United States Patent [19]
Elkins et al.

[11] **3,768,983**
[45] **Oct. 30, 1973**

[54] SINGLE CRYSTAL BERYLLIUM OXIDE GROWTH FROM CALCIUM OXIDE-BERYLLIUM OXIDE MELTS

[75] Inventors: **Perry E. Elkins**, Santa Ana; **Stanley B. Austerman**, Villa Park, both of Calif.

[73] Assignee: **North American Rockwell Corporation**, El Segundo, Calif.

[22] Filed: **Nov. 3, 1971**

[21] Appl. No.: **195,365**

[52] **U.S. Cl.** .... **23/301 SP**, 23/305, 423/122, 423/624

[51] **Int. Cl.** **B01j 17/20**

[58] **Field of Search** .... 23/305, 301 R, 300, 23/301 SP, 304; 423/624, 122, 134, 263, 275; 148/22

[56] **References Cited**

UNITED STATES PATENTS

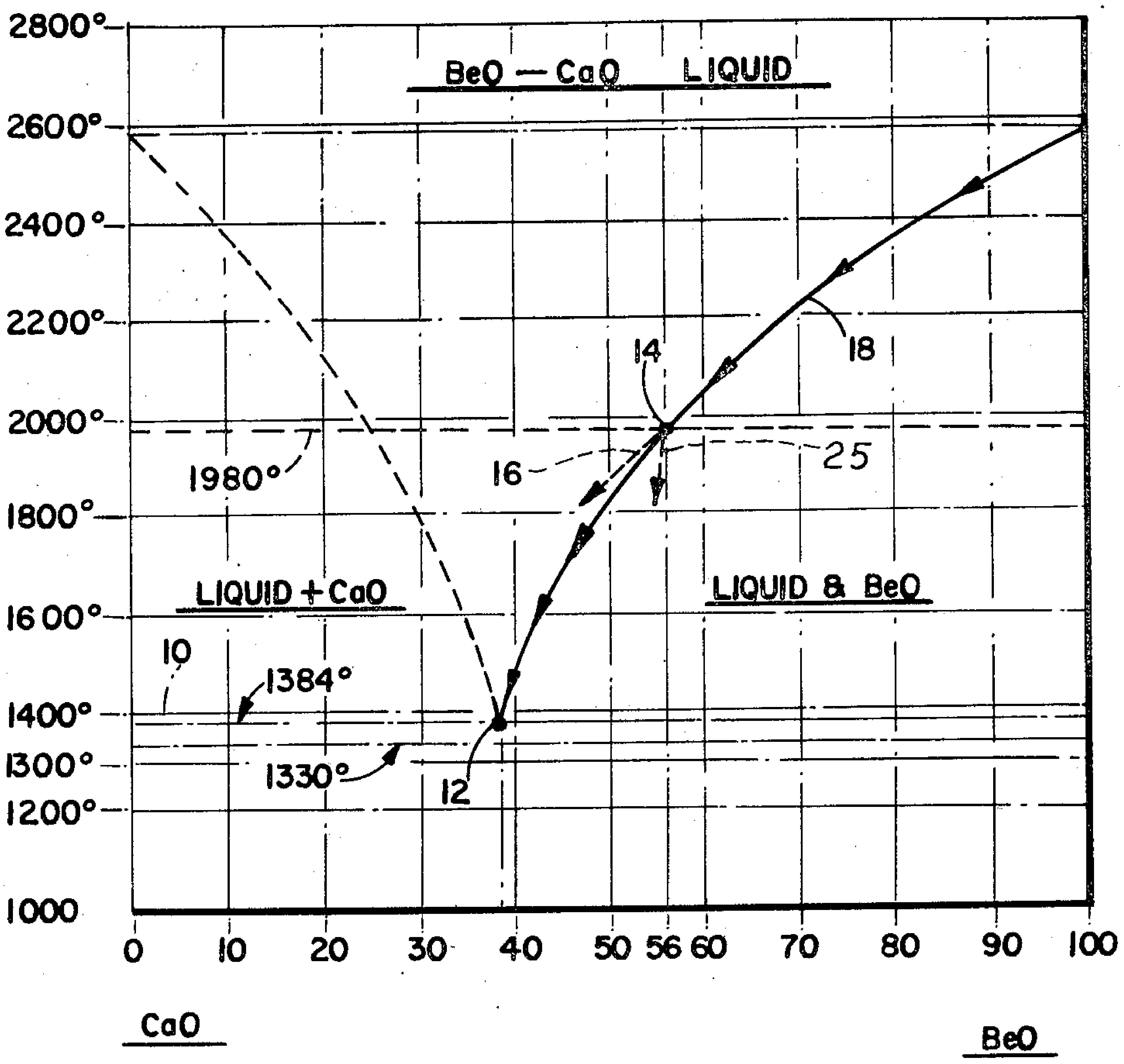
2,848,310	8/1958	Remeika	23/305
3,234,135	2/1966	Ballman et al.	23/305
3,341,302	9/1967	Flanigen et al.	23/301 R
3,345,133	10/1967	Steele et al.	23/304
3,490,959	1/1970	Krock et al.	148/22
3,595,803	7/1971	Dugger	23/305
3,650,702	3/1972	Swets	23/300

