A Mathematical Model for Solute Redistribution during Dendritic Solidification

By Sumio KOBAYASHI**

Synopsis
To quantify the solute redistribution during solidification, an approximate solution of the Brody–Flemings model of dendritic solidification has been derived on the assumption of parabolic solidification and a constant partition ratio, and compared with an exact solution of the model. It has been shown that the approximate solution has good accuracy.

Further, on the basis of the derived equation, an extended mathematical model is proposed, incorporating a thermal model of solidification into the analysis without assumption on the solidification rate. The extended model includes the treatment of multi-component alloy and β transformation, the temperature dependence of diffusion coefficients and the estimation of the diffusion path. The extended model provides the results consistent with the available data.

Key words: mathematical modeling; solidification; segregation; diffusion; carbon steel.

I. Introduction
In the earliest description with the Scheil equation for solute redistribution during solidification, the diffusion of solute into solid phase (back diffusion) was neglected.1,2) Brody and Flemings3,4) have extended the theory to include the back diffusion effects based on their solidification model; the model assumed 1) complete diffusion in liquid phase and incomplete back diffusion, 2) a plate-like dendrite geometry, 3) a constant diffusion coefficient, and 4) parabolic or linear solidification rate. Both approximate equations derived by Brody and Flemings for linear and parabolic solidification rate are, however, invalid for rapid diffusion in the solid phase.

Clyne and Kruz,5,6) and Ohnaka5,7) have modified the Brody and Flemings equation for parabolic solidification rate; both the modifications are valid for infinite and infinitesimal diffusion coefficient. Further, the present author has derived an exact solution of the solidification model of Brody and Flemings for parabolic solidification rate, and has shown that the accuracy of all the approximate solutions mentioned above are often bad.8,9)

Although the solidification model of Brody and Flemings with parabolic growth has been rigorously solved, several problems still remain in applying the model to solidification processes: 1) calculation of the exact solution is uneasy because the solution has an infinite series of the confluent hypergeometric functions, 2) no realistic method has been found to estimate the solidification rate or the local solidification time, of which value is necessary for the calculation, and 3) a parabolic solidification rate in the assumptions may be unrealistic in most of the solidification process. In particular, both the temperature at the solid–liquid interface and solute redistribution during solidification must be taken into account to determine the solidification rate.

The present paper describes a new approximate solution of the Brody–Flemings model and an extended mathematical model which incorporates a thermal model of solidification into the approximate solution derived in this paper and permits the changes of thermophysical parameters during solidification.

II. Mathematical Formulation of the Brody–Flemings Model
The assumed geometry is shown in Fig. 1. In the figure, the solidification proceeds along x-direction until the solid–liquid interface X reaches the position x=L. The length L and the position x=0 correspond to one half of the dendrite spacing, l/2, and the dendrite spine, respectively. Assumptions in the model are as follows.

1) Solute elements move in solid phase by volume diffusion with a constant diffusion coefficient D as

\[
\frac{\partial C_s}{\partial t} = D \frac{\partial^2 C_s}{\partial x^2}, \quad \text{..............(1)}
\]

where, \(C_s\): the solute content in solid.

2) Diffusion in liquid is complete.

3) Liquid and solid densities are identical and constant. Thus fraction liquid \(f_L\) and fraction solid \(f_s\) are given by

\[
f_s = X/L, \quad \text{and} \quad f_L = 1-f_s. \quad \text{..............(2)}
\]

4) The equilibrium partition ratio \(k\) applies at the interface and is constant throughout solidification process. Therefore,

<table>
<thead>
<tr>
<th>Solid</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>x = X</td>
</tr>
<tr>
<td>x = L</td>
<td></td>
</tr>
</tbody>
</table>

x=0: Dendrite spine  
x = X: Solid–liquid interface  
x = L: Midpoint between two dendrites

Fig. 1. Schematic illustration of the Brody–Flemings model of dendritic solidification.
\( C_s = kC_L \), .................. (3)

where, \( C_s \): the solute content in solid at the solid-liquid interface

\( C_L \): the solute content in the liquid.

(5) There is no mass flow into or out of a volume element.

\[ D \frac{\partial C_s}{\partial x} = 0, \quad \text{for} \quad x = 0, \quad .................. (4) \]

and

\[ \frac{k}{L} \int_0^x C_s dx + (1 - f_s) C_s = kC_0, \quad .......................... (5) \]

where, \( C_0 \): the initial alloy composition.

