

THE PLANAR TO CELLULAR TRANSITION DURING THE DIRECTIONAL SOLIDIFICATION OF ALLOYS

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Abstract—The planar to cellular interface transition during the directional solidification of a binary alloy has been studied in the succinonitrile–acetone system. The interface velocity at which the planar interface becomes unstable and the wave numbers of the initially unstable interface have been precisely determined and compared with the linear stability analysis. Critical experiments have been carried out to show that the planar to cellular bifurcation is subcritical so that a finite amplitude perturbation below the critical velocity can also give rise to planar interface instability.

Résumé—Nous avons étudié, dans le système succinonitrile–acétone, la transition d'interface de planaire à cellulaire pendant la solidification dirigée d'un alliage binaire. Nous avons déterminé de façon précise la vitesse interfaciale à laquelle l'interface planaire devient instable ainsi que les nombres d'onde de l'interface initialement instable, et nous les avons comparés avec l'analyse linéaire de la stabilité. Nous avons réalisé des expériences critiques pour montrer que la bifurcation de l'état planaire à l'état cellulaire est située en dessous de la valeur critique, si bien qu'une perturbation d'amplitude finie en dessous de la vitesse critique peut donner lieu également à une instabilité de l'interface planaire.

Zusammenfassung—Der Übergang von der planaren zur zellulären Grenzfläche während der gerichteten Erstarrung einer binären Legierung wurde am System Succinonitril–Azeton untersucht. Die Geschwindigkeit der Grenzfläche, bei der die planare Grenzfläche instabil wird, und die Wellenzahlen der zu Anfang instabilen Grenzfläche wurden genau bestimmt und mit der linearen Stabilitätsanalyse verglichen. Kritische Experimente wurden durchgeführt und es wurde gezeigt, daß die planar-zelluläre Aufspaltung unterkritisch ist. Dadurch kann eine Störung mit endlicher Amplitude auch unterhalb der kritischen Geschwindigkeit zu einer Instabilität der planaren Grenzfläche führen.

INTRODUCTION

The formation of cellular and dendritic interfaces during the directional solidification of alloys gives rise to microsegregation profiles which influence the mechanical properties of alloys. In addition, the instability of a planar interface and its subsequent reorganization into a periodic array of cells or dendrites is a general phenomenon which occurs in a variety of disciplines such as metallurgy, physics, chemistry and biology [1]. Consequently, the problem of pattern formation has received an increasing amount of theoretical and experimental interest in recent years [2–19]. Three important aspects of this study are: (1) the planar interface instability condition, (2) the type of bifurcation that exists for the planar to cellular transition, and (3) the subsequent reorganization of the unstable planar interface into a regularly spaced array of cells or dendrites.

The criterion for the instability of a planar interface was first proposed by Tiller *et al.* [2] for a solid–liquid interface which is externally driven at a constant velocity under positive temperature gradient conditions in the liquid at the interface. The onset of instability was predicted when the stabilizing effect of the thermal gradient was balanced by the destabilizing effect of the solute diffusion. This crite-

rión, which is commonly known as the constitutional supercooling criterion, ignores the stabilizing effect of the interfacial energy [3] and is valid only when the instability occurs at very low velocities [3, 4]. Furthermore, it does not address the question of wave numbers to which a planar interface becomes unstable. A more detailed model of the planar interface stability was subsequently developed by Mullins and Sekerka [3] who carried out a linear perturbation analysis which also included the stabilizing effect of the solid–liquid interfacial energy. For small velocities, the Mullins–Sekerka analysis predicts that a planar interface will be unstable when the velocity of the interface exceeds a critical velocity, V_c , given by the relationship [1]

$$v_c = 1 + 3(K_0^2\alpha)^{1/3}v_c^{1/3}, \quad \alpha v \ll 1 \quad (1)$$

where v_c is the dimensionless critical velocity, $v_c = V_c \Delta T_0 / GD$, in which ΔT_0 is the equilibrium freezing range of the alloy, G the conductivity-weighted average temperature gradient at the interface and D the solute diffusion coefficient in the liquid. K_0 is the equilibrium solute partitioning coefficient and the parameter α is given by

$$\alpha = \gamma G / 4\Delta S \Delta T_0^2 \quad (2)$$

in which γ is the solid–liquid interfacial energy, and

ΔS is the entropy of fusion per unit volume. Note that $v_c = 1$ represents the modified constitutional supercooling criterion in which the temperature gradient in liquid at the interface, G_L , is replaced by G .

At the critical velocity the Mullins-Sekerka analysis predicts the unstable wave number, k_c , to be [1]

$$k_c = (G/2\Delta T_0)(K_0/\alpha)^{1/3}v_c^{2/3}, \quad \alpha v \ll 1. \quad (3)$$

One of the major aims of this paper is to test the validity of the linear stability analysis by carrying out detailed experimental studies of the planar interface instability in a well-characterized system. Although a number of experimental studies in metal systems has been carried out to examine the conditions for the planar interface stability [20–26], the precise velocity of the interface break-up could not be determined because the interface break-up velocity was associated with the externally imposed velocity. Somboonsuk and Trivedi [27] have shown that there is a sufficiently long transient before the actual velocity of the interface approaches the externally imposed velocity so that a precise measurement of V_c requires not only the measurement of the actual interface velocity at the time of break-up, but also the dynamical values of the thermal and solute gradients at the interface. In this paper we shall report the results of directional solidification experiments in the succinonitrile-acetone system in which the actual interface velocities at the time of the planar interface instability were measured. These dynamical velocities were then correlated with the critical velocities predicted under steady-state growth conditions.

