

April 11, 1961

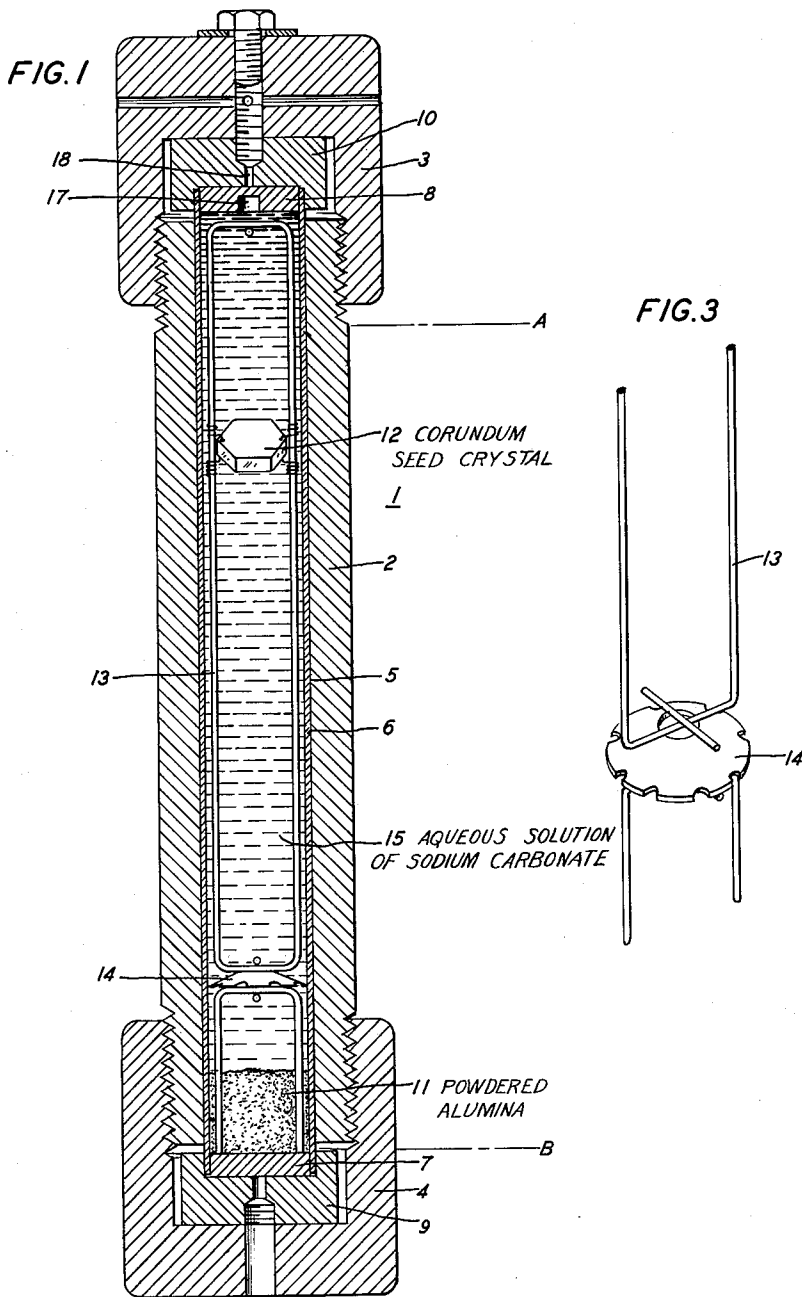
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2,979,413