(6) The local solidification rate is parabolic as expressed by

\[ f_s = \frac{\sqrt{t/t_f}}{t_f}, \quad .......................... (6) \]

where, \( t_f \): the local solidification time.

By introducing a parameter \( z \) to represent the position in the volume element as

\[ z = \frac{(x/X)^\gamma}{2\tau}, \quad .......................... (7) \]

where, \( \gamma = 8Dt_f/\tau^2 \), .......................... (8)

and by replacing \( t \) and \( x \) by \( f_s \) and \( z \), respectively, the equations of diffusion (Eq. (1)) and mass conservation (Eq. (5)) can be rearranged as follows. Appendix I should be referred for details.

\[ f_s \frac{\partial C_s}{\partial f_s} = (1 + 2z) \frac{\partial C_s}{\partial z} + 2z \frac{\partial^2 C_s}{\partial z^2}, \quad .......................... (9) \]

and

\[ \frac{k f_s}{2 \sqrt{2\tau}} \int_0^{\sqrt{z_0}} C_i \frac{dz}{\sqrt{z}} + C_i(1 - f_s) = kC_0, \quad .......................... (10) \]

where, \( z_0 = 1/(2\tau) \).

Application of the integral \( f_s^{\sqrt{z_0}} \int dz/\sqrt{z} \) with Eq. (9), differentiation of Eq. (10) with respect to \( f_s \), and elimination integral terms yield the boundary condition as

\[ (1 - f_s) \frac{\partial C_s}{\partial f_s} + (k - 1) C_s + k \frac{\partial C_s}{\partial z} = 0, \quad \text{for} \quad z = z_0, \quad .......................... (11) \]

Another boundary condition and the initial condition are

\[ \sqrt{z} \frac{\partial C_s}{\partial z} = 0, \quad \text{for} \quad z = 0, \quad .......................... (12) \]

and

\[ C_s = kC_0, \quad \text{for} \quad f_s = 0. \quad .......................... (13) \]

Separation of the variables in Eqs. (9) and (11) to (13) leads to an exact solution in the form of

\[ C_s(f_s, z) = kC_0 \sum_{n=0}^{\infty} \zeta_n \frac{F(-n/2, 1/2; 1 - z)}{F(-n/2, 1/2; -z_0)} f_s^n, \quad .......................... (14) \]

where, \( \zeta_0 = 1 \),

\[ \zeta_n = \prod_{m=0}^{n-1} \left( 1 - k \frac{F(-m/2, 3/2; 1 - z_0)}{F(-m/2, 1/2; 1 - z_0)} \right), \quad \text{for} \quad n \geq 1, \quad .......................... (15) \]

and \( F(a, c; z) \) is the confluent hypergeometric function. The derivation of Eqs. (14) and (15) is shown in Appendix II.

III. Approximate Solution of the Solidification Model of Brody-Flemings

As the first approximation, the second derivative with respect to \( z \) in the righthand side of Eq. (9) is neglected:

\[ f_s \frac{\partial C_s}{\partial f_s} = (1 + 2z) \frac{\partial C_s}{\partial z}, \quad .......................... (16) \]

The solution of Eq. (16), \( C_s \), is a function of single variable of \( f_s \sqrt{1 + 2z} \), and satisfies

\[ C_s = C_i(f_s \sqrt{1 + 2z}). \quad .......................... (17) \]

Elimination of the first derivative with respect to \( z \) from Eqs. (16) and (11) yields the following equation.

\[ (1 - (1 - \beta) f_s) \frac{\partial C_s}{\partial f_s} + (k - 1) C_s = 0, \quad .......................... (18) \]

where, \( \beta = \gamma/(1 + \gamma) \).

