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METHOD FOR GROWING CRYSTALS USING A SEMIPERMEABLE MEMBRANE

Abdul Hamid Madjid and Allen R. Vaala, State College, Walter F. Anderson, Jr., University Park, and Joseph Pedulla, Jr., State College, Pa., assignors to Research Corporation, New York, N.Y.

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ABSTRACT OF THE DISCLOSURE

A process for growing crystals wherein a first solvent is loaded with a crystallizable solute or crystal precursor and separated from a second solvent in which the crystals are less soluble, by a diffusion boundary, such that crystals are grown from nucleation sites at the diffusion boundary as the second solvent diffuses into the first solvent. This process is highly suitable for growing a wide variety of crystals, including many which have been heretofore difficultly obtainable by other crystallization methods.

BACKGROUND OF THE INVENTION**Field of the invention**

This invention relates to a process for growing crystals. More particularly, this invention relates to a process for growing crystals from nucleation sites along a diffusion boundary between a loaded first solvent and a second solvent having a lower crystal solubility than the first solvent.

Description of the prior art

Crystallization is a major processing operation which is widely used in the chemical industry to recover pure substances from impure solutions. While a wide variety of crystallization techniques are known, all involve the three basic steps of supersaturation, nucleation, and crystal growth.

Supersaturation is achieved by cooling a saturated solution of a solute-laden solvent; by evaporating a portion of the solvent; by adding a precipitating agent; by chemical reaction; or by other numerous techniques known in the art. Once formed, supersaturated solutions are difficult to handle without accidentally inducing crystallization, and accordingly it would be highly desirable to have available a crystallization technique which does not require the preparation and handling of supersaturated solutions. The necessary centers of crystalline growth or development, the nuclei, are formed by nucleation, which may be either spontaneous or induced. Induced nucleation, such as by seeding, is widely used for this purpose, since it provides a method of controlling both the extent of nucleation and the extent of crystal growth, depending upon the particular product desired. However, seeding on a large scale in order to obtain a high yield provides only a limited degree of control over these factors, since the number of nucleation sites is roughly proportional to the amount of seeded material which is added. Once the nucleation sites are formed, further crystalline growth will then occur by the precipitation of additional amounts of solute from the supersaturated solution onto the individual nuclei. Two of the most common instances in which these crystallization techniques are widely applied include purifying solute materials and growing large, single crystals.

Various crystallization techniques have been developed specifically for purifying materials. In simple recrystallization, impurities may be removed by dissolving crystals in a small amount of hot solvent and cooling. If the solvent is properly selected so that the impurities are selectively more soluble in the solvent than the main product, purer

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crystals can be obtained. However, such a method is wasteful, due to the poor yield caused by a large amount of product remaining behind in the mother liquor. Accordingly, it would be highly desirable if a crystallization technique were available which could produce a good yield of crystalline solute by not leaving a large amount of said solute behind in the mother liquor.

Another crystallization method for purifying crystallizable solute materials is fractional crystallization from melts, a technique similar to simple recrystallization but one wherein no solvent is used. Instead, melting and partial freezing are used to separate impurities. This technique is widely used in zone refining, wherein a material to be purified is packed into a narrow column and a heated molten zone moved through the material along the length of the column. Impurities are collected and become concentrated in the molten material at one end of the column, which may be readily removed. While zone refining offers several distinct advantages, it requires special equipment to pass the heated molten zone along the length of the packed column. Accordingly, it would be highly desirable if a crystallization method were available which had the benefits of zone purification without the need for expensive and complex temperature-regulating equipment.

As previously indicated, another large application of crystallization methods lies in satisfying the growing demand in recent years for large and perfect or near-perfect crystals of innumerable substances in order to exploit crystalline properties thereof. Illustrative of such crystals which are currently in demand are piezoelectric crystals, optical materials, masers and lasers, paramagnetic crystals, semi-conductors, luminescent and fluorescent materials, synthetic gems, inorganic filaments, etc. While many techniques for growing single large crystals have been proposed, only three current methods have been found to be useful for wide practical application: melt crystallization, solution crystallization, and vapor crystallization. The melt process, as presently used, requires a close temperature control of the hot and relatively cool zones, as well as careful synchronization of a pulling movement as crystal growth progresses. Solution crystallization, usually by cooling or evaporation, requires, in addition to regulation of temperature and/or pressure, means for dealing with crystals which are formed randomly throughout the crystallizer, and result in encrusted and inefficient cooling coils, plugged up outlets, and the like unless preventative measures are designed into the crystallizer. Furthermore, a suitably designed fines trap is a major factor in the operation of any controlled suspension crystallizer, since the early removal of excess nuclei results in a more efficient process. The vapor process, although widely used, requires expensive equipment, the cost of which may be prohibitive for large scale applications.

