

FINAL REPORT

on

STUDY OF CERAMIC PRODUCTS AND PROCESSING
TECHNIQUES IN SPACE

to

CALIFORNIA INSTITUTE OF TECHNOLOGY
JET PROPULSION LABORATORY
PASADENA, CALIFORNIA 91103

December 1, 1974

by

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(NASA-CR-142575) STUDY OF CERAMIC PRODUCTS
AND PROCESSING TECHNIQUES IN SPACE Final
Report (Battelle Columbus Labs., Ohio.)

N75-20562

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This work was performed for the Jet Propulsion Laboratory,
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Contract No. 953845

ABSTRACT

An analysis of the solidification kinetics of beta alumina in a zero-gravity environment was carried out, using computer-simulation techniques, in order to assess the feasibility of producing high-quality single crystals of this material in space. The two coupled transport processes included in the study were movement of the solid-liquid interface and diffusion of sodium atoms in the melt. Results of the simulation indicated that appreciable crystal-growth rates could be attained in space. Considerations were also made of the advantages offered by high-quality single crystals of beta alumina for use as a solid electrolyte; these clearly indicated that space-grown materials would be superior in many respects to analogous terrestrially-grown crystals. Likewise, economic considerations, based on the rapidly expanding technological applications for beta alumina and related fast ionic conductors, revealed that the many superior qualities of space-grown material would justify the added expense and experimental detail associated with space processing.

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1. SUMMARY

Beta alumina is a sodium aluminate having sodium content which can apparently vary from about 0.1 to more than 10 weight percent. It is a solid-electrolyte material which is currently finding increasing technological interest because of its exciting possibilities for use as battery or fuel-cell components or as electrochemical transducers. The single-crystal form of this material is ideally suited for such applications because of the marked anisotropy of electrolytic conductivity with crystallographic orientation. Detailed considerations were made, as part of this program, of the properties of polycrystalline beta alumina relative to single crystal, and it was thereby concluded that the single-crystal form is indeed to be preferred in several respects. Unfortunately, it is very difficult to grow high-quality single crystals terrestrially⁽¹⁾, so that the advantages offered by the zero-gravity environment of an orbiting spacecraft for growing crystals which are relatively defect-free appear to be particularly applicable to the beta-alumina system as well as to other materials of this general class⁽²⁾.

In this light, we have developed a computer-simulation study of the growth from the melt of single-crystal beta alumina in space in order to quantitatively assess the growth kinetics expected for this material and thereby evaluate the economic feasibility of space production. The simulation was based on two coupled transport processes: movement of the solid-liquid interface as crystal growth proceeds and diffusion of solute (sodium) atoms in the melt. A series of studies was carried out by varying input data for velocity of the moving interface and solute diffusivity. It was found that appreciable crystal-growth rates could, in principle, be attained. Likewise, a quantitative evaluation was made, again for various values of the interface velocity and solute diffusivity, of the minimum temperature gradient required at the interface in order to avoid constitutional supercooling⁽³⁾, a condition which would result in instabilities in the growth process and consequent breakdown of the planar interface.

Considerations were also made of the power required to grow beta alumina -- an important factor for space processing. It was thus found that the power input required to maintain the necessary temperature gradient at the interface and to allow for radiative heat losses is the order of 100 watt, a figure which actually would vary, depending upon such factors as the nature and configuration of heat shields, the crystal size, and magnitude of the temperature gradient required at the interface. Of course,

the total power input is increased due to power losses which occur in coupling the power source to the crystal-growth system. We believe that such losses can be minimized through the use of appropriate solar-imaging techniques.

We have also studied methods currently being used to grow beta alumina single crystals and found that it is a relatively difficult material to grow terrestrially. One of the principal drawbacks is the relatively slow grow rates that must be used; space processing offers the potential for overcoming this difficulty and making production of the material economically feasible.

2. INTRODUCTION

2.1. Background

The three principal benefits to be gained from the processing of materials in space are derived from (1) the possibility of achieving ultra-high vacuum, (2) the existence of an inexpensive heat source via solar energy, and (3) the absence of a gravitational field within an orbiting spacecraft. Of these, the last is of greatest potential importance, particularly in view of the relatively large expense associated with materials processing in space. Zero-g effects are most pronounced in kinetic processes occurring in liquid and liquid-solid systems, and to some extent, in powdered solid systems in which sedimentation is significant. The research described herein is directed at exploiting the zero-gravity environment, the specific application being the evaluation of the solidification kinetics of a very important crystalline ceramic material, beta alumina, from the liquid state. The approach taken consists of a computer-simulation study of the solidification process with the emphasis placed upon the relative importance of zero-g in determining properties of the final material. Cost-effectiveness considerations are also included because of the financial burdens and experimental complications associated with space processing.

2.2. Properties of Beta Alumina

The beta-alumina system was chosen for this study because it is a technologically significant crystalline ceramic material which can be prepared from the melt. It is a sodium aluminate, having sodium content which can apparently vary from about 0.1 to more than 10 weight percent, although the nominal formula for this material is $\text{NaAl}_{11}\text{O}_{17}$. (A related phase is β'' alumina, which has the nominal formula NaAl_5O_8 .) As pointed out by Kummer⁽⁴⁾, in his review of the properties of beta alumina, this material has a hexagonal layer structure with lattice constants $a = 5.59 \text{ \AA}$ and $c = 22.53 \text{ \AA}$. The sodium ions are situated entirely in planes 11.27 \AA apart which are perpendicular to the c-axis. These planes contain, in

loose packing, equal numbers of sodium and oxygen ions. Other ions, such as silver, potassium, rubidium, lithium, and thallium, have been substituted for sodium in the beta-alumina lattice⁽⁴⁾.

The primary reason for the great interest shown in beta-alumina and related materials over recent years results from the fact that the sodium ions exhibit very high mobility⁽⁴⁾ along the planes in which they lie while the material also exhibits relatively low electronic conductivity. (The oxygen ions situated in these planes do not exhibit this high degree of mobility). As a result, beta-alumina has found extensive application as a solid-electrolyte component in new types of batteries and fuel cells having high energy density and power density. Other applications also exist; for example, Whittingham and Huggins⁽⁵⁾ have called attention to:

"the potential use of these and related materials for a wide range of other purposes, primarily as experimental tools for the measurement of thermodynamic and kinetic data . . . their unusual properties open up a very wide vista for the use of solid electrolytes as electrochemical transducers in a great variety of scientific as well as engineering applications."

2.3. Rationale for Space Processing

Terrestrial techniques for fabricating beta alumina have been discussed by many authors (e.g., References 4, 6, and 7). For example, beta-alumina powder can be prepared by solid state reaction between powder mixtures of NaAlO_2 and alpha alumina. The powder can be densified using appropriate sintering or hot-pressing procedures⁽⁷⁾. Single crystals of this material have also been grown; for example, Stormont and Morrison⁽¹⁾ have described procedures for growing single-crystal tubes and ribbons.

The single-crystal form for beta alumina is the preferred form of this material for a number of reasons, including the following:

- (a) The conductivity of the sodium ions is highly anisotropic (high conductivity in directions normal to the c-axis). Benefits offered by this fact would be reduced if the material were polycrystalline.
- (b) The material, as used in a high-energy-density battery, might possibly be operable at lower temperatures if the single-crystal form is used⁽¹⁾.
- (c) Processes occurring as a result of the presence of grain boundaries result in degradation of properties of the electrolyte. For example, sodium ions tend to segregate at the boundaries, causing the material to take on undesirable metallic properties⁽⁸⁾. Also, fracture studies of β'' -alumina have indicated that mechanical

failure may be initiated by an intergranular weakening due to sodium segregation at grain boundaries⁽⁹⁾. Consequently, the presence of grain boundaries results in shorter useful lifetimes of the material.

- (d) There is some indication that grain-boundary diffusion in fast ionic conductors (such as beta alumina) is actually slower than intragranular diffusion⁽¹⁰⁾. This would mean that grain boundaries would tend to lower the ionic conductivities of these materials.
- (e) It is likely that significantly thinner sections of single-crystal material could be used, for application as a solid electrolyte, relative to the polycrystal, resulting in lesser amounts required for production. Thinner sections also result in a proportional enhancement of diffusive flux, as clearly shown by examination of Fick's first law.

Unfortunately, it is relatively difficult to grow large quantities of high-quality, single-crystal beta alumina under terrestrial conditions. For example, one of the problems results from the relatively slow growth rates that must be used (≤ 6 mm/hr for growth in the c direction; ≤ 12 mm/hr for growth in the a direction)^(1,8). A major limiting factor is the diffusion rate of sodium in the melt. Space processing would offer an advantage, in this respect, because the absence of convection currents in the melt, under zero-gravity conditions, would offer the possibility for attaining higher temperature gradients; this would offset the limitation imposed by the finite sodium diffusivity and thus permit faster growth rates. Also, crystals having relatively large cross-sectional area (measured along the solid-melt interface) could be grown in space since the possibility of cellular instability (which would occur terrestrially as a result of convection currents) would not exist under zero-gravity conditions.

Generally speaking, the two main advantages offered by space processing in the production of single crystals in space are containerless growth and improved homogeneity, as now described:

(a) Containerless Growth

Space processing, in this context, can be regarded as an extension of methods currently used to grow crystals terrestrially, in which surface-energy effects are used to combat gravitational forces and allow containerless growth in a one-g environment. With the removal of gravity, other effects will become dominant. These include the development of a catenary shape (instead of the typical cylindrical shape) through surface-energy forces, thermal effects (which alter surface energy), and the influence of impurity segregation at the free surfaces and at the growing interface.

