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Interface Stability and Defect Formation during Crystal Growth

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Fabietti, L. M. R.

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Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

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Interface stability and defect formation during crystal growth

Luis Maria Rodolfo Fabietti

Under the supervision of Rohit K. Trivedi

From the Department of Materials Science and Engineering

Iowa State University

Unidirectional solidification experiments have been carried out in organic crystals with the aim of improving our knowledge on the effects of constraints on the interface morphology and to increase our understanding of the growth of anisotropic materials. The experimental information shows that lateral constraints such as a sharp change in the cross-sectional area in the solid liquid interface path, can produce important changes in the microstructure if the interface morphology is planar, cellular or dendritic.

The study of anisotropic materials cover several topics. It is first shown that slight anisotropy does not influence the dendrite tip selection criterion. This conclusion is obtained from the analysis of the relationship between tip radius and velocity for dendrites growing under the steady state condition for two different materials, CBr_4 and C_2Cl_6 , which have different surface energy anisotropy values. The values of the dendrite operating parameters σ^* are compared with the predictions of the solvability theory and the morphological stability theory. The experiments show better agreement with the latter theory.

Critical experiments have been designed and carried out to find the response functions which determine the composition and temperature of the interface as a function of velocity

in faceted materials. The experiments, carried out in Napthalene-Camphor system, indicate a strong temperature dependence of the planar interface growth which can be correlated with the step growth mechanism. Experiments on the interface instability show an important dependence on the crystallographic orientation.

Unidirectional solidification experiments in zone refined Napthalene confined in very thin cells (gap size $\leq 50\mu\text{m}$) have proven to be a good method to study the defect production at the solid liquid interface. Specifically, the photoelastic properties of Napthalene provides a visual examination of the stress configuration. The photoelastic fringes correlate with the stress produced at the interface during the solidification. A finite element model is proposed that assumes the stress to be due to an inhomogeneous concentration distribution in the solid near the interface.

Unidirectional solidification experiments have been carried out with Tert Butyl Alcohol which indicate that the initial instability is similar to that for nonfaceted materials. A morphological transition which is similar to the cellular-dendritic transition in nonfaceted materials is identified.

The analysis of the transient times in unidirectional solidification experiments, carried out in the Succinonitrile-Acetone system, indicates that the presence of thermomigration and convection can produce important departures from the theoretical models which consider solute diffusion as the only mechanism present.

Interface stability and defect formation during crystal growth

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Luis Maria Rodolfo Fabietti

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GENERAL INTRODUCTION

Since the man realized his ability to manipulate the environment, the understanding of the basic laws which control the nature has been one of the most persistent work in human history. One part of that work is the area of materials science. The evolution in the field has been tremendous, from changes in shape through mechanical work to the development of new materials. Metallurgy, probably because of its association with war, was one of the most developed fields. In this field, there are historical gaps where the information has been lost, as for example the case of the Damascus swords, and hundreds of years later we can not fully understand how they were processed.

Industrial revolution and the understanding of the physics at an atomic level brought a new insight which expanded the field of application and increased the spectrum of materials available through the development of new materials and processing techniques.

Not long ago, another big step in the technological evolution occurred with the discovery of the transistor and its natural evolution, the microchip. In this case, technology had to develop new requirements, such as extreme purity and high quality in the crystals produced for use as base material.

One of the most powerful tools for the material scientist is the manipulation of the phase transformations involved in the development of any material. Vapor deposition, solidification, melting, and precipitation of second phases, are examples of chemical and structural changes, and the understanding of the laws behind them is one of the key points in the materials science research. In particular, solidification is one of the most common transformation in material processing and has been used for thousands of years as a required step in the production of pure elements and alloys. Most of the characteristics formed

during solidification will be permanent or very difficult to remove completely, so the understanding and the controlling the solidification microstructures is very important.

Solidification studies are based fundamentally on the analysis of the influence of distinct variables present during the transformation, i.e., composition, thermal gradient, rate of cooling and geometry of the mold. The interaction of these parameters gives a microstructure that is responsible for the properties of the material. The traditional approach to the problem has been to carry out solidification processes by keeping all but one of the variables constant. In this sense, unidirectional solidification experiments were and are one of the key tools in the investigation of this field. Such directional solidification has primarily been carried out to study basic principles in materials with isotropic properties under isolated conditions.

In the directional solidification studies of metals, the analysis is generally made after the solidification process is complete by cutting, polishing, and etching the material and then examining it under a microscope to determine or model the microstructure evolution for a given set of external conditions. In recent years, with the help of selected organic crystals which have similar characteristics as metals regarding the solidification process, it is possible to analyze "in situ" the formation of different morphologies of the interface under diverse experimental conditions. The morphology is both a characteristic of the material and of the external conditions imposed on the system and is the macroscopic evidence of the atomistic process involved in the transformation.

As in other areas of science, the technological requirements are the driving force for the evolution and the solidification field is not exempt of this rule. The use of nontraditional materials, i.e., composite materials for products previously made of metals, the change in the processing techniques, i.e, from heavily deformed and precipitated alloys to monocrystals of variable geometry like turbine blades and the birth and development of the

solid state electronics and related laser optics, are some of the most important examples which brought a new challenge to the material processing where the solidification plays a key role. In particular, solid state electronic materials, like Ge and Si have anisotropic growth properties and the necessity of high purity and high crystal quality is the starting point for making any integrated circuit. Therefore, the knowledge and understanding of the mechanisms which govern the solidification of these materials is of prime importance.

The purpose of this thesis is to improve our knowledge of the solidification of materials with anisotropic growth characteristics and to examine the influence of mold geometry on the development of microstructures.

The experimental approach has been to study transparent organic crystals in unidirectional solidification experiments. This successful technique allows "in situ" observation of the morphological development of the solid liquid interface under controlled experimental conditions. The similar growth characteristic of metals and semiconductors with some organic materials enables one to use transparent organic crystals as a model system to understand the dynamical process of solidification microstructural development in metals and semiconductors.

Explanation of Dissertation Format

This dissertation has been written in the alternate format. Under the scope of understanding the interaction of the solute diffusion field with the mold geometry, a simple constraint was applied to a solidification front, i.e., the cross section area of the solidification front was closed, except for a small aperture. In the actual dimensions of the experiment the gap size was $\approx 1\text{mm}$. This constraint implies a reduction in the cross section area by a factor 25. In the first section critical experiments in the Succinonitrile-

Acetone system have been carried out to study the influence of this lateral constraint in the interface morphology. It is shown that the importance of the gap depends on the unperturbed interface morphology, being most important for planar interface and not affecting the structure for dendritic interface when the interdendritic spacing is less than 5 times the gap size.

Previous studies on metals and plastic crystals assumed that the surface energy is isotropic. Although all dendrites are parabolic in shape near the tip region, there are certain differences induced by the small surface energy anisotropy. We examined the Carbon Tetrabromide-Hexachloroethane system, $\text{CBr}_4\text{-C}_2\text{Cl}_6$, which has an eutectic. Hypo and hyper eutectic alloys were prepared and unidirectional solidification experiments were carried out to obtain a dendritic interface morphology for dendrites rich in CBr_4 in one case and rich in C_2Cl_6 in the another. In the second section, experiments were carried out to distinguish between two theories on morphological dendrite tip stability. On one side, the solvability theory predicts that the stability condition depends on the surface energy anisotropy. On the other hand, the morphological stability theory obtains a similar analytical expression which is independent of the anisotropic properties of the material. The experimental values show that the growth anisotropy does not influence the tip radius selection giving a result more consistent with the marginal stability theory.

Only one variable characterizes the planar interface growth of nonfaceted materials. It is only necessary to know the interface temperature. The solid or the liquid compositions at the interface are obtained through the use of the equilibrium diagram. An increase in the growth anisotropy means that kinetics effect will become prominent. The interface temperature and composition are not longer related by the equilibrium conditions. The interface velocity enters now as a new variable, so that the composition of the solid and liquid at the interface depend upon velocity and interface temperature. These two

relationships for interface compositions are called response functions. The knowledge of the response functions allows the quantitative evaluation of the nonequilibrium conditions at the interface, i.e., it enables one to calculate departure from the equilibrium. In the third section an experimental method is given to measure these response functions. The experiments were carried out in the Naphthalene-Camphor system and a detailed analysis of the planar interface stability as a function of the orientation is presented. From the measurements of the variation in the planar interface temperature as a function of the external velocity the step growth mechanism for the interface growth has been identified.

For further study of faceted materials, a series of unidirectional experiments have been carried out in Tert Butyl Alcohol since it has an absolute entropy of fusion slightly above the marginal value suggested by Jackson to distinguish between faceted and nonfaceted materials. A material with such a characteristics should show both faceted and non faceted behavior. In the fourth section, a comprehensive study of the growth condition of TBA has been carried out showing that it is solute and not the kinetic effect which induces different morphologies.

The solid-liquid interface of faceted materials has points of high inhomogenities due to their anisotropic characteristics in surface energy, kinetic coefficient or distribution coefficient. The effects can induce stresses in the solid and they can change the morphology of the interface in a very important way. The development of stress induced near the interface during growth has been examined in the fifth section and it is shown for the first time by "in situ" observations how defects are produced in the solid liquid interface in zone refined Naphthalene. The stress distribution is associated with the stress fringes seen in photoelastic materials. A plausible model is developed which correlates these stresses with the concentration gradient in the solid.

The transient regime is a inevitable step in the solidification experiments. Current theories assume that the interface velocity is equal to the external velocity and that no

instability occurs at the planar interface during the transient time. The former assumption is contradictory with the other experimental variables. About the latter assumption, there is no information as yet about the validity of the constitutional supercooling criterion when the interface becomes unstable during the transient time. Thus, in the sixth section, an analysis of the transient times in solidification experiments has been carried out in the Naphthalene-Camphor and the Succinonitrile Acetone systems. A disagreement is found between the experimental results and the a theory based on diffusion as the only mechanism operating in the liquid for the matter transfer. The experimental results are analyzed by considering the possibilities of thermal migration and convection as possible mechanisms of mass transfer in the liquid.

SECTION I. THE DEVELOPMENT OF SOLIDIFICATION MICROSTRUCTURES IN PRESENCE OF
LATERAL CONSTRAINTS

INTRODUCTION

The ability to define processing conditions so as to obtain an optimum microstructure in the solidified material is the key aspect of the design of many technologically important processes which include casting, welding, single crystal preparation and rapid solidification techniques. Our fundamental understanding of the correlation between the processing conditions and the microstructural development has primarily come from theoretical models [1-10] and critical experimental studies [11-20] carried out under well-characterized solidification conditions. For directional solidification, the microstructure evolution is studied under fixed conditions of temperature gradient at the interface, G , the externally imposed velocity, V , and the alloy composition, C_0 . It is also often assumed that the interface is growing under steady-state condition so that its velocity is precisely the same as the externally imposed velocity. Also, the cross-section of the solidifying material is assumed to be constant.

If the solidification technique is to be used successfully to process advanced engineering components, it is important that we extend our understanding of microstructure formation to more complex conditions. Many engineering components do not have a uniform cross-section. For example: the turbine blades made by the directional solidification technique have varying cross-sections which will influence the final microstructure that forms in the finished product [21-23]; a discontinuous change in cross-section exists when an alloy is solidified in presence of discontinuous fibers [24-27]; and the ability to produce shaped single crystals of varying cross-sectional areas has important applications in device technology and instrumentation [28,29]. Two important effects arise due to the change in cross-section that will influence the microstructure of the solidified alloy. First, the heat flow may not be unidirectional so that one needs to investigate the thermal field in a

complex geometry. Detailed numerical studies of such thermal fields have indeed been carried out [22-23]. The other important effect is the change in solute field ahead of the interface, as the interface approaches the region where the cross-section changes significantly. This aspect has not been studied in detail, and it is the purpose of this paper to report critical experimental studies which elucidate the effect of discontinuities in the cross-section on the morphology of the interface.

When an interface that is moving under steady-state conditions encounters a change in cross-section, the interface velocity changes significantly from the externally imposed velocity. Since the morphological stability of the interface is governed by the local velocity of the interface, a significant change in interface morphology can occur if the cross-section is changed significantly. This change in morphology will also result into micro and macrosegregation patterns which would be significantly different from those in the uniform cross-section region. In order to understand the effect of cross-section changes on the microstructural development, we have carried out directional solidification experiments in a model transparent system, Succinonitrile-Acetone system, so that the changes in interface shapes can be examined in situ. Different experimental conditions have been examined which produce different initial microstructures in a region of constant cross-section. This has enabled us to characterize the effect of cross-section changes on the initially planar, cellular and dendritic interfaces.

EXPERIMENTAL TECHNIQUES

Directional solidification studies were carried out in a temperature stage described by Eshelman and Trivedi [30] and Mason and Eshelmann [31]. The temperature trace in the steady-state regime, produced by a calibrated thermocouple, was used to determine the temperature gradient in the sample. All experimental studies were carried out in Succinonitrile-Acetone system since all the thermophysical properties of this system have been carefully determined [12]. Both Succinonitrile and Acetone were purified before mixing, and the techniques used to purify these materials have already been described by Somboonsuk et al. [14] and Eshelman and Trivedi [30].

The major experimental difference in these studies was the design of the Hele-Shaw cell which contained the Succinonitrile -Acetone mixture. The basic designs of the cell are shown in Fig. 1. The cell design incorporated a constraint which significantly reduced the cross-section of the sample. Experimental studies were carried out with the sample cell design shown in Fig. 1a in which the angle, ϕ , was varied from zero to ninety, Fig. 1b. For very small angles, a nucleation of solid ahead of the interface was observed, so that most of the experiments were carried out with $\phi=45^\circ$. In order to observe the effect of the angle on morphological evolution, a set of experiments was also carried out with $\phi=90^\circ$.

The sample cell was made of glass slides with a gap of 150 μm between the slides. The constraints, used to change the cross-section, were also made of 150 μm thick material. Since the material used to constrain the sample may influence the thermal profile in the sample, different materials such as glass, mylar and alumina were used to check the effect of the constraint material on solidification microstructures. No significant difference was observed with these materials. Consequently, glass and mylar were used in this study. Most experiments were carried out with mylar since its thermal conductivity is closer to

Succinonitrile than that of glass. Consequently, the thermal fields were nearly unidirectional so that the changes in microstructures can be largely attributed to the effect of the cross-section change on the solute profile ahead of the interface.

(a)

(b)

Figure 1. The designs of the cell which illustrate the shape of the constraint used to change the cross-section. (a) $\phi = 45^\circ$, (b) $\phi = 90^\circ$

EXPERIMENTAL RESULTS

Experimental studies were carried out in Succinonitrile - 0.60wt.% Acetone, and the temperature gradient was maintained at 4.8 K/mm. For this temperature gradient value, the latent heat effect on the temperature gradient at the interface will be negligible for low velocities used in these experiments. Directional solidification experiments were carried out with externally imposed velocities of 0.3, 0.5, 0.8, 1.0, 2.0, and 5.0 $\mu\text{m/s}$ in the cell design shown in Fig. 1a. In the initial region that has a constant cross-section, a planar interface at 0.3 $\mu\text{m/s}$, a cellular interface at 0.5 $\mu\text{m/s}$, and a dendritic interface at and above 0.8 $\mu\text{m/s}$, were found to be stable. Experiments were also carried out at the external velocities of 0.8 and 2.0 $\mu\text{m/s}$ in the cell design shown in Fig. 1b. We shall now describe the morphological changes which occurred as these interfaces approached the constraint that altered the cross-section of the sample. First, the results for $\phi=45^\circ$ will be presented for the initial planar, cellular and dendritic interfaces. Subsequently, the results for $\phi=90^\circ$ will be described in a separate section.

Initial Planar Interface

Figure 2 shows the results of the directional solidification run carried out at the imposed velocity of 0.3 $\mu\text{m/s}$, and the sequence of photographs in this figure illustrate the changes in interface shapes as it approached the constraint. Figure 2a is the steady-state interface shape far from the constraint which clearly shows that a planar interface is stable at this velocity for a uniform cross-section sample. As the interface approaches the constraint, it initially becomes sharply curved and the velocities of different parts of the interface begin to differ significantly from the velocity that is imposed externally. The

highly curved interface, below the center of the opening of the constraint, becomes unstable and forms a cellular structure, as seen in Fig. 2b. As the interface approaches closer to the constraint, the cellular interface transforms to a dendritic interface, Fig. 2c. As the dendrites approach the constraint, their velocities increase very sharply which is evident in the much finer scale of dendrite that is seen in Fig. 2d.

The above observations correspond to a sharp decrease in the cross-section. Once the interface enters the opening in the constraint, it then sees an increasing cross-section of the sample. Here, the fine dendritic structures begin to coarsen with time, Fig. 2e. As the cross-section becomes larger, the dendritic structure first transforms to a cellular structure, Fig. 2f, and then to a planar interface, Figs. 2g and 2h. Note that during the entire experiment the externally imposed velocity, V_e , was kept constant at $0.3 \mu\text{m/s}$. However, the interface velocity was found to change significantly close to the region where the change in cross-section was imposed. In order to calculate the interface velocity, the position of the leading interface as a function of time was measured for a stationary frame of reference. Figures 3a and 3b show the position and the velocity of the interface, respectively, as a function of time. The velocity of the interface was found to increase very sharply as the interface encountered the change in cross-section. This increase in velocity of the interface caused the transitions to cellular and dendritic structures. In order to examine the change in microstructural scales, the tip radius of cellular and dendritic structures were measured and the results are shown in Fig. 4. In this figure, the variations in the interface velocity and tip radius are shown for comparison, and they are plotted versus distance with the zero on the distance scale representing the location where the cross-section is reduced sharply. Note that the velocity and the tip radius are related inversely, and that the interface has the largest velocity after it enters the constrained opening.