The linear stability analysis of Mullins and Sekerka [3] was carried out under the assumption that the amplitude of perturbation was infinitesimal. A more detailed nonlinear analysis was presented by Wollkind and Segel [7] for a small but finite amplitude of perturbation. They concluded that the planar to nonplanar bifurcation can be subcritical so that a planar interface, if subjected to large amplitude deformations, could become unstable at $v < v_c$. Thus, the second aim of this paper is to present experimental results which examine this nature of bifurcation. Our results confirmed the existence of subcritical bifurcation and showed that large amplitude cells remained stable when the interface velocity was slowly changed from $V > V_c$ to $V < V_c$. Also, very small amplitude perturbations were not observed at V just above V_c . The amplitude of the interface increased from zero at $V < V_c$ to a finite value when V was increased just above V_c . Furthermore, when the interface was maintained just below V_c for a long time, long amplitude perturbations with large wavelengths were also observed which gave rise to an unstable interface.

EXPERIMENTAL

Directional solidification studies of succinonitrile-acetone system were carried out in an apparatus

similar to that described by Jackson and Hunt [28] and Mason *et al.* [29]. The succinonitrile-acetone system was chosen since all thermophysical properties have been measured quite precisely for this system, which allows a quantitative comparison with the theory. Special care was taken to ensure that all the experimental variables were also controlled and measured accurately.

To study the instability of a planar interface, a very precise linear motion is required. Since the critical velocity for the instability is of the order of $1 \mu\text{m/s}$, any small deviation from linearity will cause significant fluctuations in the velocity. For this reason, a high precision screw needs to be aligned quite accurately and the sample motion is also required to be precisely linear. The design of the high precision stage used in this study is described elsewhere in detail [30]. The entire directional solidification apparatus was placed on a shock absorbing base to minimize any vibrational effects. The actual velocity of the sample was monitored with an electronic differentiator and a linear variable differential transformer (LVDT). The velocity was found to be constant within $\pm 0.1 \mu\text{m/s}$.

The temperature gradient at the interface was measured from the temperature profile obtained from a thermocouple which was placed inside the cell. The thermocouple was first calibrated against a standard thermometer to within $\pm 0.01 \text{ K}$. The thermocouple trace was obtained during the steady-state growth of the interface. Experiments were also carried out with two thermocouples in the cell which were positioned such that the first thermocouple traced the temperature profile of the steady-state planar interface growth at $V < V_c$ and the second thermocouple traced the temperature profile after the interface just became unstable at $V > V_c$. No significant change in temperature gradient at the interface was observed prior to and after the break-up.

Succinonitrile and acetone were purified by zone refining (with a minimum of 60 passes) and by distillation, respectively. These purified materials were mixed and filled in the cell in a dry box under a dry nitrogen environment. The concentration of acetone was varied between 0.10–0.34 wt%. Initially the composition was controlled by mixing appropriate weights of the components. However, the exact concentration of acetone in the cell was subsequently determined by measuring the planar interface temperature with a calibrated thermocouple during a steady-state run at $V < V_c$.

Another experimental variable which could affect the values of critical velocity and cell spacing is the thickness of the cell. If the cell is very thin, the interface develops a curvature along the vertical direction due to surface tension effect with the glass. Also, if the thickness is large, convection effects become very important at low velocities. Experimental runs were thus made with the thickness varying from 10 to $500 \mu\text{m}$. As shown earlier by

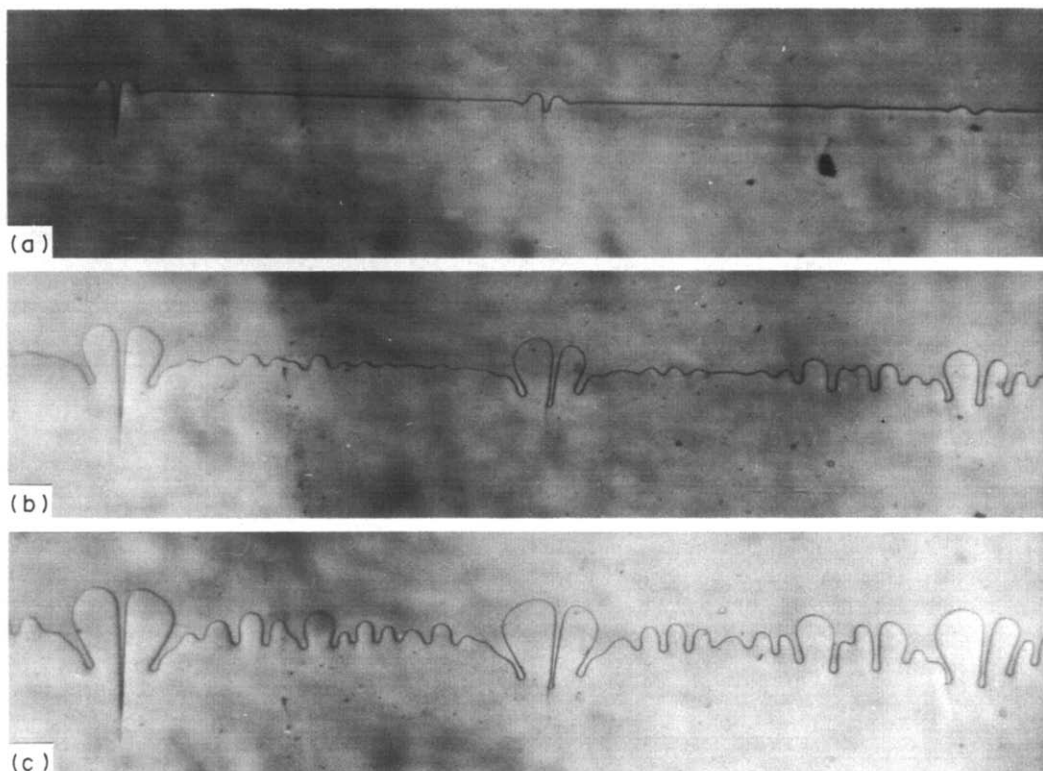


Fig. 1. The changes in the interface shape with time. The times after the instability was observed are (a) 0 s, (b) 270 s and (c) 570 s. The directional solidification of succinonitrile-0.15 wt% acetone was carried out under the conditions of $G = 3.76 \text{ K/mm}$ and $V = 0.8 \mu\text{m/s}$.

