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Diffusion dominated process for the crystal growth of a binary alloy

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Abstract

The pure diffusion process has been often used to study the crystal growth of a binary alloy in the microgravity environment. In the present paper, a geometric parameter, the ratio of the maximum deviation distance of curved solidification and melting interfaces from the plane to the radius of the crystal rod, was adopted as a small parameter, and the analytical solution was obtained based on the perturbation theory. The radial segregation of a diffusion dominated process was obtained for cases of arbitrary Peclet number in a region of finite extension with both a curved solidification interface and a curved melting interface. Two types of boundary conditions at the melting interface were analyzed. Some special cases such as infinite extension in the longitudinal direction and special range of Peclet number were reduced from the general solution and discussed in detail.

1. Introduction

The convection driven by buoyancy is greatly reduced in the microgravity environment, which may be beneficial to the crystal growth. In general, the diffusion process for crystal growth of a binary alloy will couple with the processes of heat transfer and convection driven by non-buoyancy effects such as thermal and/or solutal capillary convection and phase change convection, see for examples Refs. [1,2]. However, the diffusion dominated process during unidirectional solidification of a binary alloy may be suggested, especially in the microgravity environment under certain conditions as discussed by Coriell and co-authors [3,4], who analyzed a curved solid–liquid interface both slightly deviated from planarity [3] and with a large departure from planarity [4] in the Cartesian coordinate system. Recently, the subject was re-studied by an asymptotic theory for the case of large Peclet number in the Cartesian coordinate system, and the longitudinal coordinate was transformed by dividing by the Peclet number [5]; it seems that this solution is limited to a very small deviation of the curved solidification interface from planarity, in addition to a thin boundary layer of larger Peclet number.

Although the complete equations, including conservation of mass, momentum, energy and concentration, may be solved numerically, see for example Refs. [1,2], however, the analytical solutions for a simplified model may give the clear physical picture for mechanism studies. Recently, the influence of convection on the lateral segregation was also analytically discussed for a limited case of quasi diffusion regime [6]. The results show that

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the influence of convection has the same effect on lateral segregation as the curved solidification interface in order of magnitude.

In the present paper, the radial segregation during unidirectional solidification of a binary alloy with a curved solidification interface and curved melting interface is analyzed for a cylindrical crystal with finite extension in the longitudinal direction, and the steady-state concentration field for arbitrary Peclet number is obtained by perturbation theory based on a small geometrical parameter. Two types of boundary conditions at the melting interface, denoted as case a and case b, are discussed. In the next section, the perturbation theory for the problem is presented. The solutions for zero order and for the first order are given respectively in Sections 3 and 4. The radial segregation at the solidification interface for case b is analyzed in Section 5. Several examples of case a including large Peclet number and small Peclet number, are analyzed in Section 6. The last section is discussions and conclusions.

2. Perturbation theory

Analyzing a finite liquid region of cylindrical alloy with radius a and height l, the cylindrical coordinate (r, θ, z) is adopted as shown in Fig. 1, and the axisymmetric assumption is used. The liquid is confined by a upper curved melting interface and a lower curved solidification interface. The origin of the coordinate is located at the symmetric center of solidification interface moving with a constant pulling velocity V as discussed in Ref. [3]. Then, the basic equation of solute concentration C in the liquid may be written as

$$\nabla^2 C + \frac{V}{D}\frac{\partial C}{\partial z} = 0, \tag{2.1}$$

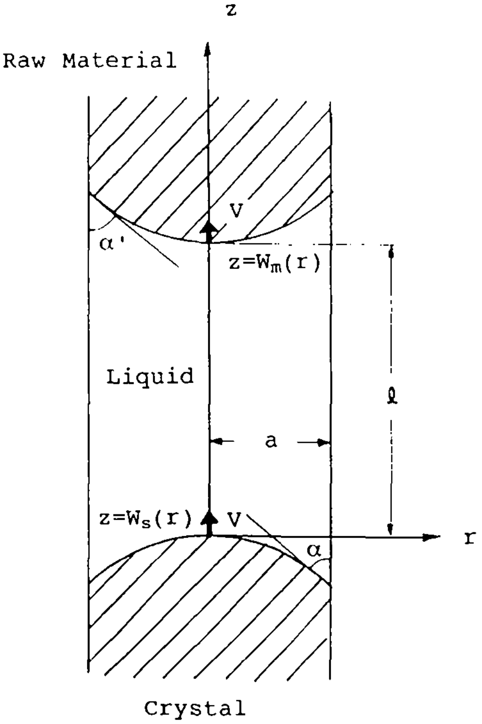

Fig. 1. The schematic diagram of diffusion crystal growth with two curved solid/liquid interfaces.

