On the solution of solute diffusion during eutectic growth

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ABSTRACT

An exact solution of solute diffusion for the stoichiometric-compound/stoichiometric-compound eutectic is derived for a planar interface. Compared with the previous work, the solution is consistent with the kinetics of triple-junction, i.e. the eutectic composition is necessarily found at the triple-junction. Adopting an averaged conservation law at the interface, a general solution is proposed for any kind of eutectics and phase diagrams. Simulation results in the Ni_5Si_2–Ni_3Si eutectic growth show that the general solution is a good approximation. The current work makes it possible to incorporate the kinetics of triple-junction into the eutectic growth model.

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1. Introduction

Eutectic alloys are important because of their low melting points, good casting properties and excellent mechanical properties [1–5]. They are important model systems for the pattern formation due to their particularly rich variety of interfacial instabilities [6,7]. They are important for designing the composition of bulk metallic glass because of their potential high glass-forming ability (e.g. alloys with lower liquidus temperature near the eutectic point) [8–10]. Therefore, it is quite an important theoretical and practical topic to model eutectic growth.

The first step for modeling is to solve the diffusion equation. In the pioneering work of Jackson and Hunt (JH) [11], the solute diffusion field in the liquid is approximately described by that of a planar interface, the concentration on the liquid side of which is given approximately by the equilibrium eutectic composition. The solution was extended recently to the multi-phase eutectic growth [12] and the eutectoid transformation with non-negligible solute diffusion in the growing phases [13]. This kind of solution [11–13] limits itself to sufficiently small undercoolings. Donaghey and Tiller (DT) [14] derived the solution in which the concentration variation along the planar interface is taken into account. In order to obtain some physical insights into rapid eutectic growth, Trivedi–Magnin–Kurz (TMK) [15] simplified the DT solution [14] to two types of phase diagram: one cigar-shaped in which the liquidus and the solidus are parallel below the eutectic

temperature and the other in which the equilibrium partition coefficients are constant and equal. An extension of the TMK solution [15] to the case where both the interface and solute diffusion are under local non-equilibrium conditions was carried out by Galenko and Herlach [16]. This kind of solution [14–16] is rigorously applicable to the dilute solid-solution alloy systems with linear liquidus and solidus, even though it is applicable to rapid solidification and widely used [17–23].

The growing phase during eutectic growth can be a solid-solution phase (SSP), a stoichiometric compound (SC) or a non-stoichiometric compound (NSC). The binary-phase eutectics are then according to the growing phases divided into six different kinds, i.e. the SSP–SSP, SSP–SC, SSP–NSC, SC–SC, SC–NSC and NSC–NSC eutectics. Their eutectic phase diagrams can deviate from the linear assumption so substantially that both the DT [14] and TMK [15] solutions cannot be used. One common ground of the JH [11], DT [14] and TMK [15] solutions is that the eutectic composition is not necessarily found at the triple-junction (TJ). This is inconsistent with the kinetics of TJ, even though it is clearly written in the textbooks [24,25] and shown by the numerical solution [26] for eutectic growth with the same boundary conditions as the JH model [11]. For example, the TJ as the interaction of interfaces should follow the interface kinetics. For a binary-phase eutectic where two solids α and β are crystallized from one liquid L (Fig. 1), the TJ belongs to and thus follows the kinetics of both the α/L and the β/L interfaces. In the case of a planar interface, the TJ is the position where the growing α and β phases, in front of which is the same liquid concentration, share the same tangent with the liquid L under equilibrium conditions or the same growth velocity under non-equilibrium conditions in the mole Gibbs energy diagram, i.e. the kinetics of TJ is closely related to the eutectic point in the kinetic

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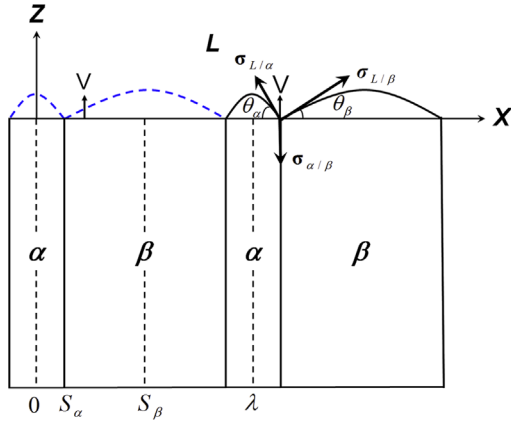*E-mail addresses:* haifengw81@nwpu.edu.cn, Haifeng.Wang@dlr.de (H. Wang).