METHOD OF GROWING CORUNDUM CRYSTALS

Filed June 14, 1957

2 Sheets-Sheet 1



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2 Sheets-Sheet 2

FIG. 2

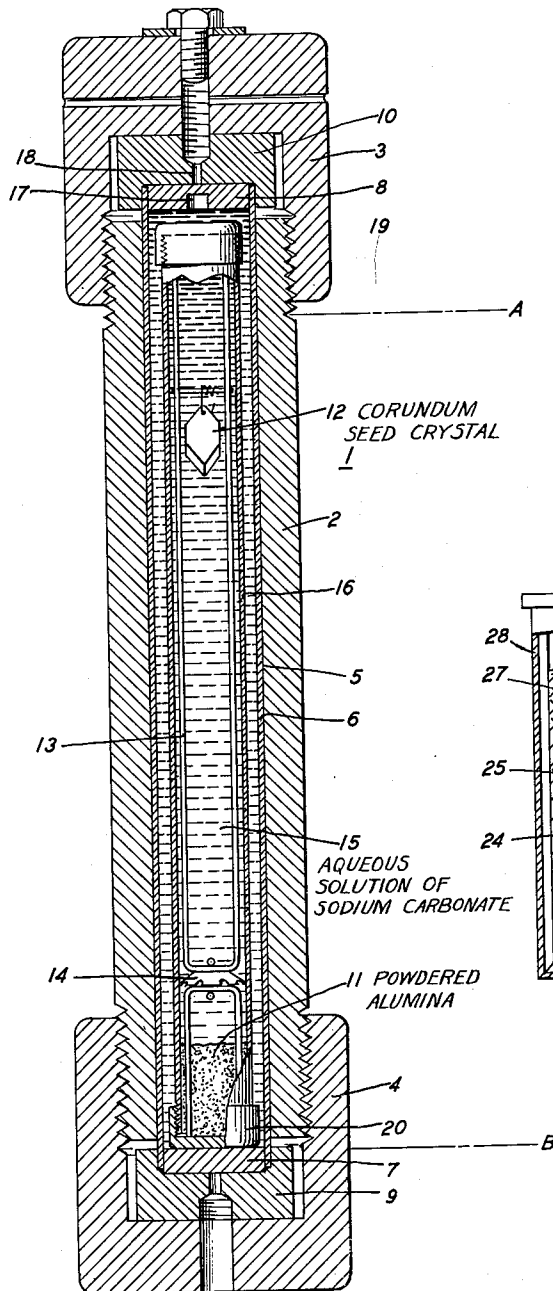
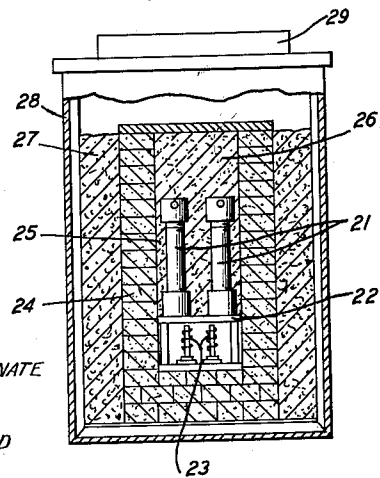


FIG. 4



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1

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METHOD OF GROWING CORUNDUM CRYSTALS

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This invention relates to methods for growing crystals of corundum. More particularly it relates to methods of growing large single crystals of corundum, of a size suitable for use as gems or for scientific and commercial uses, from seeds in aqueous media under high temperatures and pressures.

Large crystals of corundum—so called synthetic sapphire—are now grown in the art by a flame fusion process (the Verneuil process) in which Al_2O_3 is fed through a high temperature arc or flame and deposited on a boule. Crystals of corundum have also been prepared from melts of Al_2O_3 . Because of the large thermal gradients inherent in these processes, in which a solid is crystallized from a super-cooled molten material, the crystals obtained may be badly strained. Further, the growth of crystals by the more successful Verneuil method is largely constrained to rodlike growth in one dimension. By the hydrothermal synthesis of single crystal corundum to be herein described, strain free materials may be more readily obtained, and growth of the crystals can be more easily made to occur in three dimensions, so that large crystals other than rods can be prepared.

Corundum (alpha-alumina) has been synthesized from other aluminum-oxygen compounds before in the art. The patent to James W. Newsome, No. 2,642,337, granted June 16, 1953, for example, describes the conversion of alumina trihydrate ($Al_2O_3 \cdot 3H_2O$) or alumina monohydrate ($Al_2O_3 \cdot H_2O$) to corundum by heating in steam at a pressure below 2500 pounds per square inch. Similarly, the paper "A Hydrothermal Study of Equilibria in the System Alumina-Water," by A. W. Laubengayer and R. S. Weisz, Journal of American Chemical Society, 65 [2] 247-50 (1943), describes earlier attempts to synthesize corundum, and reports the hydrothermal preparation of corundum from boehmite, diaspore, gibbsite and gamma-alumina. All of the prior art processes for synthesizing corundum, however, refer only to in situ conversions of the starting material. A method which utilizes seed crystal as a nucleus on which to crystallize further material—which is essential to the controlled growth of crystals of significant size—has not heretofore existed in the art.

By the process of the present invention, however, it is possible to develop controlled growth of large corundum crystals at a rate of about 5 mils per day, on a selected crystal face or faces, and to incorporate into the crystal materials other than alumina, which change or enhance the properties of the crystals. In the process, alumina or aluminum hydrates are used as solid nutrients which are partially dissolved in an aqueous medium. The growth of the seed crystal is promoted by maintaining a temperature differential between the aqueous medium in the vicinity of the seed crystal and the medium in the vicinity of the nutrient solids. The solid nutrients, dissolved in solvent at the higher temperature, are precipitated on the seed crystal at the lower temperature.

