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An analytical model has been developed to describe solute partitioning during rapid solidification of binary alloys under local nonequilibrium conditions. The model takes into account deviations from equilibrium both at the solid–liquid interface according to the kinetic approach of Jackson et al. based on Monte Carlo simulations and in the bulk liquid using local nonequilibrium diffusion model (LNDM). The dimensionless growth parameter $\beta$ found in the Monte Carlo simulations as the important parameter for solute trapping has been modified for the local nonequilibrium diffusion case. An analytical expression has been developed for the velocity-dependent partition coefficient $K_{\text{LNDM}}(V)$ which predicts complete solute trapping and an abrupt transition from diffusion-controlled to diffusionless solidification when the interface velocity $V$ passes through the critical point $V=V_0$. The predictions are in good agreement with the experimental results, molecular dynamic studies, and Monte Carlo computer simulations.

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1. Introduction

Much of the current detailed understanding of rapid solidification of binary alloys under nonequilibrium conditions has been developed based on Monte Carlo computer simulations, which employ a detailed picture of the solid–liquid interface [1–3], and on local nonequilibrium diffusion model (LNDM) [4–7], which takes into account deviation from local equilibrium of solute diffusion in the bulk liquid. The most obvious manifestation of the deviations from equilibrium during rapid solidification is solute trapping which reduces the segregations at the solid–liquid interface. The degree of solute trapping is usually quantified by the partition coefficient $K$, defined as the ratio of the concentration of solute in the solid to that in the liquid at the interface. The effect of solute trapping has been investigated both theoretically and experimentally [1–3,5–15]. The most outstanding question in all these studies is transition to complete solute trapping $K(V)=1$ at high interface velocity $V$. Conventional modes of solute trapping result in $K(V)\to1$ only at $V\to\infty$. LNDM predicts complete solute trapping $K=1$ at a finite interface velocity [5–7]. The molecular dynamics simulations [8–10] and the experimental data [11–15] confirm the possibility of reaching the complete solute trapping at a finite interface velocity. The exact knowledge of the $K$ vs. $V$ relation is of considerable practical importance to model transition to diffusionless solidification, solute and disorder trapping, grain refinement, morphological stability and microstructure formation of commercial materials. Moreover, rapid solidification of binary alloys is of fundamental interest to physicists in the general context of the evolution of dynamic systems far from local equilibrium. To address this issue, we will incorporate the LNDM approach [4–7] into the Jackson et al. model [1–3] to take into account deviations from equilibrium both at the solid–liquid interface and in the bulk liquid.

2. Jackson et al. model

The probability that an atom will be trapped into a crystal depends on the ratio of the distance that the interface advances during this time to the distance that the atom can diffuse during this time [1–3]. The distance $L$ which a solute atom can move by diffusion during time $t$ is $L=(Dt)^{1/2}$. The parameter $L=(Dt)^{1/2}$ is usually defined as “diffusion length” and provides a measure of how far the concentration has propagated in the $X$-direction by diffusion in time $t$ in the laboratory reference frame. It is a consequence of a solution to parabolic diffusion equation (see Fig. 1 dashed line) that is valid at a relatively low interface velocity. The ratio of these two distances is the dimensionless parameter $\beta$ [1–3]:

$$\beta = \frac{Vt}{(Dt)^{1/2}} = \frac{(Vt_0u_0c)}{(D)^{1/2}}$$

(1)

where $u_0$ is the normalized difference between the rates at which atoms join and leave the crystal, and $c$ is the cube root of the atomic volume. The partition coefficient for small solute concentration takes the form [1–3]

$$K(V) = K_0^{1/(1+\beta)}$$

(2)
3. Solute diffusion under local nonequilibrium conditions

At high interface velocity the solute diffusion in the bulk liquid occurs under local nonequilibrium conditions and the solute concentration \( C(X) \) in the moving reference frame is governed by the hyperbolic diffusion equation [6]

\[
\frac{\partial C}{\partial t} + \frac{\partial^2 C}{\partial X^2} - V \frac{\partial C}{\partial X} = D \left( 1 - \frac{V^2}{V_D^2} \right) \frac{\partial^2 C}{\partial X^2} + W + \tau \frac{\partial W}{\partial t} \tag{3}
\]

where \( \tau \) is the relaxation time to local equilibrium, and \( W \) is the kinetic rate (source) function. In the laboratory reference frame the Fourier transformation \((\partial \delta x \to -i \omega, \partial \delta t \to -i \omega)\) of Eq. (3) gives the dispersion law

\[
-\omega^2 - \tau \omega^2 = -4D\chi
\tag{4}
\]