(b) Homogeneity

Crystals grown on earth are inhomogeneous for two main reasons: First, the composition of the growing crystal depends upon the rate at which the surface is growing into the melt, since this influences the concentration profile of solute ahead of the interface. Because the growing crystal surface is not usually planar, geometrical effects induce variations in growth rate across the curved surface. The composition changes across the width of the interface lead to radial compositional variations across the solidified material, an effect known as coring. Second, microscopic inhomogeneities are caused by the development of instabilities in the growing smooth surface, leading to the entrapment of impurities into the surface, the resulting effect known as grooving. (Grooving actually constitutes the onset of cellular growth. Unlike banding, which has otherwise similar characteristics in the final crystal, grooving is a process in which the growing crystal ceases to be smooth.) Both of the above problems will be most severe in the growth of beta-alumina crystals because of the high sodium content (typically, several weight percent). Both could be alleviated by space processing through the elimination of convection currents in the melt. First, the absence of convection currents would allow the design of systems in which crystals could be grown with more nearly planar surfaces than is possible at present, and also allow the establishment of steady-state concentration gradients ahead of all parts of the growing surface. Both effects would minimize coring. Second, the preservation of smooth surfaces in terrestrial technology is achieved by using slow rates of crystal growth, since the rate is made slower to permit the growth of materials with large amounts of solute. But difficulties do develop through convection currents. Generally, the liquid near a growing Czochralski crystal is colder and denser than that at the bottom of the bath. In addition, rejected solute often changes the liquid density still further. Consequently, Rayleigh instabilities develop, causing grooving; and although many ingenious means are used to alleviate the problem, space processing can potentially eliminate it entirely.

2.4. Computer-Simulation Methods Applied to Space Processing

Given that we are interested in quantitatively evaluating the efficacy of space processing for the fabrication of high-quality single crystals of beta-alumina, the question remains as to the approach to be taken. In general, space-processing procedures, because of the unique environmental conditions, cannot be evaluated completely via terrestrial experiments. This fact provides the incentive for the use of computer-simulation methods, which can be related to partially relevant experiments to predict, as accurately as possible, the results to be expected in the space environment. Such simulations take account of the best current state of the theory and, if possible, are applied to laboratory experiments to test the predictions as far as possible.

Computer-simulation methods are, in fact, finding ever-widening applications in the materials-science area in general. This stems partly

from the fact that on the one hand, kinetic processes occurring in materials are generally of an extremely complex nature, whereas on the other hand, increasingly sophisticated technological applications of materials require as complete an understanding of materials behavior as possible. Among the advantages offered by computer-simulation methods are the following:

- (a) One is freed from requirements of analytical tractability in the development of theoretical models. The physical model one uses as the basis for his simulation is limited only by the bounds of current knowledge and the time and funds allotted to prepare and execute the program.
- (b) Phenomena difficult to reproduce within the laboratory can often be more efficiently described by simulation techniques.
- (c) It is a relatively simple and inexpensive matter to alter processing and physical parameters in a given computer "experiment", then repeat the "experiment" to observe resulting changes.
- (d) Laboratory experimentation can be minimized when computer-simulation methods are used. As Bicking⁽¹¹⁾ has noted:

"In materials development, as in so many other engineering and scientific areas today, the use of computer-simulation procedures may be substituted for long hours of laboratory experimentation."

Indeed, it has been predicted⁽¹¹⁾ that, in the future, computer simulation of the behavior of materials will be the primary avenue for their development.

Computer simulations of processes occurring in materials generally take one of two principal approaches, as follows:

- (1) Macroscopic descriptions of kinetic phenomena in terms of appropriate physical models in which time-dependent relations for heat flow, diffusion of matter, etc., are solved numerically.
- (2) Atomistic calculations in which an atomic model of a crystal is "constructed" using appropriate interatomic potentials, and in which the behavior of individual atoms is thereby followed.

Our analysis of the solidification kinetics of beta alumina in zero gravity, which is described below in detail, is based on the first of these two approaches.

3. TECHNICAL DISCUSSION

3.1. Semi-Quantitative Comparison of Ionic Conductivity of Oriented Single-Crystal Beta Alumina With Polycrystalline Form

a. Introduction

As we have already discussed, the conductivity of sodium ions in beta alumina is highly anisotropic, with high conductivity existing in planes normal to the c-axis of the crystal. Possible benefits offered as a result of this phenomenon would clearly be reduced if polycrystalline material were to be used. We, therefore, sought to estimate the ionic conductivity of oriented single-crystal beta alumina relative to the polycrystalline form. The purpose of this relatively small effort was to help assess the possible economic advantages which would result from the use of oriented single crystals, made in space, for future applications as fast ionic conductors.

We developed highly simplified models, nevertheless ones which could be expected to yield ballpark results. Our concept of ionic diffusion through polycrystalline material involved the movement of ions through grain boundaries and along highly conductive planes of the grains. The total path thus consisted of a component along boundaries and a component through the grains. Two models were developed to give quantitative expression to our concepts of diffusion: a one-dimensional model and a three-dimensional model.

b. One-Dimensional Model

A system of grains was imagined to be arranged along a line. The grain sizes were selected at random from an approximately normal distribution, with mean radius of 0.09 (arbitrary units), as shown in Figure 1. Grain sizes were in the range 0 to 0.2. A stochastic (i.e., Monte Carlo) model was devised to select grain sizes at random from this array. The ionic flux was assumed to pass around grain boundaries and along the central (diametral) plane of the grains. The orientation of the conducting plane for each grain was selected at random within the range 0 to 90 degrees.

The array of grains chosen in one simulation, and the ionic diffusion path, are shown in Figure 2. The path traveled along the grain boundaries was found to be 0.466 times the path traveled through the grains.

c. Three-Dimensional Model

For a three-dimensional system of grains, diffusion along grain boundaries need not occur if, adjacent to each grain, there exists a suitably oriented grain such that diffusing sodium ions can "jump" from the conducting planes in the one grain immediately onto a set of conducting planes in the adjacent grain. For our three-dimensional model, we assumed

