Dynamics of Banded Structure Formation in Rapid Solidification

Alain Karma and Armand Sarkissian
Physics Department, Northeastern University, Boston, Massachusetts 02115
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Motivated by widespread experimental observations of the "banded structure" in rapidly solidified alloys, we have studied numerically by Green's-function method the dynamics of the planar interface under rapid directional solidification condition. We find that the formation of this structure can be explained and partially characterized quantitatively in terms of highly nonlinear "relaxation oscillations" of the interface whose spacings are controlled by latent heat diffusion but not by the thermal gradient. A comparison with experiment is presented for Al-Fe alloys.

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One decade ago, a novel unexpected microstructure, the so-called *banded structure,* was observed in rapidly solidified alloys [1]. Since then, numerous other experimental observations have revealed that the occurrence of this structure is a rather universal phenomenon common to many rapidly solidified alloys, when the growth conditions approach absolute stability. Detailed microstructural studies [1–3] have shown that this structure is composed of alternating light and dark bands lying parallel to the solidification front [Fig. 1(a)], the dark bands having a spatially periodic precipitate structure, either cellular and dendritic or eutectic, and the light bands corresponding to microsegregation-free regions.

The problem of understanding why bands form, and how to reliably predict their spacings, has continued to pose a difficult theoretical challenge. Historically, the first observations of the banded structure came as a complete theoretical surprise. On the basis of the classic Mullins-Sekerka linear stability analysis of the planar interface [4], one would have expected a steady-state dendritic and cellular-array structure to form at velocities just below the absolute stability limit (V_{as}) beyond which the planar interface is completely stable. Such a structure has actually been observed in sufficiently dilute Ag-Cu alloys [2], but at larger compositions of Cu and in many other alloys it is the banded structure which, instead, has most often been observed [1].

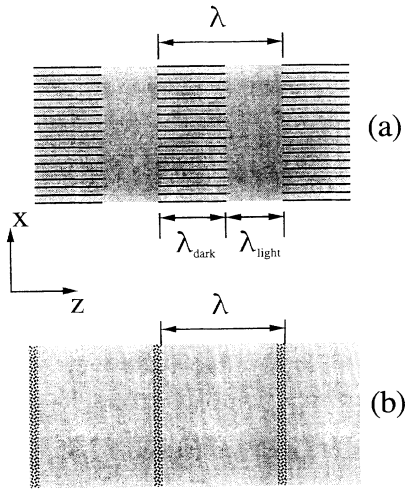

FIG. 1. Schematic drawing of banded structures as observed in longitudinal sections of rapidly solidified alloys (Refs. [1–3]). The z axis and x axis are respectively parallel to the growth direction and to the solidification front.

In order to account for the fact that the assumption of local thermodynamic equilibrium at the interface breaks down at large solidification rate, several authors have extended the Mullins-Selerka stability analysis of the planar interface to incorporate various nonequilibrium effects [5,6]. Coriell and Sekerka first redid the analysis using a velocity-dependent segregation coefficient $k(v)$ and identified a novel cellular oscillatory instability at V_{as}. More recently, Merchant and Davis [6] further extended the analysis to a model which neglects latent heat diffusion but includes both nonequilibrium segregation and a velocity-dependent liquidus, and obtained an oscillatory instability of similar physical origin as that of Coriell and Serkerka. Subsequently, Braun, Merchant, and Davis have considered the interaction of cellular (finite wave vector) and planar oscillatory modes in this model via a weakly nonlinear analysis which applies to extremely dilute alloys [7]. In an attempt to describe the actual time-periodic changes of structures, which are not describable by linear stability analysis, Gremaud and coworkers [3] have recently proposed a phenomenological model of banding based on periodic instabilities of the growth velocity. In this model, the solidification front is assumed to make abrupt quasi-instantaneous transitions in velocity when changing back and forth from a planar to a cellular and dendritic or eutectic structure, with slow quasi-steady-state changes in velocity in between these transitions.

Despite this recent progress, two main questions have remained to a large degree unanswered: (1) Do planar instabilities actually lead, in a nonlinear regime, to the supposed time-periodic changes in interface velocity which would account for the formation of bands in experimentally relevant parameter ranges? (2) What are the dominant physical factors which control the band spacings?

