

(6)p

1995/08/34

324783

N95-14548

## CONVECTION AND MORPHOLOGICAL STABILITY DURING DIRECTIONAL SOLIDIFICATION

S. R. Coriell, A. A. Chernov, B. T. Murray, and G. B. McFadden

National Institute of Standards and Technology

Gaithersburg, MD 20899 USA

### ABSTRACT

For growth of a vicinal face at constant velocity, the effect of anisotropic interface kinetics on morphological stability is calculated for a binary alloy. The dependence of the interface kinetic coefficient on crystallographic orientation is based on the motion and density of steps. Anisotropic kinetics give rise to traveling waves along the crystal-melt interface, and can lead to a significant enhancement of morphological stability. The stability enhancement increases as the orientation approaches a singular orientation and as the solidification velocity increases. Shear flows interact with the traveling waves and, depending on the direction of the flow, may either stabilize or destabilize the interface. Specific calculations are carried out for germanium-silicon alloys.

### INTRODUCTION

During the directional solidification of a binary alloy solute inhomogeneities can arise from both fluid flow and morphological instability. In microgravity buoyancy-driven fluid flow is reduced, and experiments to study the evolution of morphological patterns without the interference of fluid flow may be possible. We are carrying out theoretical studies of the interaction of fluid flow with the crystal-melt interface [1-3]. Included in this research are: (1) calculations of cellular morphologies in the absence of fluid flow; (2) evaluation of the Seebeck voltage for cellular interfaces as a method for monitoring interface morphology in metallic alloys; (3) linear stability analyses of coupled interfacial and convective instabilities; (4) calculations of the effects of time-dependent gravitational accelerations (g-jitter) on fluid flow during directional solidification. This ground based research will focus on providing theoretical interpretation and guidance for a series of space experiments to be carried out by J. J. Favier, R. Abbaschian, and colleagues on tin-bismuth alloys using the MEPHISTO apparatus and by K. Leonartz and colleagues on succinonitrile-acetone alloys. Bismuth typically grows from the melt with facets, and in this paper we will describe recent studies of morphological stability when the interface attachment kinetics is highly anisotropic.

During solidification of a binary alloy, the crystal-melt interface may become morphologically unstable [4, 5] leading to cellular or dendritic growth. Here, we consider the effect of anisotropy of interface kinetics on morphological instability during growth of a binary alloy at constant velocity. We treat growth in a direction near a singular orientation, and use a model of kinetic anisotropy based on step motion. The effect of anisotropy of surface tension and interface kinetics has previously been treated [6] in a quasi-static approximation to the diffusion field; kinetic anisotropy gave rise to traveling waves along the crystal-melt interface. In this article, we keep the full time-dependence of the diffusion field and show that the traveling waves resulting from kinetic anisotropy can provide a significant enhancement of morphological stability, especially for orientations near the singular orientation and for large growth velocities. We have recently obtained similar results for constant velocity growth from a supersaturated solution [7].

In solution growth, it is well known that a solution flowing above a vicinal face of a crystal has a strong influence on morphological stability [8-10]. If the flow is opposite to the direction of the step motion, there is a stabilization of the interface with respect to step bunching. In the absence of a shear flow, there is an apparent flow of liquid opposite to the step motion (in a reference frame attached to the moving steps) and this stabilizes the interface, preventing step bunching and the formation of macrosteps [7].

For melt growth, interface stability near a vicinal face was the subject of an earlier treatment by Yuferev [11] in which he concluded that interface stability is enhanced for very small deviations from the singular orientation. Also, Kolesnikova and Yuferev [12] have carried out weakly nonlinear calculations in the frozen temperature approximation, i.e., equal thermal properties and vanishing latent heat. A strong interaction

between a shear flow parallel to the crystal-melt interface and anisotropy of kinetics has recently been found [10].

In this article, we carry out a linear treatment of interface stability during constant velocity solidification of a binary alloy. We allow for an interface kinetic coefficient that depends on the crystallographic orientation of the crystal-melt interface. We carry out specific calculations for germanium-silicon alloys for orientations in the vicinity of a singular orientation, which occur in this alloy [13].