Figure 2. The changes in initially planar interface shape as it encounters the changes in cross-sections. $V_0=0.3 \mu\text{m/s}$

(a)

(b)

Figure 3. The changes in (a) the leading interface position and (b) the interface velocity with time for the growth condition of Fig. 2

Figure 4. The variation in the velocity and the radius of curvature of the leading segment of the interface with distance for directionally solidified alloy at $V_e = 0.3 \mu\text{m/s}$. The zero for the position corresponds to the location where the cross-section is sharply reduced

Initial Cellular Interface

When the directional solidification was carried out at $V_0 = 0.5\mu\text{m/s}$, the steady-state interface in the initial region of constant cross-section was found to exhibit a cellular structure. The dynamical changes in the interface morphologies, as the interface approached the reduced cross-section region, are shown in Fig. 5. The basic changes in the interface profiles are very similar to those for the initial planar interface case. As the effect of the constraint becomes important, the macroscopic cellular front becomes curved, Fig. 5b. The cellular region below the opening moves at a higher velocity than the regions away from the opening, and a cell to dendrite transition is observed, Fig. 5c. As the interface enters the smaller cross-section, the velocity of the leading interface increases rapidly. Once the dendrites enter the smaller cross-section, further growth of dendrites occur in a region where the cross-section is increasing. This increase in cross-section slows down the velocity of leading dendrites which tend to increase the tip radius, Fig. 5d. Also secondary branches grow out and one observes the formation of a primary dendrite from a tertiary branch, Fig. 5e. As the dendrites grow further in an expanding cross-section, a coarsening of dendritic structure is observed, Figs. 5f and 5g, which ultimately leads to the formation of a cellular structure as the cross-section increases to its initial value before the constraint.

The changes in velocity with time or position were measured. The results were found to be very similar to those for the initial planar interface case so that they will not be reproduced in this paper. The lengths of cells and dendrites as a function of position of the leading interface were also measured and the results are shown in Fig. 6. For comparison, similar results for the initial planar interface case are also shown in the figure. The length

of dendrite, which is also related to the interface velocity, is found to increase rapidly after the interface enters the reduced cross-section.

Initial Dendritic Interface

Steady-state dendritic structures in the initial uniform cross-section region were observed when the directional solidification was carried out at external velocities of 0.8, 1.0, 2.0 and 5.0 $\mu\text{m/s}$. The dendritic structure at 0.8 $\mu\text{m/s}$ was formed just beyond the cell-dendrite transition where the primary dendrite spacing was large, i.e., roughly one half of the size of the smaller cross-section of the sample. In this case, a significant influence of the constraint was observed on the morphology of the interface. For higher velocities, where the dendrite spacing was much smaller than the width of the gap in the constraint, the effect of the reduced cross-section was found to be quite small. Thus, significantly different effects of cross-section change on dendritic microstructures were observed depending upon the relative size of the opening in the constraint and the primary dendrite spacing which was established before the influence of the constraint became important. We shall, therefore, first discuss two cases of dendritic growth which show the two limiting behaviors, and then outline the changes that occurred for other velocities.

Figure 7 shows the time sequence of the interface shape for the external velocity of 0.8 $\mu\text{m/s}$. The solidification front, as it approaches the smaller cross-section region, becomes curved, although the curvature of the macroscopic interface is much smaller than that observed for the initial planar and cellular interface cases, Fig. 7b. The dendrites in the center initially show a significant decrease in the tip radius (Fig. 7b) and, as they enter the opening, they become very fine with significantly reduced secondary arm spacing. Once the leading dendrite enters the region where the cross-section begins to increase, it slows down

so that the other dendrite catches-up rapidly with the first dendrite, Figs. 7c and 7d. The dendritic interface now slows down with a sharp increase in the tip radius. This large tip radius then becomes unstable with respect to the tip-splitting, Fig. 7e, and a cellular array emerges, Fig. 7f. As the cellular array grows further, dynamical selection process for the primary spacing occurs through the cell elimination process, Fig. 7g. As some of the cells eliminate, the cellular structure begins to transform to a dendritic structure, Fig. 7h. Finally, as the cross-section becomes larger, the effect of the reduced cross-section becomes negligible and the interface regains the original structure that existed in the initial steady-state condition prior to the effect of the constraint.

Figure 8 shows the position of the dendrite tip with time for the two dendrites in Fig. 7 which enter the smaller cross-section. The velocity, which is given by the slope of the curve, increases initially, then goes through a maximum, and finally decreases. Note that when the leading dendrite slows down, the trailing dendrite speeds up until it catches up with the first dendrite. The morphological transition of dendritic structure from a higher interface velocity, Fig. 7d, to a lower interface velocity, Fig. 7h, goes through changes in the interface shapes which are very analogous to those described by Somboonsuk and Trivedi[16] for the experimental conditions in which the external velocity was reduced, while the cross-section was kept constant.

When the directional solidification experiment was carried out at higher velocities, the primary dendrite spacing became much smaller than the width of the opening in the constraint. When the primary spacing was smaller than the one fourth of the width of the constraint, no drastic effect on the interface morphology was observed. Figure 9 shows the changes in microstructure for the external velocity of $2.0 \mu\text{m/s}$. The macroscopic curvature of the interface is observed to be small and it occurs only when the solidification front is close to the reduced cross-section region. A group of dendrites goes through the

opening without any major morphological transitions. The velocity and the dendrite tip radius are, however, affected. The changes in interface velocity and the dendrite tip radius with the position of the interface were measured, and the results are shown in Fig. 10. In contrast to the low velocity results (Fig. 4) which show one peak in velocity, the results in Fig. 10 show two distinct peaks in the interface velocity versus position plot. The low velocity results exhibited the peak in the interface velocity after the interface entered the constrained opening. At higher velocities, an additional peak is observed just before the interface entered the constrained opening. The two peaks in the interface velocity also correspond to two valleys in the dendrite tip radius. No simple quantitative relationship between the interface velocity and dendrite tip radius was found in this highly dynamic condition.

The results of the variation in interface velocity due to the presence of changes in cross-section are summarized in Fig. 11. The results for the external velocity of $0.5 \mu\text{m/s}$, which are very similar to those for the $0.3 \mu\text{m/s}$ case, are not shown in the figure for clarity. The changes in interface velocity are significantly higher for low external velocity values, i.e., for the conditions of initially planar or cellular interface. The percentage change in interface velocity becomes smaller for dendritic structure, and the magnitude of this change decreases as the external velocity is increased. The experimental results for external velocities of 0.3 , 0.5 and $0.8 \mu\text{m/s}$ show only one peak in the interface velocity, whereas those for 1.0 , 2.0 and $5.0 \mu\text{m/s}$ show two peaks.

The change in cross-section has been shown to give rise to the changes in either interface morphologies or the scales of microstructures. The extent to which the presence of constraint will alter the morphology or segregation patterns was examined for the geometry used in these experiments. Figure 12 shows the interaction distance, within which changes were significant, as a function of the external velocity.

Figure 5. The effect of cross-section changes on the morphology of the solid-liquid interface. Directional solidification was carried out at $V_E=0.5 \mu\text{m/s}$ which gave rise to initial cellular interface

Figure 6. The variations in the dendrite or cell lengths with the position of the interface for directional solidification studies carried out at the external velocities of 0.3 and 0.5 $\mu\text{m/s}$

Figure 7. The changes in the interface morphology as the interface encounters the changes in cross-sections. The external velocity was $0.8 \mu\text{m/s}$, which gave rise to an initial dendritic interface

(a)

(h)

(b)

(g)

(c)

(f)

(d)

(e)

Figure 8. The position of the dendrite tip for the two dendrites which pass through the reduced cross-section, as observed in Fig. 7

Figure 9. The changes of the interface morphology with distance for the directional solidification run carried out at the external velocity of $2.0 \mu\text{m/s}$. The initial dendritic spacing was significantly smaller than the width of the opening

(a)

(b)

(c)

(d)

Figure 10. The changes in the tip radius and velocity of the leading dendrite with the position of the interface for the experimental conditions of Fig. 9

Figure 11. The variations in the velocities of the leading interface segments with position for different external velocities. The zero position represents the location of the sharply reduced cross-section

Figure 12. The magnitudes of the interaction distance, where the morphology is significantly altered, as a function of external velocity

Morphological Changes in a Channel

In all the experiments described above, the cross-section was initially reduced sharply and then increased gradually to its initial value. Since the morphological changes will also be influenced by the angle ϕ , an experimental study was also carried out with $\phi = 90^\circ$ and the size of the gap was kept at 1mm, which was identical to the gap size for the experiments with $\phi = 45^\circ$. The directional solidification experiments were carried out at the external velocities of 0.8 and 2.0 $\mu\text{m/s}$. The composition of the alloy was slightly less than 0.6 wt.% Acetone so that planar and dendritic steady-state interfaces were observed at the velocities of 0.8 and 2.0 $\mu\text{m/s}$, respectively, in the initial region of constant cross-section.

The results of experiments at the velocity of 0.8 $\mu\text{m/s}$ are shown in Fig. 13. The initial changes in the interface profile, as the interface experiences the effect of cross-section reduction before it enters the small region, are very similar to those observed earlier, and shown in Fig. 2. The interface first becomes highly curved just below the opening, Fig. 13a. Once it enters the smaller cross-section, its velocity increases rapidly which gives rise to bands of solute. Such solute bands are visible in the Figs. 13b and 13c, and they are similar to the solute bands reported earlier by Sekhar and Trivedi [27]. The increase in interface velocity inside the smaller cross-section, which we shall refer to as a channel, causes a sharp transition first to an almost single cell, Fig. 13c, and then to a dendritic structure, Fig. 13d. The single dendrite grows at an angle to the heat flow or the channel direction to satisfy the crystallographic constraint, until it encounters the side of the channel, Fig. 13e. At this point the dendrite tip, which can no longer grow in a desired crystallographic direction, becomes unstable and some secondary branches begin to grow preferentially, Fig. 13f. Since the constraint of the channel does not allow the dendritic structure to form in a specific direction, a somewhat chaotic behavior is observed in which the interface

repeatedly tries to align in appropriate crystallographic direction. The changes in interface velocity with position near the constraint were found to be very similar to those described in Fig. 4, except that the interface velocity did not decrease sharply since the cross-section was not increased in the present case.

Figures 14 and 15 show the effect of reduced cross-section on the morphological development of dendritic structure obtained at the external velocity of $2.0\mu\text{m/s}$. The dendritic array in Fig. 14a is not affected by the constraint until it comes very close to the region where the change in cross-section occurs. Close to the barrier, the two dendrites which are just below the opening begin to grow faster and their tip radii become sharper, Fig. 14b, whereas the dendrites away from the opening which see the barrier slow down and their tip region becomes very broad. One of the dendrites enters the channel and it first becomes finer as the interface velocity in the channel increases, Fig. 14c, and then it coarsens as the interface velocity decreases. The dendrite in the channel grows in the preferred crystallographic direction which is slightly different from the orientation of the channel. Thus, the dendrite continues to grow until the dendrite tip reaches the left side of the channel, Fig. 15a. As the dendrite grows in the left side of the channel and becomes nearly a half-dendrite, the liquid region on the right hand side becomes highly supercooled so that nucleation of solid at the right wall of the channel occurs, as seen in Fig. 15a. These solid nuclei then grow quite fast and form a dendritic structure, Fig. 15b, which eliminates the dendrite that was present earlier. This new dendrite again grows until its tip reach the side of the wall, Fig. 15c, at which point the tip region slows down and the secondary branches begin to become prominent. One of these secondary branches becomes unstable and forms a dendrite which then competes with the dendrite that evolves at the left hand wall of the channel, Fig. 15d. The dendrite on the right hand side predominates since it can readily grow in the preferred crystallographic direction. The process of dendrite formation and its

elimination when it reaches the left hand wall, continues as the solidification progresses. These experiments show that the crystallographic constraints are critical in maintaining the steady-state dendrite growth. A complete dendritic structure is not found to be stable inside a channel whose direction does not coincide with one of the preferred dendrite growth directions. In the present case the cross-section of the channel was such that the width of the channel was comparable to the primary dendrite spacing of the stable dendritic array. Recently Sekhar and Trivedi [27] have shown that a nearly half dendrite can grow in a steady-state manner if the width of the channel is close to half the characteristic primary dendrite spacing in infinite width sample. In this case steady-state dendritic growth is observed even when the channel direction is not the same as the preferred dendrite growth direction.

(a.)

(b.)

(c.)

(d.)

(e.)

(f.)

Figure 13. The morphological changes in the initially planar interface as it encounters a sharply reduced uniform cross-section. $V_0 = 0.8 \mu\text{m/s}$. The width of the channel is 1 mm

Figure 14. The changes in the interface morphology with time for directional solidification run at $V_0 = 2.0 \mu\text{m/s}$, where the initial steady-state conditions gave rise to a dendritic structure. Channel width = 1 mm

(a.)

(b.)

(c.)

(d.)

(a.)

(b.)

(c.)

(d.)

Figure 15. Further changes in the interface morphology with time for the experiment shown in Fig. 14. Channel width = 1 mm

DISCUSSION

We shall examine the effect of the change in cross-section of the sample on the solute field ahead of the interface, and then discuss how this change in solute field will affect the stability of the solid-liquid interface. Since the cross-section in our studies is reduced by a factor of 25, the interface largely sees a barrier to the diffusion field except at the constraint opening. The solute field will thus be analogous to the end effect so that the solute field can be approximately described by the final transient field solution given by Smith et al. [32]:

$$C_L/kC_0 = 1 + \sum_{n=1}^{\infty} (2n+1) [P(n-k)/P(n+k)] e^{-n(n+1)(1-f_L)} P$$

where P is the Peclet number which is the ratio of the length of the sample ahead of the constraint and the diffusion distance, D/V , k is the equilibrium solute distribution coefficient and f_L is the fraction of liquid within the region before the constraint opening. The above equation shows that the fractional length of the final transient is inversely proportional to P so that the length of the final transient will be proportional to D/V . Thus the solute field ahead of the interface will be affected significantly when the interface is at a distance of D/V from the constraint region. Although the end effects for cellular and dendritic interface growth have not been examined in the literature, the solute fields ahead of these interfaces have also been found to be proportional to D/V . Table 1 compares the diffusion distance D/V with the distance d_1 measured in our studies. A reasonable agreement is observed even for cellular and dendritic interfaces. It should be noted that all transient models in the literature assume that the interface velocity in the transient regime is

constant and equal to the external velocity. This is indeed not the case, since the velocity of the interface segment which passes through the opening increases, as shown in Fig. 4, and the velocity of the interface segment close to the sides of the sample decreases, as the interface approaches the constraint. Consequently, the concentration profiles will be significantly different from those predicted by the Smith et al analysis. However, their analysis will still be valid for estimating the distance at which the end effects just become important for a planar interface, i.e., the distance at which the concentration gradient at the interface just begins to change.

When the interface approaches the constraint, the interface segments which see the barrier will slow down, so that they will move slower than the interface segments which see the opening. These differences in velocities give rise to a macroscopic curvature to the advancing solidification front. The difference in the velocities is largest for the planar interface case and it becomes smaller for the cellular and dendritic interfaces. Once the interface acquires the macroscopic curvature, a lateral diffusion of solute occurs from the interface region which has the highest curvature. This additional lateral diffusion then enhances the curvature of the interface leading to a sharper concentration gradient in liquid at the leading interface region. This increase in concentration gradient then causes the interface to become unstable so that a planar interface breaks up into a cellular interface and then to a dendritic interface. Since the dendrite tip grows close to the liquidus temperature, whereas the planar interface grows at the solidus temperature, the formation of dendritic structure is accompanied by a sharp increase in velocity as the dendrite tip tends to reach a higher temperature region. Similar observations have also been made on the initial cellular interfaces. Since the velocity of the interface increases with the transition to a dendritic structure, the peak in interface velocity occurs after the interface enters the smaller cross-section.

For experiments at higher external velocities, the diffusion distance ahead of the dendritic array is quite small so that the macroscopic curvature of the dendritic array is small. In this case the interface velocity first increases due to the contribution of the lateral diffusion as the interface acquires some curvature. However, as the dendritic array approaches the opening, the solute pile up at the sides slows down the lateral diffusion effect so that the interface velocity of the leading interface segment goes through a maximum before it enters the opening. Thus, for high velocities, two peaks in interface velocity are observed: one before the opening and the other after the opening.

The morphological changes which occur near the change in cross-section can also be influenced by the convection in liquid. As reported by Glicksman et al. [11], a 4.7% volume contraction occurs during the freezing of Succinonitrile. Thus, as the interface approaches the barrier, there will be a fluid flow through the opening to compensate for the volumetric contraction. Since the cross-section is reduced by a factor of 25, the relative fluid velocity will be increased 25 times as the interface enters the constraint. This fluid flow can be significant, and it will reduce the local solute build up at the interface, thus allowing it to freeze at a higher temperature which will cause the interface to accelerate. Since the initial curvature of the interface occurs close to D/V , the instability of the interface primarily occurs due to the diffusion barrier. However, the acceleration of the interface, as it enters the opening, will be strongly influenced by the fluid flow.