where D is the diffusion coefficient and $\nabla^2 = (\partial^2/\partial r^2) + (1/r)(\partial/\partial r) + (\partial^2/\partial z^2)$ the Laplace operator in the cylindrical coordinate system. The boundary conditions may be given as

$$D\left(\frac{\partial C}{\partial z} - \frac{\mathrm{d}W_s}{\mathrm{d}r}\frac{\partial C}{\partial r}\right) + V(1-k)C = 0, \quad \text{at } z = W_s(r), \tag{2.2}$$

$$\frac{\partial C(0,z)}{\partial r} = 0, \quad \frac{\partial C(a,z)}{\partial r} = 0, \tag{2.3}$$

where k is the partition coefficient, the ratio of the solid solute concentration C_s to the liquid solute concentration C at solidification interface $z = W_s(r)$. The boundary condition at melting interface $z = W_m(r)$ may be given by two sorts, that is

$$\text{(a)}\quad C(r,z) = C_l(r), \quad \text{at } z = W_m(r). \tag{2.4a}$$

$$\text{(b)}\quad D\left(\frac{\partial C}{\partial z} - \frac{\mathrm{d}W_m}{\mathrm{d}r}\frac{\partial C}{\partial r}\right) - V(C_l - C) = 0, \quad \text{at } z = W_m(r), \tag{2.4b}$$

where $C_l(r)$ in (2.4a) and (2.4b) denote the concentration at the melting interface. Usually, the models of infinite extension were discussed as in Ref. [3–5], and associated with the condition (2.4a) when $W_m(r) = l \to \infty$. In fact, the numerical simulation of Ref. [4] cuts the region of infinite extension into a finite one, and corresponds to the boundary condition (2.4a) with finite l. Both boundary conditions (2.4a) and (2.4b) are usually applied in different articles. A symmetric condition is required as in the first relationship of (2.3) for concentration, and should be satisfied also for other quantities such as the interface configuration $\mathrm{d}W_m(0)/\mathrm{d}r = 0$ and $\mathrm{d}W_s(0)/\mathrm{d}r = 0$. Then, the problem of the diffusion process reduces to solving Eq. (2.1) with the boundary conditions (2.2)–(2.4).

As discussed in Ref. [3], the radii of the curvatures of the interfaces are usually much larger than the radius of the alloy cylinder. Therefore, a small geometrical parameter may by selected as

$$\epsilon = \frac{\max\left[\max(|W_s(r) - W_s(0)|), \max(|W_m(r) - W_m(0)|)\right]}{a} \ll 1, \tag{2.5}$$

and is independent of how large the order of magnitude of the physical parameters such as the Peclet number. By application of perturbation theory, the quantities may be expressed as follows

$$C(r,z) = \sum_{n=0}^{\infty} \epsilon^n C_n(r,z), \quad W_s(r) = \sum_{n=1}^{\infty} \epsilon^n W_{sn}(r), \quad W_m(r) = \sum_{n=1}^{\infty} \epsilon^n W_{mn}(r). \tag{2.6}$$

Substituting these expansions into the basic equation and boundary conditions, the problem may be, then, solved order by order. The equation and boundary conditions for zero order are

$$\frac{\partial^2 C_0}{\partial r^2} + \frac{1}{r}\frac{\partial C_0}{\partial r} + \frac{\partial^2 C_0}{\partial z^2} + \frac{V}{D}\frac{\partial C_0}{\partial z} = 0, \tag{2.7}$$

$$\frac{\partial C_0(r,0)}{\partial z} + \frac{V}{D}(1-k)C_0(r,0) = 0, \tag{2.8}$$

$$\frac{\partial C_0(0,z)}{\partial r} = 0, \quad \frac{\partial C_0(a,z)}{\partial r} = 0, \tag{2.9}$$

$$C_0(r,l) = C_l(r), \tag{2.10a}$$

$$\frac{\partial C_0(r,l)}{\partial z} + \frac{V}{D}C_0(r,l) = \frac{V}{D}C_l(r). \tag{2.10b}$$

The problem of zero order (2.7)–(2.10) is the problem with both plane solidification interfaces. Hence, the equation and boundary conditions for higher order could be demonstrated step by step. It could be seen that the problem for each order becomes linear, and could be solved analytically by the expansion of eigenfunctions in principle.

3. Solution of zero order

Due to the boundary condition (2.9) and the linear relationships (2.8) and (2.10), the finite Hankel transform [7] may be introduced as

$$H_i^{(0)}(z) = H^{(0)}(\alpha_i, z) = \int_0^a r C_0(r, z) J_0(\alpha_i r)\,\mathrm{d}r, \tag{3.1}$$

and the reverse transform gives the solution of zero order as

$$C_0(r, z) = \frac{2}{a^2} \sum_{i=1}^{\infty} H_i^{(0)}(z) \frac{J_0(\alpha_i r)}{[J_0(\alpha_i a)]^2}, \tag{3.2}$$

where α_i satisfies the condition

$$J_0'(\alpha_i a) = 0. \tag{3.3}$$

By application of the transfer relations, the problem of zero order reduces to the problem of an ordinary differential equation

$$\frac{\mathrm{d}^2 H_i^{(0)}}{\mathrm{d}z^2} + \frac{V}{D} \frac{\mathrm{d}H_i^{(0)}}{\mathrm{d}z} - \alpha_i^2 H_i^{(0)} = 0, \tag{3.4}$$

$$\frac{\mathrm{d}H_i^{(0)}(0)}{\mathrm{d}z} + \frac{V}{D}(1-k) H_i^{(0)}(0) = 0, \tag{3.5}$$