We report here the results of a detailed numerical study of the full dynamics of the planar interface under rapid directional solidification conditions which provides

answers to these two questions. The answers are only partial since we restrict our numerical study to the dynamics of the planar interface which therefore automatically suppresses transverse morphological instabilities (along the x axis in Fig. 1) which occur simultaneously with the zero-wave-vector (planar) instability supposed to drive banding. However, there seems to be two experimental observations which justify why an essential part of the banding phenomenon can be captured by probing the dynamics of the planar interface (an already difficult numerical task in one dimension for the coupled solutal-thermal free-boundary problem with a very small solutal/thermal diffusivity ratio). First, there is the aforementioned observation that bands are observed to be flat in the transverse direction. This indicates that during part of its cycle of oscillation the interface should indeed be planar. Second, there is the observation that the very high velocity banded structure (which precedes microsegregation-free solidification) is composed principally of microsegregation-free regions [3]. For this structure, the dark bands only consist of transverse rows of small spherical precipitates as depicted in Fig. 1(b) and $\lambda_{\text{light}}/\lambda \simeq 1$. This in turn strongly suggests that for this structure the transverse instabilities should be suppressed during most of the cycle of oscillation where the interface is planar, and that consequently its spacing λ should be predictable in terms of the period of oscillation of the planar interface. This is also in accord with the fact that during its oscillation cycle the interface accelerates abruptly into a high velocity regime, well beyond the absolute stability limit, where all transverse instabilities are suppressed. The agreement between our numerics and experiment in Al-Fe alloys seems to support our assumption that the total band spacing λ can be predicted in terms of planar oscillations for structures with $\lambda_{\text{light}}/\lambda \simeq 1$ [Fig. 1(b)]. For the generic banded structure of Fig. 1(a), we cannot with the present theory predict independently λ_{dark} and λ_{light} and the characteristics of the precipitate cellular structure inside dark bands. However, we can at least provide a crude estimate of the wavelength of this structure by using the criterion that it should be comparable to the wavelength of the fastest unstable mode of the planar interface at the minimum velocity of the oscillation cycle. Finally, in regard to question (2) above, the major finding of this study is that the temperature gradient has almost no effect on the band spacing. This spacing is controlled by the interplay of the planar instability driven by solute trapping and latent heat diffusion which dictates the changes of temperature at the interface.

The equations we solve are the usual diffusion equations for concentration and temperature, $\partial C/\partial t = D_C \partial^2 C/\partial z^2$ and $\partial T/\partial t = D_T \partial^2 T/\partial z^2$, with the boundary conditions on the interface [8]

$$T_i = T_M + mC_L - \frac{RT_M^2}{L}\frac{v}{v^*}, \tag{1}$$

$$C_L(1-k)v = -D_C\left[\frac{\partial C}{\partial z}\right]_L, \tag{2}$$

$$Lv = -c_p D_T\left(\left[\frac{\partial T}{\partial z}\right]_L - \left[\frac{\partial T}{\partial z}\right]_S\right), \tag{3}$$

where we have chosen for simplicity equal thermal diffusivities in both phases. Nonequilibrium effects are included using the phenomenological velocity-dependent forms $k = (k_e + v/v_d)/(1 + v/v_d)$ introduced by Aziz and Kaplan [9] and Jackson, Gilmer, and Leamy [10] and

$$m = m_e\{1 + (k_e - k[1 - \ln k/k_e])/(1 - k_e)\}$$

by Boettinger and Coriell [11], where k_e and m_e are respectively the equilibrium segregation coefficient and the liquidus slope. The last term on the right-hand side of Eq. (1) represents the effect of attachment kinetics where v^* is a kinetic parameter on the order of the velocity of sound in metals.

We solved the above free-boundary problem numerically by recasting it in the form of two coupled integral equations using the standard Green's-function method [12]:

$$C_L(t) = \int_0^\infty dz' C(z',0) G(z_i(t) - z';t) + \int_0^t dt' C_L(t')\left(\frac{1}{2}\frac{z_i(t) - z_i(t')}{t - t'} - k(t')\frac{dz_i(t')}{dt'}\right) G(z_i(t) - z_i(t');t - t'), \tag{4}$$

$$T_i(t) = \sqrt{\epsilon}\int_{-\infty}^\infty dz' T(z',0) G(\sqrt{\epsilon}[z_i(t) - z'];t) + \frac{L}{c_p}\sqrt{\epsilon}\int_0^t dt' \frac{dz_i(t')}{dt'} G(\sqrt{\epsilon}[z_i(t) - z_i(t')];t - t'), \tag{5}$$

where $\epsilon \equiv D_C/D_T$, $G(x;\tau) = [1/(4\pi D_C \tau)^{1/2}]\exp(-x^2/4D_C\tau)$, and $T(z,0)$ and $C(z,0)$ are the initial temperature and solute profiles at time $t = 0$ which are taken to have the usual simple exponentially decaying form corresponding to a steady-state planar interface with velocity V_0. Directional solidification conditions are imposed using the boundary conditions at infinity $\partial T^{\pm}/\partial z = G^{\pm}\exp(-V_0/D_T z)$ and $C = C_\infty$, where the + and − signs refer to the liquid and solid phases, respectively, $G^{\pm}$ are the temperature gradients in both phases with $G^- = G^+ + (L/c_p)V_0$, and V_0 is the isotherm velocity far from the interface which is the usual control parameter of directional solidification.