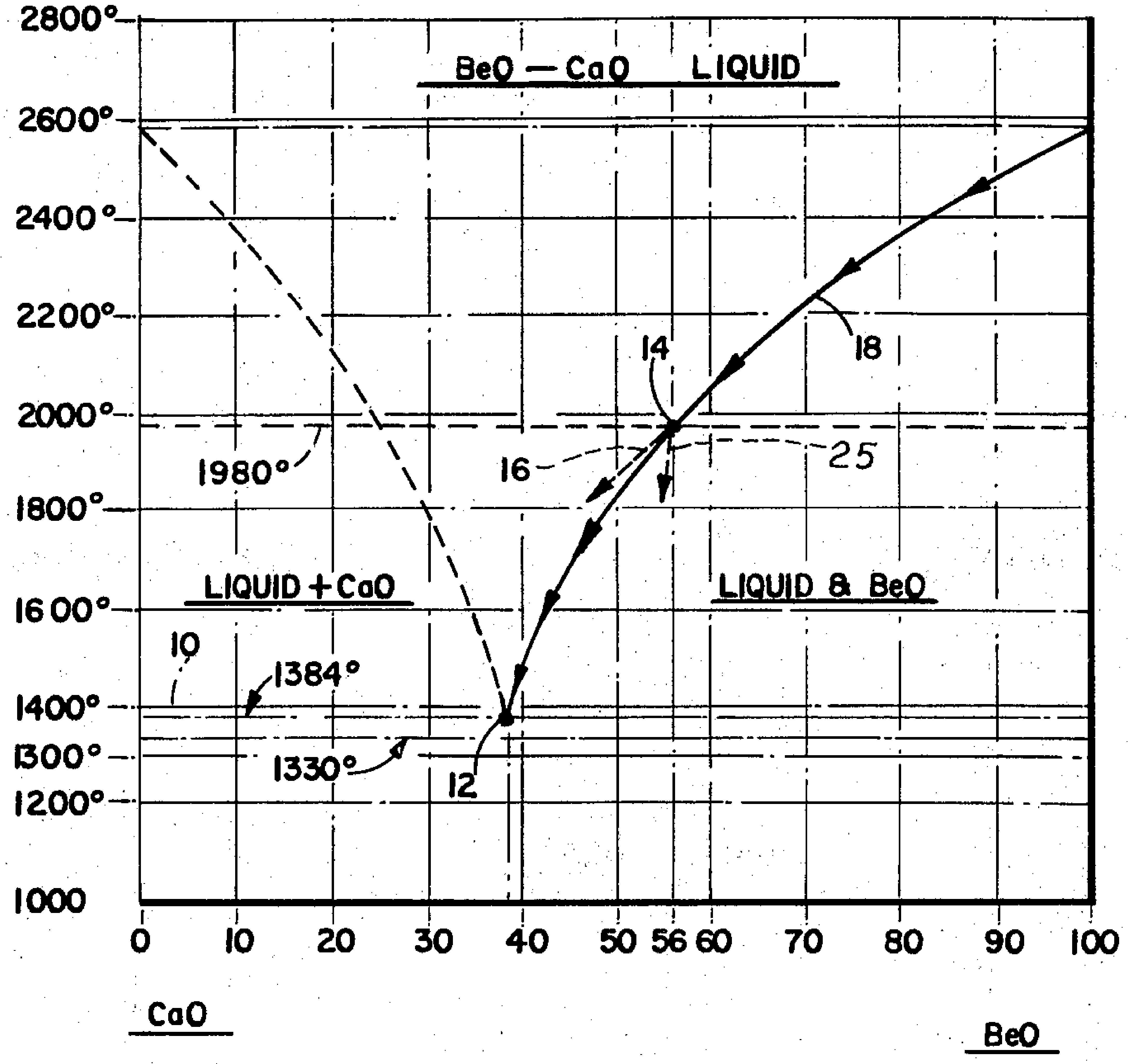
Primary Examiner—Norman Yudkoff
Assistant Examiner—R. T. Foster
Attorney—L. Lee Humphries et al.