Mason *et al.* [29], the effect of cell thickness was found to influence the results when the thickness was less than $100 \mu\text{m}$. Consequently, all the experiments were carried out for cell thickness of $150 \mu\text{m}$, where convection effects were shown to be negligible [3]. In order to eliminate any vertical temperature gradient, a unidirectional heat flow was ensured by the presence of large source and sink which kept the temperatures constant at the cell ends over the thickness of the cell. Convection of air outside the cell was minimized by placing glass shields just above and below the cell [30]. The velocities of the interface were sufficiently small that the latent heat effects were negligible compared to the imposed heat flow.

Three sets of experimental studies were carried out. For a given composition and temperature gradient, the critical velocity was calculated from equation (1). The sample was then solidified at velocity V_0 , which was below V_c , where a planar interface growth was observed. After a steady-state growth was established at V_0 , the external velocity was changed rapidly to V_E , where $V_E > V_c$. The interface location and shape were photographed continuously at 1 sec intervals, and Fig. 1 illustrates the interface break-up phenomenon. The velocity of the interface with time was then calculated from the distance vs time measurements, and this is shown in Fig. 2. The interface velocity as well as the time at which the interface just became

unstable, as seen from the photographs, were then marked on this plot. Since the break-up was observed before the interface velocity coincided with V_E , a series of runs was made with different V_E values, and the interface velocity, V_b , at which break-up occurred was measured for each V_E run, as shown in Fig. 2. The critical velocity, V_c , was then taken to be equal to the smallest V_b value where the break-up was observed. Another set of experiments was also carried

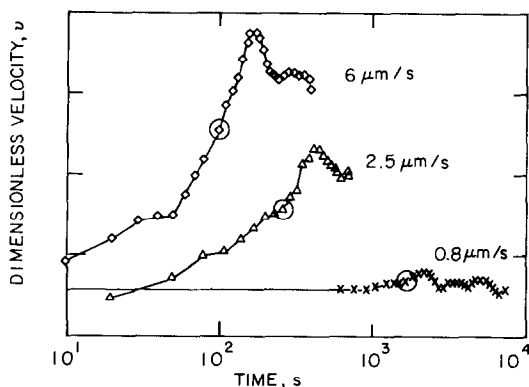


Fig. 2. The variation in the dimensionless interface velocity, v , with time when the external velocity was changed from v_0 to v_E . The circles denote the interface velocity and the corresponding time at which the planar interface became unstable.

out in which the external velocity was changed from V_0 to $V > V_c$ in small velocity steps. At each velocity, the run was made for a sufficiently long time to observe any sign of instability. The velocity at which the first break-up was observed was then noted. Since the change in velocity was sufficiently small, about $0.05 \mu\text{m/s}$ near V_c , the external velocity at which the break-up was observed was taken to be equal to the V_c .

The third set of experiments was designed to study the planar to cellular bifurcation. In this study, a planar interface was first stabilized at $V < V_c$. The velocity was then increased in small steps until the first sign of break-up was observed. At each velocity step, a constant velocity was maintained for at least 15 min or more to see if the interface became unstable. When a velocity was found at which the planar interface just became unstable, the sample was run at that velocity for a sufficient time to form a periodic cellular structure. The amplitude and wave number of this periodic structure were then measured. Next, the velocity was decreased in steps to see if the interface became planar below V_c . A velocity was determined, which was significantly less than V_c , where the cellular to planar transition occurred. Since the cellular structure was found to be stable below V_c , another experiment was carried out in which a planar interface was held just below V_c for a long time. A large amplitude fluctuation in shape was observed after about 3 h. The stability of the interface in the presence of these large amplitude fluctuations was then examined.

RESULTS AND DISCUSSION

Planar interface instability

The theoretical analysis of the planar interface instability examines the stability of a planar interface which is initially moving at a constant rate. Experimentally, the study of planar interface instability requires the velocity to be changed from $V = V_0$ to $V = V_E$, where $V_0 < V_c < V_E$. Figure 2 shows the actual change in interface velocity when the external velocity was changed from V_0 to V_E . Both the interface velocity, V_b , at which the break-up was observed and the time, τ_b , required to reach the break-up velocity were found to be functions of V_E .

To examine the critical velocity at which an instability is observed, it is important to keep the sample at a given velocity for a sufficiently long time for the solute and thermal fields to readjust. Thus, when no interface break-up is observed, the time of run must be sufficiently long for the interface velocity to equal the external velocity. When a break-up of the interface is observed, the time taken by the interface to reach V_b is a function of V_E . This variation in τ_b as a function of V_E was measured, and it is shown in Fig. 4. The time taken for the interface to reach the break-up velocity was found to be inversely proportional to V_E .