## THEORY

We consider directional solidification of a binary alloy at constant velocity  $\bar{V}$  in the  $z$ -direction and treat the morphological stability of an initially planar crystal-melt interface. We choose an  $(x, y, z)$  coordinate system (moving with the macroscopically planar interface) such that the crystal-melt interface is described by  $z = h(x, t)$ , where  $t$  is the time. Further, we consider a two-dimensional problem and assume that all quantities are independent of the  $y$ -coordinate.

The temperature fields,  $T_L(x, z, t)$  and  $T_S(x, z, t)$ , in the melt and crystal and the solute field in the melt,  $C_L(x, z, t)$ , satisfy the partial differential equations

$$\frac{\partial T_L}{\partial t} = \kappa_L \nabla^2 T_L + \bar{V} \frac{\partial T_L}{\partial z}, \quad (1)$$

$$\frac{\partial T_S}{\partial t} = \kappa_S \nabla^2 T_S + \bar{V} \frac{\partial T_S}{\partial z}, \quad (2)$$

and,

$$\frac{\partial C_L}{\partial t} = D \nabla^2 C_L + \bar{V} \frac{\partial C_L}{\partial z}, \quad (3)$$

where  $\kappa_L$  and  $\kappa_S$  are the thermal diffusivities in the melt and crystal, respectively, and  $D$  is the solute diffusivity; we neglect diffusion in the solid. We also assume that there is no fluid flow in the melt and that the thermophysical properties are independent of temperature and solute concentration. These transport equations and assumptions are most appropriate for dilute alloys.

The boundary conditions at the crystal-melt interface are

$$(\mathbf{V} \cdot \mathbf{n})(1 - k)C_L = -D \nabla C_L \cdot \mathbf{n}, \quad (4)$$

$$L_v(\mathbf{V} \cdot \mathbf{n}) = (k_S \nabla T_S - k_L \nabla T_L) \cdot \mathbf{n}, \quad (5)$$

$$T_S = T_L, \quad (6)$$

$$\mathbf{V} \cdot \mathbf{n} = \beta(p)(T_e - T_L), \quad (7)$$

where

$$T_e = T_M + mC_L - T_M \Gamma \mathcal{K}, \quad (8)$$

$\mathbf{V}$  is the solidification velocity vector,  $\mathbf{n}$  is the unit normal to the interface,  $k$  is the segregation coefficient,  $L_v$  is the latent heat per unit volume,  $k_S$  and  $k_L$  are the thermal conductivities of crystal and melt, respectively,  $\beta(p)$  is the kinetic coefficient,  $T_M$  is the melting point,  $m$  is the liquidus slope,  $\Gamma = \gamma/L_v$ ,  $\gamma$  is the surface tension, and  $\mathcal{K}$  is the mean curvature of the crystal-melt interface. We will assume that  $\beta(p) = \beta_{st}|p|$ , with  $p \equiv \tan \theta$ , where  $\theta$  measures the deviation of the interface from a singular orientation. We will denote the orientation of the planar interface relative to the singular orientation by  $\bar{p}$ , and consider that  $\bar{p} > 0$ . We fix the far-field boundary conditions by specifying the bulk alloy concentration  $C_\infty$  and the temperature gradient in the melt at the crystal-melt interface. We will perform stability calculations for germanium-silicon alloys; the required properties are given in reference [14].

In [7, 10, 14] the morphological stability of a solid-liquid vicinal interface is treated using linearized theory in two dimensions. The perturbation to the planar interface ( $z = 0$ ) with crystallographic orientation  $\bar{p}$  has the form

$$z \propto \exp(\sigma t + ik_x x). \quad (9)$$

Here  $k_x$  is the wavenumber and  $\sigma$  is the complex temporal factor,

$$\sigma = \sigma_r + i\sigma_i. \quad (10)$$

The interface is unstable if  $\sigma_r > 0$ . The dispersion relation for  $\sigma$  as a function of  $k_x$  can be obtained analytically. In the thermal steady-state approximation, i.e.,  $\kappa_L \rightarrow \infty$  and  $\kappa_S \rightarrow \infty$ , it reduces to

$$\begin{aligned} \sigma/\bar{V} = \{ & -\bar{G} - T_M \Gamma k_x^2 + ik_x \bar{V}/(\beta_{st} \bar{p}^2) + mG_c[\alpha - \bar{V}/D]/[\alpha - (1-k)\bar{V}/D]\} \\ & \{L_v \bar{V}/(2\bar{k}k_x) + (\bar{V}/\beta_{st} \bar{p}) + mG_c/[\alpha - (1-k)\bar{V}/D]\}^{-1}, \end{aligned} \quad (11)$$

where

$$\alpha = (\bar{V}/2D) + \sqrt{(\bar{V}/2D)^2 + k_x^2 + (\sigma/D)}, \quad (12)$$