2

The process of growing corundum is carried out at relatively high temperatures and pressures. Suitable equipment for creating, maintaining, and withstanding the conditions is known in the art, and is described below.

Fig. 1 is a front elevation in section of a pressure-resistant autoclave or bomb and liner which can be used in the hydrothermal synthesis of sapphire;

Fig. 2 is a front view in section of an autoclave, liner and inner liner which are useful when corundum crystals of particularly high purity are grown;

Fig. 3 is a perspective view of a baffle and wire support which are conveniently used with the apparatus of Figs. 1 and 2; and

Fig. 4 is a front elevation, partly in section, of a furnace in which several of the autoclave assemblies of Figs. 1 and 2 can be conveniently heated.

In the apparatus of Fig. 1 is shown pressure-resistant autoclave 1, made up of a heavy cylindrical tube 2 having caps 3 and 4 screwed on each end. Fitting within the bore of tube 2 is an expandable cylindrical bomb liner 5 made up of a cylindrical steel tube 6 into the ends of which are fitted circular end plates 7 and 8. The end plates are fitted into tube 6 and welded thereto, as with a helium arc torch, and then machined flush with the outer diameter of tube 6. Retainer caps 9 and 10 are forced over the ends of the liner 5 after the liner has been placed in the bomb tube 2. Screw caps 3 and 4 are then screwed on.

After one end plate 7 has been welded into position, liner 5 is charged with nutrient solids 11, for example powdered alumina or an aluminum hydroxide precipitate. One or more corundum seed crystals 12 are inserted, mounted on wire frame 13 which may conveniently have a baffle portion 14, to be later described. The seed crystal may be mounted in frame 13 by any suitable means, for example, by holes drilled in the sides. The cylindrical liner 5 is then filled to the desired level with the aqueous medium 15, for example an aqueous solution of sodium carbonate and tube 5 sealed by welding end plate 8 into position. The charged liner 5 is sealed into autoclave 1 as described above.

The liner is conveniently made of seamless low-carbon steel tubing, such as commercial steels containing not more than 0.3 percent carbon, and preferably less than 0.2 percent carbon, but any other metals withstanding the temperature and pressure of the operating conditions and resistant to corrosion by the aqueous nutrient medium may be used. Any suitable dimensions may be used in the construction of the autoclave and liner. It has been found convenient to use a liner tube 6 with a height about 8 to 12 or 16 times the diameter of the tube.

In Fig. 2 is shown an equipment much similar to that in Fig. 1. In Fig. 2, however, a sealed inner liner 16, made of a corrosion resistant material such as silver, is fitted within the steel liner 5. Seed crystals 12, wire frame 13, baffle 14, nutrient solids 11 and aqueous medium 15 are all sealed within inner liner 16. Because inner liner 16 has relatively thin walls, and is made of a material such as a noble metal, which may be of low strength, it is not intended to withstand the pressures built up within it. To prevent rupture of inner liner 16, the liner 5 is filled with water or a medium similar to medium 15 to the same percentage fill as within inner liner 16. In this manner a roughly equivalent pressure is developed inside and outside inner liner 16. Since there is no pressure difference, or only a negligible one between the pressures within and without inner liner 16, a relatively fragile material can be used in the construction of the inner liner. Threaded caps 19 and 20 are sufficient to seal inner liner 16 since high pressures need not be

3

tolerated. The outside diameter of the inner liner should be kept somewhat smaller than the inner diameter of the liner 5 so that pressure conditions outside inner liner 16 approximate those inside the inner liner. Inner liner 16 need not be pressure-tight—in fact it is advantageous if some leakage occurs through the seal made by the threaded caps. If excessive diffusion is discouraged by the seal, a slight leak will permit equalization of pressure within and without the inner liner. An outside diameter which is between 50 percent and 80 percent of inner diameter of liner is recommended. Particularly good results have been obtained with an outer diameter for inner liner 16 which is 75 percent of the inner diameter of liner 5.

Because high pressures are developed within liner 5 in the device of Figs. 1 and 2 end plate 8 may be constructed with a central portion 17 of reduced thickness, opposite an opening 18 in retainer cap 10 so as to form a safety release in case the pressure within the autoclave accidentally becomes excessive.

As an alternative to the use of a separate inner liner 16 as shown in Fig. 2, liner 5 may be plated, lined, or clad interiorly with a corrosion resistant metal, such as silver or platinum or one of the other noble metals. Because the nutrient solutions are corrosive of iron, plated interiors are preferred if iron contamination in the crystal is to be minimized.

