

[11] 3,607,115

**[54] CRYSTAL PULLING FROM MOLTEN MELTS
INCLUDING SOLUTE INTRODUCTION MEANS
BELOW THE SEED-MELT INTERFACE
6 Claims, 8 Drawing Figs.**

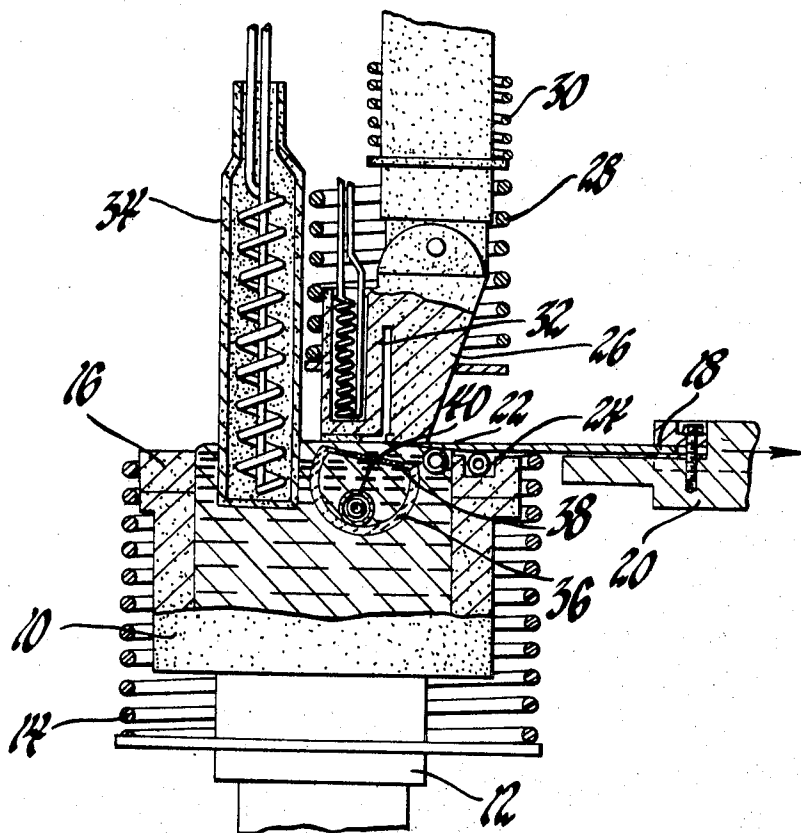
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3,258,314	6/1966	Redmond	23/301 SP
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ABSTRACT: An apparatus and method are disclosed for growing crystals from a melt of a molten solvent metal that is saturated with a solute. Heat is withdrawn through a seed contacting the surface of the melt to precipitate the solute onto said seed at the seed-melt interface. The seed is pulled away from the melt at a rate commensurate with the precipitation rates. Simultaneously, more solute is dissolved into the melt from a solute source in the melt beneath the growth interface while maintaining a close source-growth interface spacing substantially constant.