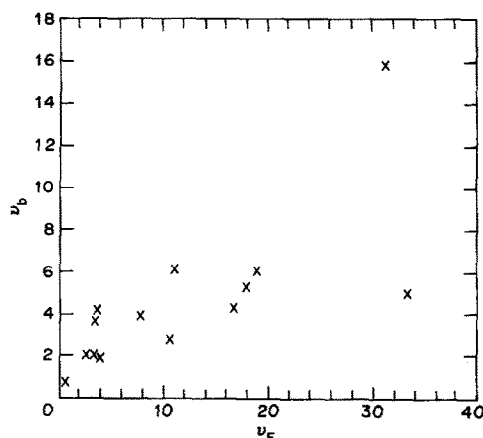


Fig. 3. The relationship between the dimensionless velocity, v_b , at the break-up and the dimensionless external velocity, v_E .

The variation in v_b as a function of $v_E - v_0$ is shown in Fig. 3 where $v = V\Delta T_0/GD$. Although there is a significant scatter in the data, v_b was found to increase as $v_E - v_0$ was increased. The lowest velocity, v_b , where the break-up was observed will be close to the v_c value. This minimum value of v_b will be denoted by v_b^* .

The theoretical value of V_c is obtained under the assumption of a steady state solute profile that is characteristic of the velocity V_c . Experimental values of the critical velocity, however, were measured under nonsteady state conditions since the interface velocity was changing when the interface became unstable. When V_E and V_0 are close to V_c , this dynamic effect may be negligible. To gain some insight into the difference between the critical values obtained during the steady-state (V_c) and during the dynamic (V_b^*) conditions, we shall now briefly examine the factors that could influence the difference between V_c and V_b^* .

There are three important physical factors that could influence the magnitude of V_b . First, the destabilizing influence of the solute field depends on the composition gradient, G , at the interface. When an

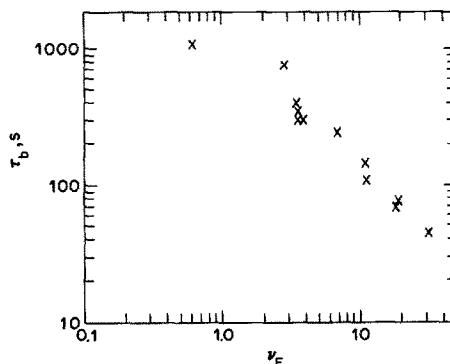


Fig. 4. The variation in the time τ_b required for the interface to break-up vs dimensionless external velocity, v_E . The external velocity was changed from v_0 to v_E .

appropriate value of G_c is reached, the interface can potentially become unstable. However, a finite time is needed for the perturbed profile to develop and during this time the interface velocity can increase beyond V_c . For this reason, the value of V_b is found to increase as the value of $V_E - V_0$ is increased.

Another factor which could also influence the value of V_b at large $V_E - V_0$ values is the change in the thermal gradient. Since thermal conductivities of the solid (K_s) and the liquid (K_L) are nearly equal in the succinonitrile system, the thermal balance at the interface would show that the change in thermal gradients in the liquid (G_L) and in the solid (G_s) at the interface are related by the equation

$$\delta(G_s - G_L) = (\Delta H/K_L)(V_b - V_0) \quad (4)$$

where δ indicates the change in gradients. Since additional heat of fusion due to an increase in interface velocity needs to be dissipated through the solid, one can obtain an upper limit on the change in average gradient by assuming that the liquid gradient changes negligibly. The maximum change in the average gradient is then given by

$$\delta G \simeq (\Delta H/2K_L)(V_b - V_0). \quad (5)$$

Thus, for large $(V_b - V_0)$, the weighted average value, G , also increases slightly, which would stabilize the interface to slightly higher values. This effect, however, is small since for $V_b - V_0 \simeq 1 \mu\text{m/s}$, the change in gradient is only about 0.1 K/mm. Thus the maximum change in gradient was less than 3% in our experiments, so that the thermal effects can be readily ignored.

When $V_E - V_0$ is small, the change in interface velocity with time was found to be a very slowly varying function, as seen in Fig. 2, so that one would not expect a significant change in interface velocity during the time it took to form observable perturbations in the interface shape. However, the interface velocity was still changing, so that the concentration gradient in liquid at the interface, G_c , was not equal to that for a steady-state interface growth at V_b . This difference in G_c at the interface could give rise to some deviation between V_b^* and V_c values. Smith *et al.* [31] have shown that when the velocity of the interface is suddenly increased, the concentration in the liquid and in the solid at the interface first increases from their steady-state values of C_∞/K_0 and C_∞ respectively, where C_∞ is the average composition of the alloy. This increase occurs because the total mass of solute ahead of the planar interface decreases as the velocity is increased, so that solute concentration in the solid must increase from its steady-state value of C_∞ . The solute concentration in the liquid will first increase and then go through a maximum and finally decrease to its steady-state value of C_∞/K_0 . This variation in interface composition will change the value of G_c in the transient regime. If C_L is the concentration in the liquid at the interface when the interface velocity is V_b , then the

concentration gradient, G_c^b is given by

$$G_c^b = -(V_b/D)C_L(1 - K_0)$$

or

$$mG_c^b = (V_b\Delta T_0/D)(K_0C_L/C_\infty). \quad (6)$$

The linear stability analysis shows the condition for the planar interface stability as

$$-G + mG_c \left[\frac{k^* - V/2D}{k^* - V/2D(1 - K_0)} \right] - (\gamma/\Delta S)k^2 = 0 \quad (7)$$

where $k^* = (V/2D) + [(V/2D)^2 + k^2]^{1/2}$ in which k is the wave number of the perturbation. For low velocities and for $K_0 = 0.1$, the term in the large bracket will be nearly unity, so that one may estimate the change in critical velocity by substituting mG_c^b in place of mG_c for the dynamical conditions. This will relate V_c and V_b^* by the following equation

$$V_c = V_b^*(K_0C_L/C_\infty). \quad (8)$$

The actual determination of V_c thus requires the measurement of C_L . Experimentally, we have determined the displacement Δx of the interface, in a reference system attached to the interface, from its steady state position to its location at V_b^* when the break-up occurred. From this displacement, the change in interface temperature was calculated and the value of C_L was then calculated from the phase diagram. This gave the relationship.