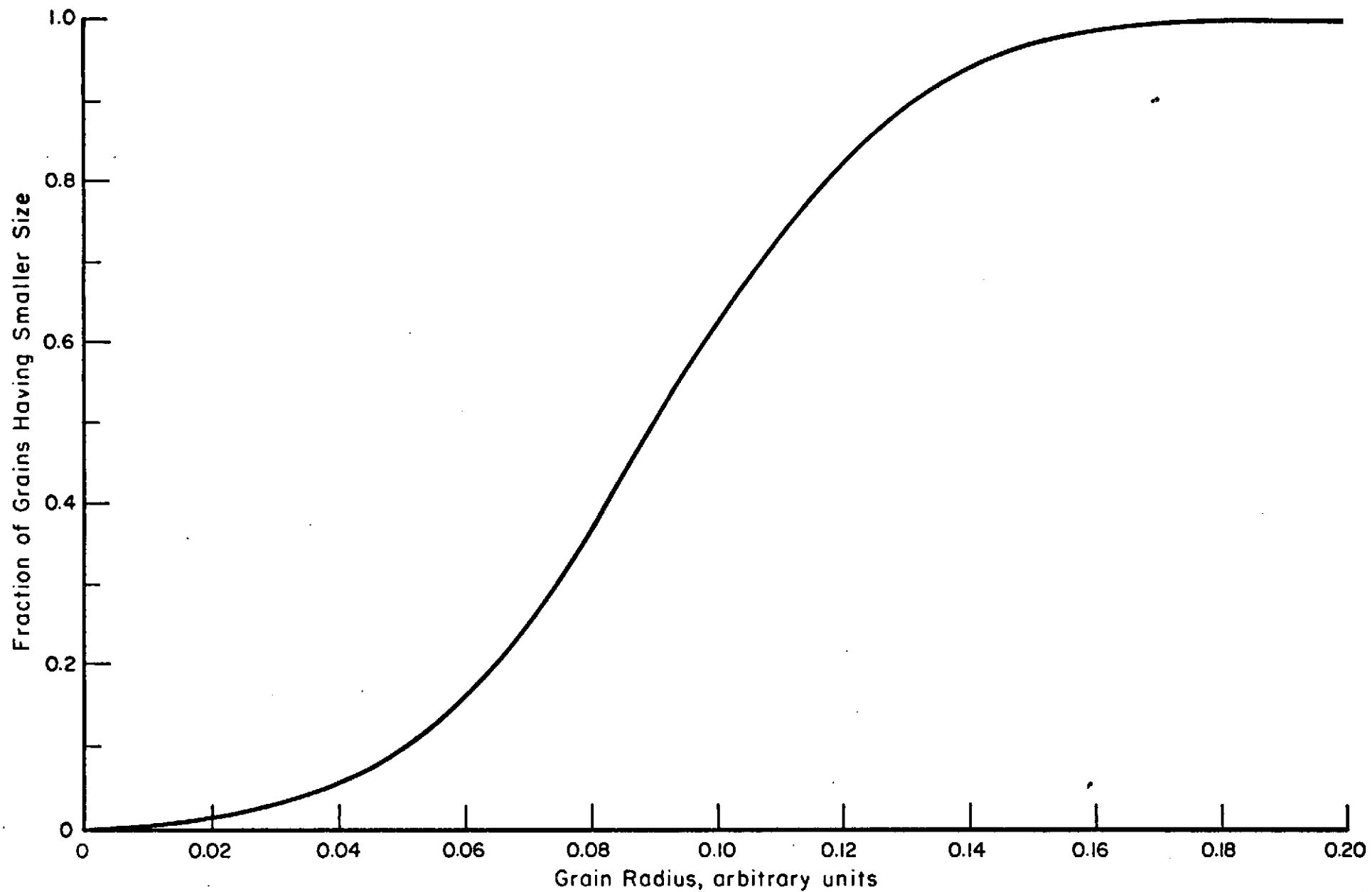


FIGURE 1. GRAIN-SIZE DISTRIBUTION ASSUMED FOR ONE-DIMENSIONAL AND THREE-DIMENSIONAL MODELS

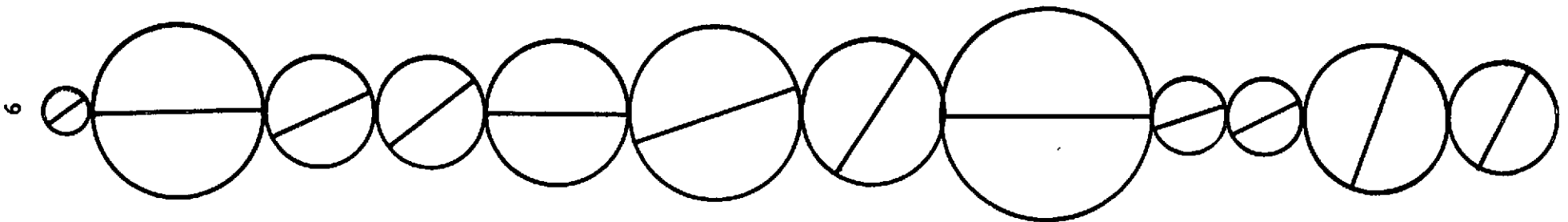


FIGURE 2. ONE-DIMENSIONAL ARRAY OF GRAINS, ILLUSTRATING RANDOM ORIENTATION OF HIGH-CONDUCTIVITY PATHS

that this condition was satisfied for every grain so that no grain-boundary diffusion therefore took place. The grain size and orientation were selected as before. Again, the diffusion distance through a given grain was taken simply to be equal to the grain diameter.

The flow through a set of grains is illustrated in Figure 3. The grains were assumed to spiral in three dimensions. During the computation, the actual diffusion distance was related to the linear diffusion path (the diffusion path in a properly oriented single crystal) and the corresponding ratio was plotted as each additional grain was picked out. The evolution of the accurate ratio, according to this model, is shown in Figure 4, which shows that the path length through polycrystalline material approaches a value of about 1.6 times the path through oriented single-crystal material.

d. Discussion

The two most obvious inadequacies of our simple three-dimensional model are the following: First, the diffusion length through a grain was taken to be equal to the grain diameter, whereas in a "real" crystalline grain, diffusion occurs along a set of parallel highly conductive planes which vary in total area. Second, the conducting planes were assumed to form a continuous path, without the need for any grain-boundary diffusion.

Recent experimental measurements of the relative ionic conductivity of single-to-poly-crystal beta alumina have indicated a conductivity ratio of roughly 5:1⁽⁵⁾. The result obtained with our three-dimensional model appears to be fairly consistent with this figure, since, in a "real" situation, some diffusion along grain boundaries is likely to occur (as was indicated by our one-dimensional model) and grain-boundary diffusion may actually reduce the overall ionic conductivity of the material⁽¹⁰⁾.

The principal result of this brief investigation of the conductive properties of beta alumina lies in the fact that the conductivity of a properly oriented single crystal is increased over that of an analogous polycrystal by a factor generally less than an order of magnitude. However, it should be noted that, for certain of the situations in which the fast-diffusing ionic species is something other than sodium, it is possible that grain boundaries may strongly inhibit diffusion, in which case single crystals would be essential. In addition, as we have indicated in Section 2.3, there are other very important reasons for preferring the use of single crystals over polycrystals.

3.2. Computer Simulation of Crystal Growth

a. General Comments

In considering the feasibility of growing ceramic crystals in space having properties which are superior to those characterizing

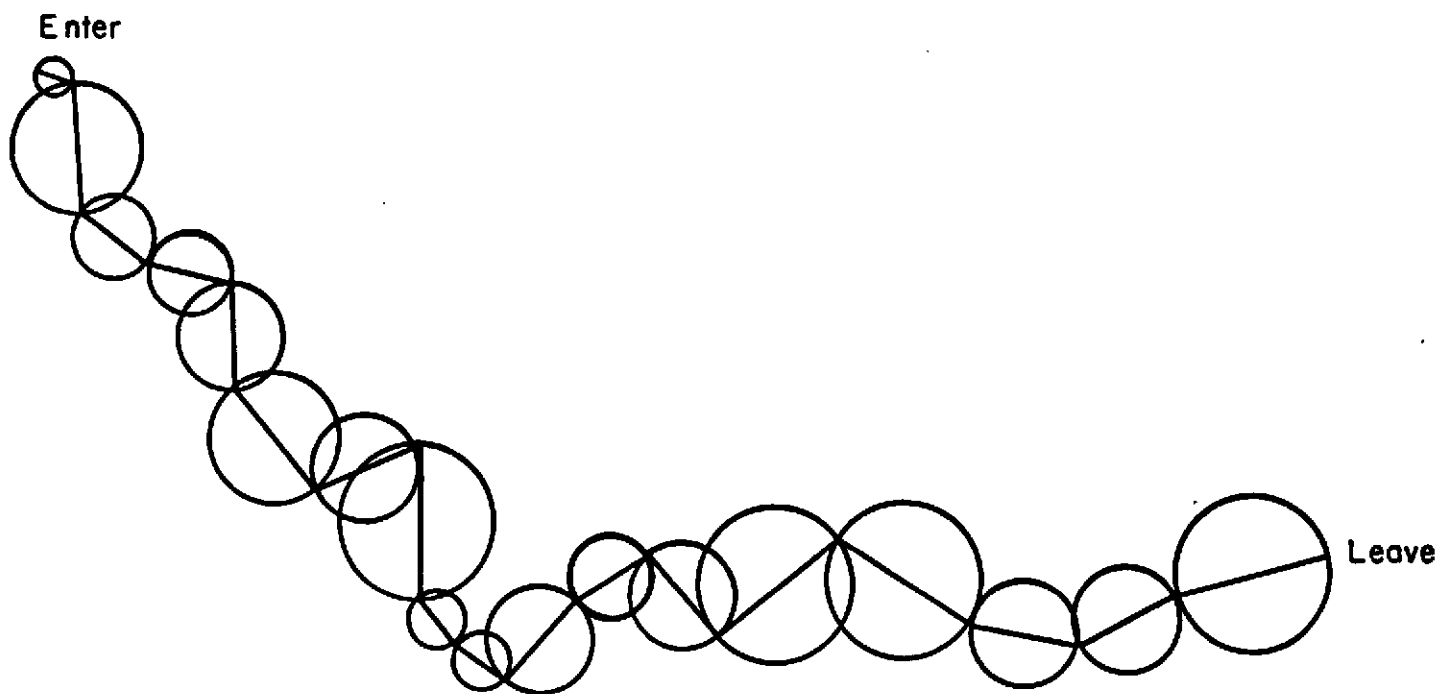


FIGURE 3. ILLUSTRATION OF THE HIGH-CONDUCTIVITY PATH THROUGH A SET OF GRAINS ORIENTED RANDOMLY IN THREE DIMENSIONS, ASSUMING NO GRAIN-BOUNDARY DIFFUSION