By integrating Eq. (18) with respect to \( f_s \), the following equation can be obtained:

\[ C_s = kC_0 \left[ 1 - (1 - \beta) f_s \sqrt{1 + 2z_0} \right]. \quad .......................... (19) \]

The second order approximate solution of Eq. (9) is obtained on the basis of the following equation.

\[ f_s \frac{\partial C_s(2)}{\partial f_s} = (1 + 2z) \frac{\partial C_s(1)}{\partial z} + 2az \frac{\partial^2 C_s(1)}{\partial z^2}, \quad .......................... (20) \]

and

\[ (1 - f_s) \frac{\partial C_s(2)}{\partial f_s} + (k - 1) C_s(2) + k \frac{\partial C_s(1)}{\partial z} = 0, \quad \text{for} \quad z = z_0, \quad .......................... (21) \]

where, \( C_s^{(n)} \): the \( n \)-th order approximation of the solution of Eq. (9)

\( \omega \): a sensitivity parameter.

Putting \( \omega = 1/2 \) and \( z = z_0 \), we can get

\[ \frac{\partial C_s(2)}{\partial z} = \beta f_s \frac{\partial C_s(1)}{\partial f_s} - \frac{1}{2(1 + \gamma)} \frac{\partial^2 C_s(1)}{\partial z^2}, \quad .......................... (22) \]

Substitution of the above equation into Eq. (21) yields

\[ (1 - (1 - \beta) f_s) \frac{\partial C_s(1)}{\partial f_s} + (k - 1) C_s^{(1)} = \frac{k}{2(1 + \gamma)} \frac{\partial^2 C_s(1)}{\partial z^2}, \quad .......................... (22) \]

Putting \( \beta = 1 - (1 - \beta) f_s \) and substituting Eq. (19) into
Eq. (22), we can get
\[
\frac{\partial C_{i}^{{\text{IN}}}}{\partial \xi} - \gamma C_{i}^{{\text{IN}}} = -kC_{0}T_{\gamma}^{2}\left[\frac{3-(1+2\beta)k}{\xi} - \frac{5-(2+3\beta)k}{\xi^{2}} + \frac{2-(1+2\beta)k}{\xi^{3}}\right],
\]
where, \( \Gamma = \frac{k(1-k)\beta^{3}}{2(1-\beta^{3})} \).

Integration of Eq. (23) under the initial condition of Eq. (13) leads to the following equation that is the second order approximation solution of Eq. (9).
\[
C_{i}^{{\text{IN}}} = kC_{0}\xi^{2}\left[1 + \Gamma \left(1 + \frac{1+\beta}{2}k\left(\frac{1}{\xi^{2}} - 1\right)\right) - 5\left(1 + \frac{2+3\beta}{5}k\left(\frac{1}{\xi} - 1\right) - 3\left(1 + \frac{1+2\beta}{3}k\ln \xi\right)\right)\right].
\]

A comparison of the second order approximate solution (Eq. (24)) with the exact solution (Eq. (14)) is shown in Fig. 2 for \( k=0.13, \gamma=0.8 \), which are the values used by Clyne et al.7 for calculating the behavior of \( P \) in \( \delta \)-Fe. The calculation results of both the equations agree well each other, although the second order approximate solution predicts slightly higher values than the exact solution for \( f_{s} \) in the vicinity of 0.97. The exact solution with the first and second order approximate solution are compared in Figs. 3 and 4 for \( f_{s}=1, k=0.1-0.8, \) and \( \gamma=0.03-10. \) All the final solute concentrations \( (f_{s}=1) \) estimated by the second order approximate solution agree well with those by the exact solution. The results by the first order approximate solution deviates appreciably from those of the exact solution when \( k \) and \( \gamma \) are small.

IV. An Extended Mathematical Model for Dendritic Solidification

1. Mathematical Model

This section incorporates the temperature or enthalpy change in the volume element with time into the approximate solution derived in the previous section. Multi-component alloys and the changes of equilibrium partition ratios and diffusion coefficients during solidification are also included.

Let us suppose a small time interval \( \Delta t \) between times of \( t_{n} \) and \( t_{n+1} (=t_{n+1}+\Delta t) \). The local solidification rate \( (=df_{s}^{2}/dt) \), the equilibrium partition ratios, the dendrite arm spacing and the diffusion coefficients could be assumed constant during the small time interval \( \Delta t \), thus Eqs. (9), (11) and (12) are applicable to estimate the change of composition during \( \Delta t \). Note that Eq. (9) is derived on the assumption of constant \( \gamma (=8Df_{s}^{2}/(df_{s}^{2}/dt)) \) as shown in Appendix I. Introduction of the initial condition
\[
C_{i} = k_{s}^{j}f_{s}^{j}C_{j,n}, \quad \text{for } f_{s} = f_{s,n} \text{ at } t = t_{n} \quad (25)
\]
leads to the following solution of the second order approximation with a similar manner shown in the previous section.
\[ C_{j,n+1} = C_{j,n} \left( \frac{\xi_{j,n+1}}{\xi_{j,n}} \right)^{\beta_j} \left[ 1 + \Gamma_j \left( P_{j,n+1} - P_{j,n} \right) \right], \]