$$H_i^{(0)}(l) = f_i \tag{3.6a}$$

or

$$\frac{\mathrm{d}H_i^{(0)}(l)}{\mathrm{d}z} + \frac{V}{D} H_i^{(0)}(l) = \frac{V}{D} f_i, \tag{3.6b}$$

where the coefficients f_i are defined as

$$f_i = \int_0^a r C_l(r) J_0(\alpha_i r)\,\mathrm{d}r. \tag{3.7}$$

The general solution of zero order is obtained as follows:

$$C_0(r, z) = a^{-2} \sum_{n=1}^{\infty} \frac{f_i}{\Delta_i} \left\{ \left[\beta_i + \frac{V}{D}(1-k) \right] \mathrm{e}^{\gamma_i z} - \left[\gamma_i + \frac{V}{D}(1-k) \right] \mathrm{e}^{\beta_i z} \right\} \frac{J_0(\alpha_i r)}{[J_0(\alpha_i a)]^2}, \tag{3.8}$$

where

$$\beta_i = \tfrac{1}{2}\left[-\frac{V}{D} - \sqrt{\left(\frac{V}{D}\right)^2 + 4\alpha_i^2} \right], \quad \gamma_i = \tfrac{1}{2}\left[-\frac{V}{D} + \sqrt{\left(\frac{V}{D}\right)^2 + 4\alpha_i^2} \right], \tag{3.9}$$

$$\Delta_i = \begin{cases} \left(\beta_i + \dfrac{V}{D}(1-k)\right)\mathrm{e}^{\gamma_i l} - \left(\gamma_i + \dfrac{V}{D}(1-k)\right)\mathrm{e}^{\beta_i l}, & \text{for case a,} \\ \dfrac{D}{V}\left[\left(\gamma_i + \dfrac{V}{D}\right)\left(\beta_i + \dfrac{V}{D}(1-k)\right)\mathrm{e}^{\gamma_i l} - \left(\beta_i + \dfrac{V}{D}\right)\left(\gamma_i + \dfrac{V}{D}(1-k)\right)\right], & \text{for case b.} \end{cases} \tag{3.10a,b}$$

Case a and case b associate with the boundary condition (3.6a) and (3.6b), respectively.

The problem of zero order can be simplified if the concentration distribution at a plane melting interface $z = l$ is uniform. In this case, the solution of the problem (2.7)–(2.10) reduces to a one-dimensional problem $C_0 = C_0(z)$, which may be described as

$$\frac{\mathrm{d}^2 C_0}{\mathrm{d}z^2} + \frac{V}{D}\frac{\mathrm{d}C_0}{\mathrm{d}z} = 0, \tag{3.11}$$

$$\frac{\mathrm{d}C_0(0)}{\mathrm{d}z} + \frac{V}{D}(1-k)C_0(0) = 0, \tag{3.12}$$

$$C_0(l) = C_l(\text{const.}) \tag{3.13a}$$

or

$$\frac{\mathrm{d}C_0(l)}{\mathrm{d}z} + \frac{V}{D}C_0(l) = \frac{V}{D}C_l. \tag{3.13b}$$

This problem of an ordinary differential equation has the solution

$$\left(\frac{C_0(z)}{C_l}\right)_{\mathrm{a}} = \frac{k + (1-k)\mathrm{e}^{-Vz/D}}{k + (1-k)\mathrm{e}^{-Vl/D}}, \quad \text{for case a,} \tag{3.14a}$$

$$\left(\frac{C_0(z)}{C_l}\right)_{\mathrm{b}} = 1 + \frac{1-k}{k}\mathrm{e}^{-Vz/D}, \quad \text{for case b.} \tag{3.14b}$$

For the case of infinite extension $l \rightarrow \infty$, the solution (3.14a) reduces to the usual one-dimensional formula (3.14b), which has been used extensively in the analysis of morphological instability.

It was pointed out [9,10], that there will be a concentration discontinuity at the melting interface for the model of mass conservation boundary condition (3.13b). It could also be seen from the relationship of case b that

$$\left(\frac{C_0(l)}{C_l}\right)_{\mathrm{b}} = k^{-1}\left[k + (1-k)\mathrm{e}^{-\mathrm{Pe}\, l/a}\right] \neq 1 \tag{3.15}$$

for finite Peclet number Pe l/a and the non-equilibrium freezing condition $k \neq 1$, where the Peclet number Pe is defined as Pe $= Va/D$. Solution of case a satisfies the continuity condition at the melting interface $[C_0(l)/C_l]_{\mathrm{a}} = 1$, however, a mass conservation condition (2.4b) cannot be satisfied by the solution (3.14a) in general. The functions depending on z in both (3.14a) and (3.14b) are the same, and the ratio of the two solutions gives

$$\frac{[C_0(z)/C_l]_{\mathrm{a}}}{[C_0(z)/C_l]_{\mathrm{b}}} = 1 + \left(\frac{1-k}{k}\right)\mathrm{e}^{-\mathrm{Pe}\, l/a}, \tag{3.16}$$

which depends only on k and Pe l/a. Both solutions of (3.14a) and (3.14b) will be the same for case $P \rightarrow \infty$, where P is the Peclet number based on length scale

$$P = Vl/D = \mathrm{Pe}\, l/a. \tag{3.17}$$

This implies that both models based on the melting interface conditions (3.13a) and (3.14) will be completely the same only for cases of infinite extension $l \to \infty$ and for the case of equilibrium freezing $k = 1$, but will be different in general. How to describe the concentration boundary condition at the melting interface is a problem, which should be studied in the future.

