Diffusionless Crystal Growth in Rapidly Solidifying Eutectic Systems

P. K. Galenko* and D. M. Herlach

Institute of Space Simulation, German Aerospace Center, Cologne 51170, Germany

(Received 25 January 2006; published 19 April 2006)

Using a local nonequilibrium model of solidification, experiments on rapid eutectic growth are analyzed. An analytical solution of a problem of rapid lamellar eutectic growth under local nonequilibrium conditions in the solute diffusion field is found. It is shown that solute diffusion-limited growth of a eutectic pattern is completely finished, and diffusionless growth of the chemically homogeneous crystalline phase begins to proceed at a critical point $V = V_D$, where V is the solid-liquid interface velocity and V_D is the solute diffusion speed in bulk liquid. A suppression of eutectic decomposition occurs in the range $V \geq V_D$ that results in a growth of homogeneous crystal phase with the initial (nominal) chemical composition of the binary system.

DOI: 10.1103/PhysRevLett.96.150602 PACS numbers: 05.70.Fh, 81.10.Aj, 81.30.Fb

Eutectic precipitation and growth is a well established phenomenon in which a liquid solidifies into a solid consisting of both an α phase and a β phase. To describe eutectic solidification, Jackson and Hunt [1] suggested a model of lamellar and rod coupled growth of α and β phases. This classic model for quasiequilibrium solidification describes the growth of α and β phases under control of the solute diffusion in bulk liquid and at the interface. The model [1] has a lot of interesting applications to interpret experiments on eutectic growth [2,3]. In particular, Trivedi, Magnin, and Kurz [4] extended the model to the case of solidification, in which the condition of quasiequilibrium at the interface is relaxed, that may play an essential role in rapid eutectic growth.

Experiments on rapid eutectic solidification give a sequence of morphological transformations with an increasing undercooling or cooling rate. In samples processed by electromagnetic levitation [5], it has been shown that a gradual transition from lamellar eutectic colonies to the anomalous (irregular) eutectic pattern occurs in a Co-25.5 at. % Sb alloy with increasing undercooling.

At higher rates of quenching (of the order of $\sim 10^5$–10^6 K/s), a transition to a completely chemically homogeneous crystalline microstructure with suppression of the eutectic transformation has been observed by Miroshnichenko [6,7]. Using x-ray and metallographic analysis, he showed that the transition has led to the crystalline phase with the initial (nominal) composition of the liquid.

Walder and Ryder [8] investigated microstructures of Ag-Cu alloys in a region of eutectic concentration in samples processed by a melt fluxing technique. For the Ag-Cu alloys, there is a critical solidification temperature at which the maximum recalescence rate rises abruptly by about 2 orders of magnitude, accompanied by significant changes in the microstructure. These authors tried to explain this behavior on the basis of a transition from diffusion-controlled growth of the eutectic to dendritic growth of a supersaturated phase.

Figure 1 exhibits a cross section of a thin film of Al-Mg alloy after quenching from the liquid by the splat-quenching method. At the surface where the quenching rate was highest, a supersaturated solid solution has crystallized. Within inner regions of the film which were cooled much more slowly, the solid has the typical eutectic microstructure. A transition from one type of structure to the other one is sharp. It testifies that the transition from one solidification mechanism to another one was sharp. For instance, it has been found that solidification with eutectic structure is finishing at a cooling rate of 5×10^5 K/s in Al-Mg alloys [9]. With the rates higher than 5×10^5 K/s, the rapid solidification gives rise to a supersaturated solid solution of an initial chemical composition. These drastic changes in microstructure can be interpreted as a sharp

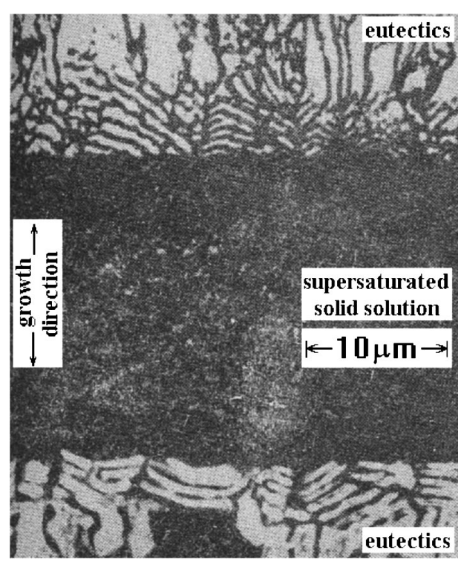

FIG. 1. Microstructure of a thin film after rapid quenching of a liquid binary Al-35 wt. % Mg system that is in a region of eutectic composition [7]. A transition in microstructure is clearly visible. The transition is sharp due to the abrupt change of solidification mechanism.