One of the most critical problems confronting those concerned with crystallization has been the need for a simple process which would be applicable to a wide variety of substances and yet not require expensive or elaborate equipment. The present invention fills such needs.

SUMMARY OF THE INVENTION

Accordingly, one object of the present invention is to provide a crystallization process which requires a minimum amount of equipment, and which is applicable for providing a wide variety of crystallizable materials.

Another object of the present invention is to provide a crystallization process which is suitable for growing large, single, perfect or near-perfect crystals.

A further object of the present invention is to provide a crystallization process which minimizes random crystal formation by controlling the number and location of nucleation sites.

Yet another object of the present invention is to provide a crystallization process in which crystals may be grown from loaded solutions which need not be saturated or supersaturated.

An additional object of the present invention is to provide a crystallization process in which growth of primary crystals is protected or enhanced.

A still further object of the present invention is to provide a crystallization process in which the growth of the primary crystal is stabilized against random thermal motion.

A more specific object of the present invention is to provide a crystallization process which provides large crystals not otherwise attainable.

A more particular object of the present invention is to provide a crystallization process which is suitable for forming large, perfect or near-perfect crystals of materials such as beta-carotene, copper or nickel tetramine sulphate, refractory materials, metal oxides, and the like.

Briefly, these and other objects are attained in one aspect of the present invention which provides a process for growing crystals in which a first solvent is loaded with a crystallizable solute or crystal precursor and is separated from a second solvent, which has a lesser degree of solubility for the crystals than said first solvent, by a diffusion boundary. The term "loaded" or used herein includes the formation of supersaturated, saturated, or concentrated solutions of crystallizable solute or crystal precursor. The term "crystal precursor" refers to materials which interact to form crystals which are chemically different from the solute. The crystals are grown from nucleation sites at the diffusion boundary which are formed as the second solvent diffuses into the first solvent. The process is highly suitable for growing a large variety of single crystals, many of which have heretofore been unobtainable by other crystallization methods.

One extremely useful application of the process of the present invention lies in preparing large, pure organic crystals with a size and yield heretofore only difficultly obtainable by conventional methods. Briefly, a crystallizable solute or crystal precursor material, suitable for either purification or the growth of large, single crystals in accordance with the present invention, is dissolved to form a loaded solution in a first solvent. A second solvent is then chosen in which the crystals to be formed have a lower degree of solubility than in the first solvent. The two solvents are then separated by a diffusion zone, for instance, by the use of a semipermeable membrane, by layering one solvent over the other, or any other suitable method. If large crystals are desired, the two solvents and the diffusion membrane will be kept at constant temperature and free from major mechanical vibrations. As the second solvent diffuses through the membrane into the first solute-laden solvent, nucleation sites are formed at the diffusion zone localized at the membrane. This diffusion zone slowly moves away from the membrane into the vessel containing the first solute-laden solvent, leading the growth of crystals from the nucleation sites at the diffusion boundary. Since supersaturated solutions need not be used, the formation of nucleation sites is initially concentrated at the diffusion membrane itself, and the formation of unfavorable nucleation sites is minimized by the diffusion of the solute through the membrane and into the bulk of the second solvent. Crystals forming in the bulk of the first loaded solvent will settle out as fines at the bottom of the first loaded solvent vessel, and thus will not interfere with the desired primary crystalline growth in the diffusion boundary area. Furthermore, the second solvent appears to have a shielding effect on the growth of the primary crystals which protects them from the random deposition of micro crystals due to the formation of random nucleation sites thereon. The second solvent appears to virtually surround the primary crystals, inhibiting thermal motion thereof as well as the formation of random nucleation sites thereon. This enhances both the

size and perfection obtainable in harvested large crystals. Additionally, the second solvent may provide a protective ambient, as in the crystallization of complex metal amines in alcohols, or the second solvent may further function as a crystal growth promotor, as in the crystallization of β -carotene from methanol.