CONCLUSIONS

Directional solidification studies in presence of changes in the cross-section have been carried out in the Succinonitrile-Acetone system whose transparent nature allowed us to examine the dynamical changes in microstructure that occur near the region of the cross-section changes. The effect of the cross-sectional change comes from the change in solute field ahead of the interface which causes the interface velocity to alter significantly. As the interface velocity changes, various morphological transitions were found to occur which could be correlated with the local interface velocity. A region in the vicinity of the cross-section change is characterized in which the microstructure and the resulting segregation pattern alter significantly.

The change in microstructure with the change in cross-section will depend upon the relative change in cross-sections and also on the external velocity. When the reduced cross-section is significantly larger than the primary dendrite spacing, only a small effect is observed due to a small change in dendrite tip radius which leads to a small change in the secondary arm spacing near the tip. This difference, however, will not be significant as the dendrite arms coarsen behind the tip region. A drastic change in microstructure, however, is found to occur when the material is solidified at low velocities and the cross-section differences are large. Such microstructural changes can be minimized by programing the external velocity to decrease or the temperature gradient to increase as the interface approaches the reduced cross-sectional area. Note that our experiments have been carried out under controlled conditions in which the temperature field is maintained constant throughout the sample. In many practical examples, such as in the growth of turbine blades, the thermal environment is different such that the smaller cross-section will be easier to

heat. This higher temperature at the reduced cross-section will tend to oppose the instability of the interface near the smaller opening.

Table 1. Interaction distances

External velocity, V_e , $\mu\text{m/s}$	D/V_e , μm	d_1 , μm
0.3	4.23	-
0.5	2.54	2.1
0.8	1.59	1.6
1.0	1.27	1.4
2.0	0.64	0.7
5.0	0.25	-

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**SECTION II. DENDRITIC GROWTH IN THE CARBON TETRABROMIDE AND HEXACHLORETHANE
SYSTEM**

INTRODUCTION

Dendritic microstructures are the most frequently observed solidification microstructures in metallic alloys. In addition, the evolution of the steady-state dendritic structures with well-developed sidebranches is one of the complex and fascinating problems in our understanding of pattern formation in physical and biological systems [1]. Consequently, a significant number of theoretical and experimental studies have been carried out to understand precisely how the microstructural scales of dendrites, viz. dendrite tip radius, primary spacing and secondary arm spacing, are related to the driving force. Often it is rationalized that the microstructural scales of dendritic morphology become finer with the increasing driving forces because a finer scale can efficiently dissipate the latent heat of fusion or can readily redistribute solute with the increase in the solidification rate. However, it has been recognized for a long time that for a given driving force an infinite number of solutions are possible which are consistent with the latent heat removal or with the solute redistribution. A mathematical solution of this problem was first obtained by Ivantsov [2]. In contrast, experimental studies show a unique selection of dendrite tip radius for a given driving force. Thus, one of the challenging problems in the theory of dendritic growth has been to understand the criterion that the system follows in selecting the unique dendrite tip radius from an infinite set of solutions of the thermal and mass transport equations.

For a number of years, it was assumed that the dendrite in an undercooled melt selects the tip radius which corresponds to the maximum in the growth rate. The invalidity of such an assumption was documented by Glicksman et al. [3] and by Huang and Glicksman [4,5] by their very careful and thorough experimental studies in a well-characterized system of pure succinonitrile. In an analogous problem of directional solidification, the experimental studies by Somboonsuk et al. [6], Trivedi et al. [7,8] and Esaka and Kurz [9] have shown the

invalidity of the criterion based on the minimum undercooling at the interface. Langer and Müller-Krumbhaar [10] subsequently examined the selection criterion based on the stability of the dendrite tip. They carried out a linear stability analysis of the Ivantsov parabola, and showed that of all possible solutions of the transport equations, only a finite number of solutions give rise to a stable tip radius. The largest stable radius was found to agree remarkably well with the experimental results of Glicksman et al. [3]. Consequently, Langer and Müller-Krumbhaar proposed the *marginal stability* criterion in which the system selects the dendrite tip radius that is just stable with respect to the tip-splitting phenomenon. The marginal stability criterion was also found to explain the experimental results on the directional solidification of succinonitrile-acetone system.

One of the drawbacks of the marginal stability criterion is that there is no rationale for the selection of the marginally stable state over all other stable states. Furthermore, Langer and Müller-Krumbhaar carried out the linear stability analysis of an isothermal paraboloid which is not the self-consistent shape when surface energy effects are present in the system. Although the surface energy effect is small, it is nevertheless very important since it must be present to stabilize the dendrite tip with respect to the tip-splitting instability. Several self-consistent models of dendritic growth have recently been developed [11-16]. They show that no self-consistent steady-state dendrite growth is possible when the effects of isotropic surface energy or interface kinetics, however small, are included in the model. It is only when the anisotropy in the interface energy is taken into account that a self-consistent, steady-state, dendrite growth is possible. Furthermore, they find that there is only one solution that is stable with respect to the tip-splitting phenomenon [17,18]. This unique dendrite tip selection criterion is called the solvability approach, which for small peclet number conditions, gives the result:

$$m_L G_C - G = \Gamma / \sigma^* R^2, \quad (1)$$

where G_C is the concentration gradient at the unperturbed interface being considered, m_L is the slope of the liquidus, R the radius of the dendrite tip and Γ is the ratio of surface energy to the entropy of fusion per unit volume. The value of $G = (K_S G_S + K_L G_L) / (K_S + K_L)$. Thus, for systems with $K_S = K_L$, $G = (G_L + G_S) / 2$, σ^* is a constant which depends on the surface energy anisotropy parameter, ϵ , and the solvability criterion predicts that $\sigma^* \sim \epsilon^{1.75}$, for $\epsilon \ll 1$. It should be noted that equation (1) also precisely describes the prediction of the marginal stability criterion, except that the value of σ^* is predicted to be a numerical constant, equal to ~ 0.025 , for all systems. In succinonitrile, where the anisotropy in the surface energy is small, both the marginal stability and the solvability criteria predict the value of σ^* to be around 0.02. Thus, it has not been possible to test these theories from the results in the succinonitrile system, so that it is necessary to examine other systems where the anisotropy parameter is slightly higher. The major aim of this work is therefore to present directional solidification results in the carbon tetrabromide and hexachlorethane system. Both, hypoeutectic and hypereutectic compositions were studied so that dendrites of carbon tetrabromide as well as of hexachlorethane can be examined. For both these cases VR^2 was found to be constant, and from these results, the values of σ^* were determined.

EXPERIMENTAL STUDIES

Directional solidification experiments were carried out, using a Hele-Shaw cell in a temperature gradient stage that is described by Mason and Eshelman [19]. The velocity with which the cell was driven externally was first calibrated by using a linear variable differential transformer and periodically checked by observing the motion of a micrometer slide under the microscope. A steady-state interface motion was ensured by examining the location of the dendrite tip with time under the microscope, which remained unaltered under steady-state growth conditions. The temperature gradient at the interface was measured by a calibrated thermocouple which was placed inside the cell.

The carbon tetrabromide and hexachlorethane system was chosen for the present study since all relevant physical properties of this system have been measured [20]. Also the value of the diffusion coefficient has been determined from the detailed experimental studies to characterize the smallest stable eutectic spacing [21]. The values of the parameters for this system are given in Table 1. The materials were first purified by the procedure described earlier by Seetharaman and Trivedi [21]. The carbon tetrabromide (CBr_4) - hexachlorethane (C_2Cl_6) system has a eutectic at 8.4 wt.% hexachlorethane. Consequently, we selected two compositions, a hypoeutectic composition with 7.9 wt.% hexachlorethane and a hypereutectic alloy containing 10.5 wt.% hexachlorethane. During the solidification of the hypoeutectic alloy, the solidification structure consists of carbon tetrabromide dendrites with interdendritic eutectic. On the other hand, the hypereutectic alloy exhibits primary dendrites of hexachlorethane with interdendritic eutectic behind the front. Typical dendritic structures for these two compositions are shown in Fig. 1.

Directional solidification experiments were carried out over the velocity range of 0.2-20.0 $\mu\text{m/s}$, and the temperature gradient was maintained at 3.0K/mm. The steady-state

dendritic structures were photographed from which the dendrite tip radius (R), primary spacing (λ_1) and the initial secondary arm near the dendrite tip, (λ_2), were measured. The results for CBr_4 and C_2Cl_6 are shown in Fig. 2. Both, R and λ_2 , were found to decrease with the increase in velocity, whereas λ_1 exhibited a maximum. These results show the same behavior as that found in the succinonitrile-acetone system [6]. The dendrite tip radii in CBr_4 and C_2Cl_6 systems were found to vary as $V^{-0.53 \pm 0.03}$ and $V^{-0.47 \pm 0.03}$, respectively. Thus, the values of VR^2 in these two systems were found to be nearly constant. The least square line for VR^2 equal to constant gave the following relationships:

$$VR^2 = 978 \pm 8 \text{ } \mu\text{m}^3/\text{s}, \quad \text{for } \text{CBr}_4, \quad (2)$$

$$VR^2 = 124 \pm 13 \text{ } \mu\text{m}^3/\text{s}, \quad \text{for } \text{C}_2\text{Cl}_6 \quad (3)$$

The initial secondary spacing near the dendrite tip was found to vary with velocity as $V^{-0.44 \pm 0.11}$ and $V^{-0.45 \pm 0.025}$, for CBr_4 and C_2Cl_6 systems, respectively. These relationships also show that $V\lambda_2^2$ is nearly constant for these two systems.

Figure 1. The shape of the dendrite tip region for: (a) CBr_4 dendrite grown directionally in CBr_4 - 7.9wt.% C_2Cl_6 at $V = 5.0 \mu\text{m/s}$ and $G = 3.0 \text{ K/mm}$, (b) C_2Cl_6 dendrite grown directionally in CBr_4 -10.5wt.% C_2Cl_6 at $V = 1.0 \mu\text{m/s}$ and $G = 3.0 \text{ K/mm}$. Mag. 144.4X

Figure 2. The variation in the (a) dendrite tip radius, (b) initial secondary arm spacing near the dendrite tip, and (c) primary dendrite spacing, with velocity for CBr_4 and the C_2Cl_6 dendrites

DISCUSSION

We shall first compare our results with the theoretical predictions of equation (1). For dendritic structures under directional solidification conditions, the temperature gradient term in equation (1) is generally negligible. Also, the value of G_C can be obtained from the solute flux balance at the dendrite tip, viz. $G_C = VC_t(k-1)/D$, where C_t is the composition in the liquid at the dendrite tip, k is the solute distribution coefficient at the dendrite tip temperature, and D is the interdiffusion coefficient in the liquid. Equation (1) can thus be simplified to the form:

$$VR^2 = \Gamma D / \sigma^* \Delta T_S, \quad (4)$$

where $\Delta T_S = m_L C_t(k-1)$. Note that, for a constant value of m_L , ΔT_S is equal to the freezing range of the alloy whose composition corresponds to the solute concentration in the *solid* at the dendrite tip. For the low velocities used in the present study, the dendrite tip temperature will be close to the liquidus temperature of the alloy. Consequently, the values of ΔT_S can be directly obtained from the phase diagram. By substituting the experimental values of VR^2 and the constant values of Γ , D , and ΔT_S , the values of σ^* were evaluated from equation (4), and the following results were obtained:

$$\sigma^* = 0.022, \quad \text{for } CBr_4, \text{ and} \quad (5)$$

$$= 0.019, \quad \text{for } C_2Cl_6. \quad (6)$$

The values of σ^* for CBr_4 and C_2Cl_6 agree with the prediction of the marginal stability criterion. The precise values of the surface energy anisotropy parameter for these materials are not known. However, the shape of the dendrite tip region and the distance between the dendrite tip and the first sidebranch perturbation show that the anisotropy in the interfacial energy is somewhat larger in these systems than in succinonitrile. Thus, according to the solvability approach the values of σ^* should be higher than 0.02 that is found for the nearly isotropic succinonitrile dendrites. Our results are thus not in conformity with the solvability approach, but they do agree remarkably well with the prediction of the marginal stability criterion.

Glicksman et al. [3] first discovered the scaling law between λ_2 and R for dendritic growth in a pure undercooled succinonitrile. Subsequently, Glicksman and Singh [22] also reported a similar scaling law for pure pivalic acid dendrites. However, the magnitude of the scaling law constant was found to be significantly higher in the latter system, and this was attributed to the greater anisotropic properties in the pivalic acid system. Similar scaling laws have also been observed in directional solidification studies [6, 23]. In these studies the ratio λ_2/R was found to be 2.0 in the succinonitrile-acetone system, whereas a value of 3.8 was found in the pivalic acid-ethanol system. An examination of our present experimental results, Fig. 2, clearly show that similar scaling law behavior is exhibited by both the CBr_4 and the C_2Cl_6 dendrites. Figures 3a and 3b show the value of λ_2/R as a function of velocity. The values of the scaling factors are found to be 3.18 and 3.47 for the CBr_4 and the C_2Cl_6 systems, respectively. These values are in between those for a nearly isotropic succinonitrile and a very anisotropic pivalic acid. Since the values of the ratios are found to be very close for the CBr_4 and the C_2Cl_6 dendrites, the anisotropic parameter in both these systems appears to be similar. Thus, we can now make a qualitative

correlation that the value of the scaling law constant increases with the increase in the anisotropic interface properties of the system.

(a)

(b)

Figure 3. The value of the ratio λ_2/R as a function of velocity for (a) CBr_4 , and (b) C_2Cl_6 dendrites

CONCLUSIONS

Directional solidification studies have been carried out in the transparent CBr_4 - C_2Cl_6 system to examine the variations in the dendrite tip radius, the primary spacing and the secondary dendrite arm spacing near the tip as a function of velocity. Two different compositions were selected for the study so as to obtain dendrites of CBr_4 and of C_2Cl_6 . The value of VR^2 was found to be constant for both these systems. Using these values, the magnitudes of the dendrite tip operating parameters, σ^* , were obtained for these two systems. The values of σ^* for the CBr_4 and C_2Cl_6 dendrites were found to be equal to 0.022 and 0.019, respectively, which are in good agreement with the marginal stability theory. Although the anisotropy in these system is larger than that in the succinonitrile system, the value of σ^* is found to be the same in three systems, which tend to support the result of the marginal stability theory.

Table 1. Properties of CBr₄ and C₂Cl₆.

Parameter	CBr ₄ dendrites in	C ₂ Cl ₆ dendrites in
	CBr ₄ - 7.9wt.% C ₂ Cl ₆	CBr ₄ - 10.5wt.% C ₂ Cl ₆
γ , mJ/m ²	9.5	14.5
ΔS , J/m ³ K	0.09	0.085
Γ , mK	1.06×10^{-7}	0.47×10^{-7}
D , m ² /s	0.8×10^{-9}	0.8×10^{-9}
ΔT_S , K	3.7	15.9

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SECTION III. NONEQUILIBRIUM EFFECTS DURING THE LEDGEWISE
GROWTH OF A SOLID-LIQUID INTERFACE

INTRODUCTION

Morphological developments of solid-liquid interfaces have been studied extensively for metallic systems in which the interface is assumed to be rough on an atomic scale so that atoms can attach themselves uniformly along the interface. In this case every element of the interface moves normal to itself. Also, the temperature and the composition at the interface are often established by the local equilibrium condition if the interface attachment kinetics are rapid; otherwise the deviations in interface temperature and compositions from their equilibrium values are directly proportional to the velocity.

In anisotropic materials a faceted interface with a lower solid-liquid interfacial energy is generally observed, and such an interface is atomically smooth except for the presence of ledges or steps. The growth of a faceted interface occurs by the motion of steps only, so that an interface element is stationary until a step passes over it which then moves the interface element through a distance given by the height of the step. Since the formation of a step interface requires some driving force, the interface temperature and concentration generally deviate from their equilibrium values. The kinetic law which relates the deviation from equilibrium with the velocity of the interface is governed by the mechanism by which the step forms. The main sources of steps are: (1) two dimensional nuclei on the growing interface, (2) a screw dislocation, and (3) a re-entrant corner due to the presence of a twin boundary intersecting the interface. These different mechanisms give rise to different kinetic laws so that by measuring the kinetic effects at the interface, it is possible to determine which of these mechanisms is actually operative in a given system.

Although kinetic effects at the interface are very important in the development of microstructure, very little attention is devoted in the literature to quantify this effect. One of the major reasons for this lack of study is that simple experiments have not been designed

to quantitatively study the interface kinetics effect. In this paper, we shall develop the basic ideas on interface kinetics and show that the directional solidification technique can be used to obtain critical information on the kinetics effects. Detailed experimental studies, carried out in a transparent organic material which grows with a faceted interface, will then be presented. For this study, the naphthalene-camphor system has been selected since the phase diagram of this system has been determined, and some of the important physicochemical properties have been measured. In order to characterize the interface temperature and the interface composition, two sets of experimental studies have been carried out to: (1) measure the interface temperature during the steady-state growth of a planar interface, and (2) determine the condition for the planar interface instability. From these experimental results, the variation in interface temperature and composition with velocity is established, and the magnitude of interface kinetics effect evaluated.