\[ P_{j,n} = \left( 1 - \frac{1 + \beta_j k_{p,j}^{L/L}}{2} \right) \frac{1}{\xi_{j,n}} - \frac{1}{5} \left( 1 - \frac{1 + 2 \beta_j k_{p,j}^{L/L}}{3} \right) \frac{1}{\xi_{j,n}} \ln \xi_{j,n}, \]

\[ \xi_{j,n} = 1 - \left( 1 - \beta_j k_{p,j}^{L/L} \right) f_{j,n}, \]

where, \( C_{j,n} \): the concentration of element \( j \) in the liquid phase at \( t = t_n \)

\( k_{p,j}^{L/L} \): the equilibrium partition ratio of element \( j \) dependent on the metallurgical phase (\( S = \delta \) or \( \gamma \)) of solid.

The parameters \( \Gamma_j, \eta_j \) and \( \xi_{j,n} \) are peculiar to the time interval between \( t_n \) and \( t_{n+1} \), and defined as follows.

\[ \Gamma_j = \left( 1 - k_{p,j}^{L/L} \right) \frac{\beta_j}{2} (1 - \beta_j k_{p,j}^{L/L}), \]

where, \( \beta_j = \frac{8D_j}{R} f_{j,n+1} - f_{j,n} \),

\[ \eta_j = \frac{8D_j}{R} f_{j,n+1} - f_{j,n} \]

\[ \xi_{j,n} = 1 - \left( 1 - \beta_j k_{p,j}^{L/L} \right) f_{j,n}, \]

Diffusion coefficient \( D_j \) is the form of

\[ D_j = D_0 \exp \left( - \frac{Q_j}{RT} \right), \]

where, \( R \): the gas constant

\( T \): the absolute temperature of the volume element considered.

The diffusion coefficient \( D_j \) and the equilibrium partition ratio \( k_{p,j}^{L/L} \) are assumed to be constant during the time interval \( \Delta t \) between times of \( t_n \) and \( t_{n+1} \), and determined from the temperature \( T \) and the metallurgical phase of solid at \( t = t_n \). The parameters \( \Gamma_j, \eta_j, \beta_j \) and \( \gamma_j \) are also assumed to be constant during the time interval between times of \( t_n \) and \( t_{n+1} \), and may be changed from time interval to time interval. The parameters \( \xi_{j,n}, \xi_{j,n+1}, P_{j,n} \) and \( P_{j,n+1} \) are calculated from the parameters \( \beta_j \) and \( k_{p,j}^{L/L} \), which are peculiar to the time interval between times of \( t_n \) and \( t_{n+1} \). Therefore \( \xi_{j,n} \) and \( P_{j,n} \) denote the values at \( t = t_n + 0 \), and \( \xi_{j,n+1} \) and \( P_{j,n+1} \) denote the value at \( t = t_{n+1} - 0 \).

The local equilibrium is assumed at the solid-liquid interface, thus the liquidus temperature of the volume element at \( (n+1) \)-th time step can be uniquely determined by the alloy composition \( C_{j,n+1} \). The temperature in equilibrium of liquid and solid is given by the following equation on the assumptions8 that the alloy is dilute solution and exhibits the Raoultian ideal behavior.

\[ \frac{1}{T_{LS}} = \frac{1}{T_{LS}} + \frac{R}{\Delta H_{LS}} \sum_j \left( 1 - k_{p,j}^{L/L} \right) \frac{C_j}{W_j}, \]

\[ \Delta H_{LS} = \frac{1}{T_{LS}} + \frac{R}{\Delta H_{LS}} \sum_j \left( 1 - k_{p,j}^{L/L} \right) \frac{C_j}{W_j}, \]

The temperature of \( \delta / \gamma \) transformation is given by

\[ \frac{1}{T_{0 \gamma}} = \frac{1}{T_{0 \gamma}} + \frac{R}{\Delta H_{0 \gamma}} \sum_j \left( 1 - k_{p,j}^{L/L} \right) \frac{C_j}{W_j}, \]

where, \( T_{0 \gamma} \): the temperature and enthalpy of \( \delta \) and \( \gamma \) phase transformation of pure iron, respectively

\( W_j \): the atomic weight of element \( j \).