In Fig. 3 is shown in detail a type of baffle 14 and frame 13 which may conveniently be used in the bombs shown in Figs. 1 and 2. While the presence of a baffle is not essential to the successful growth of corundum on a seed, growth rates are enhanced by their employment. Baffle 14 and frame 13 are preferably made of a corrosion-resistant material, such as of silver, or one of the other noble metals.

When a baffle is used in the apparatus of Figs. 1 and 2, for example, more uniform temperatures in the nutrient region and in the crystal growing region are produced, with the greatest temperature drop occurring in the baffle itself. By minimizing the temperature gradient existing within the crystal growing region, more uniform growth of all crystals in the chamber is promoted. With a baffle absent, there is greater tendency for the seed crystals uppermost in the autoclave—that is in its coolest portions—to grow at the expense of seed crystals more proximate to the warmer portions of the autoclave in the region of the nutrient solution.

The presence of the baffle also increases the circulation of the aqueous medium within the autoclave by a diffusion pumping action promoted by the temperature difference on opposite sides of the baffle. This surprising result is obtained even though only small open areas of the baffle are used to permit circulation of the aqueous medium between the nutrient chamber and the growing chamber. Thus, the total area of the openings in the baffle may be between 50 percent or 20 percent and only 0.5 percent of the total horizontal cross-sectional area of the chamber, blocked by the baffle. Small open areas between 2 percent and 10 percent promote fastest growth, and an open area of between 2 percent and 5 percent is conveniently used.

In Fig. 4 is shown a furnace in which autoclaves of the type shown in Figs. 1 and 2, or other types of high pressure assemblies may be suitably heated. Assembled autoclaves 21 are set vertically on a hot plate 22 heated from below in any suitable manner, as by electric resistance heaters 23. The hot plate, heaters and autoclaves are surrounded by a fire-brick enclosure 24, open at the top, to form a chamber 25.

The space between autoclaves 21 and the enclosure 24 is filled to a greater or lesser depth with any suitable heat resistant, heat insulating substance 26 such as Vermiculite. By filling chamber 25 with a heat insulator, uniformity of temperature within chamber 24 is promoted, and the temperature differential between the top

4

of autoclaves 21 and the bottom of the autoclaves, in contact with hot plate 22, is minimized. To increase the temperature differential between the top and bottom of the autoclaves 21, the depth of insulation 26 may be decreased, exposing the upper portions of autoclaves, and thus cooling them.

A supplementary heat insulation 27 of suitable material, for instance Vermiculite, surrounds fire-brick enclosure 24 and is contained in an outer shell 28, which may be formed of sheet metal. A sheet metal cover 29 is vented to permit escape of gases if rupture of the safety valves of the autoclaves occurs. An automatic temperature controller is conveniently used to maintain hot plate 22 at a fixed temperature.

Other convenient techniques, such as electrical resistance heaters wound around autoclaves such as those shown in Figs. 1 and 2 can be used as an alternative to the device shown in Fig. 4. Tap-offs on a single coil, or more than one coil, can be used to regulate the temperatures of different portions of the autoclave so that a temperature differential of a desired magnitude can be maintained.

Differential heating of the autoclave, however accomplished, is continued for a period of time sufficient to cause substantial growth of the corundum seed crystal suspended in the autoclave from the solid nutrient in the autoclave. After sufficient growth to produce a crystal of desired size has occurred, the whole autoclave is allowed to cool, is removed from the furnace and opened to extract the crystal.

As the solid nutrient in the bombs, either commercially available reagent grade aluminum oxide or aluminum hydroxide are convenient materials. Crystalline corundum itself can be used as the nutrient if, for example, small crystals are available for conversion into large crystals by the hydrothermal process. Corundum, or alpha alumina, is the stable aluminum species in the system under the conditions of temperature and pressure and in the presence of the components of the aqueous nutrient; therefore, any solid aluminum-containing nutrient placed in the autoclave will be converted to corundum with time, whether the initial species be aluminum hydroxide, gamma alumina, or, even, metallic aluminum. Because materials other than corundum are metastable under the conditions within the autoclave, they exhibit higher solubilities than does corundum, the stable species. Consequently if materials other than corundum are used as solid nutrients high initial supersaturations and, hence, high initial growth rates are often observed. These rates, due to the enhanced solubility of the metastable solid nutrient, fall off as in situ conversion of the nutrient to corundum proceeds.