At the high-frequency limit \( \omega \to \infty \) Eq. (4) predicts a finite speed of the diffusive wave \( V_D = (D\chi)^{1/2} \) i.e. maximum speed with which the diffusion perturbations can propagate in the bulk liquid [4–7]. For steady-state regimes, solution to Eq. (3) can be expressed as

\[
C^*(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \frac{(1-\omega\tau)\exp(-\omega x)\eta(u)}{(1-\omega^2\tau^2)^{1/2}} \, du
\tag{5}
\]

where \( \eta(u) = \int_{-\infty}^{\infty} \omega(x) \exp(\omega x) \, dx \). \( \omega = V/V_D \) is nondimensional interface velocity, \( C^*(x) = (C(x) - C_0)/C_0 \) and \( x = XV/D \). Eq. (5) results in the solute concentration in the bulk liquid

\[
C_{\text{NDM}}(x) = (C_1 - C_0) \exp(-VX/D_{\text{NDM}}(V)) + C_0
\tag{6}
\]

where \( D_{\text{NDM}}(V) \) is the effective diffusion coefficient [5–7]; \( C_0 \) and \( C_1 \) are the solute concentration in the liquid far from \( (X \to \infty) \) and at the interface \( (X = 0) \), respectively. The effective diffusion coefficient \( D_{\text{NDM}} \) is shown in Fig. 2 (curve 2) as a function of nondimensional interface velocity \( \omega = V/V_D \). For \( V > V_D \) the solute concentration ahead of the interface \( C(X) = C_0 \) as \( D_{\text{NDM}}(V) = 0 \). It implies that when the interface velocity \( V \) passes through the critical point \( V = V_D \), an abrupt transition from diffusion controlled to diffusionless solidification occurs. The result arises due to the “wave” nature of solute diffusion under local nonequilibrium conditions and has a clear physical meaning: a source of perturbations (i.e. the interface) moving with a velocity greater than the maximum speed of perturbations cannot disturb the medium ahead of itself. Expression (6) yields the solute boundary layer

\[
\delta_{\text{NDM}}(V/V_D) = \begin{cases} D(1-V^2/V_D^2)/V_0, & V < V_D, \\ 0, & V > V_D \end{cases}
\tag{7}
\]

The boundary layer \( \delta_{\text{NDM}} \) (curve 3 in Fig. 2) shrinks more rapidly with increasing interface velocity, than expected from the classical mass transport theory (curve 4 in Fig. 2) and equals zero for \( V > V_D \).

Thus at high interface velocity \( V > V_D \) when solute diffusion occurs under local nonequilibrium diffusion conditions, the solute concentration has propagated in the X-direction of the laboratory reference frame a distance \( H = V_D t \) (see Fig. 1 solid line). From the microscopic point of view the diffusive speed \( V_D \) can be treated as the maximum speed with which an individual atom moves in X-direction in the bulk liquid. In this situation the distance that a solute atom can diffuse away from the interface in the moving reference frame is \( (V_D - V)t \). Hence, the probability that an atom will be trapped into the crystal under local nonequilibrium conditions, i.e. the ratio of the distance that the interface advances during time \( t \) to the distance that the atom can diffuse

Fig. 1. Schematic concentration profiles in the laboratory reference frame illustrating the diffusive distance. Solid line—concentration profile calculated from classical parabolic diffusion equation. Diffusive distance is \( L = (Dt)^{1/2} \). At \( t = \tau \) the concentration profiles coincide.