 © 2006 The American Physical Society

transition from partition solute diffusion transformation to chemically partitionless (diffusionless) transformation at a finite solidification velocity. Such transition leads to suppression of growth of stable phases and the appearance of a region of metastable solid solutions. Thus, it has been experimentally found that [6–9]: (i) the transition from eutectic growth to a homogeneous solid solution of the initial chemical composition may proceed in systems with eutectic or near eutectic composition at high cooling rates or deep undercoolings; (ii) the transition proceeds sharply; (iii) the transition proceeds with the finite fixed cooling rate, i.e., with fixed undercooling and finite solidification velocity.

Analyzing theoretical models of rapid eutectic growth [3,4], one can note that they predict the transition to the completely diffusionless solidification only with an infinite growth velocity V of α and β phases. This fact follows from the description of solute transport using Fick's model of diffusion, which assumes infinite speed V_D for solute diffusion propagation.

A model which extends a description of rapid crystal growth to the case of the finite diffusion speed has been formulated using local nonequilibrium conditions at the solid-liquid interface and in the solute diffusion field [10,11]. Quantitative analysis showed that the transition to diffusionless growth proceeds abruptly and with the finite interface velocity V equal to the solute diffusion speed V_D in bulk liquid [11,12]. Consequently, the local nonequilibrium model qualitatively satisfies the above points (ii) and (iii) for abrupt transition to diffusionless growth at the finite solidification velocity. In this Letter, we show that, in comparison with the model including local nonequilibrium on the interface only [3,4], the further extension of the model to the case of local nonequilibrium in a solute diffusion field allows us to describe a transition from eutectic growth to an apparently homogeneous structure in eutectic systems. In comparison with the problem of a single-phase solidification [10], we describe the diffusion problem of rapid two-phase solidification in an example of lamellar coupled growth.

Consider solidification of a binary system consisting of the atoms A and B and having the eutectic point with equilibrium temperature T_e and concentration C_e. Assume that undercooling ΔT below the eutectic point in the liquid provides a motion of the interface with the velocity V comparable with the solute diffusive speed $V_D = (D/\tau_D)^{1/2}$ in bulk liquid, where D is the diffusion constant and τ_D is the time for relaxation of solute diffusion flux to its steady-state value. We neglect the diffusion in α and β phases which have the form of the lamellar eutectic microstructure. Therefore, we accept one-sided model solidification in which a steady state occurs with the solid concentration C_s equal to the initial composition C_0 [10]. For further simplification, a kinetic phase diagram of phase state is taken such that the solute partitioning for both phases is described by the functions $k_\alpha = k_\beta = k \equiv C_s/C$, where k is the solute partitioning coefficient dependent on velocity V and C is the concentration of B atoms as a solute in the liquid. Then, for a steady-state regime, the 2D equation for the solute diffusion is given by [11,13]

$$\frac{\partial^2 C}{\partial x^2} + \left(1 - \frac{V^2}{V_D^2}\right)\frac{\partial^2 C}{\partial z^2} + \frac{V}{D}\frac{\partial C}{\partial z} = 0, \tag{1}$$

which is valid in reference frame (x, z) moving at constant velocity V with the interface $z = 0$. Boundary conditions are far-field with $z \to \infty$

$$C = C_0 = C_e + \Delta C_\infty, \tag{2}$$

symmetry conditions with $x = 0$ and $x = S_\alpha + S_\beta$

$$\frac{\partial C}{\partial x} = 0, \tag{3}$$

solute balance (conservation) at the interface for the α phase $(0 \le x < S_\alpha)$

$$-D\left(1 - \frac{V^2}{V_D^2}\right)\left(\frac{\partial C}{\partial z}\right)_{z=0} = V(1-k)C^*_{l\alpha}, \tag{4}$$

and solute balance (conservation) at the interface for the β phase $(S_\alpha \le x < S_\alpha + S_\beta)$

$$\begin{aligned} -D\left(1 - \frac{V^2}{V_D^2}\right)\left(\frac{\partial C}{\partial z}\right)_{z=0} &= V(1-k)C^*_{l\beta} \\ &= V(1-k)(1 - C^*_{l\alpha}). \end{aligned} \tag{5}$$

Here ΔC_∞ is the difference between initial concentration C_0 and the eutectic concentration C_e, $C^*_{l\alpha}$ and $C^*_{l\beta}$ are the concentrations on the α phase and β phase in the liquid, respectively, S_α and S_β are half the interlamellar spacing for each phase, and $\lambda = 2(S_\alpha + S_\beta)$ is the lamellar spacing.