The physical form of the nutrient species introduced into the autoclave is not critical. As stated, reagent grade aluminum oxide, which is usually "soft heat" poorly crystallized and partially hydrated corundum, and aluminum hydroxide are the nutrient species most conveniently used. The oxide may be crystalline or powdered, of any size. However, to deter spontaneous spurious nucleation in the cooler portions of the autoclave, which would detract from growth on the seed crystal, a particle size of at least 200 mesh or greater is conveniently used. Such a particle size, which corresponds with a sieve opening of 0.074 millimeter on the United States Standard Screen Scale, discourages convection carrying of the nutrient particles to the cooler portions of the autoclave where they could act as nuclei for growth on other than the seed crystal. If aluminum hydroxide is used as the nutrient species added to the autoclave, it may be in its typical gelatinous form or in a partially dehydrated form.

The corundum seed crystal 12 of Figs. 1 and 2 may be a whole crystal, or a fragment or cut of a crystal of natural or synthetic corundum. Since there is substantial crystal growth in the direction of the primary, or c,

crystallographic axis, it is convenient to use a seed plate cut so that its faces are perpendicular to this crystallographic axis. Such a cut exposes the (0001) crystal faces. The plate can then be mounted so that the faces are perpendicular to, and grow in, the direction of the longest axis of the autoclave if there is concern over the crystal growing to the sides of the autoclave liner. Another cut which has been found convenient to give large growth rates is one exposing a (11 $\bar{2}$ 0) face of the crystal. The crystal can similarly be mounted in the bomb so that the exposed (11 $\bar{2}$ 0) face is perpendicular to the longest axis of the autoclave, though the mounting angle is not critical. A mounting of the crystal with growing faces parallel to the long axis of the autoclave minimizes possible contamination by adherence of chance particles of, for example, corrosion products.

As an aqueous medium for transporting dissolved corundum from the portion of the autoclave containing the solid nutrient to the suspended seed crystal, aqueous solutions of sodium carbonate have been found most effective. In theory, any material in which corundum can be dissolved to a greater or lesser degree, and with which corundum will be the thermodynamically solid stable phase under the operating conditions, can be utilized as a transport medium, whether the solvent be aqueous or non-aqueous, acidic, basic, or neutral.

Although aqueous solutions of sodium carbonate have been found by far the most suitable transport media under the conditions of temperature and pressure used, the invention is considered to embrace transport media made up of alkaline aqueous solutions, more particularly aqueous solutions of alkali metal compounds which react with water to give basic solutions, and more particularly aqueous solutions of the carbonates of the alkali metals, such as sodium carbonate or potassium carbonate, alone or in mixture with one another or in mixture with the hydroxides of the alkali metals, such as sodium or potassium hydroxides. When mixtures of alkali metal carbonates and hydroxides are used, those solutions are most effective which contain the highest proportions of carbonates.

Taking sodium carbonate as the preferred material for use in the aqueous bath, the concentration of the solute should be at least 0.5 molar in the aqueous medium, and preferably at least 1 M in concentration. A solution of 2 M concentration has given particularly good results. The concentration of dissolved solute is best kept below about 5 moles per liter, since at higher concentrations there is a possibility that some other aluminum species, for example sodium aluminate, may be stable in the system, rather than the corundum phase desired. As mentioned, sodium hydroxide or mixtures of sodium carbonate and sodium hydroxide may be used in the process. In general the presence of sodium hydroxide will necessitate higher temperatures and pressures and larger temperature differentials within the autoclave to give the same growth rate as an equivalent sodium carbonate solution, in which aluminum oxide is inherently more soluble. The presence of more dissolved solute, either sodium carbonate or sodium hydroxide, will favor higher growth rates.

It is not known whether the growth of crystalline corundum by the present invention is done with the aqueous nutrient solution at temperatures and pressures above the critical temperature and critical pressure of the solution or not. No discontinuous difference in growth rates is observed of corundum seed crystals at different distances from the solid nutrient, which may indicate that only a single fluid phase is present in the system under the conditions of growth, though, also, the presence of a baffle would tend to reduce any possible difference in growth rates. However, it is possible that growth may be occurring at temperatures and pressures below the critical temperature and pressure with formation of a large volume of low density fluid phase in con-

tact with the seed crystals and a second fluid phase of higher density and small volume which remains essentially in the portions of the autoclave surrounding the solid nutrient materials.

The temperature in the coolest part of the autoclave chamber should not fall below 395° and should preferably be at least 405° C. If too low a temperature is used diaspore, rather than corundum, becomes the stable phase in the system.