$$K_0C_L/C_\infty = 1 - (K_0G\Delta x/m_LC_\infty). \quad (9)$$

By substituting the above result in equation (8), and using the dimensionless velocity v , one obtains

$$v_c = v_b^*[1 - (K_0G\Delta x/m_LC_\infty)]. \quad (10)$$

For our experimental results, $K_0 = 0.1$, $G = 3.76 \text{ K/mm}$, $m_L = -3.02 \text{ K/wt\%}$, $C_\infty = 0.15 \text{ wt\%}$, $\Delta x = 0.26 \text{ mm}$, and $V_b^* = 0.84$, we obtain

$$v_c = 1.02. \quad (11)$$

The theoretical value of v_c for modified supercooling criterion is given by $v_c = 1$, and for the linear stability analysis of Mullins and Sekerka, $v_c = 1.03$. The experimentally determined value of v_c is thus very close to that predicted by the linear stability analysis.

Another experiment was carried out for $G = 3.82 \text{ k/mm}$ and $C_\infty = 0.10 \text{ wt\%}$ acetone in which a planar interface was established below V_c . The velocity was then increased in steps of $0.05 \mu\text{m/s}$, and at each velocity a sufficient time was allowed to establish the steady-state condition. The planar interface was found to be stable at $V = 1.55 \mu\text{m/s}$, but it became unstable at $V = 1.60 \mu\text{m/s}$. This experimental value corresponds to $v_b = 0.87$, and it will be close to the theoretical value of $v_c = 1.065$ if dynamical effects, as described earlier, were taken into account. These experimental results thus clearly establish the validity of the linear stability analysis in predicting the critical velocity for the planar-nonplanar bifurcation.

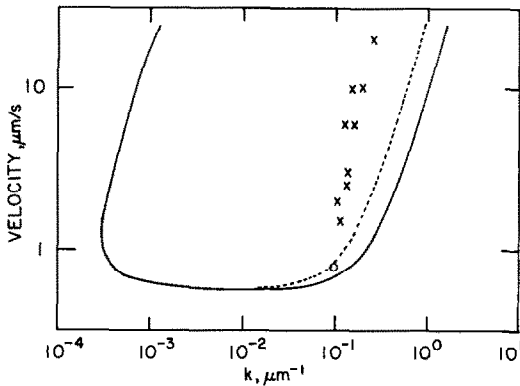


Fig. 5. The variation in the initial wave numbers of an unstable interface with the break-up velocity V_b . The solid line is the marginal stability curve and the dotted line represents the wavelengths with maximum amplification rate as predicted by the linear stability analysis of a planar interface. Experimental results are for $G = 4.28$ K/mm and $C_0 = 0.35$ wt% acetone. The open circle value is for $C_0 = 0.15$ wt%.

For the experiments described in Figs 2 and 3, the initial wavenumber of perturbation was also determined. To eliminate the effect of grain boundaries, the wavenumbers were measured at interface locations far from the boundary. The variation in initial wavenumbers with velocity V_b are shown in Fig. 5. It was found that the wave numbers increased with the increase in the velocity at which the instability was observed. The variation in the critical wavelength, λ_c , with composition is shown in Fig. 6 and the experimental value of the wavelength observed at V_b^* is also shown for comparison. The experimental value of the wavelength was found to be significantly smaller than that predicted by the linear stability analysis. The difference between the theoretical and the experimental values is significantly large so that it cannot be justified by the dynamical effects discussed previously. A more detailed discussion on the wavenumber selection will be given in a subsequent paper [32].

Planar-cellular bifurcation

The linear stability analysis of Mullins and Sekerka was carried out under the assumption that the amplitude of perturbation was infinitesimal. Therefore,

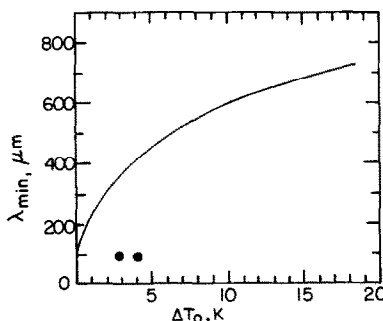


Fig. 6. A comparison of the theoretical and experimental values of the wavelength at critical velocity.

once the interface becomes unstable, the linear stability analysis cannot accurately describe the evolution of a cellular interface since higher order terms become important. Thus, the actual evolution of a cellular pattern is inherently nonlinear. In order to examine the nonlinear effects qualitatively, experimental measurements were carried out to measure the variation in amplitude with time for a specific perturbation, as shown in Fig. 7. The results are shown in Fig. 8, which clearly indicate that the nonlinear effects become quite important at very low amplitudes. Furthermore, it was found that the spacing shown in Fig. 7 increases substantially with time by the elimination of some cells, and the final spacing was significantly larger than the one shown in Fig. 7. A detailed analysis of the dynamics of cell formation will be described in a subsequent paper [33]. However, the present results show that the nonlinear effects become quite significant even for small amplitude perturbations. Consequently, it is necessary to examine the nonlinear perturbation theory to see if large amplitude perturbations would become unstable at $v < v_c$.