Fig. 2. Partition coefficient \( \beta \), Eq. (2a), (curve 1); nondimensional effective diffusion coefficient \( D_{\text{NDM}}/D \), Eq. (6), (curve 2); local nonequilibrium boundary layer \( D_{\text{NDM}} \), Eq. (7), (curve 3); local equilibrium boundary layer (curve 4); and partition coefficient \( K_{\text{NEMD}} \), Eq. (9), (curve 5) as functions of dimensionless interface velocity \( \omega = V/V_D \).

where \( K_e \) is equilibrium partition coefficient and \( A \) is a constant. For near equilibrium conditions when \( \beta \to 0 \) the partition coefficient \( K(V) \to K_e \). At the other extreme \( \beta \to \infty \) the partition coefficient \( K(V) \to 1 \). For a rough interface, the growth rate \( V \) is proportional to \( u_e [1,2] \), i.e. \( V = V_D u_e \), so that \( \beta \) is proportional to \( V \):

\[
\beta = V(a/V_D)^{1/2}
\]

where \( V_D \) is the atomic diffusion speed \( V_D \) in the Wilson–Frenkel expression for the diffusion controlled growth, or the thermal velocity of the atoms for growth which is not thermally activated [1,2]. Thus, \( K(V) \) takes the form

\[
K(V) = K_e^{1/(1 + A^\omega V)^\omega}
\tag{2a}
\]

where \( A^\omega = A(q/V_D)^{1/2} \). Taking into account that \( V_D = D/a \), we have \( A^\omega = A(V/V_D)^{-1/2} \), so that for diffusion controlled growth \( A^\omega = A/V_D \). Eq. (2a) predicts complete solute trapping \( K(V) \to 1 \) as \( V \to \infty \) (curve 1 in Fig. 2).
4. Discussion and comparison with experiment

Under local nonequilibrium diffusion conditions the modified trapping probability \(\beta_{\text{LNDM}}\) as \(V \rightarrow V_D\) implies complete solute trapping \(K^{\text{LNDM}}(V) \rightarrow 1\) at the finite interface velocity \(V = V_D\) (see Eq. (9) and Fig. 2 curve 5). Molecular dynamic studies [8–10] and the experimental data [11,12] have also shown the complete solute trapping at a finite interface velocity. The velocity dependence of the partition coefficient was measured for rapid solidification of polycrystalline Si-As alloys induced by pulsed laser melting [13,14]. The experimental results are compared with predictions of the Jackson et al. model, Eq. (2a), and LNDM, Eq. (9), on Fig. 3. The best fit is obtained for \(V_D = 2.8\) m/s, \(A = 5.5\), and \(A^* = 2.2\) s/m. The \(K\) vs. \(V\) experimental data obtained by pulsed laser melting of Ge-Si alloys [15] are shown in Fig. 4 together with the predictions of both Jackson et al. model and LNDM with \(V_D = 4.8\) m/s, \(A = 2.9\), and \(A^* = 0.8\) s/m. The values of \(A\) and \(A^*\) are in good agreement with those of Monte Carlo simulations [2,3] and theoretical prediction \(A^* = A/V_D\) for diffusion controlled growth. This implies that a best fit is obtained with approximately the same values of \(A\) for both models. The values of \(V_D\) are also consistent with those of other investigations [7–9,13,14].

The results presented in Figs. 3 and 4 show that at a relatively low interface velocity the Jackson et al. model fits the data well but the nonequilibrium partition coefficient \(K^{\text{LNDM}}(V)\) fits experimental data and molecular dynamic results better both at high and low interface velocity and predicts complete solute trapping \(K^{\text{LNDM}}(V) = 1\) for \(V > V_D\).

5. Conclusion

The work extends the most recent theory for interface kinetics due to Jackson et al. [1–3] by introducing a dimensionless parameter (trapping probability) \(\beta_{\text{LNDM}}\) that takes into account the local nonequilibrium solute diffusion effects. It can be used for Monte Carlo simulations of alloy solidification under local nonequilibrium conditions. The underlying physical picture for the extension, based on insights gained from LNDM, is that the solute concentration perturbations move with a finite velocity which may be on the order of or even less than the interface velocity. The model successfully describes the transition from diffusion controlled to diffusionless solidification with complete solute trapping for \(V \geq V_D\). The model can be used to study phase transformations and microstructure evolution during the processing of commercial materials under nonequilibrium conditions.

References