$\bar{G} = (k_S G_S + k_L G_L)/(2\bar{k})$ , and  $\bar{k} = (k_S + k_L)/2$ . In a previous treatment [6] of the effect of anisotropic kinetics on morphological stability, a quasi-static approximation was made for the diffusion field which is equivalent to setting  $\sigma = 0$  in the definition of  $\alpha$ . In this limit, the above expression agrees with eq. (13) of reference [6]. The dispersion relation can be written as a cubic polynomial with complex coefficients in the variable  $\alpha - (\bar{V}/2D)$ ; this has the advantage that all roots of the nonlinear equation can be determined. In the thermal steady-state approximation, we have numerically solved the cubic polynomial to determine the stability conditions. We have also numerically solved the ordinary differential equations as a boundary value problem to determine the stability conditions; this does not require the thermal steady-state approximation.

## RESULTS

The dispersion relationship  $\sigma_r = \sigma_r(\bar{V}, \bar{G}, c_{\infty}, \bar{p}, k_x)$  includes, as independent parameters, the normal growth rate  $\bar{V}$ , the temperature gradient  $\bar{G}$ , the impurity concentration  $c_{\infty}$  and the slope  $\bar{p}$ ; stability requires that  $\sigma_r < 0$  for all values of  $k_x$ . In principle, the slope,  $\bar{p}$ , may be fixed independently of the other processing variables by cutting the crystal to prepare an initial interface; however, only very small deviations (less than a tenth of a degree) from a singular interface make sense because large deviations are indistinguishable from a rough interface. Even such a prepared interface may be replaced (wedged out) by the nearest singular face in the course of sufficiently long growth. Under the typical conditions of faceted growth, the vicinal slope  $\bar{p}$  on a facet is, like  $\bar{V}$ , dependent on supercooling and is determined either by a dislocation step source or by two-dimensional nucleation on the most supercooled region of the facet. In these cases, the slope  $\bar{p}$  is a function of the growth rate  $\bar{V}$  which is determined by the conditions of crystal pulling (Czochralski) or crucible movement through a temperature gradient (Bridgman and related techniques). In the following, we consider stability conditions for both an independently given slope and for a slope determined by  $\bar{V}$ , i.e.,  $\bar{p} = \bar{p}(\bar{V})$ , for dislocation assisted growth and for growth by two-dimensional nucleation.

Figure 1 presents the real part of the temporal factor  $\sigma$ , i.e.,  $\sigma_r$ , as a function of the wavenumber  $k_x$  in dimensionless form for the processing conditions  $\bar{V} = 10 \mu\text{m/s}$ ,  $G_L = 50 \text{ K/cm}$ , and  $C_{\infty} = 5 \text{ at\%}$ . The upper plot with  $\bar{p} = 0.002$  is for isotropic kinetics. The lower two plots are for anisotropic kinetics with  $\bar{p} = 0.002$  and  $0.0015$ . Stabilization due to anisotropy is evident. Also, for  $\bar{p} < 0.0015$  the interface becomes absolutely stable, i.e., stable against perturbations for all  $k_x$ . Stability at  $Dk_x/\bar{V} < 5$  is common to all the curves; in this region of  $k_x$  the perturbation wavelength  $2\pi/k_x > D/\bar{V}$ , i.e., the diffusion boundary layer follows the perturbed interface and thus there is less driving force for instability. The steep drop in  $\sigma_r$  at high wavenumbers is associated with capillary stabilization, while the kinetic stabilization determines the overall level of  $\sigma_r$  at lower  $k_x$  and thus the height of the maximum.