Wollkind and Segel [7] first examined the stability of a planar interface for finite amplitude perturbations. They carried out perturbation analysis up to the third order in the amplitude, A_k , of the deformation of wave vector k . They studied the Landau equation, valid in the immediate vicinity of the bifurcation, which is given by

$$\frac{dA_k}{dt} = a_0(k)A_k - a_1A_k^3. \quad (12)$$

The condition, $a_0 = 0$, gives the bifurcation point, as predicted by the linear stability analysis. The parameter a_1 is known as the Landau constant. From the Landau equation it is predicted that a planar interface becomes unstable when $dA_k/dt > 0$, so that it is possible to have an unstable planar interface if $a_0 < 0$ and $a_1 < 0$, such that $dA_k/dt > 0$. This condition is known as the subcritical bifurcation which indicates that a planar interface will become unstable at $v < v_c$ if large amplitude perturbations are present. It also shows that for $v > v_c$ there is no continuous transition from planarity to small amplitude deformations. Such a continuous transition would, however, be observed if $a_1 > 0$, a condition known as the supercritical bifurcation, in which case the planar interface is unstable only for $v > v_c$.

In order to examine the type of bifurcation that is present in the succinonitrile-acetone system, experiments were carried out in which a planar interface was first established at $V < V_c$. The experimental conditions were as follows: $G = 3.82$ K/mm, $C_\infty = 0.10$ wt% acetone and a steady-state planar interface was established at $V = 0.5$ $\mu\text{m/s}$. The external velocity was then increased in steps to 0.75, 1.0, 1.25, 1.325, 1.40, 1.45, 1.50, 1.55 and 1.60, and at each velocity sufficient time was allowed to obtain a steady-state. It was found that $V = 1.60$ $\mu\text{m/s}$, the

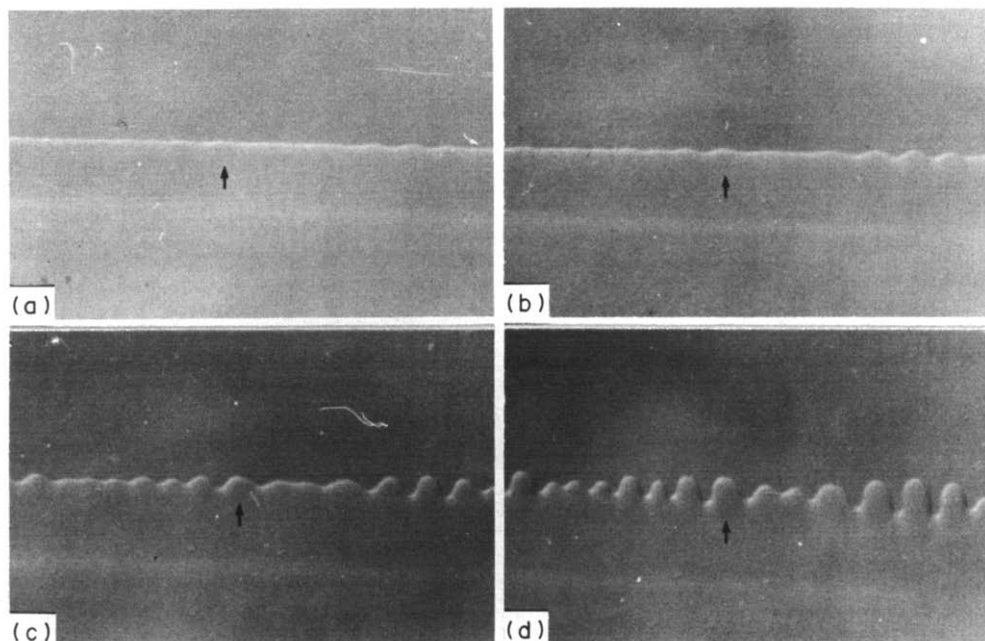


Fig. 7. The changes in interface profiles with time for the directional solidification of succinonitrile-0.10 wt% acetone under the conditions of $G = 3.82 \text{ K/mm}$ and $V = 1.75 \mu\text{m/s}$. The times after the instability was observed are: (a) 0 s, (b) 30 s, (c) 60 s and (d) 90 s. Arrows indicate the perturbation which was used to study the amplification rate.

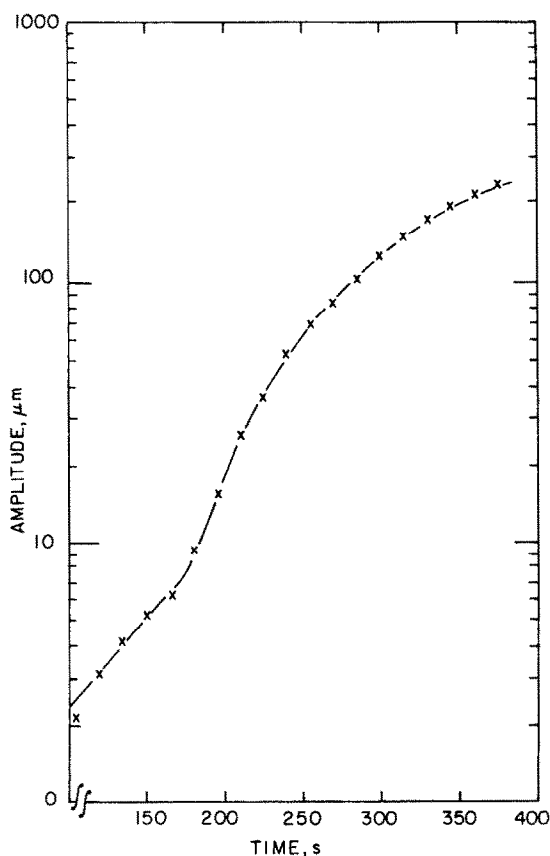


Fig. 8. The variation in the amplitude of perturbation with time for the perturbation shown in Fig. 7.