[57] **ABSTRACT**

A process for growing large single crystals substantially free of surface inclusions within several days is disclosed. This process involves the concept of promoting further growth on seed crystals from a melt composition of suitable oxides which will form a eutectic. Growth occurs as the crystal seed is rotated and pulled slowly from the melt composition. The temperature decrease of said melt is such that the temperature can be defined by the liquidus curve of the melt composition phase diagram. Growing single crystal beryllium oxide at a temperature of about 1,980° C from a melt composition having 56 weight percent beryllium oxide and 44 weight percent calcium oxide is an example of this process.

8 Claims, 1 Drawing Figure





INVENTORS
PERRY E. ELKINS
STANLEY B. AUSTERMAN

BY Joseph E. Kieninger
ATTORNEY

SINGLE CRYSTAL BERYLLIUM OXIDE GROWTH FROM CALCIUM OXIDE-BERYLLIUM OXIDE MELTS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to crystal growing and more particularly to a method of growing single crystals from a melt composition.

2. Description of Prior Art

The traditional Czochralski method of growing crystals from a liquid melt composition is well known. In this process the material from which a single crystal is to be grown is placed into a crucible and melted to form a liquid melt. The material of this melt is usually of substantially the same material as the seed crystal. The temperature of the liquid melt is maintained 1° to 2° above the melting point of the material. A single crystal seed is lowered into the liquid. Upon contact the liquid starts to solidify onto the seed. The seed is then slowly pulled from the liquid while being rotated. Continued solidification of the liquid onto the seed results in the growth of a single crystal.

The Czochralski method of growing single crystals of, for example, beryllium oxide (BeO) increases the danger of crystal cracks in the BeO. In this example, a BeO melt composition must be maintained at a temperature of about 2,450° C, the melting point of BeO. As the single crystal BeO is cooled below 2,050° C, the reported Alpha-Beta phase transition of BeO, the crystal damage that normally accompanies this phase transformation can occur thereby rendering a low yield of usuable BeO crystals.

The Alpha-Beta phase transition of BeO is also known as a crystal structure phase transformation from high temperature tetragonal to low temperature hexagonal crystal structure.

Another disadvantage of growing in particular BeO single crystals by the Czochralski method is that there is presently a very limited number of suitable crucible materials, e.g. tungsten, molybdenum and iridium, to accommodate molten BeO at its melting temperature of 2,450° C.

The flux growth method is another well known process for growing single crystals. The flux growth method differs from the Czochralski process in that the material that is to be grown is dissolved in a suitable flux, such as lithium polymolybdate. In the flux method a crucible containing a liquid solution of flux and said material is placed in a furnace. Single crystals are precipitated by lowering the temperature of the furnace causing the flux solution to become supersaturated with the material. As the material begins to precipitate out of the solution small single crystals nucleate and grow on the crucible floor and walls.

The primary obstacle in growing single crystals by the flux process is that presently good quality crystals cannot consistently be grown. The flux process produces a low yield of usuable crystals as a result of flux inclusions and surface irregularities in the crystals. Another disadvantage of the flux process is that it takes several months to grow single crystals which are of any useful size.