Fig. 1. A schematic diagram for modeling eutectic growth. A planar interface is adopted to obtain the solution of solute diffusion in the liquid.

phase diagram. Appendix A shows the equilibrium and non-equilibrium phase diagrams and the evolution of kinetic eutectic point of the Ni$_5$Si$_2$–Ni$_3$Si (γ–δ) eutectic system. As the increase of growth velocity, the eutectic composition (temperature) increases (decreases) considerably. This kinetic condition of TJ, however, cannot be incorporated into all the previous work [11–23].

The current work aims to propose a general solution of solute diffusion for the lamellar eutectic growth under rapid solidification conditions. The solution with the kinetic condition of TJ as one inevitable boundary condition is applicable to any kind of eutectics and phase diagrams. In what follows, the solute diffusion field is described firstly for the SC–SC eutectic that is quite important for the preparation of advanced materials [2–5] (Section 2). The exact solution without any assumption for the phase diagram shows that the eutectic composition is necessarily found at the TJ and is consistent with the kinetics of TJ. After that, an averaged mass conservation law at the interface is proposed to obtain the general solution. A comparative study among the JH, exact and general solutions is carried out for the γ–δ eutectic growth in the Ni–Si alloy system to show that the averaged method is a good approximation (Section 3). Our conclusions are summarized in Section 4.

2. Solution of solute diffusion during eutectic growth

Fig. 1 shows a schematic diagram of the binary-phase eutectic growth. The lamellar spacing is λ and, half widths of the lamellar α and β are S_α and S_β respectively. Attaching coordinate system to the growing interface with a constant velocity V in the Z direction, the diffusion equation in the liquid is given by

$$\frac{\partial^2 C_L}{\partial X^2}+\frac{\partial^2 C_L}{\partial Z^2}+\frac{V}{D_L}\frac{\partial C_L}{\partial Z}=0 \tag{1}$$

The boundary condition far from the interface is

$$C_L = C_\infty \text{ at } Z = \infty \tag{2}$$

and the periodic conditions are

$$\frac{\partial C_L}{\partial X}=0 \text{ at } X=0 \text{ and } X=S_\alpha+S_\beta \tag{3}$$

here C_L is the solute concentration in the liquid, C_∞ is the concentration far from the interface and D_L is the solute diffusion coefficient. A general solution of Eq. (1) with the boundary conditions Eqs. (2) and (3) is given by DT [14] as

$$C_L = C_\infty + \sum_{n=0}^{\infty} B_n \cos(b_n X)\exp\left(-\frac{VZ}{D_L}\omega_n\right) \tag{4}$$

where $b_n = 2n\pi/\lambda$ and $\omega_n = [1+\sqrt{1+(2n\pi/P_e)^2}]/2$ with $P_e = V\lambda/2D_L$ the Peclet number. The Fourier coefficient B_n ($n = 0, 1, 2, ...$) can be evaluated from the mass conservation law at the interface

$$-\frac{D_L}{V}\frac{\partial C_L}{\partial Z}\Big|_{Z=0} = \begin{cases} C_{L\alpha}^* - C_\alpha^* & , \quad 0 \le X < S_\alpha \\ C_{L\beta}^* - C_\beta^* & , \quad S_\alpha < X \le S_\alpha + S_\beta \end{cases} \tag{5}$$

where $C_{L\alpha}^*$, $C_{L\beta}^*$, C_α^* and C_β^* are the concentrations at the interface.