We suppose that the unperturbed slope  $\bar{p}$  is determined by a screw dislocation with the elementary Burger's vector intersecting the face under consideration. We also assume that the supercooling,  $\Delta T$ , and thus the value of  $\bar{p}$ , along the face is constant with  $\Delta T$  given by  $\bar{V}/(\beta_{st} \bar{p})$ . Letting  $\gamma_{st}$  be the linear energy of a step, the growth rate of the face is given by [15]

$$\bar{V} = \frac{h^2 L_v \beta_{st} \Delta T^2}{19 \gamma_{st} T_M} \quad (13)$$

and the slope is

$$\bar{p} = [h^2 L_v \bar{V}/(19 \gamma_{st} T_M \beta_{st})]^{1/2} \quad (14)$$

where  $h$  is the step height. It was shown by Voronkov [15] that the step fluctuations at the melting point decrease the step free energy for (111) Si and Ge by a factor of three or four; therefore, for the linear stability calculations for Ge, we assume that  $\gamma_{st} = \gamma h/4$ .

If the crystal face is free of screw dislocations or the supercooling is so high that step generation by two-dimensional nucleation is more effective than by the dislocation mechanism, the growth rate is [16]

$$\bar{V} = h(\bar{v}^2 J)^{\frac{1}{3}} \quad (15)$$

where the nucleation rate  $J$  ( $\text{cm}^{-2} \text{s}$ ) is obtained from

$$J = [hk_B T_M^2 \Delta T / (\omega^2 L_v)]^{\frac{1}{2}} q \beta_{st} \exp[-\pi h \gamma^2 / (k_B \Delta T L_v)]. \quad (16)$$

Here  $q$  is the density of surface sites on which nucleation is possible,  $\omega$  is the atomic volume, and  $k_B$  is Boltzmann's constant. Thus, the growth rate is

$$\bar{V} = (h^7 q^2 / \omega)^{\frac{1}{6}} \beta_{st} \Delta T^{\frac{5}{6}} [k_B T_M^2 / (\omega L_v)]^{\frac{1}{6}} \exp[-\pi h \gamma^2 / (3k_B \Delta T L_v)]. \quad (17)$$

and the slope  $\bar{p}$  is given by

$$\bar{p} = h(J/\bar{v})^{\frac{1}{3}} = (h^7 q^2 / \omega)^{\frac{1}{6}} \frac{[k_B T_M^2 / (\omega L_v)]^{\frac{1}{6}}}{\Delta T^{\frac{1}{6}}} \exp[-\pi h \gamma^2 / (3k_B \Delta T L_v)]. \quad (18)$$

Thus eq. (17) and eq. (18) give the dependence  $\bar{p}(\bar{V})$  in parametric form with  $\Delta T$  the parameter. In evaluating these expressions, we make the approximation that  $h^7 q^2 / \omega = 1$ .

In Fig. 2, we present a stability diagram in terms of the critical solute concentration as a function of the ratio of the liquid temperature gradient and the growth velocity for  $G_L = 50 \text{ K/cm}$ . The interface is stable to small perturbations for concentrations lying below the given curves. The calculations have been carried out by numerically solving the differential equations. The solid curve is the Mullins and Sekerka [4] result which for isotropic kinetics does not depend on the kinetic coefficient [6]. The dashed and dotted curves are calculated from the present model of anisotropic kinetics with  $\bar{p} = 0.01$  and  $0.001$ , respectively. Anisotropic kinetics causes a substantial enhancement of the region of stability.

The remaining two curves in Fig. 2 are for dislocation and two-dimensional nucleation controlled growth for which  $\bar{p}$  is a function of velocity. For the dislocation controlled growth,  $\bar{V} = 8.7 \times 10^4 \bar{p}^2 \text{ cm/s}$ . In the case of two-dimensional nucleation, eq. (17) and eq. (18) have been evaluated numerically to obtain  $\bar{V}$  as a function of  $\bar{p}$ .

We note that as  $\bar{p}$  becomes small, the concentration at the onset of instability becomes very large where other effects, which we have not taken into account, such as fluid flow and the concentration dependence of the distribution coefficient, liquidus slope, and diffusion coefficient, may be important. However, it is clear from the results that as a singular orientation is approached, anisotropic kinetics has a large stabilizing effect.