In the derivation of Eqs. (29) and (30), the following relations are used.

1. Activity of iron in \( i \) phase is given by

\[ a_{Fe} = 1 - A^i, \]

where,

\[ i = \delta \text{ or } \gamma \]

\( A^i = \sum_j \frac{k_{p,j}^{L/L} C_j}{W_j} \]

2. Since \( A^i < 1 \), chemical potential of iron in \( i \) phase is approximated by

\[ \mu_{Fe} = G_{Fe} + RT \ln \left( 1 - A^i \right) = G_{Fe} - RTA^i. \]

3. Chemical potential of iron in liquid phase is equal to that in solid phase.

In the present model, \( \delta / \gamma \) transformation is assumed to take place abruptly at the temperature \( T_{0 \gamma} \) within the whole volume element considered. When the measured temperature at \( n \)-th time step \( T_n \) is available, it must coincide with the liquidus temperature determined by Eq. (29). Thus the fraction solid \( f_{s,n} \) can be determined at each time step by solving the following equation.

\[ \frac{1}{T_{n}} = \frac{1}{T_{LS}^0} + \frac{R}{\Delta H_{LS}} \sum_j \left( 1 - k_{p,j}^{L/L} \right) \frac{C_j(f_{s,n})}{W_j}. \]

When the enthalpy at \( n \)-th time step \( H_n \) is available, the fraction solid can be determined by solving the following equation,

\[ H_n = \rho \Delta H \left[ f_{s,n} + f_{s,n-1} = 1 \right], \]

because the enthalpy may be related to the temperature with

\[ H_n = \rho \Delta H \left[ f_{s,n} + f_{s,n-1} = 1 \right], \]

where, \( \Delta H \): heat of fusion

\( \rho \): the density

\( \epsilon_p \): the heat capacity of steel.

If the dendrite arm spacing is not measured, the following experimental formula9 is applicable.

\[ A = AV_m, \]

\[ \lambda = AV_m \]

where, \( A, m \): experimental constants

\( V \): the cooling rate averaged between the liquidus and the solidus temperatures.

In principle the solidus temperature can be determined after solving the above equations. In the present model, however, the cooling rate \( V \) is approximated by the following equation for saving the computation time.

\[ V = \frac{T_{LS} - T}{t - t_{LS}}, \]

\[ t > t_{LS}, \]

\[ \frac{1}{T_{LS}} = \frac{1}{T_{LS}} + \frac{R}{\Delta H_{LS}} \sum_j \left( 1 - k_{p,j}^{L/L} \right) \frac{C_j}{W_j}. \]

\[ \frac{1}{T_{0 \gamma}} = \frac{1}{T_{0 \gamma}} + \frac{R}{\Delta H_{0 \gamma}} \sum_j \left( 1 - k_{p,j}^{L/L} \right) \frac{C_j}{W_j}. \]

\[ \frac{1}{T_{0 \gamma}} = \frac{1}{T_{0 \gamma}} + \frac{R}{\Delta H_{0 \gamma}} \sum_j \left( 1 - k_{p,j}^{L/L} \right) \frac{C_j}{W_j}. \]
2. Comparisons with Experimental Data

Figure 5 compares the calculated phosphorus contents in liquid phase with the experimental data of Matsumiya et al. which were obtained from the steel specimens unidirectionally solidified and quenched. The composition of the specimens are shown in Table 1. The measured cooling rate of the specimens was 2.7°C/min for a, and 15°C/min down to 1480°C and 26.5°C/min thereafter for b. The solidified structure was cellular dendritic and the arm spacing was 360 µm for each case; secondary dendrite arms with a spacing of approximately 100 µm developed for b. In the calculation all the elements shown in Table 1 were taken into account. Adopted thermophysical data are shown in Table 2. The calculated results agreed well with the experimental data for a. For b, calculation was executed for three dendrite arm spacings: the secondary arm spacing 100 µm (denoted by b in the figure), the primary arm spacing 360 µm (b'), and the average of the primary and the secondary arm spacing 230 µm (b''). The calculated results for 100 µm spacing agreed best with the experimental data, although the effects of the dendrite arm spacing on the calculated results were slight at the fractions solid where the experimental data are available.

