

May 14, 1957 J. K. DELANO 2,791,813 APPARATUS AND METHOD FOR GROWING CRYSTALS HAVING A CONTROLLED INTERNAL JUNCTION STRUCTURE Filed Oct. 28, 1954

2,791,813 Patented May 14, 1957

1

2,791,813

APPARATUS AND METHOD FOR GROWING CRYSTALS HAVING A CONTROLLED IN-TERNAL JUNCTION STRUCTURE

James K. Delano, Rye, N. Y.

Application October 28, 1954, Serial No. 465,200

6 Claims. (Cl. 22-58)

1

This invention relates to structure and method to predetermine the internal boundary or juncture definition of a growing crystal and more particularly to the structure of the vessel in which the crystal is grown, in order to create, in respect to a major-growth axis thereof, symmetrically angled strata or laminae, if the composition of the melt grows in arrays of strata or if the melt composition grows in clusters of discreet orientation, the practice of this invention forms at substantially precise planes within the growing crystal, junctures of differently angled growth of the crystal.

These multiple junctures, thus formed, are most desirable for certain usages in the electrical arts, notably in pyro and thermo electric generation, and the like. The angulated junctures of stratified growth or junctures formed by the differently orientated clusters induced by this invention, when using such metallic solutions as those composed of bismuth, antimony and the like, produce multiple energy-junctures within the crystal body, formed in extending repetition along the extent of its growth.

It is to be noted then, that if a particular melt grows 35 in strata formation that two predetermined growths of distinct inclination of strata, one to the other, on contacting in their growth as they enter the unitary or main portion of the crystal growing vessel, form a single repetitive juncture, normally bisecting the vertical axis of the vessel at their juncture faces. Three predetermined growth-sources, from respective radial seeding points, will produce three juncture faces, and so on, as the respective substantially radially disposed and predetermined seeding points or cornucopias are increased in number. 45 Each resulting precise seed-growth issuing from its capillary cornucopia forms a segment in the main body of the vessel of its own particular inclination of crystal growth in respect to the other segments. In the case of a cluster-like growth this same angulated juncture-structure 50 takes form along planes of substantially predetermined position within the crystal.

To properly utilize this invention and its novel plurality of junctured strata or cluster contacting junctures the crystal, after being grown, is cut in sections, to make these junctures available for use in the electrical arts, the plane of each section so cut being substantially normal to the major axis of the crystal's growth.

The juncture faces of the crystal may be formed according to the teaching of this invention, composed of a single metal or in combination of two or more distinct metals or alloys of different composition.

It is well known that Messrs. Obreimov and Schubnikov, see Z. Physik 1924, as well as Professor Bridgman of Harvard University in the early twenties of this century devised and originated either a vessel, tapered at its end to a capillary point or formed with a length in the crystal growing vessel of a capillary section, the aim being to allow only one lone seed to survive therefrom and to perpetuate its particular growth to form a unitary large crystal. 70

This invention is an elaboration of this theme to create a specific crystal structure having innumerable junctures formed by dissimilar angulated strata or orientated clusters as and for the purposes set forth, whereas Messrs. Obreimov, Schubinkov and Bridgman used their lone seed surviving systems to grow large single structure, or homogenous, crystals.

The objects of this invention are:

5

 The growth of a crystal body wherein pairs or a plurality of segmentally disposed strata or clusters of differential inclination or orientation are formed to gen-10 erate predetermined disposed junctures along the contacting faces of such strata or clusters.

2. The generation within the body of a growing crystal of a plurality of junctures or dissimilar inclinations formed in a plane substantially parallel with the axis of growth, the subsequent sectionalizing of said crystal along a plane normal to its axis of growth, the junctures in said cut sections defining a plurality of pole faces capable of generating opposite polarities when subjected to thermal gradients.

3. A crystal growing vessel or apparatus adapted to grow a crystal of the internal structure as described in object No. 1.