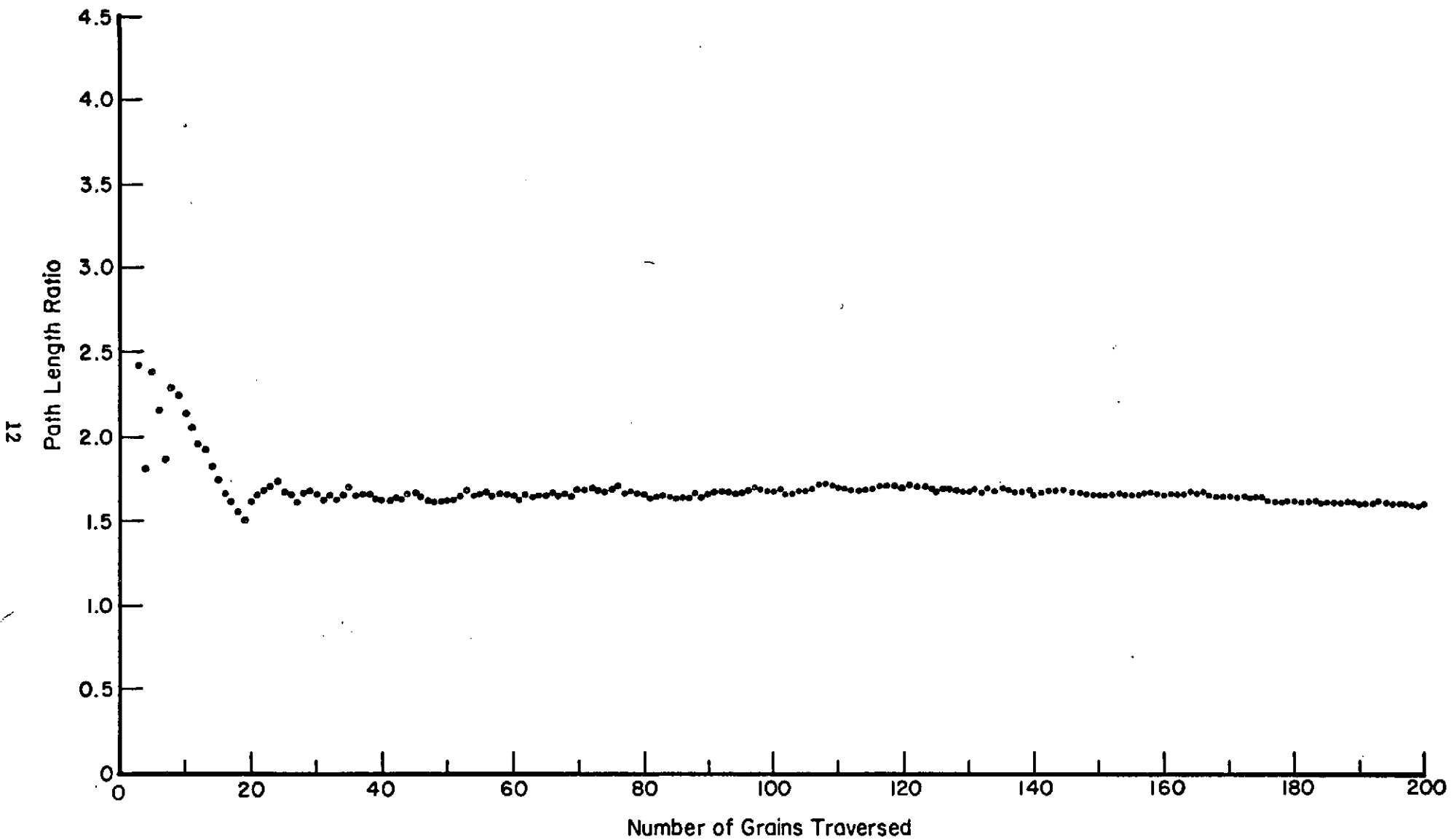


FIGURE 4. COMPUTED PATH LENGTH RATIO, FOR THE THREE-DIMENSIONAL MODEL, AS A FUNCTION OF THE NUMBER OF GRAINS TRAVERSED

terrestrially grown crystals, we must take into account the important physical processes which contribute to crystal growth. Summarized below are processes involved with growth of the prototypic crystal being analyzed in our study -- beta alumina.

1. Rejection of Solute. At any temperature in the range in which beta alumina crystallizes from the liquid, the liquid near the growing surface has a much higher sodium concentration than the solid, and the growth of the crystal is accompanied by the rejection (or partitioning) of sodium. The crystal can be grown in such a way that there is no mixing within the liquid, as in the Bridgman technique. In this case, the solute (sodium) accumulates ahead of the crystal so that eventually, after an initial transient condition, the crystal is growing with the same solute concentration as the bulk of the liquid. Alternatively, the liquid can be stirred, as in the Czochralski method; here a true steady state is never achieved.

2. Constitutional Supercooling. We find, from its phase diagram⁽⁴⁾, that beta alumina cannot be crystallized at temperatures below about 1600°C. In many crystal-growth systems, the actual minimum temperature is much higher. For example, in a Bridgman system (i.e., no stirring of the melt) the atomic fraction of NaAlO₂ in the melt must be less than approximately 0.125, and for this sodium concentration, the melt temperature must be above about 1960°C.

During crystal growth, the situation is much more complicated. The crystal growing in contact with liquid containing partitioned solute is growing at a temperature specified by the phase diagram. Ahead of the interface, as the concentration of solute falls away, the phase-diagram liquidus temperature increases sharply. This means that freezing can take place at a higher temperature ahead of the interface than at the interface itself. Consequently, there must be a temperature gradient in the liquid, with the temperature increasing with distance away from the growing crystal. If the temperature does not increase rapidly enough, so that it falls below the liquidus temperature of the liquid at any point, the liquid is said to be constitutionally supercooled. In most cases, the crystal ceases to grow as a single crystal, but grows in a cellular or dendritic manner.

3. Implications for Space Processing. The formation of a highly alloyed single crystal results in a large concentration gradient of solute and requires a large temperature gradient. This induces relatively large density gradients in the liquid which, under terrestrial conditions, might cause convection currents. Such currents, by increasing the concentration gradient of solute near the surface, lead to the breakdown of the smooth crystal-liquid interface. Furthermore, gravity imposes major restrictions upon the crystal growth process. For example, the Czochralski method has the (colder) crystal growing from the top of the melt as a device to avoid the containment of the melt. Under conditions of zero gravity the melt requires no containment.

b. Numerical Analysis

Our study of solute rejection and crystal growth was based upon a procedure described in detail elsewhere⁽¹²⁻¹⁴⁾. The modified version of the numerical scheme used in the present work is listed in Appendix A. The program is written in BASIC language, for a Hewlett-Packard 9830 system. A listing of definitions of the more important symbols is included with the appendix.

The numerical procedure is involved with the advancement of a planar and essentially infinite solid-melt interface. Calculations are based around a set of "nodes" or points spaced equidistantly along a straight line measured perpendicular to the interface. The node spacing is such that the interface moves one internodal distance during each increment of the calculation. All the node positions are moved forward at each time increments, giving a moving coordinate frame for the computation.

The crystal-growth procedure assumed for space processing was based on constrained growth, that is, the interface position being determined by the movement of the temperature profile in the crystal-growth furnace. Since the interface is at its equilibrium melting temperature, the growth rate is then given by the cooling rate (in units of temperature per unit time) divided by the magnitude of the spatial temperature gradient. A schematic illustration of the physical system is given in Figure 5, assuming steady-state growth conditions. The concentration C_0 of solute atoms in the bulk liquid is equal, under these conditions, to that incorporated into the solid. The solute concentration maintained in the liquid at the advancing interface is determined by the phase relationships⁽³⁾.

The boundary conditions were developed from the conservation relationships for a moving reference frame, the concentration of sodium in the solid at the interface being determined by the phase relationships for beta alumina⁽⁴⁾. Hence, the solute rejected at the first node, during growth, was thereby determined. The amount of solute lost from the node remote from the surface was determined by the concentration profile at that position. If there was an appreciable concentration gradient, the computation became unstable (this being simply an artifact of the numerical analysis). The time increment was therefore selected so that the concentration was virtually constant at the last nodes; the computation then became stable with no solute escaping from the computation framework at the far-field boundary.

The numerical method for treatment of diffusion between the two boundaries was based on a technique of successive substitutions and has been described in detail elsewhere⁽¹²⁻¹⁴⁾. The actual concentration changes at the nodes are found by applying the appropriate boundary condition at the moving interface.

In Figures 6 and 7 are shown some examples of beta-alumina solidification kinetics as predicted by the computer simulation. In these figures, we find the concentration profiles of the solute species, sodium, within the liquid after successive increments of crystal growth.

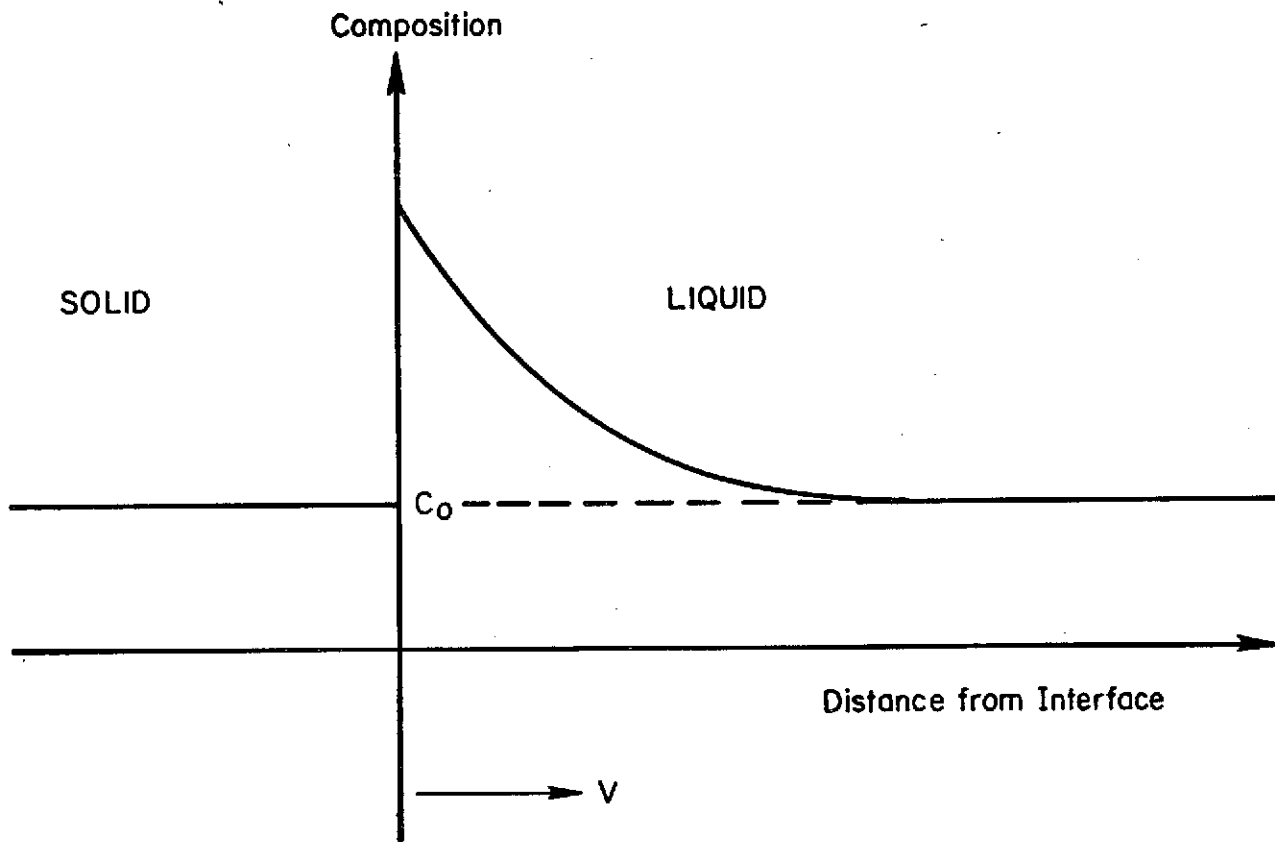


FIGURE 5. SCHEMATIC ILLUSTRATION OF THE STEADY-STATE, SPATIAL VARIATION OF SOLUTE CONCENTRATION.