For solution of Eq. (1), we introduce the notation $\tilde{C}(x, z) = C(x, z) - C_0$ and apply the method of separation of variables: $\tilde{C}(x, z) = P(x)Q(z)$. Substituting this notation into Eq. (1), one gets

$$\left(1 - \frac{V^2}{V_D^2}\right)\frac{1}{Q}\frac{d^2 Q}{dz^2} + \frac{V}{D}\frac{1}{Q}\frac{dQ}{dz} = -\frac{1}{P}\frac{d^2 P}{dx^2} = \eta, \tag{6}$$

where η is the separation variable.

The first equation

$$\left(1 - \frac{V^2}{V_D^2}\right)\frac{d^2 Q}{dz^2} + \frac{V}{D}\frac{dQ}{dz} - Q\eta = 0 \tag{7}$$

from Eq. (6) has the following solution:

$$\begin{aligned} Q(z) = Q_1 \exp\left(-\frac{V + [V^2 + 4D^2(1 - V^2/V_D^2)\eta]^{1/2}}{2D(1 - V^2/V_D^2)}z\right) \\ + Q_2 \exp\left(-\frac{V - [V^2 + 4D^2(1 - V^2/V_D^2)\eta]^{1/2}}{2D(1 - V^2/V_D^2)}z\right), \end{aligned} \tag{8}$$

where Q_1 and Q_2 are the integration constants. Solution (8) must be limited at $z \to \infty$ and it must be real for any value of η. Then it gives the following particular solution:

$$Q(z) = Q_1 \exp\left\{-\left(\frac{V}{2D(1 - V^2/V_D^2)} + \left[\left(\frac{V}{2D(1 - V^2/V_D^2)}\right)^2 + \eta\right]^{1/2}\right)z\right\}, \quad V < V_D,$$
$$Q(z) = 0, \quad V \geq V_D. \tag{9}$$

Note that, if the interface velocity V is equal to or greater than the diffusion speed, $V \geq V_D$, both constants of integration in the general solution (8) have zero value: $Q_1 = 0$ due to limited solution far from the interface with $z \to \infty$ and one has $Q_2 = 0$ for obtaining a real solution for $Q(z)$. Therefore, in particular, from solution (9) we have two radically different kinds of regimes: a regime with $V < V_D$ and a regime with $V \geq V_D$.

The second equation

$$\frac{d^2P}{dx^2} + P\eta = 0 \tag{10}$$

from Eq. (6) has the following solution:

$$P(x) = P_1 \cos(\eta^{1/2}x) + P_2 \sin(\eta^{1/2}x). \tag{11}$$

Using boundary condition (3), one can obtain integration constants P_1 and P_2 in Eq. (11). First, $P_2 = 0$ from the condition $(dP/dx)_{x=0} = 0$. Second, with $P_1 \neq 0$ one has from condition $(dP/dx)_{x=S_\alpha+S_\beta} = 0$ that $\eta_n = (n\pi/(S_\alpha + S_\beta))^2$, where n belongs to a set of integer numbers. Consequently, solution (11) takes the following particular form:

$$P(x) = P_n \cos b_n x, \qquad b_n = \frac{n\pi}{S_\alpha + S_\beta}. \tag{12}$$

Now taking Eqs. (9) and (12), using absolute values for concentration, and taking condition (2), the following solution of Eq. (1) is obtained:

$$C(x, z) = C_0 + B_0 \exp\left\{-\frac{Vz}{D(1 - V^2/V_D^2)}\right\} + \sum_{n=1}^{\infty} B_n \cos(b_n x) \exp(-\omega_n z), \quad V < V_D,$$
$$C(x, z) = C_0, \quad V \geq V_D, \tag{13}$$

where

$$\omega_n = \frac{V}{2D(1 - V^2/V_D^2)} + \left[\left(\frac{V}{2D(1 - V^2/V_D^2)}\right)^2 + b_n^2\right]^{1/2}. \tag{14}$$