Further objects of my invention are implicit in the accompanying specifications and drawings, in which: Figure 1 is a sectional elevation of the invention.

Figure 2 is a section taken along the line 2-2 in Figure 1.

Figure 3 is a section taken along the line 3-3 in Figure 1 without any crystal growing melt therein to show 30 the interior contours of the vessel.

Figure 4 is a sectional view of the resulting crystal growth from a vessel as seen in Figure 1 and indicating the lines in dot-dash of the subsequent sectionalizing of the crystal.

Figure 5 is a section comparable to Figure 2, but the vessel made of metal and formed to be parted along its mid-axis for easy extraction therefrom of the grown crystal.

Figure 6 is a plan view, partially in section, of a 40 vessel having four arced capillary seeding terminals instead of two seeding terminals as seen in Figure 1.

Figure 7 is an elevation partially in section of a modification of the invention to obtain predetermined junctures in a crystal body.

Referring to Figure 1, numeral 1 is the vessel in which the crystal of specific structure is grown. Numerals 2 and 3 are the radially formed cornucopias with capillary seedings terminals 5 and 6 preferably formed as ex-

tending divisions of the base of vessel 1. These extending divisions merge at 4 with vessel 1, which is seen in plan in Figure 3.

Around or in heating proximity to the extending divisions 5 and 6 of vessel 1 are positioned resistance coils 7 and 8 in series connection, one with the other, through lead wires 9 and 10 leading to electric supply terminals 40 and 41. A rheostat, 11, is interposed in lead wire 10 to control the heating effect from coils 2 and 3 in respect to seeding terminals 5 and 6 and the conically formed divisions 2 and 3. Likewise resistance coils 12, 14 and 16 are in similar heating relation with the main vessel 1 positioned one above the other, each of which being controlled as to their heating effect by rheostats 13, 15 and 17 respectively.

The operation of the crystal growing procedures of my invention is briefly as follows:

Vessel 1 is filled with a specific melt as previously defined and the several resistance coils viz.: 7-8, 12, 14 and 16 are energized to bring the melt to or slightly above its particular temperature necessary for a molten state. The rheostat 11 is now manipulated to reduce the temperature at the initial seed growth capillaries at 5 and 6. Due to the series winding of coils 7 and 8, a cooling factor of the same degree can be readily maintained at these divergent points, essential to a coincident starting of the seeding growth thereat. By a proper varying of the electrical energization of coils 12, 14 and 16 by control of rheostats, 13, 15 and 17 as the crystal growth progresses upwards 5 into the vessel 1, a proper gradient of temperature is maintained in the melt 21, care being taken to progressively lower the temperature of melt 21 as and at the critical point at which the actual growth of crystallization is taking place as it grows up through the divided extensions 10 2 and 3 into the body of vessel 1. The rate of growth due to the heating and cooling means illustrated can be controlled so that the twin growths are substantially equal as they progress through cornucopias 2 and 3 and contact each other and pass the apex 4 of the divisions in vessel 15 1 and the two growths form the juncture face 20 in extending array in vessel 1. The equal rate of growth of these two separate crystal growth-zones is very important to maintain juncture face 20 in vessel 1 at substantially in an axial midposition as is illustrated in Fig. 1 at numer- 20 al 20. Further describing and exemplifying the operation, as stated, various metals and alloys of different metals may be used, in the lower melting class metals such as antimony, bismuth, etc. For simplicity of describing the operation and the making of the joined finished bi-crystal I will select tin which is granulated and vessel 1 is filled through the central opening at the top, filling the extension arms 5, 6 and the central body about three-quarters full.

Current is now supplied to the heating coils 7, 8, 12, 14, 16 to heat vessel 1 and melt the contents and hold 30 the temperature slightly above the melting point. While in this molten state the vessel is shaken or vibrated which will cause any air or impurities to rise to the surface and allow the metal to settle to the extreme ends of the arms, any dross or oxides that are on the upper or open end of the central chamber can remain without affecting the result.