The rate of growth of the corundum crystal for a given percentage of aqueous fill of the free volume in the chamber increases as temperature increases. An upper temperate limit is set by the equipment presently available at about 520° C. More practical operating temperatures are below 495° C. and preferably below 450° C. in the hottest part of the chamber. With other equipment it is possible that higher temperatures could be used in the crystal growing process, but the possibility remains that in these unexplored temperature ranges the gamma-alumina or some other phase may appear in addition to or instead of the desired corundum. The lowest temperature which may be kept in the hottest portion of the autoclave is about 395° C., the low temperature limit of corundum stability in the system. Since, for crystal growth, the seed crystal must be kept cooler than the nutrient mass, operating with the nutrient at 395° C. would not permit crystal growth of corundum elsewhere in the autoclave. Consequently, the lower temperature limit of the hottest portion of the autoclave will generally be above 395° C., to permit a differential to be established in the system while maintaining all temperatures above 395° C. Thus, it is most convenient to set this low temperature limit at about 410° C. or 415° C. which permits at least a 15° C. or 20° C. internal temperature differential (assuring reasonable growth rates) though the seed crystal is kept at a temperature of as low as 395° C.

With an aqueous medium containing sodium carbonate, satisfactory results have been obtained with the operating conditions such that the externally measured mean temperature, that is the temperature average of the hottest and coolest portions of the autoclave is between 420° C. and 460° C. and preferably at about 440° C. It is important to the rate of growth of the crystal that the proper temperature differential be maintained throughout the process between the aqueous solvent bathing the mass of solid aluminum-containing nutrient and the aqueous solvent in the vicinity of the corundum seed crystal where deposition of corundum occurs. With a small temperature differential the rate of growth is low. As the temperature differential increases, the rate of growth increases. However, if the differential becomes excessive, spurious seeding may occur on the walls of the autoclave. To avoid the possibility of spurious seeding, excessive temperature differentials between the nutrient mass and the seed crystal or in other portions of the autoclave should be avoided. As shown above in Fig. 4, the temperature differential may be controlled with the apparatus shown by varying the amount of insulation surrounding the bombs in the furnace.

A temperature differential, between the hottest and coolest portion of the bomb, of 35° C. has been found most satisfactory in the process. Larger differentials up to 40° C. may be used, however. Lower temperature differentials are feasible but give slower growth rates. To eliminate veils—the outlines of the original seed crystal—which are occasionally visible in the grown crystal, the upper portion of the autoclave, during the initial heating period, may be kept at a temperature equal to or higher than that of the autoclave in the vicinity of the solid nutrient. This promotes the solution of small amounts of the seed crystal surface. When growth is then begun by cooling, relative to other warmer parts of the autoclave, the portion of the autoclave in which de-

position occurs, the outline of the original crystal is rendered invisible.

In general, temperature differentials ranging between 15° C. and 40° C. will be most often used in growing corundum crystals. A differential between 30° C. and 35° C. is preferred.

In the apparatus shown in Figs. 1 and 2, it is convenient to measure the temperature differential of the external surface of the autoclave at the levels indicated by the broken lines labeled A and B in Figs. 1 and 2. External measurement at the level A gives an indication of the internal temperature at a level which corresponds to the coolest part of the growing chamber. The external measurement at the level B gives an indication of the internal temperature in the region of the nutrient mass within the autoclave.

In steel autoclaves which are upright circular cylinders, and in which the inside diameter is approximately one-half of the outside diameter, the externally measured temperature differential gives a reasonably consistent indication of conditions within the autoclave regardless of its size. In the long autoclaves without baffles somewhat higher growth rates can sometimes be obtained in the same external temperature differential than are obtained in the shorter autoclaves.

A fair estimate of temperature conditions within the autoclaves can be made on the basis of experience. Along line B for example, the externally measured temperature would be almost identical with the internal temperature of the autoclave since all portions of the autoclave are in reasonably direct contact with heat source such as the hot plate of Fig. 4. It is a reasonable estimate that the internal (at "A") temperature is substantially lower than the measured external temperature so that in general an internal temperature differential is roughly about one-half of the corresponding externally measured gradient. In discussing values of the temperature differential earlier above, the values given refer to externally measured differentials. With the principles just stated, these values can be converted into the corresponding internal temperature values.

For example, since the hottest portions of the autoclave have an approximately equivalent external and internal temperature, the upper limits of internal temperature remain at about 520° C., with more practical operating temperatures below 495° C. and preferably below 450° C., but at least 415° C. Maximum externally measured temperature differentials of 40° C. would correspond with an approximate internal differential of 20° C., giving a maximum internal temperature, for the coolest portion of the autoclave, of 500° C., with more practical temperatures of 475° C., or preferably below 430° C. in the coolest portions of the autoclave.