planar interface became unstable after 4 min. When the first instability was observed, the sample was solidified for a long time until a steady-state cellular array was established. It was found that the amplitude of cells was quite large so that the amplitude increased discontinuously at v just above v_c . This indicated that the planar-to-cellular bifurcation is subcritical. For the subcritical bifurcation, the large amplitude cells should also remain stable for $v < v_c$. Consequently, once the cell structure was established at v just above v_c , the velocity was decreased slowly in steps and at each velocity sufficient time was allowed for the cell amplitude to change. For some velocity range, $v < v_c$, the cell structure did not change to a planar interface, but remained stable with a slightly different amplitude. The variation in the amplitude with $v < v_c$ is shown in Fig. 9. The cell structures up to $v = v^+$, as shown in Fig. 9, had strong cusps. However at $v < v^+$, the cusps disappeared and the amplitude decreased quite sharply. At the lower velocities, $v < v^+$, the sample was run for about 15 min at each velocity because of the limitation on the sample size. This time was not sufficient for the small amplitudes to decay so that the actual behavior could be indicated by the dotted line. A similar subcritical bifurcation has recently been reported by De Cheveigne *et al.* [17, 34] for the planar interface instability in an impure carbon tetrabromide system.

Figure 10 shows the variation in wavelength with velocity. Note that the wavelength increased initially as the velocity was decreased. However, at

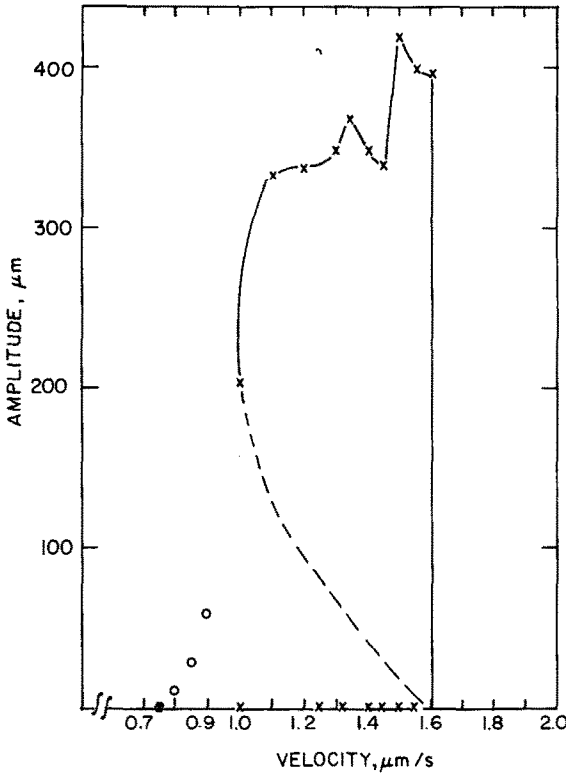


Fig. 9. The variation in cell amplitude with velocity for the directional solidification of succinonitrile—0.10 wt% acetone at $G = 3.82 K/mm$. The velocity was initially increased in steps from 0.5 to 1.6 $\mu m/s$. After the interface became unstable, the velocity was decreased in steps from 1.6 to 0.7 $\mu m/s$. Circles denote smooth interface shapes, which were unstable. The dotted line indicates a possible lower amplitude in the subcritical bifurcation curve.

$V = 1.4 \mu m/s$, a tip instability was observed which significantly reduced the wavelength. This tip-splitting continued until $V = 1.3 \mu m/s$. Below this velocity, the wavelength again increased as the velocity was decreased until $V = 0.9 \mu m/s$. This increase in wavelength occurred by the process of elimination of some of the cells. At $V < 0.9 \mu m/s$, the cusps were removed and the wavelength decreased by tip-splitting until a planar interface was again established.

We shall now examine the nonlinear stability analysis of Wollkind and Segel [7] to see the condition for the existence of the subcritical bifurcation. Coroli *et al.* [8] have given the expansion for a_1 under the condition of small velocities. For equal thermal conductivities of the solid and liquid, the sign of a_1 can be determined from the relationship [8]

$$a_1 \approx (4K_0\Delta T_0 D \Delta S / \gamma V)^{2/3} [(K_0^2 + 4K_0 - 2)/4K_0]. \quad (13)$$

Since all the parameters in the first bracket on the right hand side are positive, the sign of a_1 will be determined by the value of the second bracket, which becomes negative when $K_0 < 0.45$. Since $K_0 = 0.1$ in

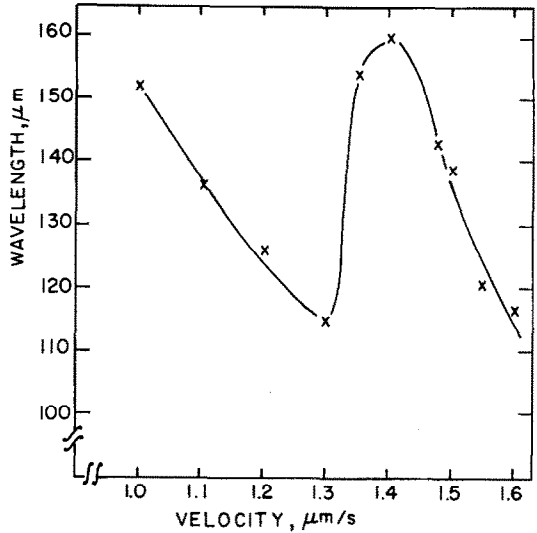


Fig. 10. The variation in wavelength with velocity during the subcritical bifurcation of Fig. 9.

the succinonitrile-acetone system, the theory predicts the existence of a subcritical bifurcation. In order to check the theory further, it would be desirable to study another solute in succinonitrile in which $K_0 > 0.5$. The existence of a subcritical transition has also been predicted by the numerical simulations of McFadden and Coriell [35] and Unger and Brown [12]. Unger and Brown [12] also predicted a second bifurcation close to the V_c where the wavelength suddenly becomes half. Our experimental results show that at $V \approx 1.3 \mu m/s$, such a change in wavelength is observed.