BASIC IDEAS

Nonequilibrium Conditions

When interface kinetics effects are significant, the temperature and the concentrations at the interface deviate significantly from their equilibrium values. It is thus necessary to characterize the effect of velocity, V , on the interface temperature T_I , and the interface compositions in the liquid, C_L , and in the solid, C_S . These nonequilibrium effects can be represented by the following two relationships, which are generally referred to as the two response functions [1]:

$$T_I = f_1 (C_S, V), \quad \text{and} \quad (1)$$

$$C_L = f_2 (C_S, V). \quad (2)$$

The second relationship gives the effect of velocity on the nonequilibrium solute distribution coefficient, i.e., $k = C_S/C_L$. The above functional relationships could be obtained from experimental studies if one could directly measure the values of T_I , C_L and C_S as a function of velocity. Although T_I can be readily measured by using a calibrated thermocouple, the values of interface concentrations cannot be measured accurately since the deviations from their equilibrium values are usually small at low velocities and they are of the same order of magnitude as the experimental errors in measuring their values. Consequently, some other means are needed to determine the functional relationships between the velocity and the nonequilibrium conditions at the interface. One often measures indirectly the nonequilibrium conditions at the interface by relating the velocity with the bulk

undercooling. However, in order to evaluate the nonequilibrium effect it is essential to measure the temperature and composition conditions precisely *at* the interface.

In this paper, we shall design critical experiments on directional solidification, and show how the results of these experiments can be used to obtain the functional form of response functions. Two sets of experimental studies are needed. In the first set of experiments, an alloy of a given composition is directionally solidified at low velocities where a planar interface is stable. After the planar interface reaches the steady-state growth condition, the temperature of the interface is measured through a calibrated thermocouple. Steady-state conditions for planar interface growth requires that the composition in the solid at the interface be equal to the alloy composition in liquid far from the interface, i.e., $C_S = C_0$, where C_0 is the alloy composition which is known. Thus, by carrying out experiments at different velocities, one obtains the functional relationship which connect the velocity, the composition in the solid at the interface and the interface temperature. The deviations in the temperature and in the compositions at the interface from their equilibrium values for steady-state planar interface growth are shown schematically in Fig. 1. The measurement of steady-state interface temperature gives the relationship between the total interface undercooling as a function of velocity, and this undercooling is represented by ΔT . In order to determine the interface undercooling, δT , the value of C_L needs to be determined, as shown in Fig. 1.

A second set of experiment is designed to evaluate the composition in the liquid at the interface as a function of velocity. The aim of these experiments is to obtain another independent relationship between the variables C_L and T_I . We propose to obtain this relationship by characterizing the critical velocity for the planar interface instability. In order to measure the critical velocity, we have carried out experimental study in a transparent system where the instability of the interface can be observed in situ. As pointed

out by Baker and Cahn [1], the general response functions must also be valid for specific experimental conditions, so that the relationship obtained through the study of planar interface instability must also be consistent with the general response function. Thus, by quantitatively measuring the steady-state planar interface temperature and the condition for planar interface instability, it is possible to characterize the nonequilibrium conditions at the interface as a function of velocity.

Growth Mechanisms

The functional relationship between the velocity and the departure from equilibrium values at the interface depends upon the mechanism that is operative for the step nucleation. For a step interface, shown in Fig. 2, the velocity of the interface is given by [2, 3]:

$$V = (h/\lambda) V_S , \quad (3)$$

where h is the step height, λ the average spacing between the steps at any given point, and V_S is the local velocity of the step. Note that if the steps are close to each other, then V_S depends upon the local spacing, λ . The spacing between the steps, in general, is governed by the mechanism of step creation as well by the dynamic processes during growth which may combine two or more steps. The dynamic process of changes in step height will cause the macroscopic orientation of the interface to change locally, and the interface will retain its orientation only if the collapse of steps occur uniformly over the entire interface. Since we are concerned in this paper with the kinetic effects at a planar interface, we shall consider the step creation process to be the dominant mechanism for establishing the step spacings.

The formation of steps can occur by the two-dimensional nucleation process, which requires finite undercooling at the interface to form a critical nucleus. If n is the number of two dimensional nuclei per unit area of the interface, and $\dot{n}$ is the nucleation rate, then the nucleation rate is given by [4, 5]:

$$\dot{n} = I_0 \exp (-\Delta G^*/RT) \quad (4)$$

where I_0 is a preexponential function, and ΔG^* is given by:

$$\Delta G^* = (\pi\gamma^2 h / \Delta S \delta T) \quad (5)$$

where γ is the interfacial free energy per unit area of the ledge interface, ΔS is the melting entropy change per unit volume, and δT is the undercooling at the interface since the nucleation of solid occurs from the liquid of interface composition.

If A is the area that needs to be covered by each nuclei, then $A = 1/n$. Thus, a single nucleation event would occur if the nuclei can grow rapidly in a time that is less than $n/\dot{n}$ or $1/A\dot{n}$. Thus, if all nuclei form at a given time, then they will form a layer of solid of height h in time $1/A\dot{n}$, so that the growth rate of the interface will be given by:

$$V = h A \dot{n} \quad (6)$$

or

$$V = V_0 N \exp \{- \pi\gamma^2 h / \Delta S \delta T RT\} \quad (7)$$

where $V_0 N$ is the preexponential factor for the nucleation process and it is a slowly varying function of undercooling compared to the exponential term.

The step growth also occurs when a dislocation with a screw component terminates at the surface. In this case, the spacing between the steps is proportional to the critical radius for nucleation [6, 7], so that the growth rate of the interface is given by:

$$V = V_s (h\Delta S/4\pi\gamma) \delta T \quad (8)$$

Since V_s , the velocity of a straight ledge, is proportional to δT , one obtains:

$$V = V_{0D} (\delta T)^2 \quad (9)$$

where V_{0D} is a constant factor for growth by the screw dislocation mechanism.

Another mechanism that plays an important role during step growth comes from the presence of re-entrant grooves on the surface. These re-entrant grooves form when multiple twins terminate on the surface, and they provide a source for the generation of steps [8, 9]. This twinned crystal requires smaller undercooling for a given velocity compared to the nucleation and the dislocation mechanisms, although no quantitative kinetic law has yet been established for this case.

Figure 1. The phase diagram showing the actual temperature and concentrations at the interface. ΔT and δT represent bulk and interface undercoolings, respectively. ΔC and δC represent the solute difference at the interface and the deviation in the liquid composition from its equilibrium value at the interface temperature, respectively

Figure 2. A schematic drawing of a ledge-wise growth of an interface

EXPERIMENTAL PROCEDURE

Directional solidification studies were carried out in the naphthalene-camphor system. The composition range studied varied from 0.5 to 3.15 wt.% camphor. The phase diagram of the naphthalene-camphor system [10] is shown in Fig. 3, and the relevant system constants are given in Table 1. As received naphthalene was first melted with sodium at 100° C to remove β -methylnaphthalene and then zone refined in a Teflon tube to avoid cracking of the tube due to the volume changes during zone refining. The zone refined naphthalene was then alloyed with very small amount of as received camphor of 99 % purity .

The naphthalene-camphor mixture was placed in a cell, of dimensions 127x25x0.15 mm. A calibrated thermocouple was placed in the sample cell. The cell, prior to filling, was sealed on all sides with a low melting point glass, except for two small openings on two sides to fill the cell with the naphthalene-camphor mixture. After the liquid in the cell was frozen, the openings were sealed with an epoxy. After the cell was filled, the composition of the alloy in the cell was determined by measuring the liquidus temperature by the ring heater method [11, 12], and this liquidus temperature was converted to composition by using the phase diagram.

Directional solidification experiments were carried out in a temperature gradient stage that is described earlier by Mason and Eshelman [13]. Three sets of directional solidification experiments were carried out: (1) to characterize the mechanism of nonplanar pattern formation for different crystal orientations (2) to measure the steady-state planar interface temperature as a function of velocity for a given composition and a specific interface orientation, and (3) to determine the critical velocity for planar interface instability of a given interface orientation for different compositions.

Directional solidification experiments were carried out in naphthalene - 0.95 wt.% camphor under temperature gradient condition of 2.5 K/mm. The velocity was varied from 0.5 $\mu\text{m/s}$ to 20 $\mu\text{m/s}$. For each velocity, the morphological development was examined in situ through an optical microscope and photographed for different times. The planar interface or the cell/dendrite tip temperature was measured with a calibrated thermocouple that was placed inside the sample. Since one of our major goals was to measure the interface temperature for steady-state planar interface growth, it was first necessary to ascertain that steady-state conditions were indeed reached when the interface temperature was measured. Two sets of measurements were made to ensure that the interface was moving at a steady state, and that the temperature gradient at the interface did not change with time.

Under transient growth conditions the temperature profile ahead of the interface will change with time. Thus, to examine this change in temperature profile directional solidification experiments were carried out by using two calibrated thermocouples that were separated by a distance of 2 mm along the growth direction. The location of the planar interface with respect to both these thermocouples was also measured from the photographs taken at every 60 seconds. The outputs of both these thermocouples are plotted in Fig. 4a as function of time. The locations at which each of these thermocouple intersected the interface are also marked in the figure. Note that initially both the thermocouples are in the hot chamber so that they show the same temperature. However, as the thermocouples move out of the hot chamber, the temperature profiles become parallel indicating that the steady state temperature distribution was attained in the sample. Figure 4b shows the temperature profiles of these thermocouples as a function of distance from the interface. It is seen that the temperature profile ahead of the interface is linear, and both thermocouples gave the same temperature condition at a given point which shows that steady state temperature conditions were established in our experiments.

In the directional solidification experiments, the presence of steady state growth conditions can be precisely established since under steady state conditions the interface, when looked under a microscope, remains at the same location with time. Thus, if one characterizes the position of the interface as seen under a microscope, even a slight deviation from steady state condition can be observed very clearly. Figure 5 shows the position of the interface as a function of time in a moving frame of reference. The interface initially recedes towards the cold chamber and then moves towards the hot chamber, and finally remains at the same location after about 40000 s. The actual velocity of the interface is the velocity observed under a microscope plus the external velocity with which the sample is pulled. Thus, the variation in the actual interface position with time in a fixed frame of reference (such as at one end of the sample) is shown in Fig. 6. Note that the large fluctuations in the interface position observed in a moving frame of reference are indeed very small perturbations in the fixed frame of reference. The variation in interface velocity with interface position is shown in Fig. 7. The results given in Figs. 5-7 clearly show that the steady state interface growth conditions were established in our experiments so that the measured interface temperature indeed corresponds to the steady-state growth condition. This is a crucial point in our experiments since the composition in solid at a planar interface is equal to the initial alloy composition only if precise steady state condition is attained experimentally.

Experimental studies were also carried out to characterize the critical velocity for planar interface instability. For these studies, experimental runs were made at several velocities to bracket the velocities which give planar or nonplanar interface. Next, a series of experiments was carried out within the small velocity bracket to determine the velocity at which first instability was observed. The sample was run at each velocity for several

hours to ensure that sufficient time was available for the formation of a perturbed interface. These experiments were repeated for several compositions.

Table 1. Properties of the naphthalene-camphor system

Pure naphthalene

Melting point	253.5 K
Molecular weight	128.17
Entropy of fusion	55.5 J/mol K
Thermal conductivity of solid	0.376 J/m s K
Thermal conductivity of liquid	0.226 J/m s K
Average surface energy	60 mJ/m ²

Naphthalene-camphor

Liquidus slope (dilute solution)	0.18 K/mol%
Solidus slope (dilute solution)	2.6 K/mol%
Solute diffusion coefficient in liquid	736 $\mu\text{m}^2/\text{s}$

Figure 3. The Napthalene-Camphor phase diagram [10]

Figure 4. The temperature trace with time from a pair of thermocouples which were placed 2 mm apart inside the cell. The time at which each of these thermocouples intersected the interface are shown with large filled circles. (a) The variation in temperature with distance from the interface, as shown by the two thermocouples readings, the zero on the X-axis is the location of the interface. (b)

Figure 5. The change in interface position with time when the interface position is measured in the moving frame of reference, i.e., the displacement of the interface as observed under the microscope

Figure 6. The variation in the interface position with time when the interface location is measured in the fixed frame of reference. The position of the interface gives the actual motion of the solid-liquid interface

Figure 7. The variation in the velocity of the interface as a function of time

RESULTS

Morphological Developments

In order to study the dynamical process of interface break-up, the naphthalene-camphor system was directionally solidified at velocities larger than that required for planar interface stability. The formation of initial perturbation and the subsequent development of periodic cellular array formation was examined in situ through a microscope. The process of interface instability and the development of cellular array was found to depend upon the crystallographic orientation of the solid-liquid interface.

Figure 8 shows a time sequence of interface pattern development. Note that the initial perturbations do not exhibit strong tendency for facet formation, and the interface instabilities are fairly smooth. As in the case of the nearly isotropic succinonitrile-acetone system [14], the initial perturbation forms at a grain boundary and this perturbation propagates along the interface, Figs. 8a-8c. Once the perturbation has acquired a finite amplitude, the anisotropy effects become important and the perturbations begin to acquire a faceted shape, Figs. 8d-8e. As the amplitude of perturbations increases further, a strongly faceted interface results. These faceted cell undergo a coarsening phenomena in that some of the cells are eliminated and the spacing between the cell increases, Fig. 8f.

The average spacing of the initial perturbations that form on a planar interface was measured for each velocity, and the results are shown in Fig. 9. In addition to the initial wavelength of perturbations, the final steady state spacing for each velocity was also measured, and these results are shown in Fig. 9. Note that a significant change in the

wavelength of cells occurs with time, i.e., from the initial formation of perturbations to the establishment of final steady-state spacing.

When a different crystallographic plane of solid formed the interface, a significantly different mechanism for the cellular pattern formation was observed, as shown in Fig. 10. In this case the perturbations occur initially only at the grain or low angle boundaries. When the grain was somewhat larger, the interface exhibited the presence of macroscopic steps. Often significant stresses form at the base of the step, as observed through the development of fringes, and these stresses relax by forming a boundary and thereby create an additional cell. Thus, the formation of cellular pattern in this case is due to the presence or generation of boundaries at the interface.

For certain boundary orientations, the instability of the planar interface occurred through the formation of a train of steps, as shown in Fig. 11. In this case, the source of the steps was at the junction of interface and the wall. The steps, once formed, propagated along the interface, the changes in the interface shape primarily occurred through the collapse of steps or through the change in interstep distances.

Interface Temperature Measurements

The interface temperatures were measured for different velocities in naphthalene- 0.95 mol% camphor system. These temperatures were measured only when the interface was growing under steady state condition, as discussed in the previous section. Also, these temperature measurements were carried out for interface orientation of Fig. 8. Since the same thermocouple was used to measure the liquidus and the interface temperature, we have characterized the interface undercooling, $\Delta T = T_L - T_I$, as a function of velocity, and the results are shown in Fig. 12. These steady state temperatures were measured for planar,

cellular and dendritic interfaces. Note that a sharp change in interface undercooling is observed at the velocity where planar to nonplanar transition takes place.

Planar Interface Instability Studies

The critical velocities for planar interface stability were determined for several compositions under known temperature gradient values in the solid and liquid. The orientation of the interface was kept constant, and it corresponded to the interface orientation shown in Fig. 8. Figure 13 shows the variation in (G/V_c) with composition, C_0 , where V_c is the critical velocity for planar interface stability.

Figure 8. A time sequence of the evolution of interface pattern when the growth rate exceeds the planar interface stability threshold. Initial perturbations are somewhat smooth and they become faceted with time. The times after solidification run was started, in minutes, are: (a) 89 (b) 89.5 (c) 90 (d) 90.5 (e) 91, and (f).120

Figure 9. The variation in the initial average periodicity of interface break-up with velocity for the interface instability sequence of Fig. 8. The final periodicity of the steady state cellular structure is also shown. The two sets of data for the initial spacing represent the results of repeated experiments to check the reproducibility of the results

Figure 10. A time sequence of the evolution of interface pattern when the growth rate exceeds the planar interface stability threshold. The instability occurs at the grain boundaries. The times after solidification run was started, in minutes, are: (a) 0 (b) 0.5 (c) 1.0 (d) 1.5 (e) 2.0, and (f).15

Figure 11. A time sequence of the evolution of interface pattern when the growth rate exceeds the planar interface stability threshold. A steplike interface is formed and the source of the steps is at the interface-wall junction. The photographs were taken at 30 s interval

Figure 12. The variation in the interface undercooling, ΔT , with velocity for steady state growth. The maximum in undercooling is observed at the planar-nonplanar transition velocity

Figure 13. A relationship between (G/V_c) and C_0 at the onset of planar interface instability

DISCUSSION

Morphological Development

The basic mechanism of instabilities on a planar interface was found to depend on the crystallographic orientation of the interface. This anisotropic behavior of pattern formation can be examined by looking at the crystal structure of naphthalene which is shown in Fig. 14. Naphthalene is an organic crystal with a distorted face-centered cubic close packing of the molecules. The unit cell is monoclinic with space group $P2_1/a$. The dimensions of the unit cell are [15]: $a = 82.18 \text{ nm}$, $b = 59.9 \text{ nm}$, $c = 86.4 \text{ nm}$ and the angle b equal to $122^\circ 55'$. There are two molecules per unit cell; one at (000) and the other at $(1/2, 1/2, 1/2)$.