It could be seen, the solution (3.8) of the infinite series presents a general form, however, each term of the series associates with a special solution of the diffusion problem which connects with a special boundary condition of the concentration distribution at the melting boundary, and may be adopted as the basic state for the analysis of morphological instability.

4. Solution of first order

The problem of first order may be written as follows:

$$\frac{\partial^2 C_1}{\partial r^2} + \frac{1}{r}\frac{\partial C_1}{\partial r} + \frac{\partial^2 C_1}{\partial z^2} + \frac{V}{D}\frac{\partial C_1}{\partial z} = 0, \tag{4.1}$$

$$\frac{\partial C_1(r,0)}{\partial z} + \frac{\partial^2 C_0(r,0)}{\partial z^2} W_{s1}(r) - \frac{\partial C_0(r,0)}{\partial r}\frac{\mathrm{d}W_{s1}(r)}{\mathrm{d}r} + \frac{V(1-k)}{D}\left(\frac{\partial C_0(r,0)}{\partial z} W_{s1}(r) + C_1(r,0)\right)$$
$$= 0, \tag{4.2}$$

$$\frac{\partial C_1(0,z)}{\partial r} = 0, \quad \frac{\partial C_1(a,z)}{\partial r} = 0, \tag{4.3}$$

$$C_1(r,l) + \frac{\partial C_0(r,l)}{\partial z} W_{m1}(r) = 0, \tag{4.4a}$$

$$\frac{\partial C_1(r,l)}{\partial z} + \frac{\partial^2 C_0(r,l)}{\partial z^2} W_{m1}(r) + \frac{V}{D}\left(\frac{\partial C_0(r,l)}{\partial z} W_{m1}(r) + C_1(r,l)\right) = 0. \tag{4.4b}$$

For simplification, only the one-dimensional solution of zero order will be used for analyzing the solution of higher order. In this case, the third term of Eq. (4.2) is omitted. It could be seen that two types of boundary conditions at the melting interface could be given as Eqs. (4.4a) and (4.4b), both conditions have been often used in the articles. Introducing the finite Hankel transform

$$H_i^{(1)}(z) \equiv H^{(1)}(\alpha_i, z) = \int_0^a r C_1(r,z) J_0(\alpha_i r)\,\mathrm{d}r, \tag{4.5}$$

then, (4.1)–(4.4) reduce into a problem of an ordinary differential equation

$$\frac{\mathrm{d}^2 H_i^{(1)}}{\mathrm{d}z^2} + \frac{V}{D}\frac{\mathrm{d}H_i^{(1)}}{\mathrm{d}z} - \alpha_i^2 H_i^{(1)} = 0, \tag{4.6}$$

$$\frac{\mathrm{d}H_i^{(1)}(0)}{\mathrm{d}z} + \frac{V}{D}(1-k)H_i^{(1)}(0) = g_i, \tag{4.7}$$

$$H_i^{(1)}(l) = bh_i \tag{4.8a}$$

or

$$\frac{\mathrm{d}H_i^{(1)}(l)}{\mathrm{d}z} + \frac{V}{D}H_i^{(1)}(l) = h_i, \tag{4.8b}$$

where α_i is defined by (3.3), and coefficients g_i and h_i are

$$g_i = -\left(\frac{\mathrm{d}^2C_0(0)}{\mathrm{d}z^2} + \frac{V}{D}(1-k)\frac{\mathrm{d}C_0(0)}{\mathrm{d}z}\right)\int_0^a rW_{s1}(r)J_0(\alpha_i r)\,\mathrm{d}r, \tag{4.9a}$$

$$h_i = -\left(\frac{\mathrm{d}^2C_0(l)}{\mathrm{d}z^2} + \frac{V}{D}\frac{\mathrm{d}C_0(l)}{\mathrm{d}z}\right)\int_0^a rW_{m1}(r)J_0(\alpha_i r)\,\mathrm{d}r, \tag{4.9b}$$

and constant $b = [\mathrm{d}C_0(l)/\mathrm{d}z]/\{[\mathrm{d}^2C_0(l)/\mathrm{d}z^2] + (V/D)[\mathrm{d}C_0(l)/\mathrm{d}z]\}$, which gives the influence of the melting interface.