We summarize here the main results of our numerical study. A more complete exposition of both results and methodology will be presented elsewhere [13]. Motivated by the recent experiments of Gremaud and co-workers, we have performed our calculations for Al-Fe alloys [14], and further restricted our attention here to the case of

Al-Fe 2 wt.% ($C_\infty = 2$). By performing a morphological stability analysis of the planar interface for the present choice of model and parameters [13] (the same analysis neglecting latent heat diffusion was performed in Ref. [6]), it can easily be shown that all spatially periodic perturbations of the form $\exp(iqx + \omega t)$ become restabilized when $V_0 > V_{as} \cong 2.95$ m/s. For $V_0 < V_{as}$ there is a finite band Δq of unstable wave vectors which increases in width with decreasing V_0, and for $V_0 < V_c \cong 1.42$ m/s there is an oscillatory instability at zero wave vector. Here, our primary concern has been to understand the dynamical evolution of the planar interface triggered by this zero-wave-vector instability in the velocity range $V_0 < V_c$.

Plots of interface velocity versus interface position are shown in Fig. 2. For clarity, the initial transients are not shown and only the final cycles are displayed. For other velocities, not displayed here, we have found that the amplitude of limit-cycle oscillations increased initially as the square root of $V_c - V_0$ which indicates the supercritical nature of the bifurcation. Two important features of the oscillations appear upon decreasing V_0. First, small amplitude oscillations evolve rapidly as V_0 is decreased into "relaxation oscillations" characterized by the relatively short time spent by the interface in a high velocity regime as compared to the longer time spent in a low velocity regime. Clear signatures of the relaxational character of these oscillations are the presence of sharp peaks in the plots of velocity versus position (Fig. 2), these peaks becoming increasingly sharper with decreasing V_0. The second important feature is the evolution towards temporal chaos via a period doubling sequence of bifurcations shown in Fig. 2. Chaotic oscillations were observed to persist when decreasing V_0 beyond the smallest value displayed here.

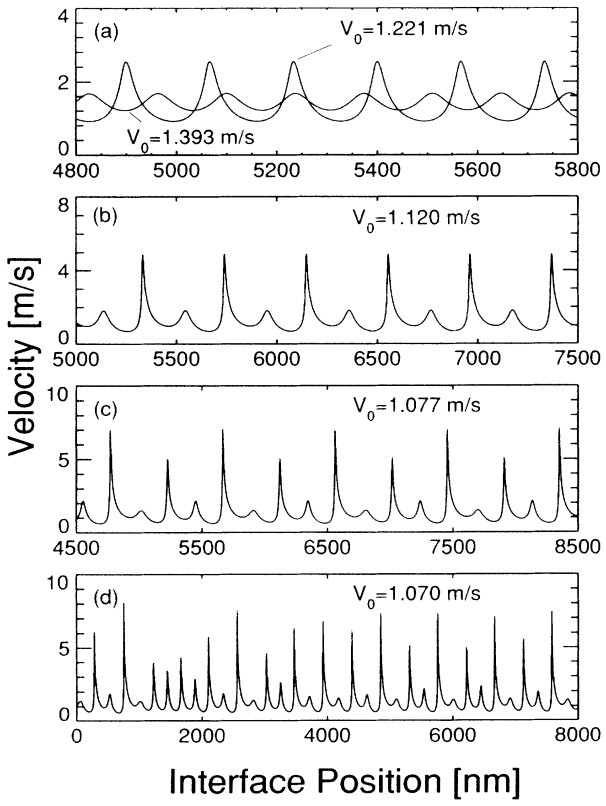

FIG. 2. Interface velocity vs interface position for different V_0: (a) period-1, (b) period-2, (c) period-4, and (d) chaotic oscillations. The total spacing λ of banded structures composed predominantly of microsegregation-free regions [Fig. 1(b)] is assumed here to be determined by the spacing of velocity minima which increases from about 135 nm in (a) to an average value of 240 nm in (d).