The growth rates of different crystallographic planes in naphthalene are significantly different, and the planes with the lowest growth rate will bound the crystal after some transient time. These bounding planes are generally low index planes which belong to the cusp orientations in the Wulff plot. The atomic density of planes in pure naphthalene decreases in the following order [15]: $\{001\}$, $\{111\}$, $\{011\}$, $\{110\}$ and $\{210\}$. Note that the presence of impurity can alter the above sequence or include some additional planes in the sequence. The surface energies of different planes have not been measured, but the average value is found to be $61 \pm 11 \text{ mJm}^{-2}$, and the anisotropy in the surface energy has been estimated to be about 20% [15].

Because of the strong anisotropic nature of the naphthalene crystal, the kinetic effects will be significant, and both the kinetic coefficient and the solute distribution coefficient may differ significantly for different planes. However, growth of any particular interface orientation can be readily examined by directional solidification studies under the conditions

of stable planar interface growth. When the growth conditions are altered to obtain a nonplanar interface, the anisotropic effects become dominant, and the planes with the slowest growth rate are exhibited as shown in Figs. 8 and 10. By measuring the angle between the planes and the direction of cells with respect to the heat flow direction, it is possible to characterize the growth direction or orientation of cells. These low index planes exhibited in the experimental results of Figs. 8, 10 and 11 are shown in Fig. 14. The cellular structure in Fig. 13a has (102) plane in the direction of growth, and the cell is bounded on the sides by planar faces (001) and (110). In contrast, Fig. 14b shows the growth of the crystal with (101) plane in the direction of growth and the cell is bounded by (001) and (101) planes. Since the atomic density in the plane growing in the heat flow direction is high, this plane is quite stable with respect to perturbations in its shape. Consequently, the instability of this plane occurs through the formation of defects. The crystallographic directions for the orientation shown in Fig. 11 are given in Fig. 14c. In this case the steps are macroscopic and the interface advances through the motion of steps only. The low energies of {100} orientations of steps and terraces makes it difficult for the interface to perturb appreciably and develop higher energy orientations.

The initial wavelength of perturbation for crystal orientation studied (Fig. 8) was found to decrease as the velocity was increased. One can qualitatively understand this behavior by examining the predictions of the linear stability analysis of planar interface stability. The range of unstable wavenumbers as a function of velocity was calculated by using the results of Mullins and Sekerka [16], and the result is shown in Fig. 15. Since the precise kinetic law is not yet known, the theoretical calculations neglected the interface kinetic effect. The experimental results of initial and final wavenumbers of perturbed interface as a function of velocity are also superposed onto this diagram. The variations in

observed wavelengths with velocity was found to be qualitatively similar to those in the succinonitrile-acetone system [17].

The mechanism of coarsening of cellular spacing was also observed to be the same as in the case of succinonitrile or metals. The increase in spacing occurred through the elimination of certain cells, as seen in Fig. 8f. The decrease in spacing by tip splitting was observed in the sequence of pattern formation shown in Fig. 10. In this case, the mechanism of creation of cell was somewhat different in that the splitting of cell was accompanied by the creation of a boundary. It appears that the formation of a small groove is accompanied by a large gradient of solute which sets up significant amount of stresses. These stresses are then relieved by the formation of a boundary [18].

Steady State Planar Interface Temperature

The effect of velocity on the temperature of the planar interface growing under steady state conditions is shown in Fig. 12. The undercooling is found to vary with velocity which indicates that appreciable interface kinetic effects are present in this system. In absence of interface kinetics effects, the planar interface undercooling will be constant and equal to the equilibrium freezing range of the alloy. In order to determine the mechanism of step creation, a relationship between the velocity and undercooling is required. Figure 16 shows the relationship between the velocity and undercooling, and the least square analysis of these results give the following relationship:

$$\ln V = 0.600 - (2.43/\Delta T), \quad (10)$$

or

$$V = 1.822 \exp \{-2.43/\Delta T\} \quad (11)$$

The velocity was also plotted against ΔT and ΔT^2 , and the correlation was not found to be as good as that for the exponential relationship given by equation (11). The exponential relationship between the velocity and undercooling shows that the process of two-dimensional nucleation is operative for the growth of the interface.

By substituting the value of $\Delta T = T_L - T_I$, and noting that for steady state planar interface growth $C_S = C_0$, the relationship between the interface temperature and velocity is obtained as:

$$T_I = T_M + mC_S + [2.43/\ln(0.549V)], \quad (12)$$

where m is the slope of the liquidus line. Equation (12) gives a relation between interface temperature with velocity and solute composition in solid at the interface, and thus it describes the first response function, i.e., equation (1).

Planar Interface Instability Condition

In order to specify the conditions of nonequilibrium, the composition in the liquid at the interface must also be characterized. We can indirectly characterize the value of C_L by examining the condition of planar interface instability. In order to correlate C_L with the critical velocity, V_C , we shall assume that: (1) the planar interface is growing very close to the steady-state condition when it begins to become unstable, so that the composition in solid at the interface is equal to the alloy composition, and (2) the constitutional supercooling criterion is valid, so that $G = mG_C$, where G is the average temperature gradient at the

interface and G_c is the concentration gradient at the interface when the interface just begins to become unstable. The concentration gradient at the interface can be related to the velocity of the interface through the solute flux balance, which gives:

$$G = -m (C_L - C_S) V_c / D \quad (13)$$

Rewriting the above equation, we obtain:

$$C_L = C_S - (GD/mV_c) \quad (14)$$

The above equation relates C_L with V and C_S , and thus it gives the second response function, i.e., equation (2).

Interface Kinetic Effects

The interface kinetic effects for a specific orientation of the naphthalene crystal was characterized by the two response functions, given by equations (12) and (14). These two equations give the interface temperature and interface composition in the liquid as a function of velocity and alloy composition. Since both the response functions were determined experimentally for composition of 0.95 mol % camphor, Fig. 17 shows the experimental values of interface temperature and the compositions in the solid and in the liquid for $V = 1.0 \mu\text{m/s}$.

The present experimental study is restricted in that the interface temperature variation with velocity were examined only for one composition. A more general relationship would require the study over a range of compositions. Similarly, we have used the planar interface instability condition to obtain the second response function. If one

thinks of functions given by equations (1) and (2) as equations of surfaces in three-dimensional plots describing the interface temperature and interface composition as a function of V and C_S , then we have obtained equations of specific sections of these surfaces. This restriction is mainly due to the fact that the quantitative evaluation of the second response function was possible only by using the planar interface instability condition. A more general relationship would require actual measurements of interface compositions which are difficult to obtain precisely through currently available experimental techniques. The limited experimental study presented in this paper shows for the first time the magnitudes of the nonequilibrium process at the interface, and it demonstrates an experimental technique to quantify these nonequilibrium processes.

Figure 14. Crystallographic orientations of the naphthalene crystal. Figures (a) to (c) correspond to the interface orientations shown in Figs. 8, 10 and 11, respectively

Figure 15. A comparison of the wavelength of the initial instability with the prediction of the linear stability analysis

Figure 16. The relationship between V and ΔT for steady state planar interface growth conditions

Figure 17. The representation of experimental results on interface temperature and compositions under nonequilibrium conditions onto a phase diagram

CONCLUSION

Detailed experimental study is carried out in the naphthalene-camphor system to examine the mechanisms of the planar interface instability and to quantitatively characterize the nonequilibrium effects that are present at the interface. It is shown that appreciable interface kinetic effects are present in this system, and the kinetic effects are highly anisotropic so that the mechanism of planar interface instability is strongly influenced by the orientation of the interface. Lower atomic density planes such as the {210} planes were found to become unstable through the formation of smooth perturbations. On the other hand, the high atomic density planes such as {001} planes were found to be very stable and the perturbation of this interface orientation required the formation of defects.

Interface kinetics effects play a key role in the development of solidification microstructures. However, quantitative measurements of the interface kinetic effects have not been available in the literature. In this study, we have used the directional solidification technique to obtain for the first time the response functions for the nonequilibrium conditions that exist at the interface during growth.

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SECTION IV. SOLIDIFICATION MORPHOLOGIES IN TERT BUTYL ALCOHOL

INTRODUCTION

Most solidification experiments have been focused on metals and plastic crystals since these materials exhibit nearly isotropic growth behavior and they have negligible kinetic effects. Thus, from the physical and mathematical point of view, it is simpler to analyze the experimental results in these systems. As an example, the lack of measurable kinetic effect allows the use of the equilibrium conditions at the interface so that it is possible to evaluate the interface composition if the interface temperature is known. However, there are several important materials which grow under nonequilibrium conditions at the interface. Semiconductors, superconductors and most of the organic crystals belong to this group. The anisotropy in the physical properties, such as surface energy, kinetic coefficient and partition coefficient, produces a strong orientation dependence in the growth rate. The anisotropy is usually more than a change in the rate of growth of different planes; it may also change the growth mechanism of the solid liquid interface.

Solid-liquid interfaces can be divided in two groups: rough interfaces which are characteristic of metals and plastic crystals, and angular faceted interfaces that correspond to semiconductors, superconductors and the majority of organic crystals. Jackson [1] proposed a simple model to predict the conditions for faceted or rough solid:liquid interface based on the entropy of fusion value. According to this model, if $\Delta S/R$ is less or equal to 2, where ΔS is the entropy of fusion and R is the universal constant of gases, the interface will be rough and it will grow in a continuous way, i.e., all the solid surface sites are equally probable for an incoming liquid atom. On the other hand, when $\Delta S/R$ is greater than 2, the interface has preferential places for attachment of new atoms and the growth will be controlled by the step mechanism, i.e., an atomically flat interface will grow only when one step passes over it. The step growth mechanism produces facets in the solid liquid interface. The Jackson criterion is based on thermodynamic considerations and it fails to consider the

influence of solidification conditions, namely the effect of velocity on the nature of the interface, as has been observed in several experimental publications [2-6].

Cahn [7] resolved this inconsistency by proposing a model that is based on kinetic considerations. His model predicts a faceted growth for small driving forces and a transition to continuous growth when the driving force overcomes a critical value. This critical force can be high or small enough to be undetectable in solidification experiments and materials with only one kind of behavior may be observed.

According to Cahn [7] and Cahn et al. [8], the relationship between the velocity and undercooling will depend on the driving force for the transformation. In pure materials, the growth can be characterized as classical, transitional or continuous depending upon the particular mechanism of growth that is operating. A step growth is expected for low driving forces where the interface undercooling is proportional to the square root of the velocity. In contrast, a continuous regime exists when the driving force exceeds a critical value and the interface undercooling is directly proportional to the velocity. Between these two regimes, the kinetics behavior will deviate from both the above laws. When impurities are present, or in alloys, the presence of solute may change the growth law. The interface undercooling will be a function of both the velocity and the interface composition. To determine which effect predominates, one has to study the relationship between the interface velocity and undercooling. For pure materials, if the effect is only kinetic, the driving force is a monotonously increasing function of the total undercooling and the relationship between velocity and undercooling will be linear for continuous growth and nonlinear for the growth of atomically smooth surfaces. That is not necessarily the situation in the presence of solute because the change in the interface undercooling has a component due to the solute accumulation in front of the interface.

Most of the solidification experiments reported in the literature, have been carried out for both extremes of the spectrum, i.e., for metals and plastic crystals or for highly faceted materials like Napthalene, Salol or Silicon. In the transition zone, both faceted and continuous growth may be present simultaneously. In order to examine the interface characteristics in the transition zone, unidirectional solidification experiments have thus been carried out in Tert Butyl Alcohol (TBA) which has a value of $\Delta S/R = 2.7$. Purified TBA and the mixture of purified TBA with water were unidirectionally solidified to examine the conditions for the planar interface stability and the dynamics of the cellular morphological development.

MATERIAL

Tert Butyl Alcohol has a value of $\Delta S/R = 2.7$ and it was first classified by Timmermans [9] as a plastic crystal. However, this characterization is questionable because of the complex crystalline structure, which is still not known. The crystal structure has been postulated to be more complex than a cubic structure required for a plastic crystal [10,11]. The crystal structure of TBA has been studied by different techniques [11-15], and the scheme of the possible structures of TBA is shown in Fig. 1. This scheme is not unique since there are disagreements in the literature about the temperatures of transformations and earlier experimental observations show that Crystal III can often be melted without transforming it into crystal I. Moreover, the crystalline structure, called Crystal III, can not be reproduced easily. Crystal I and Crystal II can be in equilibrium with the melt, and Crystal III can be nucleated sometimes by undercooling the liquid.

Morphologically, we observed two crystal structures of TBA: one when the cold chamber in the solidification apparatus was below 10 °C, Fig. 2a, which we believe is Crystal II structure, and the other which we shall call needles or fingernails depending on the particular orientation that was present (Figs. 2b and 2c). These latter structures are of Crystal I. This needle structure, which looks like a hollow cylinder for most of its length except near the tip region, exhibits faceted characteristics, as shown in the Fig. 2c

The binary mixture of TBA and water was also directional solidified. The equilibrium diagram of TBA-Water system [16] is available and it is shown in Fig. 3.

Figure 1. Scheme of the possible crystalline structures of Tert Butyl Alcohol

Figure 2. Crystalline structures of TBA. (a) Crystal II. Magnification 44 X. (b) Crystal I. Magnification 44 X. (c) Crystal I. Tip morphology. Magnification 120X

(a)

(b)

(c)

Figure 3. Tert Butyl Alcohol-Water equilibrium diagram [16]

EXPERIMENTAL PROCEDURE

As received TBA was first dried and then distilled. The material was dried by stirring the liquid in molecular sieves for one day. This treatment absorbs most of the water present in TBA. The residues of molecular sieves left in suspension in the liquid was next removed by distillation. The dried and distilled TBA was used for directional solidification studies. Also, two other samples were prepared in a dry chamber by adding distilled water of predetermined amount. These samples contained 0.5 and 1.0 wt.% water.

Unidirectional solidification experiments were carried out for all the three samples in a solidification apparatus for transparent materials which is described by Mason and Eshelman [17]. The solidification cell was made of glass by fusing two microscopy slides. The gap between the slides was about 150 μm and the sides of these cells were sealed by fusing low melting point powder glass except for two small apertures left for liquid to be introduced. The cells were filled with the TBA-water mixture by capillary action through one of the openings. Once the cell was full, it was allowed to freeze very quickly. Finally, inert epoxy was used to close the small openings.

After the epoxy was dried, the cell was transferred to the microscope stage and the material was melted and solidified several times until the needles had grown parallel to the heat flux. The sample was held stationary in a positive thermal gradient until a planar interface was reestablished prior to the experimental study.

In high magnification experiments, a reticule was inserted into the photographic eye piece to define a moving reference system. The stationary state is defined when the interface does not change its position as a function of time in this reference system. The interface temperature was measured with a calibrated thermocouple. The trace of the thermocouple output as a function of time in the liquid showed that the temperature gradient was linear. It

has been shown [18] that the thermal field reaches the steady state value quite rapidly so that it is possible to correlate the position and temperature values with certain confidence and, a continuous value of the interface temperature can be obtained. In this context, if $T_i(t) = f(t)$, then $v(t) \propto f'(t)$, where $T_i(t)$ is the interface temperature as a function of time and $v(t)$ is the interface velocity.

RESULTS AND DISCUSSION

Morphological Analysis

Figure 4 shows the planar interface instability sequence for the dried and distilled sample for the external velocity of $V=0.5 \mu\text{m/s}$. Although the sample was distilled and dried, some residual water impurities remained which caused the instability of the planar interface. This sequence serves as an example to show the main features involved in the transformation and it is similar to those seen at other velocities and higher compositions. The sequence will be analyzed in the three main morphologies, planar, cellular and dendritic.

Planar interface instability

After some transient time, the perturbations are first produced at the grain boundary. For some orientations, as seen in Fig. 4b, facets can be seen growing normal to the heat flow direction. The instabilities far from the grain boundary are smooth as in the case of metals or plastic crystals [18]. The solid solubility of water in pure TBA is negligible, therefore it is not clear at what undercooling the interface should become unstable since there is no steady state regime for the planar interface.

The velocity of the cells is lower than the external velocity and therefore, the interface undercooling continues to increase during this stage. The cells then show lateral facets which grow perpendicular to the heat flow direction. The growth rate of this faceted plane is lower than the velocity in the heat flow direction. The low growth rate for the bounding planes introduce an important constraint in the cell elimination process, so that, the final dendritic spacing is very close to the value of the initial wavelength perturbation. Figure 5 shows the variation in the cellular spacing as a function of the external velocity for

different compositions and thermal gradients. The spacing decreases when the velocity or the gradient is increased as it happens in nonfaceted [19] as well as in faceted materials [20]. In contrast to other systems, viz., faceted system like Naphthalene and non-faceted system like Succinonitrile [18] the primary spacing in TBA is fixed by the initial wavelength of the perturbation.

Cell to dendrite transition

At certain point of the cell growth, a second structure can be seen to grow in the liquid. This structure has the shape of a fingernail with a curved tip. We will call this structure dendrite or fingernail.