Examples of materials which can be crystallized by the present invention, but would be quite difficult to obtain by prior art techniques, include complex heavy metal ammonium salts, such as copper tetramine ammonium sulfate monohydrate and other copper, nickel, and heavy metal complexes, such as nickel tetramine, hexamine, etc., complexes (nitrates, sulfates, chlorides, etc.). By using the zone diffusion process, crystals of these rather unstable materials may readily be prepared in good yield, particularly from crystal precursor materials.

As an additional example, refractory crystals can be prepared by the process of the present invention. Metal oxides, such as iron (II) oxide, iron (III) oxide, and the like may also be prepared. Furthermore, the process of the present invention does not require the use of a distinct membrane to separate the two solvents, since, under suitable circumstances, a virtual membrane created by layering one solvent over the other may be used. Thus, it will be apparent to those skilled in the art that the process of the present invention is applicable to a wide variety of crystallization techniques and may be utilized for a large number of different purposes in which conventional crystallization techniques have serious drawbacks.

These and other objects, features, and advantages of the invention will become more fully apparent to those skilled in the art from the following description and examples of preferred embodiments of the invention, which are presented by way of example and not by way of limitation.

DESCRIPTION OF PREFERRED EMBODIMENTS

While concentrated or supersaturated solutions may be used in the process of the present invention, the description below will be given in terms of using saturated solutions, since they are simple to prepare and handle, and since the use of unsaturated solutions yields only small crystals.

A first solvent or mixture of solvents for the crystallizable solute or crystal precursor is saturated with solute by any suitable means.

A second solvent or mixture of solvents is provided which has less solubility for the crystallizable solute or crystalline product than the first solvent. Preferably, but not necessarily, the second solvent should also be miscible with the first solvent. Immiscible solvents may be used, provided the two solvents and the solute can diffuse thru each other to a minimal degree.

A diffusion boundary is then selected to separate the two solvents. In the case of immiscible solvents or solvents of different densities, this may comprise a virtual membrane which is created by slowly layering the loaded solvent over the zone solvent, or vice versa.

Preferably, the loaded solvent will be denser than the second solvent so that crystal growth will extend downward from the interface, allowing crystal fines to settle away from the growing crystal.

However, in most instances, it will be more convenient to separate the loaded solvent from the zone solvent by a semipermeable membrane. Selection of a suitable membrane will depend on the particular purpose at hand, and a wide variety of membranes suitable for the purpose may be used. Crystals will grow on almost any membrane, but the growth characteristics will vary among different membranes.

Since the diffusion process of the present invention is useful at both high and low temperatures, using a wide variety of solvents, including water, organic solvents, high temperature solvents, such as molten metal or metal salts, fluxes etc., it will be appreciated that the selection of a

particular membrane will be determined largely by the environment in which it is to be used and the type of crystals which it is desired to grow.

Suitable membranes that have been successfully used include glass frits; wood charcoal; porous stainless steel; porous plastic, graphite or ceramic discs; mammalian membranes such as intestines, bladder and parchment; plastic films such as cellophane; cheesecloth; felt, etc.

The rate of crystalline growth and the size of crystal obtained may be controlled both by the choice of membrane, as discussed above, and by varying the ambient temperature. Highly porous membranes and high temperatures generally result in rapid crystal growth, while less porous membranes and low temperatures give slower growth but larger crystals. It will be appreciated that osmotic pressure phenomena in the growing vessel may also be a factor in certain cases, and that oxidation or reduction properties of the solvents will be a factor in growing refractory crystals.

Preferably, but not necessarily, the first solvent, second solvent, and membrane will be kept at constant temperature and free from major mechanical vibrations, although techniques for varying ambient temperature during crystallization are known and may be utilized if desired. Depending on the solute and solvents used, crystals will start growing, usually at the membrane, within a few hours or days. Initial growth is fairly rapid, typically forming long sword-like crystals as the tip of the crystal is led by the travelling diffusion boundary. After a few days, diffusion transport of solute thru the solvent becomes a major factor, and growth is most noticeable in thickness of the crystals.