The interface velocity is V and the concentration of solute in the melt at large distances from the interface is C_0 .

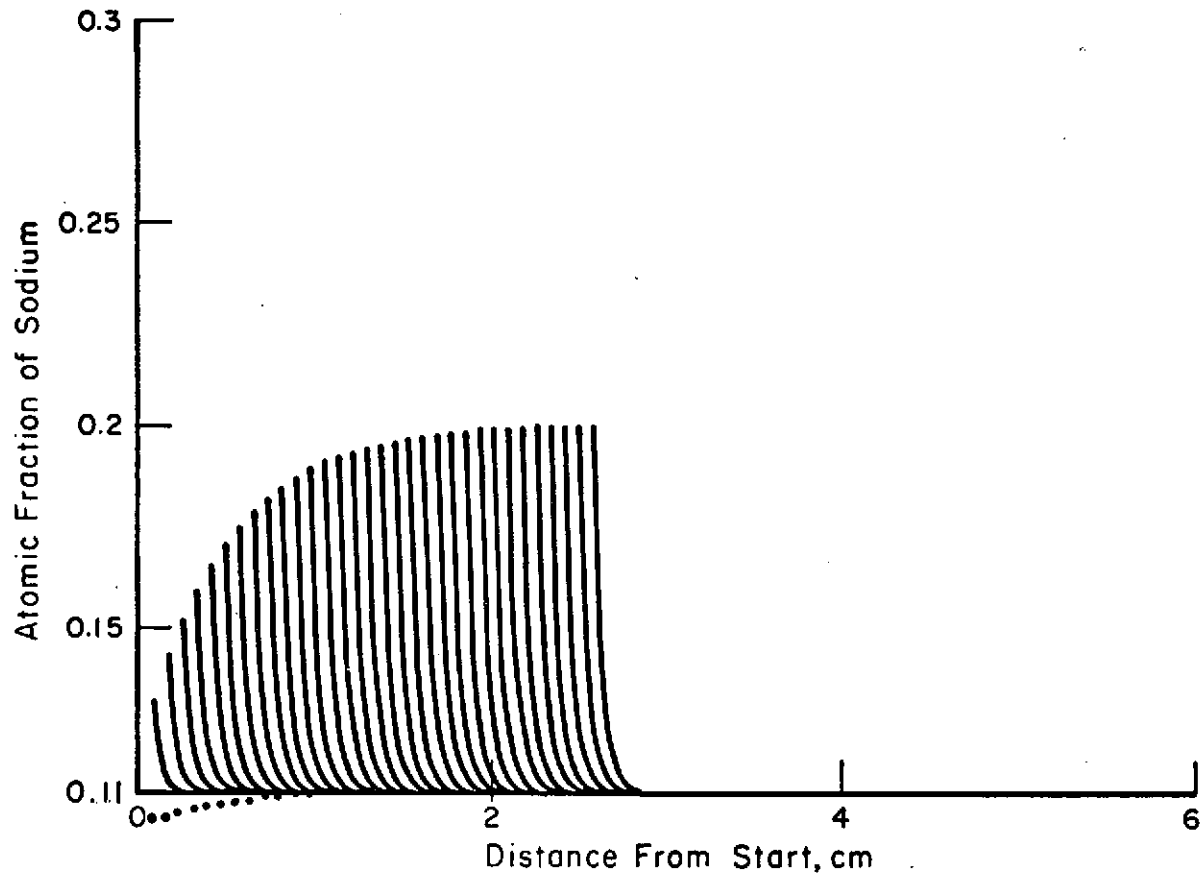


FIGURE 6. SIMULATED SOLIDIFICATION KINETICS FOR BETA ALUMINA, ASSUMING GROWTH RATE OF 10^{-3} cm/sec, SODIUM DIFFUSIVITY IN THE MELT OF 5×10^{-5} cm²/sec. SOLID CURVES REPRESENT CONCENTRATION PROFILES OF SODIUM IN THE MELT AT VARIOUS TIMES. DOTS REPRESENT SODIUM CONTENT IN THE SOLID AT INDICATED POSITIONS.

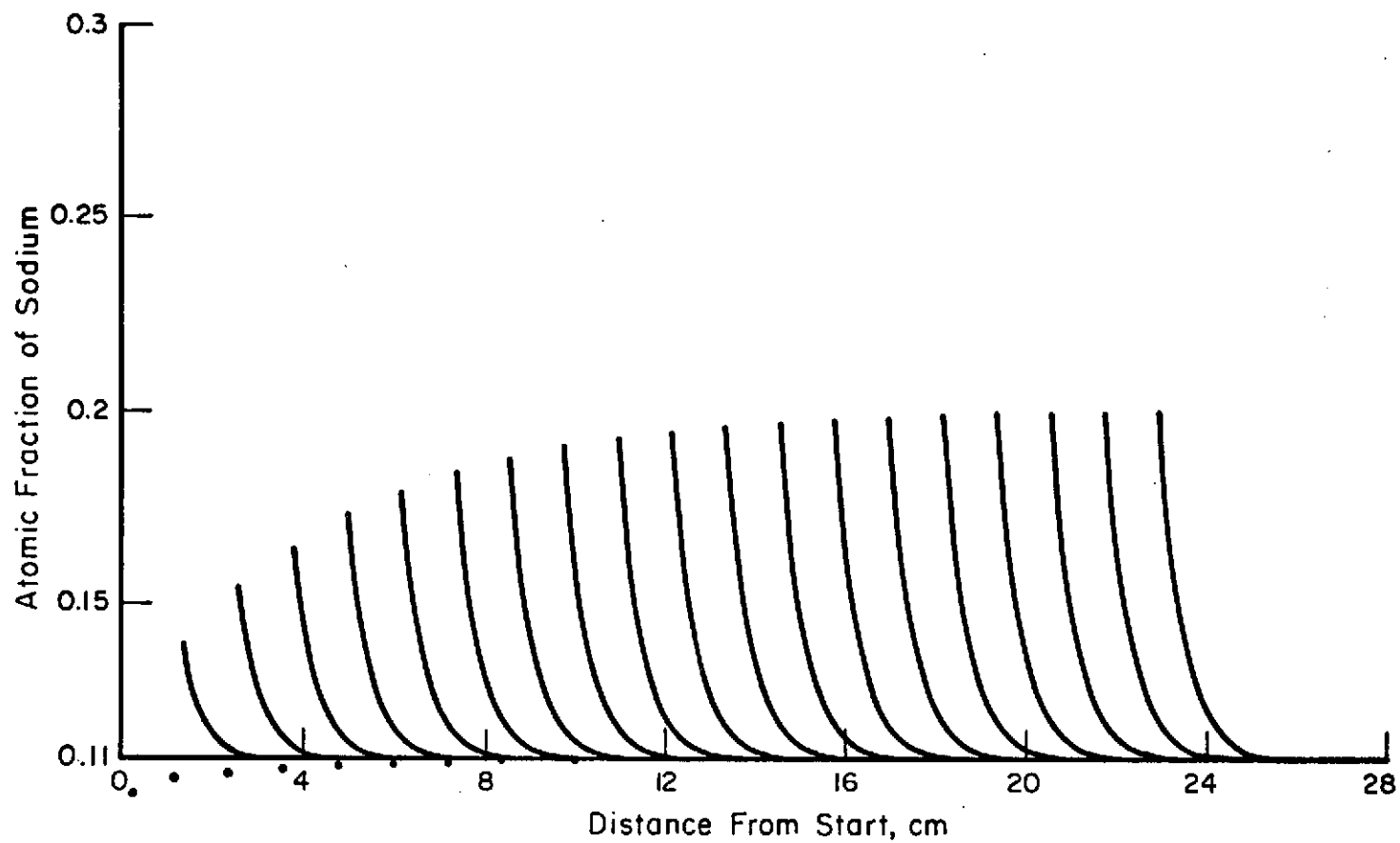


FIGURE 7. SIMULATED SOLIDIFICATION KINETICS FOR BETA ALUMINA. Conditions are the same as for the situation illustrated in Figure 6, except the growth rate here is reduced to 10^{-4} cm/sec.

The dots show the solute concentration in the crystal at various positions. Figure 6 corresponds to a relatively rapid growth rate of 10^{-3} cm/sec, while Figure 7 shows growth at 10^{-4} cm/sec. Note, in Figure 7, the broad solute-enriched region ahead of the growing surface, extending almost 2 cm into the liquid.

3.3. Constitutional-Supercooling Considerations

We also examined the "constitutional-supercooling" considerations of the growth process using data developed in the simulation. Figures 8 and 9 show the minimum permissible melt temperatures for 10^{-3} and 10^{-4} cm/sec growth rates, respectively. This latter information was generated using the steady-state concentration profile developed by the procedure listed in Appendix A. The numerical scheme, in BASIC language, used to obtain Figure 8 and 9 is listed in Appendix B. Here, the computed steady-state concentration profile is seen to be stored in file 8 and brought into the computation at line 240.