SUMMARY OF THE INVENTION

This invention relates to a process of growing single crystals by promoting further growing on a single crystal seed from a melt composition. The melt composition contains a mixture of selected oxides which can form a eutectic composition. The advantage of such a melt composition is that it melts at a lower temperature than a melt composition of only the material to be crystallized. The temperature of the melt composition is lowered to the liquidus temperature, that is, where solid material with the same composition as the seed comes out of the solution. When the temperature of the melt composition is stabilized at the liquidus temperature, a seed crystal is lowered into the surface of the melt. Material of the same type as the seed precipitates from the melt composition and grows on the seed crystal. Growth of the seed material from the melt composition occurs while the seed is rotated and slowly pulled from the melt. During the growth process on the crystal, the seed type material concentration in the melt is reduced; and the melt temperature is lowered such that the temperature can be defined by the liquidus curve of the respective melt composition phase diagram. After 10 to 15 hours of growth, a large single crystal boule substantially free of inclusions is recovered from the melt.

An example of a preferred embodiment of this invention is to grow a beryllium oxide, BeO, single crystal from a melt composition containing 56 weight percent BeO and 44 weight percent CaO at a temperature of 1,980° C.

Other objects and advantages of this invention will be apparent from the following detailed description wherein a preferred embodiment of the present invention is clearly shown.

BRIEF DESCRIPTION OF THE DRAWING

The drawing shows a phase diagram of a BeO-CaO mixture.

DETAILED DESCRIPTION

This invention involves a process of growing large single crystals by promoting the growth on seed crystals from a melt containing a mixture of suitable oxides. As shown in the drawing, the BeO-CaO melt will be used to describe the growth of beryllium oxide, BeO, crystals by this process. BeO single crystals can be grown from BeO-CaO melt compositions containing 40 or more weight percent BeO. Preferably, the mixture should melt below 2,050° C, the reported Alpha-Beta phase transition temperature of BeO which usually causes crystal damage. A melt composition having 56 weight percent BeO and 44 weight percent CaO as shown in the drawing is such a melt composition. This melt composition does not exceed the Alpha-Beta phase transformation temperature of BeO and therefore is not subjected to the risk of crystal destruction. It should also be noted that by utilizing this type of mixture the melt composition temperature is substantially below 2,450° C, the melting temperature of BeO.

The mixture containing, for example, 56 weight percent BeO and 44 weight percent CaO is heated to form a melt in an iridium crucible at about 1,980° C, the liquidus temperature **14** where solid BeO seed material comes out of the melt.

After the melt composition is stabilized at the liquidus temperature **14**, a BeO seed crystal is lowered into the surface of the melt. The BeO crystal seed is attached to a pull rod which is operated by conventional mechanical means. Localized cooling of the melt composition below the liquidus temperature **14** in the area of the BeO seed results in BeO material coming out of the super-saturated melt and precipitating onto the single crystal BeO seed.

The growth process of BeO onto the seed continues while the seed is rotated and slowly pulled from the melt until equilibrium is re-established between the seed and the melt. During the BeO growth on the seed, the concentration of the seed material in the melt is reduced. The melt temperature is then lowered to conform to the liquidus curve **18** of the BaO-CaO phase diagram as illustrated in the drawing.

The lowering of the melt interface temperature is critical for growth to proceed. That is, when BeO is removed from the melt, the melt composition becomes richer in the other oxide component CaO and the liquidus temperature **14** decreases. If the temperature is lowered at too slow a rate during the pulling of the crystal seed, the melt-solid temperature represented by dashed arrow **16** becomes higher than the instantaneous liquidus temperature **14** of the melt composition resulting in the crystal breaking away from the melt causing all growth to cease.

Conversely, if the temperature is lowered at too rapid a rate for the pull rate of the crystal, the melt-solid temperature **25**- tends to become substantially lower than the liquidus temperature **14** as illustrated. The result is excessive super-saturation resulting in spontaneous nucleation of BeO throughout the melt and growth on the seed becomes polycrystalline.

The preferred condition is to couple the pull rate of the crystal seed and temperature decrease such that the actual melt-solid temperature is only 2° or 3° lower than the temperature on the liquidus line **18.** Thus, conditions at the crystal-melt interface would follow the liquidus curve **18** of the phase diagram during the growth run. As the system is further cooled from the liquidus temperature **14** towards the eutectic temperature **10,** BeO continues to crystallize until reaching the eutectic temperature **10,** the temperature at which the eutectic mixture **12** is formed.

After a 15 hour growth run utilizing the foregoing process, a large BeO single crystal substantially free of surface inclusions is pulled from the melt composition.

