in claim 1, wherein said vertical mold and said vertical seed receptacle are rotatable relative to each other about the vertical, said vertical seed receptacle having a reference mark on the exterior surface thereof, said vertical mold having means on the exterior surface thereof cooperable with said reference mark for determining the relative angular position between said vertical mold and said vertical seed receptacle.

References Cited in the file of this patent

UNITED STATES PATENTS

1,793,672	Bridgman	Feb. 24, 1931
2,214,976	Stockbarger	Sept. 17, 1940
2,679,080	Olsen	May 25, 1954
2,879,189	Shockley	Mar. 24, 1959
2,972,525	Emeis	Feb. 21, 1961