In Eq. (13), the Fourier coefficients can be found from balances (4) and (5). Integration along the interfaces of the α phase and β phase is given by

$$-D\left(1 - \frac{V^2}{V_D^2}\right)\int_0^{S_\alpha}\left(\frac{\partial C}{\partial z}\right)_{z=0} dx = V(1 - k)\int_0^{S_\alpha} C_{l\alpha}^* dx,$$
$$-D\left(1 - \frac{V^2}{V_D^2}\right)\int_{S_\alpha}^{S_\alpha+S_\beta}\left(\frac{\partial C}{\partial z}\right)_{z=0} dx = V(1 - k)\int_{S_\alpha}^{S_\alpha+S_\beta}(1 - C_{l\alpha}^*) dx, \tag{15}$$

where $C_{l\alpha}^*$ is the interfacial concentration given by Eq. (13) for $V < V_D$ and $z = 0$. After integration, one gets

$$B_n = \frac{S_\alpha S_\beta b_n V(1 - k)}{[\omega_n D(1 - V^2/V_D^2) - V(1 - k)]\sin(b_n S_\alpha)},$$
$$B_0 = \frac{1 - k}{k}\frac{C_0 S_\alpha - (1 - C_0)S_\beta}{S_\alpha + S_\beta}, \tag{16}$$

where it has been taken into account that, in a steady-state regime of solidification, solid concentration is defined as the initial concentration C_0; therefore, it has been taken $C_{l\alpha}^* = C_0/k(V)$.

A comparison with previous solutions may be outlined. First, the solution given by Eqs. (13), (14), and (16) shows that, in contrast with the classic solution of Jackson and Hunt [1], the term with $V/2D$ is not negligible in comparison with b_n given by Eq. (12) for exponent (14). In the present description, the term $V/[2D(1 - V^2/V_D^2)]$ in the exponent becomes a valuable function of V, particularly with $V \sim V_D$. Second, solutions (13), (14), and (16) transform into the previous solution [3] for local equilibrium diffusion in the limit $V_D \to \infty$. Third, excluding periodicity, i.e., when $b_n = 0$, solution (13) describes concentrational profiles for a single-phase solidification with finite solute diffusion speed V_D [10,13].

As follows from Eq. (13) and qualitatively shown in Fig. 2, diffusion ahead of the solid-liquid interface is finishing and diffusionless growth without solute redistribution begins at the critical velocity $V = V_D$. Miroshnichenko [7] provided an experimental diagram "maximal undercooling ΔT prior to solidification" as a function of "cooling rate $\partial T/\partial t$" in small samples of a number of aluminum alloys (including the Al-Mg alloy discussed in Fig. 1). He showed that, for samples with linear size of a few millimeters or centimeters, the cooling rates of the order of

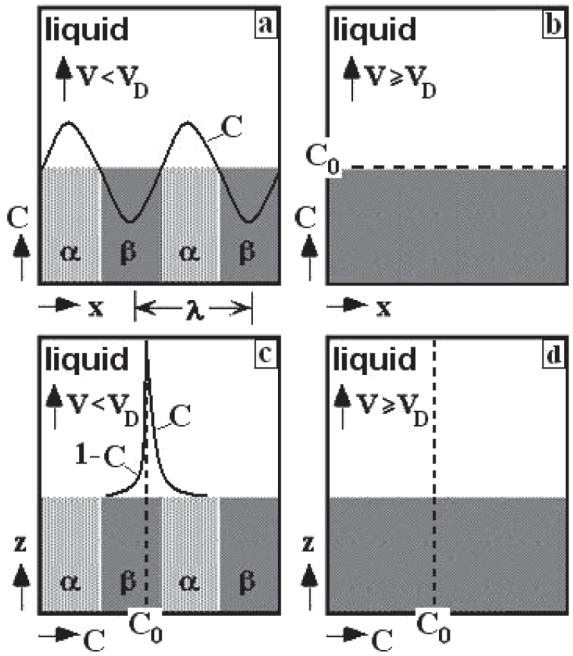

FIG. 2. Concentrational profiles $C(x, z)$ predicted by solutions (13)–(16). The dashed line shows initial (nominal) concentration C_0. (a),(b) Transverse solute distribution along the x axis. (c),(d) Longitudinal solute distribution along the z axis.

10^5–10^6 K/s provide undercooling of 150–300 K. Assuming the sample size as $l = (1\text{–}3) \times 10^{-3}$ m and isotherm associated with the growth interface, one may evaluate the growth velocity as $V \cong (\partial T/\partial t)(l/\Delta T) = (10^5\text{–}10^6) \times (1\text{–}3) \times 10^{-3}/(150\text{–}300) \cong 1\text{–}10\,\mathrm{m/s}$. This numeric evaluation shows that the interface can move with the velocity of the order of the diffusion speed $V \sim V_D \approx 1\text{–}10$ m/s [10–12]. Therefore, one may assume that the critical velocity $V = V_D$ is accessible and diffusionless solidification for eutectic systems is possible.