The solution of the first order problem (4.1)–(4.4) is obtained as

$$C_1(r,z) = a^{-2}\sum_{i=1}^{\infty}\left\{\Delta_i^{-1}\left[g_i\mathrm{e}^{\gamma_i l} - bh_i\left(\gamma_i + V\frac{1-k}{D}\right)\right]\mathrm{e}^{\beta_i z} + \left[bh_i\left(\beta_i + V\frac{1-k}{D}\right) - g_i\mathrm{e}^{\beta_i l}\right]\mathrm{e}^{\gamma_i z}\right\}$$
$$\times\frac{J_0(\alpha_i r)}{[J_0(\alpha_i a)]^2} \tag{4.10a$'$}$$

and it reduces as follows for the plane melting interface $b = 0$

$$C_1(r,z) = a^{12}\sum_{i=1}^{\infty} g_i\frac{\exp[-\gamma_i(l-z)] - \exp[-\beta_i(l-z)]}{[\gamma_i + (V/D)(1-k)]\exp(-\gamma_i l) - [\beta_i + (V/D)(1-k)]\exp(-\beta_i l)}\frac{J_0(\alpha_i r)}{[J_0(\alpha_i a)]^2} \tag{4.10a}$$

for case a, and

$$C_1(r,z) = a^{-2}\sum_{i=1}^{\infty}\left\{\frac{g_i}{\Delta_i}\left[-\left(\beta_i + \frac{V}{D}\right)\exp(\beta_i l + \gamma_i z) + \left(\gamma_i + \frac{V}{D}\right)\exp(\beta_i z + \gamma_i l)\right]\right.$$
$$\left. + \frac{h_i}{\Delta_i}\left[\left(\beta_i + V\frac{1-k}{D}\right)\exp(\gamma_i z) - \left(\gamma_i + V\frac{1-k}{D}\right)\exp(\beta_i z)\right]\right\}\frac{J_0(\alpha_i r)}{[J_0(\alpha_i a)]^2} \tag{4.10b}$$

for case b, where Δ_i is defined by (3.10b). The solution (4.10) is valid in the region $0 \le r < a$ and $0 \le z \le l$, and connects the curvature of interfaces via the coefficients g_i and h_i defined in (4.9). It is convenient to express the functions $W_{s1}(r)$ and $W_{m1}(r)$ as a series in r, and only the terms $n < 3$ will be kept for simplicity, that is,

$$W_{s1}(r) = w_{s0} + w_{s1}r + w_{s2}r^2, \quad W_{m1}(r) = w_{m0} + w_{m1}r + w_{m2}r^2. \tag{4.11}$$

According to the selection of the origin of the coordinate system, it gives $w_0 = 0$. The symmetric condition requires $w_1 = 0$. A contact angle at the corner of the interface is satisfied by

$$\tan\left(\frac{\pi}{2} - \alpha\right) = \pm\frac{\mathrm{d}W_{s1}(a)}{\mathrm{d}r}, \tag{4.12}$$

where the signs + and − correspond, respectively, to a concave and a convex curve of the solidification interface. The relation (4.11) may, then, be reduced as

$$W_{s1}(r) = \pm\frac{1}{2a}\mathrm{ctg}\,\alpha r^2. \tag{4.13a}$$

Similarly, the melting interface may be written as

$$W_{m1}(r) = l \mp \frac{1}{2a} \text{ctg } \alpha' r^2, \tag{4.13b}$$

where α' is a characteristic angle at the melting interface and may have a similar meaning as α in physics or may be introduced only as a mathematical approximation to express the configuration of the melting interface. By application of the relationship of the Bessel function [8] $xJ_0(x) = (\mathrm{d}/\mathrm{d}x)\{x[\mathrm{d}J_0(x)/\mathrm{d}x]\}$, using the condition (4.9) and the solution of zero order (3.14), the coefficients g_i and h_i of (4.9) are obtained as follows:

$$g_i = \begin{cases} \pm C_l \dfrac{\text{Pe}^2 \text{ctg } \alpha}{a\alpha_i^2} \dfrac{k(1-k) J_0(\alpha_i a)}{k + (1-k)\exp(-\text{Pe } l/a)}, & \text{for case a,} \\ \mp C_l \dfrac{a(1-k)}{\alpha_i^2} \left(\dfrac{V}{D}\right)^2 \text{ctg } \alpha \, J_0(\alpha_i a), & \text{for case b,} \end{cases} \tag{4.14a,b}$$

$$h_i = \pm C_l \frac{a(1-k)}{\alpha_i^2} \left(\frac{V}{D}\right)^2 \text{ctg } \alpha' \exp\left(-\frac{Vl}{D}\right) J_0(\alpha_i a). \tag{4.15}$$

In this case, the concentration distribution of first order (4.10) may be written as

$$\frac{C_1(r, z)}{C_l} = \pm \text{Pe}^2 \text{ctg } \alpha \frac{k(1-k)}{k + (1-k)\exp(-\text{Pe } l/a)} F_1(r, z), \quad \text{for case a,} \tag{4.16a}$$

$$\frac{C_1(r, z)}{C_l} = \pm \left[(1-k)\text{Pe}^2 \exp(-P) \text{ctg } \alpha'\right] F_2(r, z) \pm \left[(1-k)\text{Pe}^2 \text{ctg } \alpha\right] F_3(r, z), \quad \text{for case b,} \tag{4.16b}$$