The transition from cell to fingernail can be divided in two steps according to the sequences shown in the Fig. 6. First a set of faceted planes is observed to take form in the cell which causes "flattening" of its sides. This transition from a rounded to a semifaceted cell can be explained on the basis of the kinetic effect on some growing planes. The planes with lower kinetic coefficient will have a lower rate of growth and they will last longer because the highest growth rate planes will disappear faster. This morphological change is then induced by the growth process and does not imply a change in the kinetic of growth. Second, once the facet has been formed there is a faceted-nonfaceted intersection at the tip of the cell. At the intersection, there is a discontinuity in the growth direction and velocity as shown in the Fig. 6a. The shape will be maintained only if the faceted plane can adjust its composition to keep the liquid concentration gradient lower at the intersection point. The experiments show that the velocity of the cellular tip does not change during some time after the fingernail shoots into the liquid. It means that the solute distribution in front of that part of the interface has not been altered significantly by the first stages of the fingernail development. Therefore, it is probable that at the intersection point the liquid concentration gradient is increased over the limit of stability which causes the formation of a dendritic

needle. Figure 6b shows the fingernail shape at the beginning of the growth taken from a highly magnified picture. This shape shows that the cell does not grow more than a certain distance when the fingernail is already growing. The solute rejected by the inner lateral plane increases the solute in front of the initial cellular interface which decreases the liquid concentration gradient in front of the tip.

Finally the fingernail starts to surround the cell keeping a hollow morphology.

Dendritic interface

Figure 7 is a dendritic tip showing several features of the fingernail morphology: i) The fingernail structure is open at the tip as can be seen in the Figs 7a and 7b. ii) The tip of the dendrite is rounded. iii) The fingernails have different layers that grow with time which causes the coarsening of the dendrite. iv) A faceted morphology can be seen close to the tip.

General Kinetics

Figures 8-10 show the interface position measured in a fixed reference system for dried and distilled TBA for different velocities.

Figure 11 shows a high magnification experiment carried out with an external velocity of $V=0.3 \mu\text{m/s}$. The position was plotted from a moving reference system. Figure 12 shows the interface position from a fixed reference system. The arrows indicate when the planar to cellular and cellular to dendritic interface transitions occur. As it was explained above, these data can be transformed to interface undercooling by using the temperature gradient value and to interface velocity by a point to point numerical derivation. A plot of the interface velocity as a function of the interface undercooling is shown in the Fig. 13. The

experimental points show that the interface velocity has a small dependence on the interface undercooling until the fingernail shoots up into the liquid. Once the fingernail grows faster than the external velocity, the undercooling starts to be reduced so that the plot has a looped shape. Finally, the tip velocity goes back to the external velocity value at some fixed undercooling. The scattering in the experimental points at the stationary state reveals departures from the stationary state regime. The tip undercooling at steady state as a function of the external velocity has been measured for TBA-0.5wt.% water and the results are shown in the Fig. 14. The general behavior coincides with the tip undercooling-velocity dependence in highly faceted materials like Napthalene [20].

The fingernail suffers a coarsening effect mentioned above but the velocity of this process is considerably smaller than the growth velocity in the heat flux direction. Figures 15-18 show the width of the cell as a function of time compared with the cell amplitude. The cell amplitude was defined as the distance from the cell tip to the cell base.

As a matter of comparison, an experiment on the Succinonitrile-Acetone system was also carried out. Figure 19 shows the interface velocity as a function of undercooling for an external velocity $V=1 \mu\text{m/s}$. The similarity between this result with the Fig. 14 may indicate that the growth process for TBA is primarily controlled by solute diffusion in the liquid as it is known to happen in the Succinonitrile system.

Figure 4. TBA dried and distilled. Planar interface instability and subsequent development. External velocity $V = 0.5 \mu\text{m/s}$. The times after the solidification started, in minutes (a) 16, (b) 65, (c) 71

(a)

(b)

(c)

Figure 4. (Continued) (d) 76, (e) 99, (f) 106

(d)

(e)

(f)

Figure 5. Cell spacing as a function of the external velocity

(a)

(b)

Figure 6. Cell to fingernail transition. a) Faceting of the lateral planes. b) Side view of a fingernail growing and rejecting solute into the liquid

(a)

(b)

Figure 7. Tip structure. (a) focused close to the objective. (b) focused far from the objective. Magnification 120 X

Figure 8. TBA dried and distilled. Interface position as a function of time from a fixed reference system. External velocity $V = 0.5 \mu\text{m/s}$

Figure 9. TBA dried and distilled. Interface position as a function of time from a fixed reference system. External velocity $V = 1 \mu\text{m/s}$

Figure 10. TBA dried and distilled. Interface position as a function of time from a fixed reference system. External velocity $V = 2 \mu\text{m/s}$

Figure 11. TBA-0.5wt.% water. Interface position as a function of time from a moving reference system. External velocity $V = 0.3 \mu\text{m/s}$. Temperature gradient, $\nabla T = 1.5 \text{ K/mm}$

Figure 12. TBA-0.5wt.% water. Interface position as a function of time from a fixed reference system. External velocity $V = 0.3 \mu\text{m/s}$. Temperature gradient, $\nabla T = 1.5 \text{ K/mm}$

Figure 13. TBA 0.5wt.% water. Relationship between interface velocity and total interface undercooling. External velocity $V = 0.3 \mu\text{m/s}$. Temperature gradient $\nabla T = 1.5 \text{ K/mm}$

Figure 14. TBA-0.5wt.% water. Interface undercooling as a function of the external velocity

Figure 15. TBA dried and distilled. Cell amplitude and width as a function of time. External velocity $V = 0.5 \mu\text{m/s}$

Figure 16. TBA dried and distilled. Cell amplitude and width as a function of time. External velocity $V = 1 \mu\text{m/s}$

Figure 17. TBA dried and distilled. Cell amplitude and width as a function of time. External velocity $V = 2 \mu\text{m/s}$

Figure 18. TBA dried and distilled. Cell amplitude and width as a function of time. External velocity $V = 5 \mu\text{m/s}$

Figure 19. Succinonitrile=1wt.% Acetone. Relationship between interface velocity and total interface undercooling. External velocity $V = 1 \mu\text{m/s}$

CONCLUSIONS

The pattern formation in TBA is shown to occur in three stages; first the planar interface becomes unstable with perturbations that are smooth; as these perturbations grow in the nonlinear regime, the small amplitude cells become faceted on sides and the tip growth is reduced; finally, a fingernail type of instability initiates from one side of the faceted cell. These morphological changes clearly show the significant effect of the interface anisotropy properties on pattern formation. However, the precise role of the kinetic effects is difficult to evaluate quantitatively since it is difficult to isolate the solute effects from the interface kinetic effects. The overall relationship between the interface velocity and interface undercooling in TBA system is very analogous to that in the nearly isotropic Succinonitrile-Acetone system. Our experimental results thus indicate that the relationship between velocity and kinetic undercooling at the interface cannot be derived from the relationship between velocity and total interface undercooling when solute effects are present in the system. In order to obtain definite quantitative information on the kinetic effects at the interface, it is necessary to precisely measure not only the interface temperature but also the interface compositions which is not possible at this time.

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SECTION V. STRESSES AT THE SOLID LIQUID INTERFACE

INTRODUCTION

Modern technology routinely employs solid state properties of carefully grown crystals for new applications. Examples of this are the miniaturization of the electric circuits and the use of solid state crystals in the area of optic related lasers. In these two particular fields, one of the principal requirements is the perfection in the crystal structure. The ability to manipulate the perfection in a very controlled way is a critical requirement. In the microchip production, for example, the goal is to achieve a silicon matrix as perfect as possible in order to control the amount of dopants. In the field of optics materials, the uses of solid state modulators like (ADP) and (KDP) and the production of high quality crystals for the laser optics and amplifications are of vital importance in modern technology. Considerable work has been done to study the defect production in the material processing, in particular during the solidification process [1-9].

If defects are defined as changes in the perfect periodicity of the lattice, they can be divided in two categories, chemical and structural defects. Chemical defects are due to the presence of impurities or second phase precipitates and structural defects are due to dislocations, grain boundaries and stresses. These two categories are interrelated because the presence of an impurity can induce stress and inversely a stress field can induce impurity accumulation.

Mainly, defects are produced during the phase transformations involved in the synthesis and in the subsequent cooling. If the phase transformation is a liquid to solid, the control of defect production is achieved by adjusting the critical variables during the solidification, in particular, temperature gradients and cooling rate.

If the material is nonfaceted as in the case of metals and plastic crystals, the planar interface has a uniform solute distribution. Faceted materials can produce inhomogeneous

solute distribution because, each facet has its own partition coefficient and the amount of solute rejected will depend on the orientation. The intersection of facets of different orientations is a potential cause for nonuniform solute distribution. According to Hurle and Cockayne [10] the following mechanisms of defect production during solidification and subsequent cooling can be identified:

- a) Non steady state convective motion of the melt
- b) In nonfaceted materials, cellular and dendritic interfaces produce solute accumulation in localized sites
- c) In faceted materials, anomalous distribution of solute due to the presence of facets
- d) Dislocation generation or rearrangement during the cooling to room temperature
- e) Generation of precipitates and point defects during cooling
- f) Entrapment of particulate material and gas bubbles during the crystal growth.

However, these are not the only mechanisms. We have been able to identify other sequences of defect production at the interface. These defects are initiated at the solid-liquid interface as a result of the dynamical changes in the interface shape during growth. The stresses produced at the interface can be observed in situ in photoelastic materials.

Photoelasticity is the property of some optically homogeneous materials which become birefringent under stress. The transparency to visible light of these materials allows the visualization of the stress configuration through a set of fringes characteristic of these phenomenon. Theories have been developed to correlate the fringes with the stress field, but there is not much information about the photoelastic effects when the unstressed material is anisotropic like in the Napthalene case.

Photoelasticity theory for isotropic materials assumes a linear relation between optical axis and principal directions of stress. The main result is that for the plain stress condition, the isochromatic fringes correspond to points where the difference in the

principal stresses σ_1 - σ_2 produces a light path difference that is proportional to an integer number of wavelengths. When white light is used, the different colors correspond to different stress values.

Unstressed polycrystalline birefringent material, placed between polarizers, will show different colors depending on the orientation of each grain. When stress is applied or when an internal stress develops during processing, the interaction between the "natural" optical axis and the stresses will give a set of fringe pattern. Internal stresses are caused by gradients of different origin, like differences in temperature, concentration, surface energy or the elastic constants. They can also be produced by the interaction of the solid-liquid interface region with the walls of the container. Stresses can be produced by the following different mechanisms during solidification:

- a) The solid-liquid interface grows by incorporating atoms from the liquid. The mechanism will depend on the driving force and on the particular orientation for a given material. In a faceted material like Napthalene, the growth mechanism is by steps, i.e., an interface site remains atomically flat and grows only when one step passes over it. It implies that the lateral velocity is much higher than the normal velocity and this high velocity can produce solute trapping or growth accidents that can give origin to chemical and structural inhomogeneities. If the solid can not accommodate or release the stress created by the defect, a continuous increase in the stress field takes place.
- b) Surface energy anisotropy can cause grain boundary movement during the solidification. This movement can be defect assisted or can be produced by atomic jumps through the grain boundary. In the first case, if the dislocations can not arrive to the grain boundary, stresses will be created. Dislocations can be blocked, for example, by the inhomogeneities generated through the mechanism pointed in a).

- c) Morphological perturbations in the solid liquid interface can produce a non uniform solute distribution and the concentration gradient in the solid will give a stress configuration.
- d) In the particular case of Napthalene, normal stresses to the interface can be expected because the change in the liquid volume due to the elimination of gas trapped in the solid can induce a sharp increment in the pressure.

In order to examine the mechanism of stress production, critical experimental studies have been carried out. This paper presents, for the first time, in situ experimental observations of stress fringes produced at the solid liquid interface when Napthalene is grown under unidirectional solidification conditions. Based on some of the experimental results, we have explored the mechanism which assumes that stresses are produced by a solute distribution. A finite element model is presented in which the fringe patterns can be correlated with an inhomogeneous concentration distribution. This model was made for the sequence of observations made in the present study, and is a first approach to the problem. In order to make a correlation with experiments, an additional assumption has been made that the observed fringes correspond to σ_1 - σ_2 as in the case of isotropic materials, where σ_1 and σ_2 are principal stresses.

EXPERIMENTAL PROCEDURE

As received naphthalene was first melted with metallic sodium at 100 °C during 1 hour to remove β -methylnaphthalene. The material was then introduced in a Teflon tube and zone refined with 10 ring passes. Teflon tube was used to avoid the shattering of the glass tubes due to expansion during the purification procedure. A glass cell, made of two microscope slides fused together leaving a gap $\leq 50 \mu\text{m}$ between them, was filled with the purified material. The cell was then introduced in a unidirectional solidification apparatus designed for transparent materials and described elsewhere [11]. Polarizers were installed in the light path to use the birefringence properties of Naphthalene for photographing the stress fringes. Unidirectional solidification experiments were carried out at low enough velocities to obtain a planar interface growth. The planar interface was photographed with color films at regular time intervals.

RESULTS

Unidirectional solidification experiments were carried out at moderate velocity for the present study. The planar interface was photographed with color films at regular time intervals. The sequence shown in the Figs. 1-3 were taken in the same experiment at different interface positions. The external velocity for these experiments was $V=30 \mu\text{m/s}$. From these figures, stress fringes can be seen to be associated with the changes in the interface structure. The fringes seems to be related in particular to the grain boundaries.

The sequence in Fig. 1 shows the nucleation of a new grain due to the increased undercooling produced at the base of the grain boundary by the change in the interface profile during growth. Fig. 1a, shows that the fringes are first related with a change in the grain boundary growth direction. After few seconds, a groove is created and a curved interface is generated. This curved interface can now induce a concentration distribution which is able to produce stresses described by the numerical model indicated earlier. Once the new grain is nucleated the concentration distribution due to the curved interface disappears with the stress configuration since solute atoms can migrate to grain boundary and relieve the stresses. The presence of stresses in the Fig. 1a, before the interface is curved, indicate that the concentration variation may be dictated by the variation in the temperature along the grain boundary groove.

The Fig. 2 shows the production of a crack in the solid-liquid interface due to the accumulation of stresses at one point of the interface. Again, changes in the grain boundary orientation are seen to be correlated with fringes. However in this case, the concentration of stress occurs close to the grain boundary. This stress concentration is high enough to produce a boundary in the grain.

Fig. 3 shows another crack or new grain boundary production.

Figure 1. New grain produced by nucleation after the solid liquid interface has been deformed by the presence of stress. Times relatives to Fig. a. a) $t=0$ sec, b) $t=4$ sec, c) $t=6$ sec, d) $t=22$ sec. Magnification, 50 X

Figure 2. Crack induced by the stress configuration. Times relatives to Fig. a. a) $t=0$ sec, b) $t= 10$ sec, c) $t=14$ sec, d) $t=16$ sec. Magnification, 50 X

Figure 3. New grain boundary produced by the stress configuration. Times relative to Fig. a
a) $t=0$ sec, b) $t=6$ sec, c) $t=12$ sec, d) $t=16$ sec. Magnification 50 X

DISCUSSION

Theoretical Model

One of the possible mechanisms for the production of stresses in the solid near the interface is due to the development of concentration gradient in the solid. A finite elements model has therefore been developed to show that a solute distribution can cause the stress patterns similar to the one shown in the Fig. 1.

The model is based on the following assumptions:

- a) The material is isotropic (diffusion and elastic coefficients). All constants are assumed to be temperature independent.
- b) The relationship between temperature and composition at the interface is known.
- c) The interface is growing under stationary conditions. In other words, the concentration far from the interface is equal to the initial composition.
- d) The numerical values of the constants are given in the Table 1.

Table 1. Numerical values of constants used for Napthalene in the finite element model

Poisson's ratio	0.33
Young's modulus	9×10^9 Pa
coefficient of concentration expansion, α	1.22×10^{-4} /mol %
Initial composition, C_0	0.01 mol %
Liquidus slope, m	1 K/mol %
Thermal Gradient, G	1400 K/m
Pressure	3×10^4 Pa

Solution methodology

- a) Compute the concentration profile of the solute in the crystal.
- b) From the concentration profile of the solute, compute the elastic stress solution for the crystal. The problem geometry and the boundary conditions of the problem are shown in Fig. 4 (a) and Fig. 4(b). The concentration distribution analysis and stress analysis were carried out with ANSYS version 4.4.

The interface profile of the Fig. 1c was first digitized. Then a set of coordinate (x,y) points were taken along the interface. The spacing between points was reduced along the curved regions in order to obtain a fine mesh in that region.

Concentration distribution solution

The relationship between temperature and composition has to be carried out experimentally when kinetic effects are present. As a first approach, and assuming that the solute effect is more important than the kinetic departure from equilibrium, we can apply the equilibrium diagram relationship between composition and temperature. Thus, the concentration distribution at steady state condition were obtained by solving the problem outlined in Fig. 4. The concentration of the solute on the liquid-solid interface was obtained by solving the equation

$$C = \frac{G \cdot x}{m} + C_0 \quad (1)$$

where C_0 is the uniform concentration away from the interface, G is the thermal gradient, m is the slope of the liquidus line and x is the distance measured from the interface and is positive towards the solid.

For the concentration distribution analysis of the solute, the FEM mesh is built over the entire region of the solid using two dimensional eight noded isoparametric solid element, having one degree of freedom at each node, i.e., composition. The concentration profile is obtained by solving the Fick's second law of diffusion over the selected volume. For the steady state case, this can be written as

$$\nabla^2 (D \cdot C) = Q \quad (2)$$

where D is the diffusion coefficient, C is the concentration of solute and Q is the production rate of solute.