With $V \geq V_D$, atoms have no time to move out of the interface due to atomic diffusion jumps. They become "frozen" in comparison with intensive attachment of atoms to the interface, which provides crystal growth. In such a case, transformation can be considered as diffusionless transformation and, following solution (13), a suppression of eutectic precipitation and growth occurs. Even though the initial content of the liquid is equal to the eutectic concentration, solidification with $V \geq V_D$ proceeds without eutectic decomposition, and a chemically homogeneous solid grows with an initial content $C = C_0$.

As a final note, solution (13) has a general meaning: A source of concentrational inhomogeneities, i.e., a solid-liquid interface, moving at a velocity V equal to or higher than the maximum speed V_D of these inhomogeneities cannot disturb the medium ahead of itself. With regard to the considered growth of lamellar eutectic microstructure, solution (13) proves the existence of the experimentally observed transition (i) from eutectic microstructure to homogeneous solid solution of initial concentration that occurs (iii) at a fixed solidification velocity $V = V_D$. With regard to the above point (ii), one may note that the solution (13) gives two different regimes for $V < V_D$ and $V \geq V_D$. The latter one satisfies boundary conditions (4) and (5) only for zero diffusion fluxes: $J_\alpha = V(C^*_{l\alpha} - C^*_{s\alpha}) = 0$ and $J_\beta = V(C^*_{l\beta} - C^*_{s\beta}) = 0$. It requires the conditions $C^*_{s\alpha}/C^*_{l\alpha} = 1$, $C^*_{s\beta}/C^*_{l\beta} = 1$, and $k(V \geq V_D) = 1$, which are main features of the diffusionless process. These conditions have to lead to infinite interlamellar spacing. Indeed, as has been shown in Ref. [3], $\lambda \propto k(1-k)^{-1}$ with large V. At $k(V \geq V_D) = 1$, one gets $\lambda \to \infty$, which means infinite increasing of interlamellar spacing and transition to the only phase [14]. Therefore, for further proving existence of the abrupt transition (ii), it is necessary to analyze the self-consistent model of eutectic solidification which must take into account nonequilibrium solute trapping [described by a specific form of nonequilibrium solute partitioning function $k(V)$] and slopes of liquidus and solidus in the kinetic phase diagram. In such a case, one may expect to describe the abrupt transition from the diffusion-limited growth to diffusionless growth at $V = V_D$ as has been shown for dendritic growth [11] and growth of a planar interface [12].

This work was performed with support from the German Research Foundation (DFG), Project No. He 1601/13.

*Electronic address: Peter.Galenko@dlr.de

[1] K. A. Jackson and J. D. Hunt, Trans. Metall. Soc. AIME **236**, 1129 (1966).
[2] W. Kurz and P. R. Sahm, *Gerichtet Erstarrte Eutektische Werkstoffe* (Springer, Berlin, 1975); R. Elliot, *Eutectic Solidification Processing* (Butterworths, London, 1983).
[3] W. Kurz and D. J. Fisher, *Fundamentals of Solidification* (Trans Tech Publications, Aedermannsdorf, Switzerland, 1992), 3rd ed.
[4] R. Trivedi, P. Magnin, and W. Kurz, Acta Metall. **35**, 971 (1987); W. Kurz and R. Trivedi, Metall. Trans. **22A**, 3051 (1991).
[5] B. Wei, D. M. Herlach, and F. Sommer, J. Mater. Sci. Lett. **12**, 1774 (1993).
[6] I. S. Miroshnichenko, in *Growth and Imperfections of Metallic Crystals*, edited by D. E. Ovsienko (Naukova Dumka, Kiev, 1972), p. 385.
[7] I. S. Miroshnichenko *Quenching from the Liquid State* (Metallurgia, Moscow, 1982).
[8] S. Walder and P. L. Ryder, J. Appl. Phys. **74**, 6100 (1993).
[9] I. S. Miroshnichenko and I. M. Galushko, in *Kinetics and Mechanism of Crystallization*, edited by N. N. Sirota (Nauka i Tehnika, Minsk, 1973), p. 356.
[10] P. Galenko and S. Sobolev, Phys. Rev. E **55**, 343 (1997).
[11] P. K. Galenko and D. A. Danilov, Phys. Lett. A **235**, 271 (1997); J. Cryst. Growth **197**, 992 (1999).
[12] P. K. Galenko, Mater. Sci. Eng. A **375–377**, 493 (2004).
[13] P. K. Galenko and D. A. Danilov, Phys. Rev. E **69**, 051608 (2004).
[14] A question about selection of the α phase or β phase is a specific task which can be considered through analysis of the function $\lambda = f(V, \Delta T)$.