This system of temperature gradient control symbolized by rheostats 11, 13, 15 and 17 must be necessarily indexed by a similar series of thermometers (not shown) extend- 40 ing in comparable elevations with the respective heating coils 7-8, 12, 14 and 16 along the extent of vessel 1. The requirements for melting and crystallizing of many metals at higher temperatures beyond which resistance type of heating is to be noted and as these requirements are 45 known and available for melting at higher temperatures, drawings and descriptions were omitted from the specification. The method of melting and controlled cooling as described for the resistance type is the same for either type.

It has been proved by actual practice that in a conically formed capillary terminus of a vessel as above described and illustrated at 5 and 6 that there is a crowding out of other crystal seeds by the most favorably disposed or situated seed and that the angulation of this precise 55 surviving seed growth will persist even if the configuration, or axis of the extending vessel in which the crystal grows forms a 90-degree arc. The stratification or clusterorientation will not be altered as the crystal proceeds to grow therethrough.

In Figure 5 a modification of the unitary glass vessel 1 is shown, wherein vessel 1 is composed of two metallic ceramic halves respectively, 22 and 23, with extending flanged portions 24 and 25 suitably secured, one to the other. The melt 21, when it has crystallized as previously explained, may be easily extracted in toto by the parting of sections 22 and 23. Likewise the resistance coil as indicated by 26 to maintain the necessary temperature gradient as it follows the crystal growth is sustained in ceramic insulation 27 held by supports 28 and 29. It is 70 evident to those skilled in this art that these supports may be movable up or down along the axis of vessel 1 in accordance with the desired shifting temperature gradient so essential to the equalized crystal growth.

In Figure 6 is shown in plan and partially in section 75

a crystal growing vessel having four distinct seeding terminals viz.: 30, 31, 32 and 33, formed by the radially disposed arcuate members 30a, 31a, 32a and 33a, all of equal length, which together form the closure for the base of the circular main vessel, portion 42, shown in section. The respective coincident crystal growths initiated at capillary terminals 30, 31, 32 and 33 under identical temperature gradient control as heretofore described, produce four different angulated crystal growths due to the divergent radial positions of the members 30a, 31a, 32*a* and 33*a*. The respective crystal growths extend under their equal rate of growth until they arrive into the unitary circular portion 42 of the vessel whereat they form junctured-segments as indicated by numerals 35, 36, 37

and 38, composed, if the melt forms a stratified growth of differently angulated faced junctures or if the melt forms into a series of clusters, create juncture faces of differently orientated crystal clusters.

Referring to Figure 7, this illustrates a modification of the invention. Instead of relying on radially formed extending portions which terminate at capillary ends as seen at 5 and 6 in Figure 1, to obtain a plurality of differentially angulated strata or clusters of crystal orientations therefrom to produce the juncture faces 20 in repetitive array 25 in vessel 1, the desired differential of strata or cluster orientation may be produced in members 43 and 44 by positioning a plural seeding of crystals, that is, a small fragment of crystal as seen at numerals 57 and 58, wherein by a prior microscopic examination thereof, it has been ascertained that the inclination of the crystal seeding fragments are such and such and that the crystal fragments have a cluster orientation or a strata formation. In this manner, by the proper placement of crystal seedings 57 and 58 opposite the open ended conical capillary openings 35 45 and 46 respectively, proper differential inclination or orientation, one in respect to the other, can be obtained, resulting in the desired junctured-growth.

In brief, the operation is as follows, and in substance identical to conditions prevailing in Figure 1. When the vessel 42 is filled with a melt 21 similar to that from which the crystal seedings 57 and 58 were grown and electric resistance coils 48, 49 and 55 are energized through rheostats 50 and 51 from terminals 52, 53 and 52' and 53' in extent similar to coils 7-8, 12, 14 and 16 as has already been described, the crystal seedings 57 and 58 will propagate through portions 43 and 44 past apex 54 and grow to produce juncture 20 from the resulting dual growths as represented by numerals 18 and 19, similar to those junctures 20 already described. It is noted that 50 the crystal seeding fragments 57 and 58 are physically sustained and forced tight against the capillary orifices 45 and 46 in the conical tubular extensions 43 and 44 of vessel 42 by a block 47 which, due to its mass, acts as a chilling agent as well as a physical support for seedings 57 and 58, so that the temperature of seedings 57 and 58 is kept below their melting point as when resistance coils 48, 49 and 55 initially heat up to a molten state the melt 21 in vessel 42.