The FEM for the diffusion equation after the transient term is removed is given by

$$[K_e] \{C_e\} = \{Q_e\}$$

where $\{C_e\}$ is the nodal concentration vector and $\{Q_e\}$ is the nodal solute production rate vector and

$$[K_e] = \text{element diffusivity matrix} = \int_{vol} [B]^T [D] [B] d(vol)$$

$$\text{where } [D] = \begin{bmatrix} D_x & 0 \\ 0 & D_y \end{bmatrix}$$

D_x and D_y are the diffusion coefficient in x and y directions respectively

$$[B] = \{L\} \{N\}^T$$

$\{N\} = \{N(x,y)\}$ = element shape function

$$\{L\} = \left\{ \begin{matrix} \partial/\partial x \\ \partial/\partial y \end{matrix} \right\} = \text{vector operator}$$

Since $[K_e]$ is assumed not to vary with concentration, the problem is linear, and the solution is obtained after one iteration.

Elastic stress solution

The elastic stress distributions were obtained by solving the problem as shown in the Fig. 4 (b). The concentration distribution of the solute as calculated by concentration analysis part is then used as an input to stress analysis part.

For the stress analysis, the FEM mesh is built over the entire region of the solid using two-dimensional eight noded isoparametric solid element, having two degrees of freedom at each node, translations in the nodal x and y directions. Plane stress analysis is carried out by assuming that the strain is produced due to the concentration difference which follows the relation

$$L = L_0 (1 + \alpha \Delta C)$$

where

α = coefficient of concentration expansion

$\Delta C = C_0 - C$ concentration difference from the reference concentration

L_0 = original length

L = length at concentration C

α is assumed to be linear for the small range of concentration difference

The stress is related to the strain by

$$\{\sigma\} = [M] (\{\epsilon\} - \{\epsilon^C\}) \quad \text{or} \quad \{\epsilon\} = \{\epsilon^C\} + [M]^{-1} \{\sigma\} \quad (3)$$

where

$\{\sigma\}$ = stress vector

$[M]$ = elasticity matrix

$\{\epsilon\}$ = strain vector

$\{\epsilon^C\}$ = concentration strain vector

For the two dimensional case, the concentration strain vector is

$$\{\varepsilon^C\} = \begin{Bmatrix} \alpha_x \Delta C \\ \alpha_y \Delta C \end{Bmatrix}$$

where

$\Delta C = C - C_0$ and C is the current composition at point of question and C_0 is the reference,

strain free, composition

Expanding Eq. 3 we can write

$$\varepsilon_x = \alpha_x \Delta C + \frac{\sigma_x}{E_x} - \frac{\nu_{xy} \sigma_y}{E_y}$$

$$\varepsilon_y = \alpha_y \Delta C + \frac{\sigma_y}{E_y} - \frac{\nu_{yx} \sigma_x}{E_x}$$

$$g_{xy} = \frac{\tau_{xy}}{G_{xy}}$$

FEM form of the elastic stress equation which is derived on the principle of virtual work for this case can be given by

$$[K_e] \{U\} - \{F_e^C\} = \{F_e^{Pr}\}$$

where

$$[K_e] = \text{element stiffness matrix} = \int_{vol} [B]^T [M] [B] d(vol)$$

$$[M]^{-1} = \begin{bmatrix} \frac{1}{E_x} & \frac{-\nu_{xy}}{E_y} & 0 \\ \frac{-\nu_{yx}}{E_x} & \frac{1}{E_y} & 0 \\ 0 & 0 & \frac{1}{G_{xy}} \end{bmatrix}$$

$[B]$ = strain displacement matrix based on the element shape functions

$\{U\}$ = nodal displacement vector

$\{F_e^C\} = \int_{vol} [B]^T [M] \{e^C\} d(vol) =$ element concentration load vector and

$\{F_e^{Pr}\} = \int_{areap} [A_n]^T \{P\} d(areap) =$ element pressure vector

$[A_n] =$ matrix of shape function for normal motion at the surface

$\{P\} =$ applied pressure vector

areap = area over which pressure acts.

Model results

In the Fig. 5 is shown the concentration profile and the numerical values obtained from the calculations. It may be noted that the concentration in the vertex of the groove can change up to a factor of ten from the initial value. When this solute distribution is used as an input for solving the stress problem, the distribution of points where $\sigma_1 - \sigma_2$ has the same value, should produce experimentally observed stress fringes. The Fig. 6 shows the spatial distributions of $\sigma_1 - \sigma_2$ values calculated by the finite element model.

Although the agreement is adequate considering the approximations made in the model, the main difference between the numerical and the experimental result is that the fringes in the numerical solution do not terminate at the solid liquid interface. The discrepancy could be due to the presence of very fine bubbles in the liquid. An increase in the internal pressure is created when bubbles initially trapped in the solid escape to the liquid region. This pressure sometimes is high enough to break the glass cell. The pressure would give a normal component to the stress at the interface, thereby shifting the $\sigma_1 - \sigma_2$ values. Calculations were also carried out considering pressure value of 30 KPa. The numerical results, shown in the Fig. 7, indicate that pressure could be the reason why the stress fringes impinge on the interface.

(a)

(b)

Figure 4. Theoretical model boundary conditions. (a) Concentration boundary conditions.

(b) Stress boundary conditions

Figure 5. Concentration profiles as solved by FEM

Figure 6. $\sigma_1 - \sigma_2$ profiles without normal pressure

Figure 7. σ_1 - σ_2 distribution when a normal pressure of 30KPa is applied. The units are dyn/cm²

CONCLUSIONS

It has been shown that stress fringes associated with the defect production at the interface can be experimentally detected in solidification experiments of organic crystals. A numerical model based on the concentration distribution could predict the stress pattern. However, the matching of theoretical and observed fringes requires that the internal pressure in the cell be taken in account.

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**SECTION VI. ANALYSIS OF THE INITIAL TRANSIENT BEHAVIOR
IN UNIDIRECTIONAL SOLIDIFICATION EXPERIMENTS**

INTRODUCTION

Solidification of alloys, in principle, is a diffusion controlled process. Therefore a transient time is expected when a change in the growth conditions occurs faster than the characteristic time for the diffusion field to adjust to the new situation. In particular, when a unidirectional solidification experiment starts, the planar interface rejects solute into the liquid. The solute built-up at the interface diffuses into the liquid at a rate proportional to the concentration gradient. If the constitutional supercooling criteria for instability is not fulfilled, the planar interface reaches the stationary state of growth. Otherwise, the interface becomes unstable in the transient time and transforms to a cellular or dendritic interface.

For fixed experimental conditions, i.e., external velocity and temperature gradient, the partition coefficient, k , will determine the amount of solute rejected at the interface and the diffusion coefficient of solute in the liquid, D , the amount removed from it. For small k , and large D , for example, the transient period or the equivalent transient distance, can be an important part of the total sample length.

There are two important reasons for understanding the controlling mechanisms of this transient time, first, if the transient period is long, the interface usually breaks-up before reaching the steady state as assumed by the theoretical models. Indeed, it is not yet known if the constitutional supercooling criteria is valid under this circumstance. On the other side, there is a practical interest to determine when the solid composition becomes constant. If, for example, we are trying to produce uniform composition materials the length of this period determines how much of the sample is wasted during the transient.

In faceted materials, the equilibrium diagram is no longer useful and the behavior of the interface during the transient time has not been thoroughly investigated so far. However, in

principle, the basic solute diffusion profile during the transient period should be analogous to that for nonfaceted materials if appropriate boundary conditions are taken in account

Two important aspects of the transient regime in Napthalene-Camphor and Succinonitrile-Acetone systems will be investigated in this study:

- a) The interface velocity during transient period is not equal to the external velocity as it is usually assumed. Thus the response of the interface to the change in the external velocity will be examined.
- b) If the planar interface becomes unstable during the transient period, then the validity of the constitutional supercooling will be determined by considering the local constitutional criteria.

EXPERIMENTS

It was explained in the Section III how the Napthalene was purified and alloyed with the Camphor and how the position as a function of time was measured.

Zone refined Succinonitrile was mixed with acetone to produce a 0.62wt.% acetone alloy. The alloy was then introduced into glass cells with calibrated thermocouples inside. Unidirectional solidification experiments were carried out in the equipment described elsewhere [1].

Two kinds of measurement were made: a) interface position as a function of time and b) liquid temperature far from the interface and interface temperature as a function of time. To measure the position of the interface as function of time, a graduated reticule was attached to the eyepiece of the camera that is attached to the microscopy. In this way, a moving reference system was created and all the position measurements were carried out from it.

The temperature was measured in the liquid through a calibrated thermocouple connected to a microcomputer used to control the time interval between readings and to store the data. The product of the external velocity and the time between measurements is the distance traveled by the thermocouple per unit time. The thermal gradient in the liquid can be obtained by fitting a polynomial function to the temperature and distance data. The interface temperature was measured directly when the thermocouple intersected the interface.

In order to be able to extrapolate the position values to temperature values through the gradient measurement, a set of experiments was designed to check the assumption of a stationary temperature profile in the liquid. A cell with two calibrated thermocouples separated by a distance of several mm was run at different velocities in the unidirectional

solidification apparatus. The temperature of each thermocouple was recorded as explained above and then plotted considering the distance between them. In Fig. 1 the trace of each thermocouple is shown as a function of time and in Fig. 2, the thermocouple outputs are shown as a function of their distance from the interface. There is no detectable difference between the two temperatures traces and we can correlate each position with a temperature value that is time independent. Thus, the transformation between position and temperatures is straightforward because the thermal gradient is constant in the region of interest.

Finally, we assumed that local equilibrium holds, in the case of Succinonitrile, at the interface which allows one to transform temperature to composition values. In these experiments the interface position and temperature were recorded from the start until the first interface perturbations were observed.

Figure 1. Succinonitrile-Acetone system. Thermocouple output as a function of time. The large open circles indicate where each thermocouple intersects the interface.
 $V = 5 \mu\text{m/s}$. $\nabla T = 1.5 \text{ } ^\circ\text{C/mm}$

Figure 2. Succinonitrile-Acetone system. Thermocouples output taking in account the distance between them. Both temperatures are plotted as a function of the their distance to the interface

RESULTS

Napthalene-Camphor System

Figures 3-8 show the interface position as a function of time measured from the moving reference system. The experimental points follow a pattern that is not what one expects in a continuous process, i.e., the solute build-up in front of the interface is assumed to be a monotonously increasing function and not a quasi periodical one. Figures 3-8 show jumps in the interface velocity at more or less regular intervals of time. Figure 9 shows the period between these changes as a function of the external velocity. If this period is related to the diffusion field, one expects some relationship between the experimental value and the characteristic time for the diffusion processes (D/V^2) where D is the diffusion coefficient and V the external velocity.

Thus, we can define a nondimensional time period/ (D/V^2) . Figure 10 shows the plot of (period $\cdot V^2$) as a function of the external velocity. The stepped shape of the distribution of points may indicate a change in the kinetic process when the external velocity approaches $1\text{ }\mu\text{m/s}$.

Succinonitrile-Acetone System

Interface velocity measurements

Figures 11-14 show the interface position as a function of time in the moving reference system for a set of external velocities and different thermal gradients. To transform to a coordinate system fixed to the cell we have to add a $V_{\text{ext}} \cdot t$ term but as can be seen in Fig. 15 that reference system is not sensitive enough to detect interface position changes in the order of tens of microns. The interface positions versus time were measured

until the planar interface became unstable. It must be noted that in the moving reference system, when the interface is moving with the external velocity, its position as a function of time remains constant.

According to Figs. 11-14, the interface does not move with the external velocity and always becomes unstable before reaching it. Figure 16 shows the variation in the break up velocities as a function of the thermal gradient for a fixed value of the external velocity. The break-up velocity tends asymptotically to the external velocity value.

Concentration profiles in the transient regime

The transient solute distribution in unidirectional solidification experiments was first analyzed by Tiller et al. [2] assuming:

- a) The interface velocity is constant and equal to the external velocity.
- b) The rate of approach of C_s to C_0 with x is proportional to $(C_0 - C_s)$ at any x , where C_s is the solid composition at the interface, C_0 is the initial composition and x is the distance from the origin of the sample. This condition gives an exponential dependence to the solution. The final expression in the Tiller model

$$\frac{C_s(x)}{C_0} = \left\{ (1-k) \left[1 - \exp\left(-k \frac{V}{D} x\right) \right] \right\} \quad (1)$$

where V is the external velocity, D the diffusion coefficient and k the partition coefficient. Smith et al. [3] solved the time dependent diffusion equation keeping the hypothesis of constant interface velocity. Their solution for the initial transient time gives the solute composition variation in the solid as:

$$\frac{C_s(x)}{C_0} = \frac{1}{2} \left\{ 1 + \operatorname{erf} \left(\frac{\sqrt{(V/D)x}}{2} \right) \right\} + (2k-1) \exp(-kq(V/D)x) \operatorname{erfc} \left[\frac{(2k-1)}{2} \sqrt{(V/D)x} \right] \quad (2)$$

where $q=1-k$

In addition, Smith et al. [3] solved the problem of a sudden change in the interface velocity, assuming that the initial state was stationary. The solid concentration profile in this case is given by

$$\begin{aligned} \frac{C_s(x)}{C_0} = & 1 - 0.5 \operatorname{erfc} \left(\sqrt{\frac{(V_1/D)x}{2}} \right) + \\ & + q \left(\frac{0.5 - V/V_1}{k - V/V_1} \right) \exp \left[-\frac{V}{V_1} \left(1 - \frac{V}{V_1} \right) \frac{V_1}{D} x \right] \operatorname{erfc} \left[\left(\frac{V}{V_1} - 0.5 \right) \sqrt{(V_1/D)x} \right] + \\ & + \left(\frac{2k-1}{2} \right) \left(\frac{1 - V/V_1}{k - V/V_1} \right) \exp(-kq(V_1/D)x) \operatorname{erfc} \left[(k-0.5) \sqrt{(V_1/D)x} \right] \quad (3) \end{aligned}$$

where V is the stationary state velocity, V_1 is the new velocity, and x is the distance from the point at which the velocity has been changed.

Our experimental measurements show that the interface velocity is not constant and it is lower than the external velocity, therefore we expect to overestimate the solid composition as a function of the distance with these approximations. However, the result shows that the degree of agreement between theoretical and experimental points depends on the thermal gradient value as is shown in the Fig. 17 for the case of $V_e = 1 \mu\text{m/s}$.

This result is not compatible with the theory which assumes a solute distribution totally independent of the thermal field. A twofold approach toward a new model was then tried. The empiric one was to use Smith's solutions (2) and (3) with the following modifications : it was applied the experimental value of the velocity as a function of time in equation (2); the values of V and V_1 used in the equation (3) were taken as the velocity at time t and the velocity at the time $t+\Delta t$ respectively.

The second approach was to obtain the exact solution to the transient problem by taking into consideration the coupling between solutal and thermal fields and allowing the velocity to be a function of time, i.e., to solve

$$D \frac{\partial^2 Y}{\partial x^2} + V(t) \frac{\partial Y}{\partial x} = \frac{\partial Y}{\partial t}$$

where Y can be concentration or temperature and with the suitable boundary conditions.

The exact solution was obtained by Grayhack [4] using the Green's function method. Figures 18-22 show the different results for a set of different experimental conditions. The important result is that approximations with the equations (3) and specially (2), fit the experimental points better than the exact solution. This may indicate that there are other mass transfer mechanism besides diffusion.

The constitutional supercooling criteria

The constitutional supercooling criteria can be written in the following way

$$G \geq -m \frac{V_b}{D} C_l(1-k) \quad (4)$$

where m is the slope of the liquidus line, C_I is the composition of the liquid at the interface when the planar interface just becomes unstable, G is the thermal gradient, D the diffusion coefficient, k the partition coefficient and V_b is the break-up interface velocity.

The above result can also be expressed in terms of interface undercooling. Note that

$$-mC_I(1-k) = \Delta T' \quad (5)$$

where $\Delta T'$ is the interface undercooling when the planar interface becomes unstable, and it is defined in Fig. 23.

Thus,

$$G \geq \frac{V_b}{D} \Delta T' \quad (6)$$

The correlation between experimental points and the theoretical predictions from the relationship in equation (6) can be seen in Fig. 24.

Figure 3. Naphthalene-Camphor system. Planar interface position as a function of time.

External velocity $V=0.5 \mu\text{m/s}$

Figure 4. Naphthalene-Camphor system. Planar interface position as a function of time.

External velocity $V=0.75 \mu\text{m/s}$

Figure 5. Naphthalene-Camphor system. Planar interface position as a function of time.

External velocity $V=1 \mu\text{m/s}$

Figure 6. Naphthalene-Camphor system. Planar interface position as a function of time.

External velocity $V=1.2 \mu\text{m/s}$

Figure 7. Naphthalene-Camphor system. Planar interface position as a function of time.

External velocity $V=1.35 \mu\text{m/s}$

Figure 8. Naphthalene-Camphor system. Planar interface position as a function of time.