This invention is applicable for growing single crystals in the form of boules or thin wafers. The foregoing process is utilized when growing bowles as contrasted to thin wafers. When growing thin wafers, the seed crystal is not pulled from the melt, rather the melt temperature is lowered slowly at a rate of about 10° to 20° C per hour. A preferred rate is 15° C per hour. During the temperature decrease BeO will come out of the melt composition and deposit on the seed. Large wafers have been grown in 10 hours on the surface of the melt. The single crystal BeO wafer can be recovered from the melt by pulling the pull rod out with the attached crystal at a rapid rate.

EXAMPLE I

A mixture containing 50 weight percent BeO and **50** weight percent CaO is melted in an iridium crucible at a temperature of 1,900° C. The temperature of the melt is lowered to about 1,800° C, the liquidus temperature of the melt. A BeO seed crystal is lowered into the melt by conventional mechanical means. The melt in the area of the seed was cooled below the liquidus temperature causing BeO to come out of the melt and precipitate onto the BeO seed. The BeO seed continued to grow while it was rotated and slowly withdrawn from the melt. The temperature of the melt was decreased during the growth of the BeO seed to follow the liquidus line of the phase diagram of the BeO-CaO system. A large BeO single crystal boule weighing 7½ grams substantially free of surface inclusions was grown in 24 hours.

EXAMPLE II

A mixture containing 56 weight percent BeO and 44 weight percent CaO was melted in an iridium crucible. The temperature of the melt was lowered to about 1,980° C, the liquidus temperature of the melt composition. A BeO seed crystal was lowered into the upper portion of the melt composition by conventional mechanical means.

The melt region near the crystal seed was cooled to below the liquidus temperature. BeO came out of the melt and precipitated onto the BeO seed. The melt temperature was lowered slowly at a rate of about 10° to 20° C per hour. After 10 hours a large wafer was grown on the surface of the melt. The single crystal BeO wafer was then removed from the melt by pulling out the seed rod and the attached seed crystal at a rapid rate.

This invention permits BeO crystals to be grown from other melts such as strontium oxide, SrO,-beryllium oxide, BeO, and barium oxide, BaO, -beryllium oxide, BeO. CaO crystals can also be grown from a calcium oxide, CaO, -beryllium oxide, BeO melt where the melt composition is less than **40** weight percent BeO and the mixture of CaO-BeO will melt below the CaO phase transformation temperature. By utilizing this method, many oxides can be grown in crystal form such as strontium oxide could be grown from SrO-BeO melts or titanium dioxide, TiO_2, could be grown from TiO_2-BeO melts.

A third oxide can be added to a mixture of BeO-CaO to improve crystal quality. Oxide such as Ba, Sr, Mg, Al, Na, K, Y, La, and the rare earth elements may shift the eutectic composition and the melting temperature thereof and thereby improve crystal quality.

We claim:

1. A process for growing beryllium oxide single crystals comprising the steps of

providing a mixture containing at least beryllium oxide and calcium oxide, wherein the concentration of beryllium oxide in said mixture exceeds the beryllium oxide concentration required for a eutectic composition of beryllium oxide-calcium oxide,

heating said first mixture to form a melt,

lowering the temperature of said melt to its liquidus temperature, and

placing a beryllium oxide seed crystal into the surface of said melt whereby beryllium oxide from said melt grows on said seed crystal.

2. The process recited in claim **1** whereby said seed crystal is slowly rotated and slowly withdrawn from the melt during growth to form a boule about the seed crystal.

3. The process recited in claim **1** wherein the melt temperature is lowered at a rate of about 15° C per hour.

4. The process recited in claim **1** wherein said first mixture includes a third oxide compound.

5. The process recited in claim 4 wherein said third oxide compound is selected from the group consisting of barium, strontium, magnesium, aluminum, sodium, potassium and the rare earth elements.

6. The process recited in claim 1 wherein the beryllium oxide concentration in said first mixture varies from 40 to 70 weight percent.

7. The process recited in claim 1 including the step of continuously lowering the temperature of said melt while beryllium oxide from said melt grows on said seed crystal to cause the temperature of the melt to substantially follow the liquidus temperature curve of the melt towards the eutectic temperature.

8. The process recited in claim 1 wherein a thin wafer of single crystal material is formed on the surface of said melt adjacent to said seed crystal.

* * * * *