where

$$F_1(r, z) = \frac{\left[\exp(\gamma_i l) - b\left(\gamma_i + V\dfrac{1-k}{D}\right)\right]\exp(\beta_i z) + \left[b\left(\beta_i + V\dfrac{1-k}{D}\right) - \exp(\beta_i l)\right]\exp(\gamma_i z)}{(\Delta_i a)(\alpha_i a)^2} \times \frac{J_0(\alpha_i r)}{J_0(\alpha_i a)} \tag{4,17a'}$$

in general, or

$$F_1(r, z) = \sum_{i=1}^{\infty} \frac{\exp[-\gamma_i(l-z)] - \exp[-\beta_i(l-z)]}{[\gamma_i + \text{Pe}(1-k)]\exp(-\gamma_i l) - [\beta_i + \text{Pe}(1-k)]\exp(-\beta_i l)} \frac{J_0(\alpha_i r)}{(\alpha_i a)^2 [J_r(\alpha_i a)]} \tag{4.17a}$$

for the special condition of the plane melting interface $b = 0$,

$$F_2(r, z) = \sum_{i=1}^{\infty} \frac{[\beta_i a + \text{Pe}(1-k)]\exp(\gamma_i z) - [\gamma_i a + \text{Pe}(1-k)]\exp(\beta_i z)}{(\Delta_i a)(\alpha_i a)^2} \frac{J_0(\alpha_i r)}{[J_0(\alpha_i a)]}, \tag{4.17b}$$

$$F_3(r, z) = \sum_{i=1}^{\infty} \frac{[\beta_i a + \text{Pe}]\exp(\beta_i l + \gamma_i z) - [\gamma_i a + \text{Pe}]\exp(\beta_i z + \gamma_i l)}{\Delta_i a(\alpha_i a)^2} \frac{J_0(\alpha_i r)}{[J_0(\alpha_i a)]}. \tag{4.17c}$$

The solution (4.16a) shows that the geometrical factor ctg α of the solidification interface is proportional to the non-uniform concentration distribution $C_1(r, z)$. This conclusion agrees generally with the one in Ref. [3].

5. Radial segregation at solidification for case b

Usually, the relative difference of concentration is introduced to describe the radial segregation at the solidification interface

$$\zeta = \frac{\Delta C}{C_l} = \frac{C(a,0) - C(0,0)}{C_l}. \tag{5.1}$$

For the one-dimensional basic state (3.14), the formula (5.1) is reduced into

$$\zeta = \frac{C_1(a,0) - C_1(0,0)}{C_1}. \tag{5.2}$$

Parameter ζ is a function depending generally on the coefficients k, Pe, α, α' and l/a. Substituting the solution (4.12) into the definition (5.1), a detailed expression can be obtained, and the factors of radial segregation ζ can be analyzed.

Sometimes, the case of a larger Peclet number Pe $\gg$ 1 was discussed. In this case, the solute boundary layer will be extremely thin. Therefore, the following detailed analyses will be concentrated on the case of a limited Peclet number, that is

$$\mathrm{Pe} = \mathrm{O}(1) \tag{5.3}$$

or less. The zeros of the Bessel function for the condition (3.3) are

$$\alpha_1 a = 3.8317, \quad \alpha_2 a = 7.0156, \quad \alpha_3 a = 10.1735,... \tag{5.4}$$

Both conditions (5.3) and (5.4) imply that

$$\mathrm{Pe}^2 \ll (2\alpha_i a)^2. \tag{5.5}$$

Therefore, the coefficients β_i, γ_i and Δ_i defined by (3.9) and (3.10) may be simplified as

$$\beta_i a = -\alpha_i a, \quad \gamma_i a = \alpha_i a, \quad \Delta_i a = -2(\alpha_i a)^2 \mathrm{sh}(\alpha_i l). \tag{5.6}$$

By using the relationships (5.6) and the formula (4.12b), coefficient ζ may be obtained as

$$\zeta = \pm(1-k)\mathrm{Pe}^2\left[\mathrm{e}^{-P}\mathrm{ctg}\,\alpha' I_\mathrm{m} + \mathrm{ctg}\,\alpha\, I_\mathrm{s}\right], \tag{5.7}$$

where the constants I_m and I_s are independent of the physical parameters and defined by

$$I_\mathrm{m} = \sum_{i=1}^{\infty} \frac{1}{\mathrm{sh}(\alpha_i a)} \frac{J_0(\alpha_i a) - 1}{(\alpha_i a)^3 [J_0(\alpha_i a)]^2} = -0.0067, \tag{5.8}$$

$$I_\mathrm{s} = \sum_{i=1}^{\infty} \frac{\mathrm{ch}(\alpha_i a)}{\mathrm{sh}(\alpha_i a)} \frac{J_0(\alpha_i a) - 1}{(\alpha_i a)^3 [J_0(\alpha_i a)]^2} = -0.219. \tag{5.9}$$

The radial segregation as shown in the formula (5.7) is contributed by the curvatures of both the melting interface (4.9b) and the solidification interface (4.9a), they associate, respectively, with the first term and second term in the right hand side of (5.7). The constants I_m and I_s are both negative, so the total contribution of both interfaces are added. The absolute value of I_m is one order of magnitude smaller than the one of I_s. The melting interface may give similar important contribution as the solidification interface only if ctg α' exp($-P$) is one order of magnitude larger than ctg α, otherwise, the contribution of the curved melting interface will be relatively smaller in comparison with the one of the solidification interface in the general cases.