With a more common differential of about 35° C., the externally measured mean temperature range of between 420° C. and 460° C. can be translated to an internal mean temperature range of between about 410° C. to about 450° C. The preferred mean external value of 440° C. would correspond with a preferred internal mean temperature of about 430° C.

To obtain a practical rate of growth it is preferable to fill the free space of the chamber, excluding the space occupied by nutrient, seed, baffle, and supporting means to at least 65 percent with the liquid aqueous growing medium at room temperature. As the degree of fill is increased, temperature conditions remaining the same, higher pressures are generated within the autoclave and the growing rate increases markedly. The upper limit to the degree of fill to be used is set only by the ability of the bomb to withstand the pressure which is generated. A fill of about 85 percent has been found very satisfactory, but a fill of 90 percent will give better results in an autoclave designed to withstand the pressure. At the higher percentages of fill, lower temperatures may also

be used to accomplish the same results as can be achieved with a lower fill and higher operating temperatures.

An estimate of internal pressures within the autoclave, for the percentages of fill and in the temperature ranges given, can be made from high-temperature data on water, or from the perfect gas law. Such comparisons with different real, or with ideal, systems will give an approximation to actual conditions within the autoclave. On this basis operating pressures within the autoclaves can be estimated as between 12,000 pounds per square inch and 55,000 pounds per square inch. The higher growth rates are obtained with the higher pressures, and still higher pressures would be desirable if equipment could be designed to withstand such pressures.

A practical rate of growth can be achieved with the seed crystals suspended near the top of the autoclave chamber, where they secure the benefit of the full temperature differential within the autoclave. However, crystals may be suspended at lower points only a small distance above the nutrient mass. As noted earlier, there is no large difference in the growth of seed crystals suspended closely above or far removed from the nutrient solid especially when a baffle is present in the system.

The crystals when removed may have their surfaces covered with other phases formed within the autoclave at lower temperatures. These phases, which are not substantial in quantity and can be physically removed with ease from the crystals by washing or scraping, are produced as the bomb is cooled after deposition of corundum under the principal operating conditions.

As mentioned earlier, iron has been found as an inclusion in corundum crystals grown in autoclaves of the kind shown in Fig. 1 if the walls of the liner 5 are left unplanted. Other materials can be introduced into the crystal by adding them to the nutrient solution by design. For example, synthetic ruby has been prepared by adding a chromium compound to the nutrient. Sodium dichromate, $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, present to give a concentration of 3.7 milligrams of chromium per cubic centimeter of nutrient solution has given single crystals of corundum containing chromium in a concentration between 0.3 percent and 3 percent by weight, as determined by spectrographic analysis. The chromium in the crystal is believed to be Cr^{3+} , probably present as Cr_2O_3 .

Larger or smaller amounts of chromium between 0.01 percent and 5 percent may be added to the crystals. As before, since only one chromium species will be in equilibrium with the nutrient solution under operating conditions, almost any chromium compound such as the chromates, dichromates, chromium halides, sulfate, etc., or even metallic chromium, may be initially added to the system. Sodium dichromate has been found convenient as an additive. The chromium containing compounds can be added to the nutrient solution to give concentrations of chromium in solution between 0.1 milligram per cubic centimeter and 30 milligrams per cubic centimeter, but equivalent concentrations of other materials may be used.

Still other inclusions, as of cobalt, titanium or nickel, for example, can be introduced into the corundum crystal by addition of compounds of these materials to the nutrient solution.

Following are examples of the practice of the invention herein described:

Example 1

A cylindrical liner formed of seamless low carbon steel tubing having a wall thickness of $\frac{1}{16}$ inch, welded closed with low carbon steel caps as shown in Fig. 1 and defining a growing chamber about 1 inch in diameter and about 12 inches in length, was charged with 40 grams of reagent grade Al_2O_3 . The material (poorly crystallized corundum) was of such a size as to pass a No. 100 sieve but not a No. 200 sieve. An aqueous solution of 2 M sodium carbonate sufficient to fill 80