We have compared in Fig. 3 one of the computed cycles with the oscillation cycle (1-2-3-4-1) proposed by Gremaud and co-workers. We note that in the cycle (1-2-3-4-1), the fast acceleration (1-2) and deceleration periods (3-4) are assumed to be horizontal in the (T,V) plane, while, in the computed cycles, the interface warms up and cools down considerably during the fast acceleration and deceleration periods. Also, in their model the spatial period of the cycle (1-2-3-4-1), which determines the total band spacing, is inversely proportional to the strength of the temperature gradient. In contrast here, spatial periods of computed cycles which can be read off directly from Fig. 2 do not depend sensitively on the strength of the temperature gradient (spatial periods were found to change by no more than a few percent when G^+ was varied from 0 to 10^7 K/m). These differences can be attributed to the fact that interfacial temperature changes are controlled predominantly by latent heat diffusion and not by the temperature gradient. This in turn indicates that the widely used "frozen-temperature approximation" (no latent heat diffusion), which has provided useful qualitative insights into the origin of the banding phenomenon [3,6,7], fails dramatically

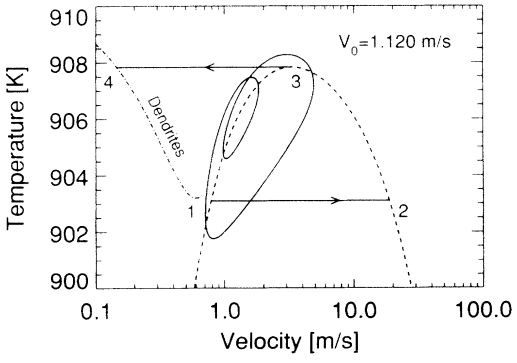

FIG. 3. The cycle (1-2-3-4-1) corresponds to the model of Gremaud and co-workers, where the steady-state dendrite branch and planar branch [defined by Eq. (1) with $C_\ell^0 = C_\infty / k(V_0)$] are represented by dash-dotted and dashed lines, respectively. The closed solid line corresponding to the computed cycle of Fig. 2(b) ($V_0 = 1.12$ m/s) is displayed for comparison.

to describe this phenomenon quantitatively. This can be understood by noting that during the fast acceleration period, driven by solute trapping of impurities, the interface is displaced by an amount $\Delta z \sim D_c/V_0$ over a short time scale $\Delta t \sim D_c/V_0^2$. Thus, in the absence of latent heat (frozen-temperature approximation), the interface warms up during this period by an amount $\Delta T \sim G^+ D_c/V_0$ which is negligible in comparison to the amount $\Delta T \sim (D_c/D_T)^{1/2} L/c_p$ by which it warms up when latent heat is present.

In regard to experiment, Gremaud and co-workers have reported band spacings between 205 and 300 nm for banded structures with a light bandwidth/band-spacing ratio $\lambda_{light}/\lambda \geq 0.75$ [3]. For comparison, the spatial periods of computed oscillations, which can only be used in principle to predict λ for structures where $\lambda_{light}/\lambda \simeq 1$, fall in the range 135–240 nm in Fig. 2. The wavelength of the most unstable mode of the planar interface at the minimum velocity of the oscillation cycle [$\simeq 0.5$ m/s in Figs. 2(c) and 2(d)] is predicted to be around 65 nm while the measured wavelength of the cellular precipitate structure within dark bands is about 25 nm [3]. This discrepancy is not surprising in view of the crudeness of the criterion used here to estimate this wavelength. A theory that incorporates transverse modes will be needed to better characterize the dark bands. Finally, our prediction that the total band spacing is controlled by latent heat diffusion and does not depend sensitively on the strength of the temperature gradient may explain why banded structures formed under a variety of conditions in different alloys often have comparable spacings. This prediction could be tested experimentally by strongly varying gradient conditions in one particular alloy and measuring the corresponding changes in band spacings.

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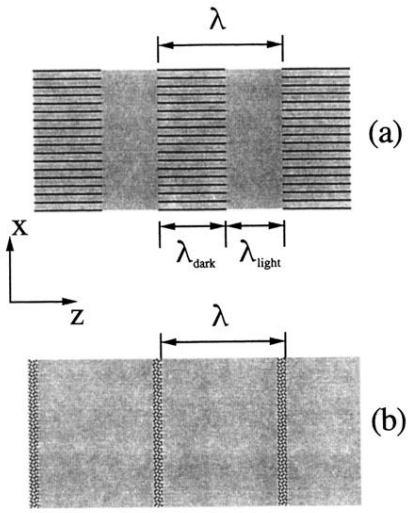

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