The formula (5.7) shows that the radial segregation during unidirectional solidification of a binary alloy with both curved solid/liquid interfaces may be expressed by a parameter ζ, which is proportional to the factors $(1-k)$, Pe^2, l/a, ctg α and ctg α'. This result is similar to the ones in Refs. [3,4] for a binary alloy with only one curved solid/liquid interface (2.7), where the proportional factors are $(1-k)$, $W_s(a) - W_s(0)$ and Pe, instead of Pe^2.

6. Examples for case a

Due to the relatively small influence of the melting interface in general, the case a will be analyzed to emphasize the influence of a curved solidification interface in this section, that is, a plane melting interface $b = 0$ is assumed.

6.1. Case of large Peclet number $\mathrm{Pe} \gg \alpha_i a$ $(i \leq N < +\infty)$

The zeros of the Bessel function (3.3) will tend to infinity as i becomes infinite, and condition $\mathrm{Pe} \gg \alpha_i a$ cannot be satisfied for very large i except $\mathrm{Pe} \to \infty$. However, the series of eigenfunction will be truncated in finite terms $i \leq N$ in the calculation, and the larger the index i, the smaller the contribution. In this case, the relationship (3.9) reduces to

$$\gamma_i = \frac{1}{a}\frac{(\alpha_i a)^2}{\mathrm{Pe}}, \quad \beta_i = -\frac{\mathrm{Pe}}{a}, \tag{6.1}$$

where the terms of $(a\alpha_i/\mathrm{Pe})^2$ in order of magnitude were omitted. The solution of $H_i^{(1)}(z)$ is simplified as

$$H_i^{(1)}(z) = \pm\frac{a}{k\mathrm{Pe}}\frac{1-\exp[\mathrm{Pe}(l-z)/a]}{[(1-k)/k]+\exp[\mathrm{Pe}\,l/a]}g_i, \tag{6.2}$$

where only coefficients g_i depend on index i in the right hand side of (5.2). Then, the solution of first order (4.10a) was given as

$$C_1(r,z) = \frac{a}{k\mathrm{Pe}}\frac{\exp[\mathrm{Pe}(l-a)/a]-1}{\exp(\mathrm{Pe}\,l/a)+(1-k)/k}\left(\frac{2}{a^2}\sum_{i=1}^{\infty}\frac{g_i J_0(\alpha_i r)}{[J_0(\alpha_i a)]^2}\right). \tag{6.3}$$

Due to the basic state (3.14a), the relationship (4.9a) gives

$$g_i = -C_l\frac{k(1-k)}{k+(1-k)\exp(-\mathrm{Pe}\,a/l)}\left(\frac{a\mathrm{Pe}}{l}\right)W_{s1}(r), \tag{6.4}$$

and (6.3) reduces to

$$\frac{C_1(r,z)}{C_l} = \frac{\mathrm{Pe}}{a}\frac{1-k}{k}\frac{\exp[\mathrm{Pe}(l-z)/a]-1}{\exp(\mathrm{Pe}\,l/a)+(1-k)/k}W_{s1}(r). \tag{6.5}$$

The radial non-uniformity of concentration at the solidification interface (5.2) may be written as

$$\zeta = \frac{1-k}{k}\frac{\mathrm{Pe}}{a}[W_{s1}(a) - W_{s1}(0)]. \tag{6.6}$$

The result (6.6) is quite similar to the one in Ref. [3] and different from the one in Ref. [5]. It shows that the radial non-uniformity may be obvious even if the shape of solidification interface has a small deviation from planarity.

6.2. Case of small Peclet number

The case of a small Peclet number requires

$$\mathrm{Pe} \ll 1. \tag{6.7}$$

After neglecting the terms of O(Pe), the coefficients (3.9) reduce to

$$\beta_i = -\alpha_i + \mathrm{O}(\mathrm{Pe}), \quad \gamma_i = \alpha_i + \mathrm{O}(\mathrm{Pe}), \tag{6.8}$$

and the solution of $H_i^{(1)}(z)$ is given as

$$H_i^{(1)}(z) = -\alpha_i^{-1} \frac{\mathrm{sh}[\alpha_i(l-z)]}{\mathrm{ch}(\alpha_i l)} g_i. \tag{6.9}$$

Then, the concentration of first order may be written as follows:

$$C_1(r, z) = -a^{-2} \sum_{i=1}^{\infty} \frac{g_i \mathrm{sh}[\alpha_i(l-z)]}{\alpha_i \mathrm{ch}(\alpha_i l)} \frac{J_0(\alpha_i r)}{[J_0(\alpha_i a)]^2} \tag{6.10}$$

or

$$\frac{C_1(r, z)}{C_l} = \mp \mathrm{Pe}^2 \mathrm{ctg}\, \alpha \frac{k(1-k)}{k + (1-k)\exp(-\mathrm{Pe}\, l/a)} \sum_{i=1}^{\infty} (\alpha_i a)^{-3} \frac{\mathrm{sh}[\alpha_i(l-z)]}{\mathrm{ch}(\alpha_i l)} \frac{J_0(\alpha_i r)}{[J_0(\alpha_i a)]^2} \tag{6.11}$$

for the condition of the solidification interface shape given by (4.13a).