While not wishing to be bound by any particular theory of the present invention, it is believed that the membrane provides a sufficient but not an excessive number of nucleation sites as a sharp concentration gradient zone becomes established between the two solvents while diffusion takes place through the membrane. The establishment of this sharp concentration gradient zone is a major factor in the crystalline growth process. This zone forms at the membrane and slowly moves away from the membrane into the vessel containing the solute in the first solvent, leading growth of crystals from the nucleation sites. As will hereinafter become more fully apparent, by controlling the number and location of nucleation sites and by exerting a protective effect around growing primary crystals, the diffusion zone process of the present invention is applicable to a large variety of materials and conditions, and in many cases will yield good results where conventional methods for growing crystals fail.

As previously indicated, the diffusion zone process has, as one important feature, an inherent reduction and selection of nucleation sites. Since supersaturated solutions need not be used, the formation of nucleation sites may be initially concentrated at the membrane itself. The formation of unfavorable sites is minimized by diffusion of the solute through the membrane and into the bulk of the second solvent. This aspect is emphasized by the use of a saturated solution as opposed to supersaturated solutions, and the concentration of crystal growth only at favorable sites appears to contribute to an improved quality of harvested crystals. Virtually all of the active nucleation sites will be located in the diffusion boundary or in the bulk of the loaded first solvent. Crystals forming in the latter will settle out as fines at the bottom of the loaded solvent vessel, and thus will not interfere with the desired primary crystalline growth in the diffusion boundary area.

A further advantage of the present method may be due to the shielding functions of the second solvent. The presence of excessive nucleation sites is detrimental to growing large crystals in any crystallization technique. Microcrystals tend to deposit randomly on growing primary crystals before the latter have reached an appreciable size, causing the formation of undesirable polycrystalline

conglomerates. In the diffusion process, the second solvent appears to have a shielding effect on growing primary crystals which protects them from the random deposition of microcrystals thereon.

Another advantage of the zone diffusion process is that the second solvent virtually surrounds primary crystals and inhibits thermal motion thereof as well as the formation of random nucleation sites thereon. This protective function can be best noticed with using a polar solvent having small molecules, such as water. The presence of such molecules in the growing region appears to inhibit thermal motion of long, chain-like tails, and enhance the size and perfection obtainable in harvested large crystals.

Other advantages of the zone diffusion process are in cases where the second solvent may provide a protective ambient, as in growing complex metal amines in alcohols, and in cases where the second solvent may additionally function as a growth promotor, as in growing β -carotene in methanol.

Suitable solvents may be selected on the basis of solubility properties for the desired crystals and include water, methanol, ethanol, benzene and other organic solvents, and chemical solutions which dissolve other chemicals, such as ammonia, copper-ammonia solutions, etc.

Any crystallizable solute material may be used, or crystal precursor materials may be used, in which case the crystals formed will be chemically different from the solute, as in growing copper tetramine sulfate monohydrate from a copper sulfate solute in an ammonia solvent. Solutes may be inorganic salts, elemental metals, or organic compounds or their salts. Illustrative examples of solutes which have been used satisfactorily include copper sulfate, nickelous nitrate, nickelous sulfate, nickelous chloride, ammonium chloride, selenium, β -carotene, and cellulose (the cellulose gives an amorphous growth).

Suitable temperatures will be determined by the thermal stability of the materials being used or harvested, their temperature-solubility profiles, and the size of crystals to be harvested. Temperatures of from about -10° C. to about $+25^{\circ}$ C. have been used satisfactorily in liquid solvent-solute systems, while temperatures of from about 700° C. to about 800° C. have been used in melt crystallization systems. Crystals which have been grown at low temperatures include copper sulfate, copper tetramine sulfate monohydrate, nickel hexamine nitrate hydrate, nickel hexamine sulfate hydrate, nickel sulfate, cobalt salts, ammonium chloride, selenium, cellulose, sodium sulfite, and β -carotene. Crystals which have been grown at high temperatures include iron oxide and boron crystals. Pressures are not critical except as they affect the temperature-solubility properties, and any suitable pressure may be used, although atmospheric pressure will generally be most convenient.