percent of the free space of the chamber at room temperature, exclusive of the solid nutrient already present, was added. A baffle and wire support, as shown in Fig. 1 were then inserted in the chamber. The baffle had an open area which was 5 percent of the horizontal cross-sectional area of the liner. The support had mounted thereon 5 corundum seeds in the form of cylindrical plates about 0.03 inch in thickness, cut with their faces parallel to the (00.1) face of the crystal and mounted with the faces vertical to the long axis of the autoclave. The crystals were mounted about $\frac{3}{8}$ inch apart, with the uppermost seed situated about $\frac{3}{4}$ inch from the top of the chamber. The lowest seed was about $1\frac{1}{2}$ inches from the top of the baffle, and about 4 inches from the top of the nutrient solids. The liner was sealed and inserted in a stainless steel bomb of appropriate size to receive the liner tightly, and of a structure as shown in Fig. 1. The autoclave was then placed in the furnace of Fig. 4. The temperature of the hot plate and the amount of surrounding insulation were adjusted so that the externally measured temperature of the autoclave, along level B of Fig. 1, was maintained at 450° C., and the external temperature at line A was maintained at a temperature at 30° C. lower than the temperature at B, that is at 420° C. These conditions were maintained for thirty days, at which time the autoclave was cooled and the crystals removed. It was found that all crystals had grown at almost identical rates, about 0.006 inch per day. The crystals had a light white adherent coating of a phase formed on cooling the autoclave. This was easily removed with hot dilute sodium hydroxide after scraping. The presence of iron inclusions gave a green tinge to the crystals, which otherwise were clear and unflawed.

Example 2

A silver inner liner, of the kind shown in Fig. 2 above, having an inside diameter of $\frac{13}{16}$ inch, a wall thickness of $\frac{1}{16}$ inch, and an inside length of $10\frac{15}{16}$ inches was loaded with a 40 gram charge of alumina nutrient, a sodium carbonate solution to an 80 percent fill, and seed crystals suspended from a silver support, with a silver baffle, just as in Example 1 and sealed with silver screw caps. The charged inner liner was then placed in an outer liner filled to the same 80 percent of free volume as the silver inner liner. The outer liner was then mounted in an autoclave as in Fig. 2. Growing conditions similar to those in Example 1 were maintained for a similar period, and then the autoclave was cooled and dismantled. After washing, the crystals formed were found to be free of any iron inclusions. The growth rate was the same as that in Example 1.

Example 3

The run of Example 2 was repeated under the same conditions and in the same apparatus, except that 3.69 milligrams of chromium per cubic centimeter of solution, added as sodium dichromate, were dissolved in the aqueous sodium carbonate solution placed in the silver inner liner. Upon cooling and dismantling, the crystals found were red corundum (synthetic ruby) containing about 0.2 percent by weight of chromium.

Example 4

The run of Example 2 was repeated under the same conditions and in the same apparatus, with the exception that the nutrient, rather than being reagent grade aluminum oxide, was a 40 gram charge of aluminum hydroxide, $Al(OH)_3 \cdot nH_2O$. The rate of growth obtained with this material as nutrient was about 0.007 inch per day.

Example 5

Using the apparatus shown in Fig. 2, as described in Example 2 above, and with a nutrient charge of 40 grams of aluminum hydroxide as in Example 4, the aqueous bath used was a 1 M solution of sodium hydroxide, NaOH, rather than sodium carbonate. A growth rate of about 0.003 inch per day was observed with this choice of solid nutrient and aqueous bath for a 10 day run.

Example 6

Using the apparatus shown in Fig. 2, as described in Example 2 above, the growth parameters were modified as follows: Concentration of Na_2CO_3 solution—1 molar; percent of fill—70 percent; temperature measured externally at B—492° C.; temperature measured externally at A—472° C. Under these conditions, a growth rate of 0.005 inch per day was observed on corundum seed crystals mounted in the silver inner liner.

Though specific embodiments have been shown and described, it is to be understood that they are illustrative only, and are not to be construed as limiting the scope and spirit of the invention.

What is claimed is:

1. The method of growing crystals of synthetic ruby in a closed system which comprises depositing corundum containing chromium ion impurities on a seed crystal of corundum from an aqueous medium containing corundum and a soluble chromium compound dissolved therein, said aqueous medium being present in an amount sufficient to occupy at least 65 percent of the free space within said closed system at room temperature and being in contact with a mass of solid corundum, said mass of solid corundum being at a temperature higher than that of said seed crystal, the temperature differential between said mass of solid corundum and said seed crystal being not greater than about 20° C., the temperature of said seed crystal being at least 395° C., and the temperature of said mass of solid corundum being not more than 520° C.

2. The method as described in claim 1 wherein the aqueous medium contains sodium carbonate dissolved therein.

3. The method as described in claim 1 wherein the concentration of dissolved chromium compound in the aqueous medium is equivalent to between 0.1 milligram of chromium ion per cubic centimeter of solution and 30 milligrams of chromium ion per cubic centimeter of solution.

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