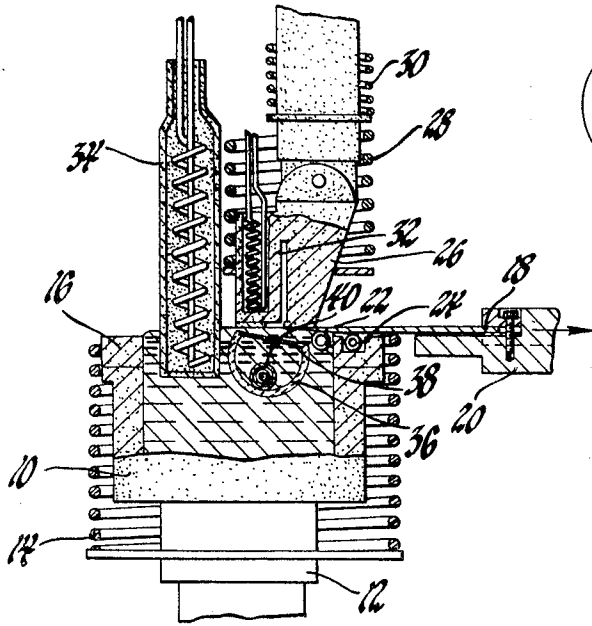


Fig. 1

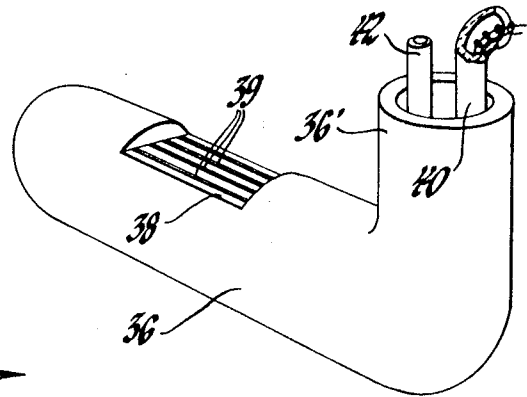


Fig. 2

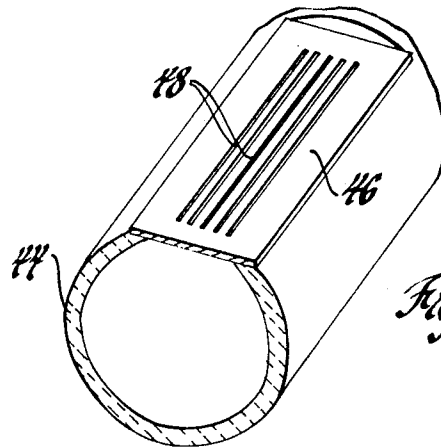


Fig. 3

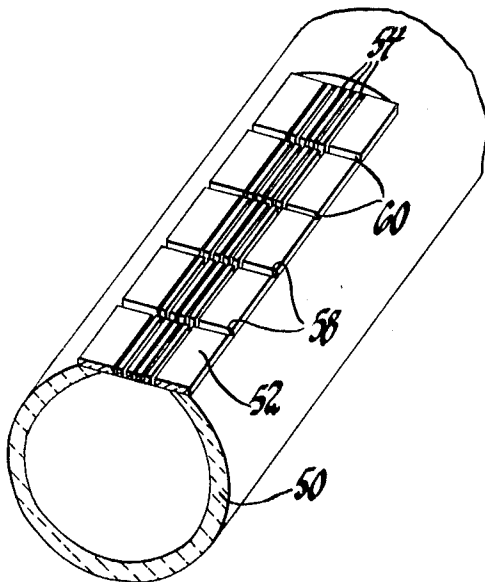


Fig. 3a

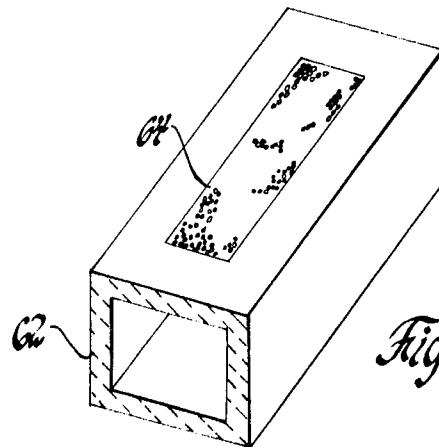


Fig. 3b

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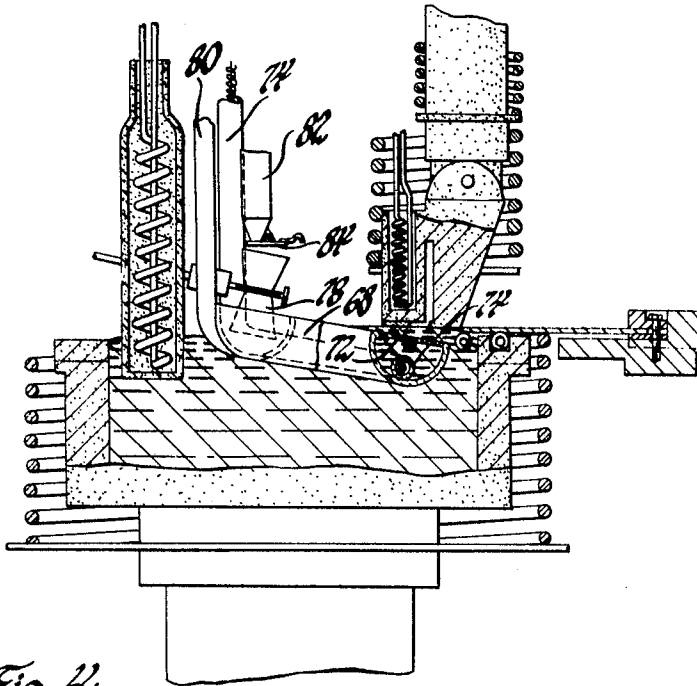