As previously indicated, the zone diffusion process is applicable to a wide variety of cases, and yields excellent results in many circumstances where conventional methods fail. In order to obtain a still better appreciation of the present invention, the following examples are presented by way of illustration.

EXAMPLE 1

Beta-carotene is an example of an organic crystal in which the use of conventional crystallization methods, such as evaporation or saturated solution techniques, gives crystals of small size and poor quality. This is probably due to thermal motion in the long, chain-like molecule, as well as the presence of excessive nucleation sites both in the mother liquor and randomly deposited on primary growing crystals. By using methanol as the second solvent in the diffusion zone process, conducted at room temperature, beta-carotene crystals were grown within 24-48 hours from a loaded benzol solvent using fresh bovine bladder membrane which had been stripped clean. Growth was noticed after 24-48 hours at room tempera-

ture, the crystals formed being slender and sword-like and up to 1 quarter inch long. Over the next 4 to 8 weeks, the crystals grew to a length of up to 1 and a half inches, and formed into spade shapes as they increased both in width and length. Growth also occurred at minus 10° C., but the initial growth stage was prolonged to 1 or two weeks. X-ray diffraction patterns showed the crystal to be more perfect than those obtained by conventional methods.

EXAMPLE 2

Copper tetramine sulphate monohydrate is another material for which the application of conventional crystal growing techniques gives poor or no results. By using the zone diffusion process, crystals of this rather unstable material have been harvested. An aqueous ammoniated copper sulphate solution was prepared by adding a slight excess of copper sulfate to an aqueous household ammonia solution, and used as the first solvent. Methanol was used as the second solvent, and with a cellophane membrane (from a package of Chesterfield cigarettes) separating the two solvents, crystal of copper tetramine sulphate monohydrate could be harvested.

After several weeks at room temperature, growth reached 1 quarter inch, and continued to about 1 and a half inches after 6 to 8 weeks.

EXAMPLE 3

This example illustrates preparing refractory crystals using the zone diffusion process. Borax was melted in a crucible, and approximately one part red ferric oxide was dissolved into three parts of the borax melt. The mixture was poured into a sack-like receptacle of very fine mesh stainless steel screen, which was tied tightly around the mixture after it solidified.

The wrapped material was placed in a graphite crucible, covered with molten lithium chloride, heated slowly in a nitrogen atmosphere to 750° C., and maintained at 750° C. for 25 hours. The material was then cooled to room temperature, sliced open, and washed to dissolve water-soluble material. Small, shiny, jet black, pyramidal crystals of ferrous oxide were recovered from various locations on the stainless steel mesh.

EXAMPLE 4

This example demonstrates the zone diffusion process using a virtual membrane to grow crystals. A loaded first solvent was prepared by saturating benzene with β -carotene, and methanol was used as the second solvent. A small orifice ($\frac{1}{4}$ – $\frac{1}{2}$ inch diameter) permitted layering the solvents without initial mixing. β -Carotene crystals grew from the edges of the opening, but not as well as when a membrane was used, as in Example 1, to provide nucleation sites.

It will be appreciated that while the foregoing disclosure relates to only preferred embodiments of the invention for growing single crystals via the zone diffusion proc-

ess described herein, it is capable of numerous modifications or alterations which may be made by those skilled in the art without departing from the spirit and scope of the invention as set forth in the appended claims.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A process for growing crystals which comprises:
 - (a) loading a first solvent with a crystallizable solute or crystal precursor;
 - (b) selecting a second solvent in which the crystals to be grown are less soluble than in said loading solvent;
 - (c) separating said solvents by a semipermeable membrane; and
 - (d) diffusing said second solvent through said membrane into said first loaded solvent so that crystals are grown in said first loaded solvent from said membrane.
2. The process of claim 1, further including the step of recovering said crystals.
3. The process of claim 1, in which said second solvent is miscible with said first solvent.
4. The process of claim 1, in which said crystallizable solute or crystal precursor is an organic material.
5. The process of claim 1, in which said first solvent, said second solvent, and said crystallizable solute or crystal precursor are in the melt phase.
6. The process of claim 1, in which said crystallizable solute or crystal precursor is selected from the group consisting of β -carotene, metallic ammonium salts, metallic oxides, and refractory oxides.

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NORMAN YODKOFF, Primary Examiner
 R. T. FOSTER, Assistant Examiner

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