As  $\bar{p}$  becomes very small or  $\bar{V}$  becomes very large, the thermal steady-state approximation is no longer valid. For example, in the thermal steady-state approximation, for  $\bar{p} = 0.001$  and  $\bar{V} = 0.001$  and  $0.01 \text{ cm/s}$ , the critical concentrations are 7.8847 and 5.4579 at%, respectively; whereas the numerical values are 7.8852 and 7.6689 at%. Thus for  $\bar{p} = 0.001$ , the thermal steady-state approximation underestimates the critical concentration. The thermal steady-state approximation fails because the wavespeed is sufficiently large that  $k_s^2$  is no longer much greater than  $\sigma_i / \kappa_s$ .

Near a singular orientation, due to anisotropy the value of  $T_M \Gamma$  may be much less than the value used in our calculations [14]; therefore, we have also carried out a few calculations with  $T_M \Gamma$  reduced by a factor of 100. For  $\bar{p} = 0.001$  and  $\bar{V}$  ranging from 0.001 to 0.1  $\text{cm/s}$ , the critical concentrations are essentially unchanged. Similarly, for dislocation controlled growth, the results for the critical concentrations are again unchanged. Thus, in the strongly kinetically controlled regime the value of the capillary constant is unimportant. Capillarity is still important at large wavenumbers, but in the kinetically controlled regime the onset of instability occurs at relatively small wavenumbers.

## CONCLUSIONS

In the calculations described above, we have assumed that the melt is stagnant. It is well known that fluid flow can alter the conditions for stability [10, 17]. For an ideal fluid and anisotropic kinetics, Chernov [10] has shown that a flow parallel to the interface and opposite in direction to the step motion stabilizes the interface while a flow in the direction of the step motion destabilizes the interface. We are carrying out numerical calculations of the linear stability of a crystal-melt interface in the presence of a parallel shear flow. The method is similar to that previously used for isotropic kinetics [18]; in addition, we have developed a pseudospectral algorithm to treat the problem. Qualitatively, the results are in agreement with Chernov [10] for an ideal fluid.

## References

- [1] B. V. Saunders, B. T. Murray, G. B. McFadden, S. R. Coriell, and A. A. Wheeler, *Phys. Fluids A4* (1992) 1176-1189.
- [2] B. T. Murray, S. R. Coriell, G. B. McFadden, A. A. Wheeler, and B. V. Saunders, *J. Crystal Growth* 129 (1993) 70-80.
- [3] R. J. Braun, G. B. McFadden, B. T. Murray, S. R. Coriell, M. E. Glicksman, and M. E. Selleck, *Phys. Fluids A5* (1993) 1891-1903.
- [4] W. W. Mullins and R. F. Sekerka, *J. Appl. Phys.* 35 (1964) 444-451.
- [5] S. R. Coriell and G. B. McFadden, in D. T. J. Hurle (ed.) *Handbook of Crystal Growth 1 Fundamentals, Part B: Transport and Stability*, North-Holland, Amsterdam, 1993 pp. 785-857.
- [6] S. R. Coriell and R. F. Sekerka, *J. Crystal Growth* 34 (1976) 157-163.
- [7] A. A. Chernov, S. R. Coriell, and B. T. Murray, *J. Crystal Growth* 132 (1993) 405-413.
- [8] A. A. Chernov and T. Nishinaga, in *Morphology of Crystals*, Ed. I. Sunagawa (Terra, Tokyo, 1987) pp. 207-267.
- [9] A. A. Chernov, *Contemp. Phys.* 30 (1989) 251-276.
- [10] A. A. Chernov, *J. Crystal Growth* 118 (1992) 333-347.
- [11] V. S. Yuferev, *Phys. Chem. Mech. of Surfaces* 2 (1985) 1916-1925.
- [12] E. A. Kolesnikova and V. S. Yuferev, *Soviet Phys.-Cryst.* 34 (1989) 7-10.
- [13] J. P. Dismukes and L. Ekstrom, *Met. Trans.* 233 (1965) 672-680.
- [14] S. R. Coriell, B. T. Murray and A. A. Chernov, *J. Cryst. Growth* (1994) in press.
- [15] V. V. Voronkov, *Sov. Phys. Cryst.* 17 (1973) 807-813.
- [16] A. A. Chernov, *Modern Crystallography III. Crystal Growth*, Springer Ser. Sol. St., vol. 36 (Springer, Berlin, 1984).
- [17] S. H. Davis, in D. T. J. Hurle (ed.) *Handbook of Crystal Growth 1 Fundamentals, Part B: Transport and Stability*, North-Holland, Amsterdam, 1993 p. 859-897.
- [18] S. R. Coriell, G. B. McFadden, R. F. Boisvert, and R. F. Sekerka, *J. Crystal Growth* 69 (1984) 15-22.