Similarly, the non-uniformity of concentration at the solidification interface may be demonstrated by using the formula (6.11). Considering the case of infinite extension $l \to \infty$ it gives $\mathrm{Pe}\, l/a = Vl/D \to \infty$. Therefore, the solution (6.11) reduces into

$$\zeta = \mp \mathrm{Pe}^2 \mathrm{ctg}\, \alpha (1-k) I_1, \tag{6.12}$$

$$I_1 = \sum_{n=1}^{\infty} (\alpha_i a)^{-3} \left(1 - \frac{1}{J_0(\alpha_i a)}\right) = 0.0561 \tag{6.13}$$

for the condition of the solidification interface shape given by (4.9). The solution (6.12) shows that the relative non-uniformity of concentration at the solidification interface is proportional to $(1-k)$, which agrees with Ref. [3]; it is proportional to ctg α, which agrees with the case of a larger Peclet number; and it is proportional to Pe^2, which is different from the case of a larger Peclet number.

3. Case of Pe = 1.

In this case, the relationship (3.9) gives

$$\beta_i = \frac{1}{2a}\left[-1 - \sqrt{1 + (2\alpha_i a)^2}\right], \quad \gamma_i = \frac{1}{2a}\left[-1 + \sqrt{1 + (2\alpha_i a)^2}\right], \tag{6.14}$$

by a similar approach, the demonstration gives

$$\zeta = \pm \mathrm{Pe}\,\mathrm{ctg}\,\alpha \frac{k(1-k)}{k+(1+k)\exp(-\mathrm{Pe}\,l/a)} I_2. \tag{6.15}$$

$$I_2 = \sum_{i=1}^{\infty} \frac{\left(1-\dfrac{1}{J_0(\alpha_i a)}\right)\mathrm{sh}\left[\sqrt{(\alpha_i a)^2+\frac{1}{4}}\left(\dfrac{l}{a}\right)\right]}{(k-\frac{1}{2})(\alpha_i a)^2\mathrm{sh}\left[\sqrt{(\alpha_i a)^2+\frac{1}{4}}\left(\dfrac{l}{a}\right)\right]+\sqrt{(\alpha_i a)^2+\frac{1}{4}}\,\mathrm{ch}\left[\sqrt{(\alpha_i a)^2+\frac{1}{4}}\left(\dfrac{l}{a}\right)\right]}. \tag{6.16}$$

The partition coefficient k has only a limited influence on the constant I_2, so the relative non-uniformity of concentration ζ at the solidification interface is proportional mainly to $k(1-k)/[k+(1-k)\exp(-l/a)]$, which value is between $(1-k)$ and $k(1-k)$.

7. Discussions and conclusions

The perturbation theory is applied successfully to analyze the radial solute segregation during unidirectional solidification of a binary alloy with a curved solid–liquid interface. The perturbation expansion is based on a small geometrical parameter, therefore, there is no limitation on the magnitude of physical parameters in general. The diffusion process was solved by the method of finite Hankel transforms for each order problem in a cylindrical region with finite extension, and a detailed configuration of the solidification interface was discussed.

From the view point of physics, the non-uniformity of concentration at the solidification interface depends closely on the configuration of the interfaces, which can only be given by the physical condition in the pure diffusion process discussed in the present paper. A general series formula (4.11) was suggested, and the constants w_n should be determined by the physical condition. More physical condition were suggested, and more terms can be involved. This method can be applied to a more general physical process, and is not limited to the suggestion (4.11).

In the present paper, the radial segregation of a pure diffusion process was analyzed for a crystal growth model of a binary alloy with cylindrical configuration and finite extension in longitudinal direction. The boundary condition at the melting interface was also given by the mass conservation conditions [1–3]. The results of two types of boundary conditions at the melting interface were compared for one-dimensional models, they had the same function dependence on the longitudinal coordinate z but a difference in a factor depending on parameter k^2 and P. Both solutions were the same only if $P \to \infty$ or $k = 1$. It seems that the diffusion in the melting phase probably needs to be discussed in the future.

The influence of a curved melting interface on the radial segregation at the solidification interface was studied. Quantitative results show that the influence of a curved melting interface is relatively smaller in comparison with the one of a curved solidification interface in general cases. It should be pointed out that the non-uniformity of solid concentration at the melting interface may also induce a non-uniformity concentration distribution at the solidification interface, and this influence appears in the zeroth order relationship in the present paper.

As examples, the cases of larger Peclet number, smaller Peclet number and Pe = 1 were discussed in detail for case a. The conclusions in the present paper are similar to the ones in Refs. [3,4] in some sense. The results in the cylindrical coordinate system of the present paper could by easily demonstrated in the Cartesian coordinate system by the method of finite Fourier transform. However, the cylindrical problem seems more reasonable in comparison with a plane problem.

From the view point of physics, how to suggest the boundary condition at the melting interface and what is the influence of the melting conditions on the field in melt liquid and then the solidification interface, these subjects are still interesting for future studies.

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