A numerical analysis was carried out, using the method listed in Appendix C and written in BASIC language, to predict the minimum necessary temperature gradient in the liquid, at the solid-melt interface and under steady-state conditions, for avoidance of constitutional supercooling (see Woodruff's⁽³⁾ discussion of this phenomenon). The results are summarized in Table 1. It can be seen that, for given solute concentration (11 atomic percent was the value assumed here), the gradient increases with increasing crystal-growth velocity and decreases with increasing solute diffusivity. This is consistent with what one would expect on a qualitative basis, i.e., that for given temperature conditions, increasing the solute diffusivity should retard the onset of instability whereas increasing the growth velocity should enhance the onset of instability.

3.4. Power-Input Requirements

An important factor in considerations of the feasibility of space processing is the power required to operate the experimental apparatus. Clearly, the total power available aboard an orbiting spacecraft is limited. We have thus carried out calculations of the total power required in order to grow beta-alumina crystals from the melt. Two sources of power consumption were considered: (1) that necessary to achieve a temperature gradient in the melt, at the advancing solid-melt interface, at the minimum level required for maintenance of a stable, planar, crystalline interface, and (2) that lost by radiation to the surroundings from the hot alumina surface. We shall, for present purposes, consider the alumina system (melt plus solid) to be contained within a right circular cylinder of length 10 cm and diameter 1.5 cm, and also assume that the nominal system temperature is 2000 deg C.

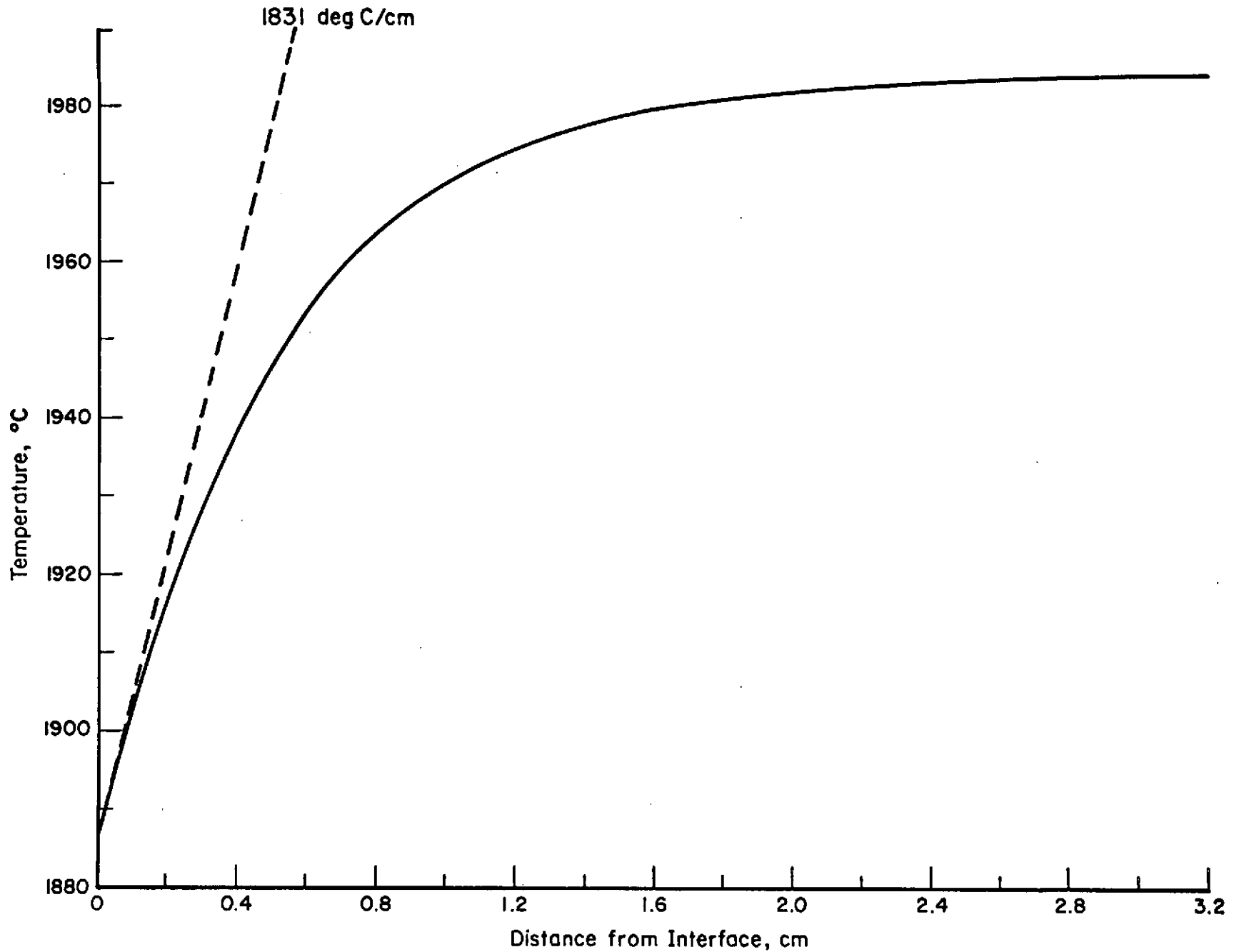


FIGURE 8. MINIMAL MELT TEMPERATURES AHEAD OF MOVING INTERFACE REQUIRED FOR STABLE GROWTH. CONDITIONS CORRESPOND TO THOSE LISTED FOR FIGURE 6. DASHED LINE ILLUSTRATES TEMPERATURE GRADIENT IN THE MELT AT THE INTERFACE.

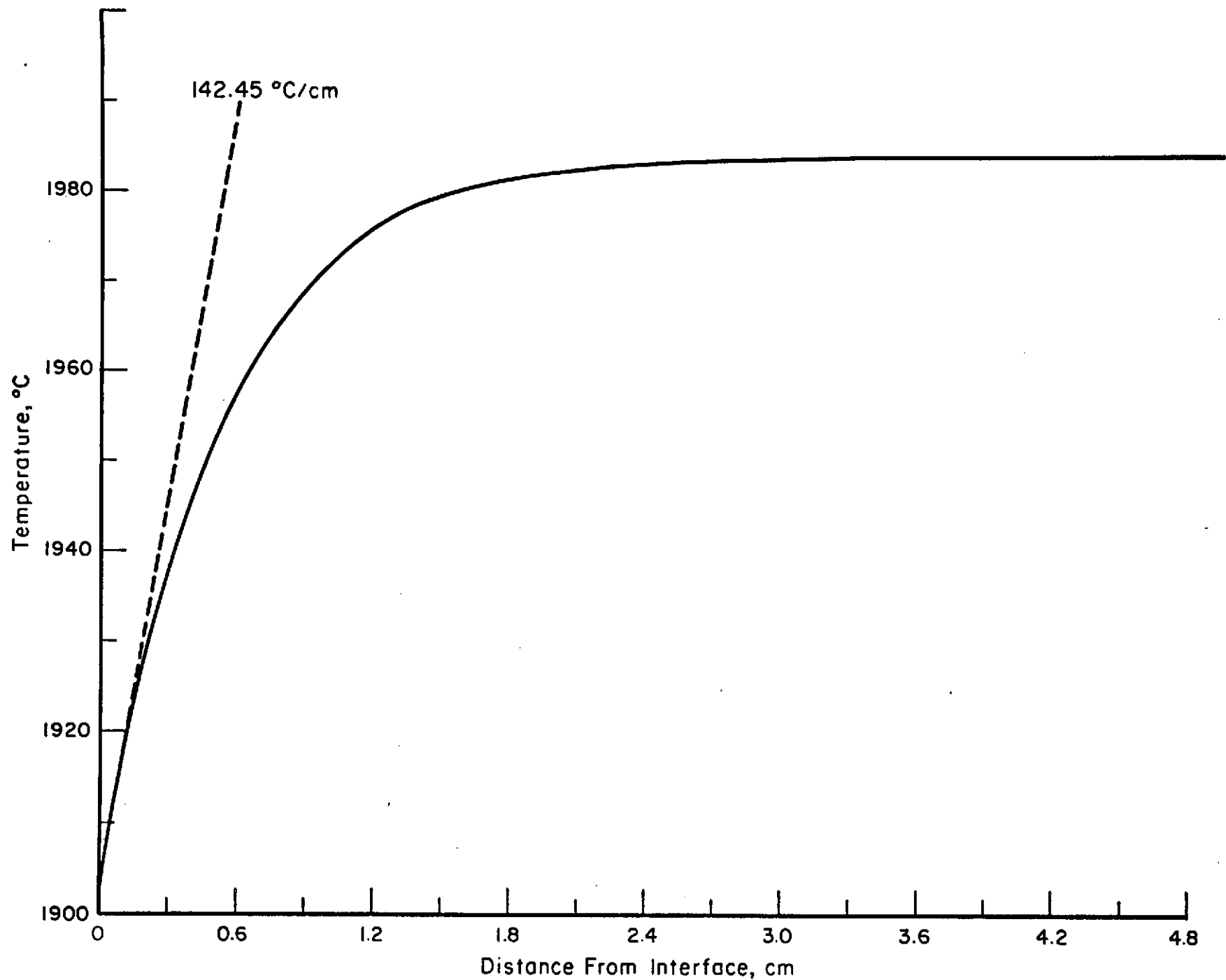


FIGURE 9. MINIMAL MELT TEMPERATURES AHEAD OF MOVING INTERFACE REQUIRED FOR STABLE GROWTH. CONDITIONS CORRESPOND TO THOSE LISTED FOR FIGURE 7.