Fig. 4

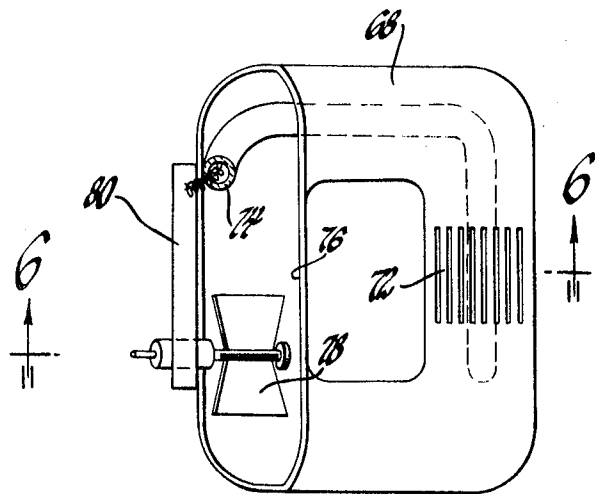


Fig. 5

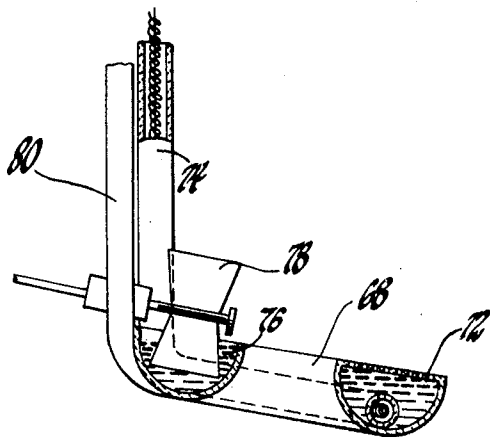


Fig. 6

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CRYSTAL PULLING FROM MOLTEN MELTS INCLUDING SOLUTE INTRODUCTION MEANS BELOW THE SEED-MELT INTERFACE

CROSS REFERENCES TO RELATED APPLICATIONS

U S. Ser. No. 795,561 Bleil, filed Jan. 31, 1969.

BACKGROUND OF THE INVENTION

Crystals have been grown in the past from liquid melts of the crystalline materials. Crystals have also been grown from supersaturated aqueous solutions of the crystalline material. U.S. Pat. No. 3,031,275 Shockley describes a technique for growing crystals from a melt floating on the surface of a liquid with which the melt is immiscible. I have found a method and apparatus by which metal and semimetal elemental and alloy crystals can be produced using many of the desirable features of these prior techniques, without also incurring the ancillary disadvantages of each.

Moreover, this invention can be used to produce continuous thin ribbon crystals. In my earlier U.S. Pat. application Ser. No. 795,561, I describe a novel technique for horizontal crystal growing which can be used to provide elemental thin crystalline ribbons of high purity. By modifying that technique in accordance with this invention, a variety of advantages can result. Ribbon growth temperature can be significantly reduced. Compound and mixed crystal, i.e. alloy, ribbons of constant composition are readily formed. The length of the ribbon produced is not inherently limited by the starting volume of the melt.

SUMMARY OF THE INVENTION

It is, therefore, a principle object of this invention to provide an improved method and apparatus for growing crystals, particularly alloy crystals, from a saturated melt. A further object of the invention is to provide an apparatus and method for producing thin ribbons of alloy crystals. These and other objects of the invention are attained by heating a solvent metal to a predetermined temperature at which it is molten, and saturating the solvent metal with a solute that will produce the crystal desired. A source of additional solute is located within the melt beneath the crystal growth interface. A close spacing is maintained between the source and the growth interface as growth proceeds. A crystalline seed is placed in contact with the melt above the source and heat withdrawn through the seed to precipitate the solute onto the seed. Concurrently, the crystalline seed is moved away from the melt at a rate commensurate with the rate of the solute precipitation. Simultaneously, additional solute is dissolved into the melt from the source beneath the growth interface to maintain melt composition substantially constant in the growth area.