Since our results indicated the presence of a subcritical bifurcation, an experiment was carried out in which the sample was held close to but just below V_c , where a planar steady-state interface was established. For this experiment, the theoretical critical velocity was $0.55 \mu m/s$, and the experimental velocity was kept constant at $0.50 \mu m/s$ where a planar interface was present. After about three hours at this velocity, a finite amplitude perturbation with large wavelength was observed. This perturbation could either be due to fluctuations over a long period of time or due to convection effects. However, when the amplitude of perturbation became large, the interface became unstable, as shown in Fig. 11. The perturbation initiated at the low temperature part of the interface and then propagated along the interface. Note that the flat part of the interface was always stable.

One may examine this result by considering a very simple model which assumes that for long large wavelengths, the depressed part of the interface could be considered planar with little influence from the interface away from it. At the location where the interface became unstable, the interface temperature was lower so that the equilibrium interface concentration was higher. By measuring the displacement, Δx , the temperature and the composition of the

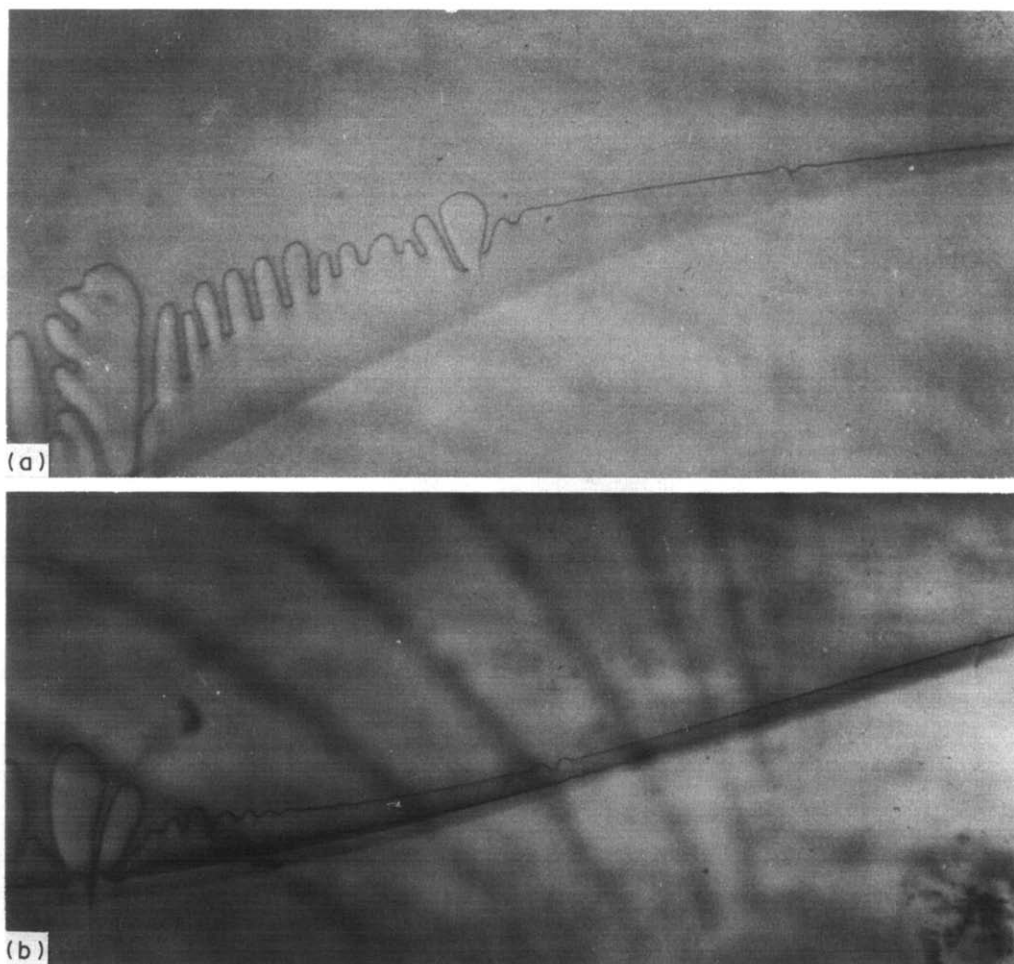


Fig. 11. Large amplitude, long wavelength, instability in succinonitrile -0.34 wt% acetone which was directionally solidified at $G = 4.0$ K/mm and $V = 0.5$ $\mu\text{m/s}$. The interfaces shapes are for time: (a) 3.6 h and (b) 4.5 h.

interface were calculated from the equilibrium phase diagram. By using a localized model, the critical velocity for this composition condition was calculated and was found to be 0.41 $\mu\text{m/s}$, which is slightly below the experimental velocity, so that the instability of the interface would be predicted.

CONCLUSION

Directional solidification experiments in the succinonitrile-acetone were carried out under conditions close to the critical conditions for the planar interface instability. It was found that the critical velocity of the interface agrees with that predicted by the linear stability analysis. The initial wave numbers of the unstable interface were significantly larger than those predicted by the linear stability analysis. The planar-to-cellular bifurcation was shown to be subcritical so that large amplitude perturbations were found to give rise to a non-planar interface below the critical velocity.

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