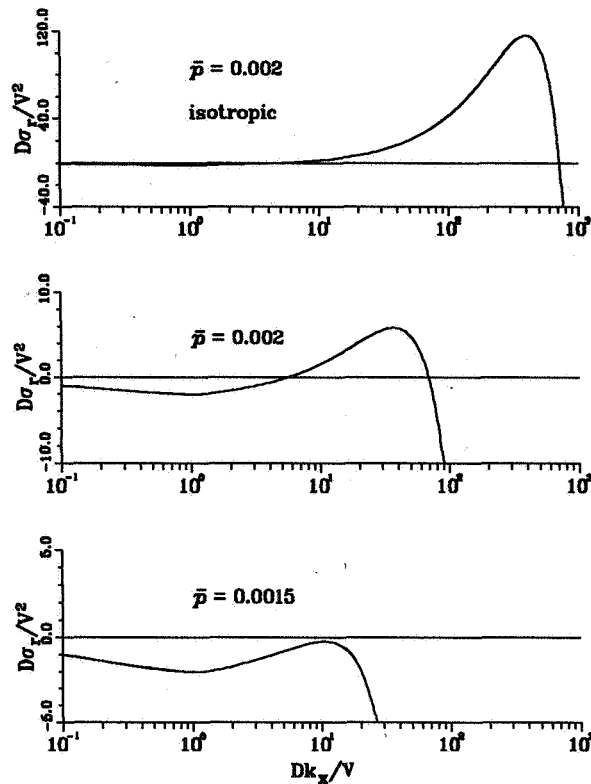


Figure 1: The real part of the temporal growth rate as a function of the spatial wavenumber for three values of the crystallographic orientation with respect to the growth direction for  $\bar{p} = 0.002$  and  $0.0015$ . The upper plot is for isotropic kinetics, while the two lower plots are for anisotropic kinetics.

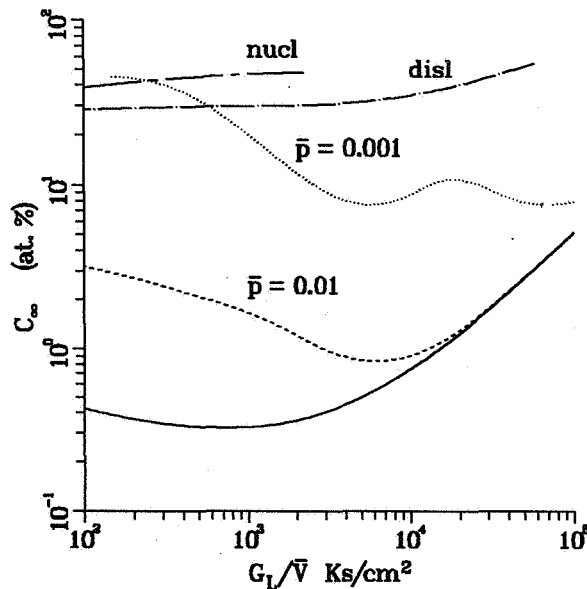


Figure 2: The silicon concentration at the onset of instability during directional solidification of germanium-silicon alloys as a function of the liquid temperature gradient divided by the growth rate with  $G_L = 50$  K/cm. The interface is morphologically stable for concentration values below the curves. The solid curve is based on the Mullins and Sekerka theory with isotropic kinetics; the remaining curves are for anisotropic kinetics. The dashed and dotted curves correspond to  $\bar{p} = 0.01$  and  $0.001$ , respectively. The curves labeled "nucl" and "disl" correspond to nucleation and dislocation controlled growth for which  $\bar{p}$  is a function of  $\bar{V}$ .