BRIEF DESCRIPTION OF THE DRAWING

Other objects, features and advantages of the invention will become more apparent from the following description of preferred examples thereof and from the drawing, in which:

FIG. 1 shows an elevational view in partial section of a horizontal crystal-growing apparatus that includes a solute source beneath the growth interface;

FIG. 2 shows an enlarged isometric view of the solute source shown in FIG. 1;

FIGS. 3, 3a and 3b show fragmentary isometric views of alternative solute sources for the apparatus shown in FIG. 1;

FIG. 4 shows a horizontal crystal-growing apparatus with a recirculating solute source;

FIG. 5 shows an enlarged plan view of the solute source shown in FIG. 4; and

FIG. 6 shows a sectional view along the line 6-6 of FIG. 5.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As already indicated, this invention involves alloy crystals by precipitation of a solute onto a crystalline seed from a melt saturated with that solute. A source of solute is provided in the

melt within a predetermined distance from the growth interface, with this spacing being maintained substantially constant during crystal growth. Moreover, this invention also contemplates providing a surface geometry on the solute source that will aid in controlling the geometry of the growth interface. While this latter concept may not be of appreciable significance for vertical crystal growing, it is of special importance when horizontally growing crystals in accordance with this invention. Shaping the source surface can permit one to produce crystalline ribbons of different surface geometries, as formed. It is in this latter connection that this invention has particular benefits in that it can provide thin, wide monocrystals flat on one side and of predetermined shape on the other.

It should also be noted that this technique can be used to produce monocrystals or polycrystalline material, as one desires. It can be used to produce substantially elemental crystals, mixed crystals and crystals of compounds. However, the composition of the crystals produced will always be a function of the solid solubility of the melt solvent in the crystal being formed. Hence, for ultimate purity in elemental crystals this technique would not be preferred. However, it provides a precise technique for producing elemental crystals containing selected amounts of other substances, for producing crystals of solute-solvent compounds of selected composition, and the like. Since for all practical purposes this technique produces crystals containing two or more elements I prefer to refer to it as an alloy crystal-growing technique. The crystal, of course, may not be a true alloy but a mixture. However, for convenience of expression I shall refer to it as an alloy.

The actual composition of the crystal will thus depend on the solute-solvent combination used, the temperature of the melt, etc. Consequently, the invention has a wide applicability from the production of elemental and compound semiconductor monocrystals to the crystals of a variety of metals.

Further, this invention can be used for vertical crystal growing, as will become apparent. However, the maximum benefits of the invention are more fully realized when it is used in combination with the horizontal crystal-growing apparatus I have described and claimed in my earlier U.S. Pat. application Ser. No. 795,561.

Reference is now made to FIG. 1 to illustrate that preferred use. Except for the additional provision of the solute source, the apparatus shown in FIG. 1 is essentially the same and operated essentially the same as described in my earlier-filed patent application Ser. No. 795,561, which is intended to be incorporated herein by reference. For this reason the similar aspects of apparatus and method shall only be briefly described here.

A rectangular crucible 10 rests on a crucible support 12 within a conventional crystal-growing enclosure (not shown) which provides a suitable environment for crystal growth. The crucible is surrounded by a radio frequency heater 14. The crucible is slightly overfilled with the desired melt, so that the free surface of the melt extends slightly above the lip 16 of crucible 10.

One end of the lower surface of a crystalline seed 18 contacts the surface of the melt while the other end is secured to a seed holder 20 for pulling the seed horizontally away from the melt.

A melt of 95 percent indium-5 percent germanium can be used to grow germanium crystals containing small amounts of indium at a growth temperature of approximately 400° C. A melt of 75 percent silver-25 percent germanium can be used to produce germanium crystals containing small amounts of silver at a growth temperature of 700° C. In such instance the seed 18 is of germanium in which the major faces of the seed are parallel and in the (111) plane. When horizontally pulled, the direction of pull is $\langle 211 \rangle$.

The upper surface of the end of the seed touching the melt is contacted by a heat sink 26, which is maintained at an appropriate temperature by means of an encircling radio frequency type heater 28. Cooling coils 30 surround the heat sink support.

A special heater 22 is recessed under the melt surface beneath the seed adjacent crucible lip 16 over which the seed is pulled. Heater 22 lies parallel the crucible lip, and transverse to the ribbon being formed, to supply ribbon heat lost by radiation. A spring-loaded roller 24 in the crucible lip 16 supports the ribbon as it is pulled over the lip. Hence, ribbon growth is restricted to the end of the ribbon under the heat sink.