The calculated local solidification times, $t_{LS}$, were 1115 s for a and 169 s for b, while those calculated numerically by Matsumiya et al. were 960 s for a and 108 s for b. The changes of fraction solid calculated with time is shown in Fig. 6 for a and b. The calculated solidification rates were similar to those of parabolic solidification.

Figure 7 compares the calculated characteristic temperatures with the results of a series of thermal analysis by Kobayashi et al. The experimental data were obtained from the cooling curves of steel specimens solidified in a furnace at a constant cooling rate of 0.5 K/s. The composition of the specimens is shown in Table 3. The measured average secondary arm spacing was 360 µm. Heat transfer between specimen and furnace was modeled by the following equation.

$$\frac{dH}{dt} = c_p \frac{T_F - T}{\tau}, \quad \text{(36)}$$

where, $T_F$: the measured furnace temperature

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Two cases were calculated by using the measured value of dendrite arm spacing and the values estimated from Eq. (34) with $A=143$ (2 is in $\mu m$) and $m=0.41$. In the figure, the calculation results of Kobayashi et al. by the finite difference method are also shown. All the calculated results agreed well with the experimental data. In particular, the difference between the three calculation methods is not distinguished at the beginning temperatures of solidification and the diffusion distance are known. In most cases, however, the local solidification time and the diffusion distance are not known. The extended mathematical model is useful to estimate the microsegregation effects because it can calculate the solidification rate and the diffusion distance. In the extended model, the local solidification time and the diffusion distance are determined from the temperature of considered volume element which is measured directly or indirectly. Since the present model is easily extended to include the equation of heat conduction, the microsegregation effects can be estimated on the basis of the present model even when the measured data are not available.

In the present model, the average cooling rate, $V$, in Eq. (34) is approximated by Eq. (35) and the empirical formula on secondary arm spacing (Eq. (34)) is used to estimate the arm spacing during solidification, although the formula is based on the arm spacings measured after solidification is finished. However, this approximation will be appropriate because of the following reasons:

1. At the initial and intermediate stage of solidification ($f_s \leq 0.7$), microsegregation is scarcely affected by the diffusion distance.
2. The estimated arm spacing will be valid at the final stage.
3. The accuracy of the estimation is insensitive to the calculated microsegregation effects as shown in Figs. 5 and 7.

An apparent weak point of the present model will be in the assumption of single phase in solid, which leads to abrupt occurrence of $\delta/\gamma$ transformation. However, the calculated results based on the present model agreed well with the experimental data of thermal analysis. This agreement will be due to the following reasons. Since, at the initial and intermediate stage of solidification, the effects of back diffusion on solute segregation is small, the present assumption will not lead to a serious error. At the final stage of solidification, the solidification rate will be governed by the redistribution of elements such as sulphur and phosphorus, which are easily segregated. These elements in the solid phase are concentrated in the vicinity of the solid–liquid interface at the final stage of solidification; and the redistribution of these elements will be only sensitive to the metallurgical phase of solid next to the liquid–solid interface but measured ones were approximately 360 $\mu m$. Calculated fraction solid at the maximum cooling rate was approximately 0.99 for the carbon range above 0.15 wt%. This result coincides with that of the finite difference method.

### V. Discussion

Ohnaka has compared the calculation results of Eq. (20) with other approximate solutions on the basis of the experimental data by Matsumiya et al. and showed that Eq. (24) agreed best with the experimental data of the case $a$. The approximate solution of the Brody–Flemings model will be directly applicable to calculate microsegregation, if the local solidification time and the diffusion distance are known. In most cases, however, the local solidification time and the diffusion distance are not known. The extended mathematical model is useful to estimate the microsegregation effects because it can calculate the solidification rate and the diffusion distance. In the extended model, the local solidification time and the diffusion distance are determined from the temperature of considered volume element which is measured directly or indirectly. Since the present model is easily extended to include the equation of heat conduction, the microsegregation effects can be estimated on the basis of the present model even when the measured data are not available.