If α and β are both SC, the concentrations in the solid C_α and C_β are the constant, and so are the concentrations at the interface C_α^* ($=C_\alpha$) and C_β^* ($=C_\beta$). Combining Eq. (4) with Eq. (5) yields

$$C_\infty = f_\alpha C_\alpha + f_\beta C_\beta \tag{6}$$

$$B_n = \frac{2}{n\pi\omega_n}(C_\beta - C_\alpha)\sin n\pi f_\alpha \quad , \quad n \ge 1 \tag{7}$$

where $f_\alpha = S_\alpha/(S_\alpha+S_\beta)$ and $f_\beta = S_\beta/(S_\alpha+S_\beta)$ are the volume fractions of α and β in the solid, and $\overline{\omega}_n = [-1+\sqrt{1+(2n\pi/P_e)^2}]/2$. In contrast to all the previous work [11–16], it is the global mass conservation law (Eq. (6)) but not the Fourier coefficient B_0 that is derived. Therefore, one more boundary condition is needed. From the kinetics of TJ (Appendix A), the liquid concentration at TJ C_L^{TJ} equals to the eutectic composition C_E

$$C_L^{TJ} = C_E \tag{8}$$

Then, integrating Eqs. (4) and (8), we have

$$B_0 = C_E - C_\infty - \sum_{n=1}^{\infty} B_n \cos(n\pi f_\alpha) \tag{9}$$

In other words, the kinetic condition of TJ is inevitable to derive the exact solution (Eqs. (4), (7) and (9)) for the SC–SC eutectic.

If the growing phase is the SSP or the NSC, the solid and liquid concentrations vary along the interface and the partition coefficient is generally concentration dependent. In this case, the diffusion equation cannot be solved analytically. Since what concerned in the eutectic growth model are the averaged interface kinetic conditions [11–13,15,17–23], an averaged mass conservation law at the interface (i.e. the averaged method)

$$-\frac{D_L}{V}\frac{\partial C_L}{\partial Z}\Big|_{Z=0} = \begin{cases} \overline{C}_{L\alpha}^* - \overline{C}_\alpha^* & , \quad 0 \le X < S_\alpha \\ \overline{C}_{L\beta}^* - \overline{C}_\beta^* & , \quad S_\alpha < X \le S_\alpha + S_\beta \end{cases} \tag{10}$$

is proposed currently to obtain an analytical solution. Here $\overline{C}_{L\alpha}^*$ ($\overline{C}_{L\beta}^*$) and $\overline{C}_\alpha^*$ ($\overline{C}_\beta^*$) are the averaged concentrations of liquid and solid at the α/L (β/L) interface. Similarly, combining Eq. (4) with Eq. (10), we have

$$C_\infty = f_\alpha \overline{C}_\alpha^* + f_\beta \overline{C}_\beta^* \tag{11}$$

$$B_n = \frac{[2\sin(n\pi f_\alpha)/\omega_n n\pi](\overline{C}_\beta^* - \overline{C}_\alpha^*)}{[1-\sum_{m=1}^{\infty} 2\sin^2(m\pi f_\alpha)/\omega_m m^2\pi^2 f_\alpha f_\beta]}, \quad n \ge 1 \tag{12}$$

One can see, the kinetic condition of TJ (Eq. (8)) is also inevitable to obtain B_0 (Eq. (9)). Since no assumption is applied for the properties of eutectic system, Eqs. (4), (9) and (12) are actually a general solution for any kind of eutectics and phase diagrams. For the SC–SC eutectic system, $\overline{C}_\alpha^* = C_\alpha$ and $\overline{C}_\beta^* = C_\beta$ and the general solution is a good approximation; please see the calculation results in Section 3. Otherwise, there can be one, two or three averaged interface kinetic conditions at the α/L or the β/L interface depending on the different interface kinetics for the SC [27], SSP [28,29] and NSC [30–32]. In this case, not only $\overline{C}_{L\alpha}^*$ and $\overline{C}_{L\beta}^*$ but also $\overline{C}_\alpha^*$ (only α is not a SC) or $\overline{C}_\beta^*$ (only β is not a SC) or $\overline{C}_\alpha^*$ and $\overline{C}_\beta^*$ (both α and β are not SCs) should be determined by the eutectic growth model, the derivation of which is out the scope of current work.