Heat sink 26 has an appendage 32 thereon for controlling temperature and melt surface height at the end of the growing seed. Appendage 32 has a heater therein for more precise temperature adjustments adjacent the growth interface. A graphite bulb 34, having a heater therein for more precise temperature adjustments adjacent the growth interface. A graphite bulb 34, having a heater therein is lowered into the melt at a rate commensurate with the crystalline growth to maintain the free melt surface at a constant height above the lip 16 of the crucible.

The solute source is a graphite or ceramic tube 36, the construction of which is more clearly shown in FIG. 2. The source tube 36 lies transverse to the ribbon being grown. It has a flat surface portion 38 with a plurality of slots 39 which are positioned beneath the growing end of the seed beneath and parallel to the growth interface. The slots provide a permeable opening in the source under the ribbon growth region. For best results, the flat surface portion 38 should be maintained within about one-eighth inch of the growth interface. Close spacing of surface 38 to the growth interface is desirable to increase the rate of crystal growth and regulate growth interface geometry. Transport of the solute from the source to the growth interface is diffusion controlled. Hence, the closer the spacing of the source to the growth interface, the faster growth can be achieved. Analogously, the closer the source surface geometry parallel the natural growth geometry, the easier the system is to control. The natural ribbon growth interface in the system shown is not perfectly horizontal. Hence, the source surface 38 is canted somewhat to be substantially parallel to it. However, in some instances one may prefer a different relative orientation.

There is also a concurrent indiffusion of the melt solvent into the source through the slots 39 in the tube 36, while the source is diffusing out. Hence, it is desirable that the volume of solute in tube 36 be appreciable to avoid any significant solute concentration changes during crystal growth that would adversely affect the rate of growth or the length of the ribbon to be produced.

Of course, for most systems the source should at least be at the melt temperature and preferably slightly higher, to prevent the melt and source from freezing. For this reason a source heater 40 is included in tube 36. Tube 42 extending into the source tube 36 can be used to introduce additional solute into tube 36 should it be desired. As can be seen, tube 36 bends at a right angle to extend up above the surface of the melt at a point removed from the growth interface. This not only increases source volume but provides a ready access to the tube interior.

The source opening through which the solute diffuses can be formed in a plurality of ways, only some of which are shown. The openings should be large enough to permit the solute to diffuse out but not so large as to permit droplets of solute to pass through. The type, geometry and dimensions of the source openings can thus be varied widely, and to some extent be a function of the solute-solvent system involved.

FIG. 2 shows a series of parallel, longitudinally oriented slots 39 in an integral flat portion of source tube 36, providing the source openings. FIGS. 3, 3a and 3b show alternative forms of source apertures which can be used. FIG. 3 shows a source tube 44 having a separate flat plate 46 secured over a longitudinal opening therein. The plate 46 has a series of parallel, longitudinally oriented slots therein, analogous to that shown in FIG. 2.

In FIG. 3a, source tube 50 also has a flat plate 52 secured over to a longitudinal opening therein, with a plurality of slots 54 running the length of the plate providing means for the

solute to diffuse out of the tube. However, in addition, transverse grooves 58 and 60 are provided in plate 52 to alter the rate of diffusion of the solute out of tube 50 in those areas where the grooves intersect. This difference in rate of diffusion will affect solute concentration in the adjacent areas of crystal growth, which in turn will affect the rate of growth in the related regions of the crystal being formed. Hence, by contouring plate 52 one can contour the lower surface of the ribbon which is being grown.

FIG. 3b shows that the source tube containing the source need not be cylindrical but can be rectangular in cross section, as source tube 62 shows. It also shows that a porous barrier need not be slots but can be of any porous body, such as a sintered metal structure 64. It might also be a screen. It should also be noted that the porous barrier need not be flat. In fact, in some instances it may be preferred that it be curved both radially and/or axially.

FIG. 4 shows a ribbon growth apparatus analogous to that shown in FIG. 1. However, the construction of the source in this embodiment of the invention provides means for continuously circulating a different means and adding more solute to the source. FIGS. 5 and 6 show the source in greater detail. The source is a substantially annular closed container 68 having a flat upper surface. One portion 72 of this flat surface has a plurality of parallel longitudinally oriented slots therein, similar to those already described providing a porous partition between the solvent and the solute. It is registered beneath the growth interface in the manner already described. A heater 74 extends down through an opening 76 into the annulus and extends around and under the porous portion 72, lying beneath the growth interface. Opening 76 is also large enough to accommodate impeller 78 which continuously recirculates the solute in annulus 68 to maintain its temperature and concentration uniform throughout. The annulus is positioned within the melt in support member 80. As the solute is consumed during ribbon growth, or as solvent concentration in the annulus rises, additional solute can be added by means of feeder tube 82, when spring-biased gate 84 is opened.