It is to be noted that the degree of laminations or strata 60 indicated in Figures 1, 4 and 7 by the numerals 18 and 19 are purely illustrative and are shown only to indicate their approximate inclination one to the other.

In Figure 4, the dot and dash lines 60 and 61 are the cutting lines normal to the growth of the crystal through which a section of the crystal is cut. When wires 63 and 64 are secured to section 65, so cut, and a thermal gradient is present, voltage is generated, as indicated.

65

Figs. 1, 6, 7 may be used for producing bicrystal sections of distinctly different metals and alloys. By employing a different metal in the separate arms and a mixture of the two selected metals in the tube or center section, the melt will on crystallizing cause the mixed metals to join its own type and set up a boundary between the two growths.

4

What I desire to protect by U. S. Letters Patent is encompassed in the following claims.

I claim:

1. The method of growing in a vessel predetermined junctures in a crystal grown from a melt which consists 5 in initiating substantially coincident but separated plural seed-growths of differential stratification in the melt thereof, continually promoting respective seed-growths therefrom by regulated heating to rise into a single compartment of said vessel at substantially equal growth rates 10 whereby the crystal formed in said vessel is composed of component portions of said plurality of coincident but initially separate growths, thereby forming junctures at their respective contacting faces within said crystal.

2. The method of growing in a vessel predetermined 15 junctures in a crystal grown from a melt which consists in initiating substantially coincident but separated plural seedings in the melt thereof from a plurality of radially conically formed terminations of said vessel, continually promoting respective surviving seed-growths therefrom by 20 regulated heating to rise into a single compartment of said vessel from said terminations at substantially equal growth rates whereby the crystal formed in said vessel is composed of component portions of said plurality of coincident but initially separate growths, thereby forming 25 junctures at their respective contacting faces.

3. An apparatus for growing crystals from a melt comprising a vessel, a plurality of depending substantially conical tubular portions forming in aggregate the closure of the base of said vessel, means to heat said vessel and 30 said extending portions thereof and means to control said heating means and adapted to provide a gradient of temperature along the extent of said apparatus.

4. In a vessel of the character described, a substantially

a plurality of radially and downwardly disposed substantially conically shaped portions forming closures at the opposite end of said vessel, each of said radially disposed tubular portions communicating and opening into said substantially tubular end section.

5. In a vessel of the character described for growing crystals, a substantially tubular main body section forming the upper part of said vessel and a plurality of curved tubular portions of substantially conical shape communicating with the bottom of said main tubular body portion and with each other and each of said conical tubular portions being closed at its bottom or pointed end.

6. In a vessel of the character described, a substantially tubular section comprising one end of said vessel, a plurality of radially and downwardly disposed substantially conically shaped portions forming closures at the opposite end of said vessel, each of said radially disposed tubular portions communicating and opening into said substantially tubular end section, means to heat said vessel and said extending portions thereof, and means to control said heating means and adapted to provide a gradient of temperature along the extent of said apparatus.

References Cited in the file of this patent UNITED STATES PATENTS

1,256,929	Schaller Feb. 19, 1918
1,733,752	Ramage Oct. 29, 1929
1,793,672	Bridgman Feb. 24, 1931
2,683,676	Little et al July 13, 1954
2,694,024	Bond et al Nov. 9, 1954

OTHER REFERENCES

Article by Chalmers, publ. in Proc. Royal Society of tubular section comprising one end of said vessel and 35 London, series A, vol. 162, pp. 120-127, 1937.