TABLE 1. MINIMUM TEMPERATURE GRADIENT (IN deg C/cm) IN THE MELT AT THE SOLID-MELT INTERFACE REQUIRED FOR MAINTENANCE OF PLANAR GROWING SURFACE OF BETA ALUMINA

Growth Velocity, 10^{-4} cm/sec	1	288	144	96	72	58	48	41	36	32	29
	2	576	288	192	144	115	96	82	72	64	58
	3	864	432	288	216	173	144	123	108	96	86
	4	1152	576	384	288	230	192	165	144	128	115
	5	1440	720	480	360	288	240	206	180	160	144
	6	1728	864	576	432	346	288	247	216	192	173
	7	2016	1008	672	504	403	336	288	252	224	202
	8	2304	1152	768	576	461	384	329	288	256	230
	9	2592	1296	864	648	518	432	370	324	288	259
	10	2880	1440	960	720	576	480	411	360	320	288
		5	10	15	20	25	30	35	40	45	50
		Solute Diffusivity, 10^{-5} cm ² /sec									

a. Heat Conduction

We assume that the thermal conductivity of the liquid beta alumina is about 0.0075 cal/sec-cm-deg C (taken to be one half that of solid, dense alpha alumina⁽¹⁵⁾ at 1900 deg C). On this basis, it is a simple matter to show that the rate of heat conduction along the cylinder axis, at steady state, and assuming a temperature gradient of 1000 deg C/cm, is about 31 watt per cm² cross sectional area. For our prototypic cylinder of 1.5 cm diameter, the total amount of heat being conducted is about 55 watt. It should be noted that the actual minimum temperature gradient required for stable advancement of the planar interface is a function of such factors as the partition coefficient, interface velocity, and solute diffusivity in the melt⁽³⁾. One finds, from Table 1, that a gradient of about 1000 deg C/cm, or higher, would permit stable growth of the beta alumina crystal at, for example, a velocity of about 7 $\mu\text{m}/\text{sec}$ for a solute diffusivity of $1 \times 10^{-4} \text{ cm}^2/\text{sec}$.

b. Heat Radiation

The heat lost by radiation from the alumina surface can be estimated from well-known results of radiation theory. We thus find⁽¹⁶⁾, ignoring radiation from the ends of the cylinder, that

$$\dot{q} = \epsilon\sigma(T_a^4 - T_s^4)/N$$

where \dot{q} is the rate of radiative heat flow across unit area of the alumina surface, ϵ is a heat-exchange factor, σ the Stefan-Boltzmann constant, T_a the absolute alumina temperature, T_s the absolute temperature of the surrounding heat shields (assumed cylindrical and concentric with the alumina), and N is the total number of heat shields. Assuming specular reflection of radiation, we can set⁽¹⁶⁾

$$\frac{1}{\epsilon} = \frac{1}{\epsilon_a} + \frac{1}{\epsilon_s} - 1$$

where ϵ_a is the emissivity of the alumina (taken to be unity) and ϵ is the emissivity of the heat shields (taken to be 0.05). We take $T_a = 2273$ deg K, $T_s = 300$ deg K, and $N = 10$, in which case we find $\dot{q} = 0.757$ watt/cm². For our prototypic system, this amounts to a heat-loss rate of about 36 watt.

c. Discussion

The net rate at which heat is supplied to the system, to both maintain the necessary temperature gradient and account for radiative losses amounts to about $55 + 36 = 91$ watt. It must be borne in mind, however, that the total amount of power input required to operate the experimental

setup depends upon the manner in which the system is coupled to the power source. For example, one of us (W. O.) has carried out analogous calculations for a crystal-growth system in which coupling of power was achieved rather inefficiently using an image furnace for which only a relatively small fraction of the power generated by the furnace was actually delivered to the system. It is anticipated, however, that more efficient power coupling can be achieved in space using solar-imaging techniques. But it is clear that the method of power coupling will represent an all-important factor in determining the total power needed from the source.

4. MARKET CONSIDERATIONS

Beta alumina has already been put to many kinds of uses including, as we have noted above, applications as components in batteries and fuel cells having high energy density and as electrochemical transducers for the measurement of thermodynamic and kinetic data. These more recent applications follow its use for decades as a refractory material⁽¹⁷⁾. However, looking toward the future, one of the most promising and extensive uses for beta alumina may be as components in load-leveling devices used to store electricity⁽¹⁸⁾. It is estimated that such devices will be required to store about one third of all the electrical energy generated in this country. Thus, for example, by 1980 the estimated power capacity required for the United States will be about 0.544×10^{12} watt⁽¹⁹⁾. Assuming that about one-quarter watt of power can be transmitted across each cm^2 of beta alumina surface⁽¹⁸⁾, and assuming a nominal membrane thickness of 0.15 cm, this amounts to a total of $0.1088 \times 10^{12} \text{ cm}^3$ of beta alumina or, assuming a density of 3.29 gm/cm^3 ⁽²⁰⁾, a total mass of about $3.6 \times 10^8 \text{ kg}$. This enormous figure, of course, represents an upper limit, since other types of electrical-energy-storing devices will be used in addition to storage batteries using beta alumina. Also, the amount of material used in a given application will vary with its quality (e.g., thinner sections of material can be used if the form is single crystal).

The principal significance of the above calculation lies in the fact that very large quantities of beta alumina are likely to be required over the next decade. The quality of the material required will vary widely, depending upon details of the proposed applications. It is evident, however, that those situations in which maximum efficiency of operation is imperative can benefit most from the use of high-quality single crystals. In these instances, space processing offers the best hope for producing such high-quality material. Clearly, however, such situations will have to be selected on a priority basis, since, at least at this time, the supply of material generated through space processing seems unlikely to be able to meet the demands.

One additional example of an application for beta alumina, for which space processing would appear to be most desirable, is its use in sodium-halogen batteries, which are used, for example, as components of cardiac pacemakers^(21,22). For such cases, in which highest quality, longest lifetime, and maximum operating efficiency (and consequently,

high-quality beta alumina) are of particular importance, the benefits offered by space processing must indeed be placed at a high level of significance.

5. CONCLUSIONS

As we have pointed out (Section 2.3), the single-crystal form of beta alumina is much to be preferred over the polycrystalline form for applications as a fast ionic conductor, the single crystal having both superior properties and longer useful lifetimes. Unfortunately, single crystals of this material are relatively difficult to fabricate terrestrially, and relatively slow growth rates must be used⁽¹⁾ which render the terrestrial process uneconomical. In addition, terrestrially grown single crystals are likely to contain inhomogeneities, products of the growth process, which effectively decrease the ionic transport rates. These reasons, in view of the expanding technological applications of the fast ionic conductors, provide the incentive for turning to space processing as a possible alternative for generating high-quality single-crystal material.

In this research, we have utilized a computer-simulation approach to predict the solidification behavior of beta alumina under zero-gravity conditions. This approach provides a comprehensive means for utilizing best current knowledge of solidification theory as applied to this specific problem. Results of the simulation indicate that growth rates could be attained in space, the order of several cm/hour, for crystals having large cross-sectional area; hence, although growth rates would still be relatively slow, the volumetric rate of production could be high. This would make the utilization of space processing economically feasible.

6. RECOMMENDATIONS

In view of the results obtained from this research, which indicate the potential value of space processing for the fabrication of single crystals of beta alumina, we recommend that the following procedures be carried out:

- (1) Extend the scope of the computer-simulation study to include such factors as variations of melt density with both solute concentration and temperature. This will permit us to quantitatively assess the magnitude of convection currents to be expected with terrestrial growth of beta alumina and thereby evaluate the extent and nature of inhomogeneities incorporated into such crystals. This will also provide us with a quantitative

comparison between the best-possible terrestrially-grown crystals and the space-grown material, an essential factor in evaluating the relative desirability of space processing. In addition, comparison can also be made between predicted microstructures and existing experimental data for terrestrially grown crystals; this would yield quantitative assessment of the accuracy of the simulation.

- (2) Design an apparatus to grow ceramic crystals in space from the melt; then make such appropriate modifications of this apparatus as may be necessary to meet any particular requirements for growth of beta alumina. An important aspect of this design will be the nature of the coupling between the power source and the apparatus. We believe that the feasibility of utilizing appropriate solar-imaging techniques should be investigated, since these could yield relatively simple and efficient means for coupling solar energy to the crystal-growth system. This portion of the research would also yield an assessment of the potential rate of production of material attainable by space-processing methods.
- (3) A wide range of crystalline ceramic materials is currently being investigated for possible uses as fast ionic conductors. Many of these are difficult to manufacture on earth in single-crystal form, and space processing offers a practical alternative. Extension of the work reported here to these other important materials would therefore be of great interest to those involved with development of their applications. Such extension can readily be carried out via computer-simulation techniques, using appropriate phase-diagram data.

These additional studies would require an effort of approximately 6 man-months plus associated computer expenses.

7. NEW TECHNOLOGY

No new technology was achieved from work carried out on this program.