External velocity $V=1.5 \mu\text{m/s}$

Figure 9. Napthalene-Camphor system. Time interval between changes in the growth law as a function of the external velocity

Figure 10. Naphthalene-Camphor system. Nondimensional period as a function of the external velocity. Note the sharp change when $V \approx 1 \mu\text{m/s}$

Figure 11. Succinonitrile-Acetone system. Interface position as a function of time in the moving reference system. External velocity $V_E = 1 \mu\text{m/s}$ (a) Thermal gradient $\nabla T = 5.6 \text{ }^\circ\text{C/mm}$. (b) $\nabla T = 7.4 \text{ }^\circ\text{C/mm}$. (c) $\nabla T = 4.2 \text{ }^\circ\text{C/mm}$. (d) $\nabla T = 2.1 \text{ }^\circ\text{C/mm}$

Figure 12. Succinonitrile-Acetone system. Interface position as a function of time in the moving reference system. For $V = 2 \mu\text{m/s}$ the thermal gradient was $\nabla T = 3 \text{ }^\circ\text{C/mm}$. For $V = 1.5 \mu\text{m/s}$, $\nabla T = 1.3 \text{ }^\circ\text{C/mm}$

Figure 13. Succinonitrile-Acetone system. Interface position as a function of time in the moving reference system. Thermal gradient $\nabla T = 4^\circ\text{C/mm}$

Figure 14. Succinonitrile-Acetone system. Interface position as a function of time in the moving reference system. $V_e = 0.4 \mu\text{m/s}$. $\nabla T = 9.5 \text{ }^\circ\text{C/mm}$

Figure 15. Succinonitrile-Acetone system. Interface position as a function of time in the fixed frame of reference. $V_E = 1 \mu\text{m/s}$. Thermal gradient $\nabla T = 7.4 \text{ }^\circ\text{C/mm}$

Figure 16. Interface break-up velocity as a function of the thermal gradient for the same external velocity $V = 1 \mu\text{m/s}$

Figure 17. Succinonitrile-Acetone system. Normalized solid composition as a function time. External velocity $V_E = 1 \mu\text{m/s}$. (a) $\nabla T = 2.1$ °C/mm. (b) $\nabla T = 4.2$ °C/mm. (c) $\nabla T = 5.6$ °C/mm. (d) Tiller solution. (e) Smith et al. solution. (f) $\nabla T = 7.4$ °C/mm

Figure 18. Succinonitrile-Acetone system. Solid profile concentration as a function of time. External velocity, $V_e = 0.5 \mu\text{m/s}$. Thermal gradient $\nabla T = 4 \text{ }^\circ\text{C/mm}$. (a) Grayhack model. (b) Equation (3) modified. (c) Equation (2) modified. (d) Equation (2). (e) Experimental points

Figure 19. Succinonitrile-Acetone system. Solid profile concentration as a function of time. External velocity, $V_e = 2 \mu\text{m/s}$. Thermal gradient $\nabla T = 3 \text{ }^\circ\text{C/mm}$. (a) Grayhack model. (b) Equation (3) modified. (c) Equation (2) modified. (d) Equation (2). (e) Experimental points

Figure 20. Succinonitrile-Acetone system. Solid profile concentration as a function of time. External velocity, $V_e = 1 \mu\text{m/s}$. Thermal gradient $\nabla T = 7.4^\circ\text{C/mm}$. (a) Grayhack model. (b) Equation (3) modified. (c) Equation (2) modified. (d) Equation (2). (e) Experimental points

Figure 21. Succinonitrile-Acetone system. Solid profile concentration as a function of time. External velocity, $V_e = 1 \mu\text{m/s}$. Thermal gradient $\nabla T = 4.2 \text{ }^\circ\text{C/mm}$. (a) Grayhack model. (b) Equation (3) modified. (c) Equation (2) modified. (d) Equation (2). (e) Experimental points

Figure 22. Succinonitrile-Acetone system. Solid profile concentration as a function of time. External velocity, $V_e = 1 \mu\text{m/s}$. Thermal gradient $\nabla T = 2.1 \text{ }^\circ\text{C/mm}$. (a) Grayhack model. (b) Equation (3) modified. (c) Equation (2) modified. (d) Equation (2). (e) Experimental points

Figure 23. Schematic equilibrium diagram showing the undercooling value used in the constitutional supercooling criteria calculations

Figure 24. Succinonitrile-Acetone system. Constitutional supercooling criteria. Equation (6). The full line represents the theoretical value

DISCUSSION

Naphthalene-Camphor System

According to the Fig. 10 there is a change in the nondimensional period between perturbations when the external velocity is around $1 \mu\text{m/s}$. This sharp change in the nondimensional time, suggests a change in the interface kinetics. Due to the faceted characteristic of this system, the equilibrium condition does not hold at the interface, therefore we are not able to correlate these positional changes of the interface with changes in composition which restricts the analysis.

Another possible reason for the oscillatory behavior is convection in the liquid. We expect the convection, if present, to be essentially the same for all the experiments because the thermal gradient was very similar for all velocities and therefore the period should be independent of the characteristic time for diffusion. However, when the interface advances it rejects solute into the liquid. Therefore, we can not rule out the possibility of an instability in the convection pattern produced by solute built-up due to change in the liquid density in front of the interface.

Succinonitrile-Acetone System

In this system the oscillatory behavior observed at the Naphthalene interface is not produced, except in one case of high thermal gradient. The possibility of using the equilibrium condition at the interface allows a more complete analysis of the experimental results.

One of our experimentally determined parameters was the value of the interface velocity during the transient regime. The experiments show, Figs. 11-14, that the interface velocity always is lower than the external velocity.

Actually, the assumption of constant velocity during the initial stages has a contradictory meaning in a unidirectional solidification experiment of alloys with a positive thermal gradient. The isotherms move with the external velocity, therefore, the only way for the interface to reduce or increase the temperature is to move initially at a lower or higher velocity than the imposed velocity.

The experimental points suggest, in principle, that the constitutional supercooling criteria is no longer valid in the transient. However, the discrepancy in the concentration profiles may indicate that something more has to be taken in account that is not included in the theoretical values.

The concentration profiles indicate an important departure from the theoretical values. See Figs. 17-22. The experimental points show that the concentration increases faster than the predictions of the exact model.

The principal differences between the exact model and Smith's solutions is that the former takes into account the changes in the interface velocity and considers the coupling between the solute and the thermal fields in a diffusive process. These results indicate that the interface is not following the behavior of a truly diffusive process.

There are two possible causes for the discrepancies, and both are related to the matter transfer process in the liquid. The implicit assumption in our analysis was that the only mechanism present was diffusion, but other mechanisms may be present, viz. a) thermosolutal diffusion, and/or b) convection.

Thermosolutal diffusion

Soret effect is called the phenomena of interaction between the solutal and thermal gradients. If we take it into account, then the continuity equation is written as [5]

$$V (C_i - C_s) = D G_c + f(G, C, T) \quad (7)$$

with

$$f(G, C, T) = D' C_i (1 - C_i) G \quad (8)$$

where D' is the thermal diffusion coefficient.

Using this expression in the constitutional supercooling criteria, equation (4),

$$G \geq \frac{m}{D} \{ V_b (C_i - C_s) + D' C_i (1 - C_i) G \} \quad (9)$$

or using the same procedure as before

$$G \geq \frac{V_b}{D} \Delta T' + G (T_f - T_i) (1 - C_i) S_T. \quad (10)$$

where T_f is the melting temperature of pure Succinonitrile and $S_T = \frac{D'}{D}$ is called the Soret coefficient. Rearranging terms and using the equal sign

$$\frac{V_b \Delta T'}{D G} = 1 - (T_f - T_i) (1 - C_i) S_T. \quad (11)$$

Figure 25 shows a plot of $\frac{V_b \Delta T'}{D G}$ as a function of $(T_f - T_i) (1 - C_i)$. The dotted line represents the constitutional supercooling criterion theoretical value when the Soret coefficient is null. The experimental points show that the Soret effect can be one reason why some of the experimental points do not agree with the theoretical prediction of the constitutional supercooling. However, the three experimental points with the lowest gradient value are seen to deviate from the linear relation. According to the equation (11), if $\frac{V_b \Delta T'}{D G}$ is greater than 1, then S_T is negative. Some cases have been reported in the literature where the Soret coefficient changes the sign as a function of concentration [6] but such a change usually implies much higher concentrations.

Convection effects

There are two kinds of convective driving forces that may be present in directional solidification experiments. One is due to the dependence of the liquid density on the temperature (natural convection) and the other is due to the dependence of the surface tension on the temperature (Marangoni convection). The experimental boundary conditions determine which is most important. In particular, in our experimental set-up where there is no liquid free surface, the only convection possible is the natural one.

As a first approximation the experimental set-up can be thought of as a horizontal layer of liquid with two walls at different temperatures. Birik [7] has solved this problem with the assumption that the walls were separated by an infinite distance. According to his model, the average velocity of the liquid due to natural convection is given by

$$v(\text{avg}) = \frac{G \rho \beta d^3}{192 \nu}, \quad (12)$$

where G is the thermal gradient, ρ the liquid density, β the coefficient of thermal expansion, ν the kinematic viscosity and d is the thickness of the liquid layer. Figure 26 is a plot of the $\nu(\text{avg})$ as a function of the thermal gradient for $d=150\text{ }\mu\text{m}$. As it was pointed by Verhoeven et al. [8] that this model overestimates the value of $\nu(\text{avg})$ because of the infinite distance assumption. The velocity values predicted by the model are very high and should be easily detected in an experiment. Thus, an experiment was carried to evaluate the liquid velocity. A cell containing an Succinonitrile Acetone alloy with SiO_2 particles dispersed was placed in the thermal gradient stage. The average size of the particle was around $20\text{ }\mu\text{m}$. The experiment showed a liquid movement with low temperature gradient, $G=1.5\text{ }^\circ\text{C/mm}$ and no motion was detected when the temperature gradient was high, $G=8\text{ }^\circ\text{C/mm}$. These results showed that the Birik model is very simple as it does not explain the nature of the problem and a new consideration of the problem was examined.

Figure 27 shows a schematic side view of part of the experimental apparatus. As can be seen in the figure, the cell is heated and cooled at the bottom by conduction and at the top part by air conduction convection and radiation. The main part, where the interface is usually localized, is in contact with air at room temperature or if some care is taken it is possible to get a more or less close chamber in that region. The common hypothesis in these experiments is that the heat is conducted through the glass slides and the experiment is truly unidirectional. This is a acceptable assumption for a range of bath temperatures which will not introduce noticeable vertical gradients.

There are two possible configurations for vertical temperature gradient in the Succinonitrile-Acetone system for the range of temperatures used. These possible configurations are shown in the Fig. 28 together with the tentative flow directions that could be induced by the temperature distribution. As an indication of the this vertical gradient, the

interface sometimes shows the appearance that is illustrated in the Fig. 29 (a) which indicates the profiles shown in Figs 29 (b) and (c).

The configuration of a horizontal layer of liquid heated from below is known as the Bénard's problem [9,10]. The solution shows that when the nondimensional Rayleigh number is greater than some critical value that is fixed by the boundary conditions the system becomes unstable and convection is possible. The Rayleigh number is given by

$$R = \frac{g \alpha \beta_T d^4}{K \nu}$$

where g is the acceleration due to gravity, α is the thermal expansion coefficient, β_T is the temperature gradient, K is thermal diffusivity, ν is the kinematic viscosity and d is the depth of the liquid layer. For our experimental conditions, $R \approx 0.01$. In the simplest case of the Bénard problem, where both surfaces are free, the critical number is $R_c = 27 \pi^4 / 4 \approx 650$. According to this calculation the system should be very stable and no convection could be induced by the vertical gradient. However, the Bénard's problem plus a horizontal temperature gradient was solved by Weber [11] and by Birik et al. [12] in two different approaches and they found that there is always a liquid motion with such a configuration. The presence of solute can change the stability conditions drastically [13]. In this case, a solute Rayleigh number is considered which is defined as follows

$$R_s = \frac{g \alpha' \beta_c d^4}{D \nu},$$

and again a critical condition for instabilities can be found. However, the possibility of interaction between the thermal gradient as the destabilizing element and the solute gradient

as the stabilizing or destabilizing effect give rise to several possible configurations that are beyond of the scope of this analysis.

It has been shown that the presence of solute can induce instabilities in thermally stable systems [14]. The influence of solute as a trigger for convective movements is very complex in our geometry because there is a competition between the Soret effect in the vertical direction, and the thermal gradient and the solute gradient induced by differences in density in the horizontal direction.

Following again the Birik [7] model in our experiment, the convection will be clockwise if we only take into account the horizontal gradient. The vertical gradient in the hot chamber will always oppose this motion. On the other side, if the cold chamber is cooler than the room temperature, this gradient will oppose too and a balance could be achieved where no convection effect will be present, see Fig. 27 (b). However, if the cold chamber is hotter than room temperature, the vertical gradient will help the motion induced by the horizontal temperature difference and the convection effects might be pronounced. The temperatures and velocities for the experiments are shown in the following table.

Table 1. Experimental conditions of temperature gradients and velocities

Hot bath temperature °C	Cold bath temperature °C	Horizontal Thermal Gradient °C/mm	External velocity $\mu\text{m/s}$
85	30	4.2	1
70.5	40	2.1	1
95	6	5.6	1
95	0	7.4	1
85	30	3	2
85	30	4	0.5
85	30	4	0.75
70	45	1.3	1.5
98	0	9.5	0.4

As can be seen in the table, the highest gradients are obtained using a cold bath temperature below the room temperature. On the other hand, low and medium gradients indicate that cold bath temperatures are above the room temperature. As an explanation of the experimental results in Fig. 25, we believe that when the cold chamber is hotter than room temperature, barrier for the convection is very small. It should be noted that in this condition the motion of particles was detected. This process is faster than the Soret effect in the horizontal direction causing an overall decreasing of solute in front of the interface. The net result looks like as if the Soret coefficient has changed sign.

In the opposite case, the system is stable against convection motions and the process is only diffusion controlled with the addition of Soret effect. It was explained above that Soret effect depends on the temperature gradient and this can explain why the concentrations profiles depend on the gradient. In this situation, where the cold chamber is at lower temperature than the ambient, the solute rejected at the solid-liquid interface will be pushed down by the vertical Soret effect, producing an accumulation of solute of lower density at the colder bottom of the cell, that condition could eventually produce a liquid motion upwards until the solute gradient has disappeared. This effect might change the rate of growth, as for example is shown in the Fig. 14 that was run at the highest horizontal gradient and it indicates a series of anomalies in the growth not detected in other experiments in the Succinonitrile-Acetone system..

As a final conclusion we believe that in these experiments Soret effect and convection may be present and these are the reason why a theory based only on diffusion process can not explain the experimental results.

Figure 25. Succinonitrile-Acetone system. The circles are the experimental values and the dotted line represents the constitutional supercooling criteria when the Soret effect is not present

Figure 26. Succinonitrile-Acetone system. Average liquid velocity as a function of the thermal gradient. The values were calculated using equation (12) from the Birik [7] model

Figure 27. Schematic side view of the experimental cell position between the chambers

(a)

(b)

Figure 28. Temperature distribution and possible flow directions. (a) Cold chamber hotter than room temperature. (b) Cold chamber colder than room temperature

Figure 29. Picture of the interface showing the existence of a vertical gradient (a).

Possible interface profile for positive gradient (b). Possible interface profile for negative gradient (c)

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FINAL CONCLUSIONS

Traditionally, solidification experiments have been carried out under idealized conditions in which, the mold geometry is simple and the material properties are isotropic. For these conditions, all the possible morphologies of the solid-liquid interface, i.e.; planar, cellular and dendritic, of isotropic materials have been experimentally investigated. This approach which is useful in testing theoretical models of isotropic materials does not cover two important areas in the solidification field. These are, 1) the interaction between the shape of the mold with the solid liquid interface and 2) the solidification of faceted materials. These two aspects of solidification were investigated in this thesis work and the principal achievements can be summarized as follows.

Experiments carried out in organic materials allowed us for the first time to investigate, in situ, the influence of changes in the cross-section of the sample on the interface morphology. The change in cross section has been found to significantly alter the development of the microstructure. Morphological transitions which change the microsegregation profiles have been characterized for different growth conditions, and these changes in interface shapes have been rationalized by using the theoretical model of morphological stability.

Theoretical models for dendritic growth, based on mass and thermal transport in the liquid, predict a range compatible of tip radius for a given velocity. The uniqueness of the solution is obtained only through a tip selection criteria. The theoretical model of steady state dendritic growth predicts a strong influence of surface energy anisotropy on the dendrite tip radius value. Unidirectional solidification experiments with materials which have slightly different anisotropic characteristics, viz., CBr_4 and C_2Cl_6 , have been carried out to test the theoretical models.

A detailed study on the unidirectional solidification of faceted materials was carried out. The characterization of the growth mechanisms and the relationship between interface morphology and experimental conditions have been established. Furthermore, experiments were designed and carried out to determine the temperature and composition, at the interface under nonequilibrium conditions.

For the first time it has been shown how defects are produced at the solid liquid interface during unidirectional solidification experiments in faceted materials.

The experiments carried out on the Tert Butyl Alcohol system showed that a morphological transition with both characteristics, faceted and nonfaceted can be induced by the solute in a way that is similar to the cellular to dendrite transition in nonfaceted materials.

The transient period in unidirectional solidification experiments has been shown to be more complex from the physical point of view than that assumed in the earlier theories. It has been shown that the constant interface velocity assumption in the transient regime is not compatible with the experimental design and that the influence of convection and thermomigration can critically affect the results.

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