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scarcely affected by the metallurgical phase in the vicinity of dendrite spine. Thus the assumption will be also valid at the final stage. However more rigorous treatment of $\delta_f$ transformation is to be desired and is a subject for further research.

This method can be modified with a few efforts to the columnar geometry of solidification which was approximately treated by Ohnaka, although there is no experimental evidence to deny the planar geometry assumed in the present paper. Such the modification will be presented elsewhere.

VI. Conclusions

To quantity solute redistribution during solidification, the Brody–Flemings model of dendritic solidification has been mathematically formulated by introducing a new variable $z$ shown in Eq. (7), and a set of equations (Eqs. (9) and (11) to (13)), which represents the Brody–Flemings model, has been derived. Adopted assumptions are: (1) planar dendrite, (2) parabolic solidification rate, and (3) a constant partition ratio, a constant dendrite arm spacing and a constant diffusion coefficient throughout solidification.

On the basis of the derived equations, approximate solutions of the Brody–Flemings model have been obtained. By comparing with an exact solution of the model, it has been shown that the second order approximate solution (Eq. (24)) has good accuracy.

Furthermore, on the basis of the derived equations, an extended mathematical model for solute redistribution during solidification has been proposed, incorporating a thermal model of solidification into the analysis without assumption on the solidification rate. The extended model includes the treatment of multi-component alloy and $\delta_f$ transformation, the temperature dependence of diffusion coefficients and the estimation of diffusion path. In the extended model, the equilibrium partition ratio, diffusion coefficient and dendrite arm spacing are assumed to be constant during a small solidification time interval $\Delta t$, and the change of the liquidus temperature, within the time interval $\Delta t$ is calculated on the basis of the second order approximate solution of the Brody–Flemings model. The solidification rate during $\Delta t$ is determined from the requirement that the calculated liquidus temperature is consistent with the incorporated thermal model. Thus solute redistribution during solidification is calculated with time step by time step.

The extended model provides the results consistent with the experimental data obtained by Matsumiya et al. and by Kobayashi et al.

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$$f \frac{\partial C_s}{\partial f_s} = \left( 2z + \frac{D}{2} \left[ \frac{df_z^2}{dt} L_z \right] \right) \frac{\partial C_s}{\partial z} + \frac{2zD}{2} \frac{df_z^2}{dt} \frac{\partial C_s}{\partial z^2}. \quad \text{(A-6)}$$

By defining

$$\gamma = \frac{8D}{\lambda^2 \frac{df_z^2}{dt}}, \quad \text{(A-7)}$$

Equation (9) is derived, because \(L = \lambda/2\). The definition of \(\gamma\) (Eq. (A-7)) includes the relation represented by Eq. (8).

**Appendix II**

**Exact Solution of the Brody-Flemings Model for Dendritic Solidification**

Mathematical formulation of the model is given by Eqs. (9) and (11) to (13). Application of the separate variable method to Eq. (9) shows that the solution is in the form of

$$C_s(f_s, z) = \sum_{n=0}^{\infty} u_n(z) f_s^n, \quad \text{(A-8)}$$

where the function \(u_n(z)\) satisfies the following ordinary differential equation

$$z \frac{d^2 u_n}{dz^2} + \left( z + \frac{1}{2} \right) \frac{du_n}{dz} - \frac{n}{2} u_n = 0. \quad \text{(A-9)}$$

This is the confluent hypergeometric equation and the solution, satisfies the boundary condition of Eq. (12) at \(z=0\), is given by

$$u_n(z) = A_n F\left( -\frac{n-1}{2}, \frac{1}{2}; -z \right), \quad \text{(A-10)}$$

where \(A_n\) is a constant parameter to be determined by the initial and boundary conditions of Eqs. (11) and (13), and \(F(a, c; z)\) represents the confluent hypergeometric function defined by

$$F(a, c; z) = \sum_{r=0}^{\infty} \frac{(a)_r (c)_r}{r!} \left( -z \right). \quad \text{(A-11)}$$

(a) and (c) are the Pochhammer symbols defined by

\( (a)_r = a(a+1)(a+2)\ldots(a+r-1) \), \( (a)_0 = 1 \), etc.

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