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APPENDIX A

LISTING OF PROGRAM FOR SOLIDIFICATION SIMULATION

A-1

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```

10 DIM BS(20),CS(20),TS(20)
20 DATA 3000,0.11,100,0.01,2000,1600,0.1,0.35,0.125,5E-05,20,900
30 READ T2,T3,G1,G2,T5,T6,P4,P5,P6,C1,J1,L1
40 T1=01=X1=02=X2=T8=0
45 G9=T3
50 R1=G2/G1
60 G5=(P4-P6)/(P4-P5)
70 R3=R1*T2
80 M1=(G5-1)*R3
90 E1=(P6-G5*P5)*R3
100 I1=4
110 D1=R3
120 D2=2*D1
130 D3=D1*D2
140 J2=J1-1
150 DISP "MIN. INIT TEMP";T6+(T5-T6)/(P5-P4)*(P5-T3);
160 WAIT 10000
170 G2=C1*T2
180 A1=C2/D2
190 D4=D1+R3
200 SCALE -1,40,0,0.35
210 YAXIS 0,0.05
220 XAXIS T3,1
230 FOR I2=0.05 TO 0.3 STEP 0.05
240 PLOT -1,I2,0
250 LABEL (*),I2
260 NEXT I2
270 REM INIT T ARRAY
280 FOR I2=1 TO J1
290 T[I2]=T3
300 NEXT I2
310 FOR L2=1 TO L1
320 T1=T1+T2
330 X2=X2+R3
340 G9=T3
350 FOR I2=1 TO J2
360 T[I2]=T[I2+1]
370 NEXT I2
380 T[J1]=T3+T8
390 N=J1
400 GOSUB 660
410 FOR I2=2 TO J2
420 N=J2-I2+2
430 GOSUB 720
440 NEXT I2
450 N=1
460 GOSUB 790

```

LISTING OF PROGRAM FOR SOLIDIFICATION SIMULATION

```

470 T[1]=T[1]+T4
490 FOR I2=2 TO J1
500 T4=T4*A1/B[I2]+C[I2]
510 T[I2]=T[I2]+T4
530 NEXT I2
535 T8=T4*0.5
540 IF L2/I1#INT(L2/I1) THEN 640
550 S3=FNL(2)
560 C9=P6+G5*(T[1]-P5)
570 OFFSET X2,0
580 PLOT 0,C9
590 PEN
600 FOR I2=1 TO J1
610 PLOT D1*(I2-0.5),T[I2]
620 NEXT I2
630 PEN
640 NEXT L2
650 END
660 REM OUTER
670 S3=FNL(N-1)
680 S[1]=S3+S2*3*D1
690 B[N]=A1+D1
700 C[N]=(-C2*S[1]+Q1)/B[N]
710 RETURN
720 REM CENTRE
730 S3=FNL(N)
740 S[2]=S[1]
750 S[1]=S3+S2*D1
760 B[N]=A1+C2*(1-A1/B[N+1])/D2+D1
770 C[N]=C2*((S[2]+C[N+1]/D2)-S[1])/B[N]
780 RETURN
790 REM INNER
800 S[2]=S[1]
810 B[N]=A1
820 D5=A1*B[1]/B[2]-B[1]-D1
830 T4=(T[1]*M1+E1-C[2]*B[1]-C2*S[2])/(D5-M1)
840 RETURN
850 DEF FNL(N)
860 P1=T[N-1]
870 P2=T[N]
880 P3=T[N+1]
890 L3=(4*P2-P3-3*P1)/D2
900 S2=(P3-2*P2+P1)/D3
910 RETURN L3
920 END
930 FOR N=1 TO 20
940 PRINT T[N];
950 NEXT N
960 END

```

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Definitions of Important Symbols

C1	Diffusivity of solute in melt
C2	Time increment multiplied by C1
C9	Sodium concentration in the solid
D1	Node spacing
G1	Temperature gradient in the melt at the interface
G2	Rate of cooling
I1	Number of computation loops between plots
J1	Number of space subdivisions
L1	Number of calculation loops
P4	Composition of solid at temperature T5
P5	Eutectic liquid composition
P6	Eutectic solid composition
Q1	Rate of solute removal from the melt, such as by evaporation (set at zero for this work)
R1	Rate of interface movement
T2	Time increment for each calculation loop
T3	Bulk concentration of sodium in liquid
T5	Temperature of intersection of liquidus and solidus lines of phase diagram
T6	Eutectic temperature
T7	Liquid composition at interface
T8	Minimum bulk temperature of liquid
T9	Initial liquid temperature
W1	Length of boule
X1	Amount of growth

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APPENDIX B

LISTING OF PROGRAM FOR ANALYSIS OF
CONSTITUTIONAL SUPERCOOLING

B-1

APPENDIX B

LISTING OF PROGRAM FOR ANALYSIS OF
CONSTITUTIONAL SUPERCOOLING

```

10  DIM CS[40],TS[40]
20  DEF FNT(C1)=(C1-P5)*(T5-T6)/(P4-P5)+T6
30  FIND 8
40  DATA 1000,0.11,100,0.01,2000,1600,0.1,0.35,0.125,5E-05,20,900
50  READ T2,T3,G1,G2,T5,T6,P4,P5,P6,C1,J1,L1
60  T1=Q1=X1=Q2=X2=T8=0
70  C9=T3
80  R1=G2/G1
90  G5=(P4-P6)/(P4-P5)
100 R3=R1*T2
110 M1=(G5-1)*R3
120 E1=(P6-G5*P5)*R3
130 I1=4
140 D1=R3
150 D2=2*D1
160 D3=D1*D2
170 J2=J1-1
180 DISP "MIN. INIT TEMP ";FNT(T3);
190 WAIT 10000
200 C2=C1*T2
210 A1=C2/D2
220 D4=D1+R3
230 REM INIT C ARRAY
240 LOAD DATA 8,C
250 FOR I2=1 TO 40
260 T[I2]=FNT(C[I2])
270 NEXT I2
280 B1=INT(T[1]/10)
290 B2=INT(T[40]/10)+1
300 SCALE -2*D1,39*D1,B1*10-10,(B2+1)*10
310 FOR I2=2 TO 40
320 PLOT I2*D1,T[I2]
330 NEXT I2
340 PEN
350 S3=FNL(2)
360 G7=S3
362 FOR I2=0 TO D1 STEP 0.1*D1
364 PLOT D1+I2,T[1]+I2*(S3+I2*S2)
366 NEXT I2
370 PEN
390 X1=(B2*10-T[1])/G7+D1
410 PLOT D1,T[1]
420 PLOT X1,B2*10
430 PLOT X1-D1,B2*10,1

```

B-1 a

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440 LABEL (*)G7
470 XAXIS B1*10,DI
480 YAXIS DI,10
490 FOR B3=B1 TO B2
500 PLOT -0.9*D1,B3*10,0
510 LABEL (*)B3*10
520 NEXT B3
540 PLOT 4*D1,7.5*B2+2.5*B1,0
550 LABEL (*) "MINIMAL MELT TEMPERATURES AHEAD OF THE INTERFACE"
555 PLOT 4*D1,7.5*B2+2.5*B1,0
557 CPLOT 0,-1
560 LABEL (*)"FOR STABLE GROWTH."
565 PLOT 4*D1,7.5*B2+2.5*B1,0
567 CPLOT 0,-3
570 LABEL (*)"MINIMUM TEMPERATURE GRADIENT = ";G7;" DEG/CM"
572 PLOT 5*D1,5*(B1+B2),0
574 LABEL (*)"GROWTH RATE";R1;"CM/SEC"
580 PLOT 5*D1,B1,1
582 CPLOT 0,1
590 LABEL (*)"POSITION";D1;"CM. UNITS"
600 END
610 DEF FNL(N)
620 P1=T[N-1]
630 P2=T[N]
640 P3=T[N+1]
650 L3=(4*P2-P3-3*P1)/D2
660 S2=(P3-2*P2+P1)/D3
670 RETURN L3
680 END
690 FOR N=1 TO 20
700 PRINT T[N];
710 NEXT N
720 END

```

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APPENDIX C

LISTING OF PROGRAM FOR ANALYSIS OF
TEMPERATURE-GRADIENT REQUIREMENTS

C-1

APPENDIX C

LISTING OF PROGRAM FOR ANALYSIS OF
TEMPERATURE-GRADIENT REQUIREMENTS

```

10 DIM BS[20,10]
20 DATA 3000,0.11,100,0.01,2000,1600,0.1,0.35,0.125,5E-05,20,900
30 READ T2,T3,G1,G2,T5,T6,P4,P5,P6,C1,J1,L1
40 T1=Q1=X1=Q2=X2=T8=0
50 C9=T3
60 G5=(P4-P6)/(P4-P5)
70 G3=1/G5
80 E2=P5-P6*G3
90 C3=(P4-P5)/(T5-T6)
100 FOR I3=1 TO 20
110 FOR I2=1 TO 10
120 C1=I2*5E-05
130 R1=I3*5E-05
140 B[I3,I2]=--R1*(T3*(G3-1)+E2)/C1*C3
145 IF B[I3,I2]<T1 THEN 150
147 T1=B[I3,I2]
150 NEXT I2
160 NEXT I3
170 SCALE -0.1*R1,R1,-0.1*T1,T1
180 FOR I2=1 TO 10 STEP 2
190 FOR I3=1 TO 20 STEP 19
200 PLOT I3*5E-05,B[I3,I2]
210 NEXT I3
220 PEN
230 CPLOT -8,-1
240 LABEL (242)I2*5E-05
242 FORMAT F8.5
250 NEXT I2
260 XAXIS 0,0.1*R1
270 YAXIS 0,T1*0.1
280 FOR I2=1 TO 10
290 PLOT -0.09*R1, 2*0.1*T1,0
300 LABEL (*)I2*0.1*T1
310 NEXT I2
320 FOR I2=1 TO 9
330 PLOT I2*0.1*R1,-0.09*T1,0
340 LABEL (*)I2*0.1*R1*1E+06
350 NEXT I2
500 PRINT "          DIFFUSIVITY, 1E-5 UNITS"
510 FOR I2=1 TO 10
520 PRINT I2*5;
525 NEXT I2
530 PRINT
540 FOR I3=1 TO 20
545 PRINT "GROWTH VELOCITY =" ; I3*5E-05
550 FOR I2=1 TO 10

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560 PRINT B[I3,I2];  
570 NEXT I2  
580 PRINT  
590 NEXT I3  
600 END
```

C-2