The preferred temperature and rate at which crystals should be grown will obviously be a function of the solvent system which is employed, as well as the quality of crystal desired. Solvents for use in growing germanium crystals include indium, gold, silver and copper. Bismuth crystals can be grown with silver as a solvent. Silicon crystals can be grown in gold, silver and aluminum solvents. Antimony and tellurium crystals can be grown with gold as a solvent. Bismuth can be used as a solvent to grow crystals of copper, indium and mercury. Tin crystals can be grown with iron as a solvent. Such crystals will contain varying minor amounts of the solvent metal.

In view of the foregoing, it can be appreciated that this invention is especially useful for horizontally pulling thin, flat crystalline ribbons. However, it should also be acknowledged that it can be used in the more conventional vertical Czochralski crystal-growing technique. Crystal boules of any size suitable cross section can be conveniently vertically pulled on a substantially continuous basis. In such instance, the crystal-pulling means, itself, will function as a heat sink to conductively remove heat from the crystal. The cooler parts of the crystal-growing apparatus will also absorb heat radiated from the freshly grown crystal. Hence, no special heat sink need be provided.

It is to be understood that although this invention has been described in connection with certain specific examples thereof no limitation is intended thereby except as defined by the appended claims.

I claim:

1. An apparatus for horizontally growing crystalline bodies which comprises means for containing a liquid melt of a solvent metal and a solute, means for maintaining said melt at a selected temperature, means for holding a crystalline seed in contact with said melt to form a seed-melt interface, means for withdrawing heat from said melt through said seed to precipitate solute onto said seed at said interface, solute

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source means for substantially continuously introducing solute into said melt adjacent said interface to maintain the solute concentration in said melt substantially constant during solute precipitation onto said seed, means for horizontally pulling said seed away from said melt at a rate commensurate with the rate of progressive melt solidification onto said seed means for maintaining the surface of the melt at a substantially constant level during crystal growth, said solute-introducing means being an immovably supported, substantially closed container having a surface portion within the melt under the seed-melt contact interface, said surface portion being substantially directly below and within about one-eighth inch below the seed-melt interface, and said surface portion having at least one opening therein through which solute diffuses to the seed-melt surface.

2. The apparatus for growing crystalline bodies as defined in claim 1 wherein means is provided for maintaining the surface of the melt at a substantially constant level during crystal growth, and the solute introducing means is an immovably supported, substantially closed container within the melt having a surface portion under the seed-melt contact interface, the surface portion is generally parallel to and within about one-eighth inch below the seed-melt interface, and the surface portion has a porous opening therein through which solute diffuses to the seed-melt interface.

3. An apparatus for horizontally grooving a crystalline ribbonlike body which comprises means for containing a liquid melt of a solvent metal and a solute, means for maintaining said melt at a selected temperature, means for maintaining said melt at a substantially constant level, means for horizontally holding a crystalline seed with one end in contact with

said melt, means for removing the heat of fusion from said one end of said seed to produce progressive precipitation of said solute on said one end, means for suppressing the net loss of the heat of fusion from the balance of said seed contacting said melt to regulate progressive precipitation of said solute thereon, a substantially closed solute container means disposed within the melt container and having a surface portion generally parallel to and within about one-eighth inch below said melt level, a porous opening in said surface portion through which solute passes to substantially continuously introduce solute into said melt under said seed-melt contact region, and means for horizontally pulling said seed away from said melt at a rate commensurate with the rate of progressive solute precipitation on said one end thereof to thereby produce a flat crystalline ribbon of predetermined thickness.

4. The apparatus for horizontally growing a crystalline ribbonlike body as defined in claim 3 wherein the surface portion of the solute container is generally flat and includes a thin wall and the porous opening in said flat surface portion is at least one slot lying transverse to the direction of crystal pull.

5. The apparatus for horizontally growing a crystalline ribbonlike body as defined in claim 3 wherein the surface portion of the solute container is generally flat and includes a thin porous sheet through which the solute diffuses into the melt.

6. The apparatus for horizontally growing a crystalline ribbonlike body as defined in claim 3 wherein the surface portion of the solute container under the seed-melt contact interface is grooved in the direction of crystal pull to produce a ribbon of predetermined cross section.

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