A semi-analytical model of microsegregation in a binary alloy

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Abstract

At small Fourier diffusion numbers semi-analytical microsegregation models, of the form suggested by Brody and Flemings, are known to perform poorly in the analysis of solidifications controlled by a parabolic solid growth. The basic inconsistency in the development of this class of models is highlighted. It is shown that an alternative, consistent development, for solidifications controlled by a constant cooling rate, results in the same microsegregation model. Comparison with predictions — maximum concentration and eutectic fractions — obtained with a numerical, constant cooling rate solution show a significant improvement in model performance. Further modification — based on curve fitting in the low Fourier number range — leads to a constant cooling rate microsegregation model that provides accurate predictions of microsegregation levels across a wide, practical range of parameters. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

During the solidification of a dendritic alloy the solute rejected at the solid/liquid interface is redistributed, at the local scale of the secondary dendrite arm spaces ($\lambda \sim 20–100 \mu m$), by mass diffusion. This process, referred to as microsegregation, controls the composition of the microstructure and the fraction of eutectic that will form.

Models of microsegregation for dilute binary eutectic alloys can be obtained by invoking a solute mass balance over the secondary arm spacing.

Typically, a plate-like morphology is assumed. Thus the problem domain is a one-dimensional region of size $\lambda/2$, separated into solid and liquid fractions by a sharp, moving interface (see Fig. 1). Other assumptions, employed in developing basic microsegregation models, are: (i) constant physical properties in the solid phase, (ii) thermodynamic equilibrium at the solid/liquid interface, (iii) a closed system, i.e., the average composition in the solution domain remains fixed at the nominal solute composition, $C_0$, and (iv) straight liquidus and solidus lines in the phase diagram. Under these assumptions a limiting case microsegregation model is the Gulliver–Scheil [1] equation. This model, which assumes complete mass diffusion in the liquid phase and zero diffusion in the solid
phase, can be written in the convenient explicit form

\[ f = \left(1 - \frac{C_1}{C_0} \right)^{1/(k-1)} \]  

(1)

where \( f \) is the solid fraction in the secondary arm space, \( C_1 \) is the concentration in the liquid phase and \( k \) is the partition coefficient. This is often a useful first cut model since in many alloys the level of diffusion in the solid is relatively small. The assumption of a zero solid diffusion, however, will overpredict the extent of microsegregation in particular the fraction of eutectic phase that forms at the end of the solidification. There have been a number of attempts to modify the Gulliver–Scheil equation and account for finite diffusion in the solid phase. A well-known class of modified equations assumes a parabolic growth rate for the solid phase, i.e. in each half of the arm space (see Fig. 1)

\[ X_s = \left(1 - f_{\text{end}}\right)\lambda \sqrt{\frac{t}{t_f}} \]  

(2)

where \( t_f \) is the local solidification time and \( f_{\text{end}} \) represents the fraction of the eutectic phase, on final solidification. Under this additional assumption Brody and Flemings [2] carry out a solute balance in the arm spacing in which the diffusion in the solid phase – often referred to as the back diffusion – is modeled by imposing a diffusion boundary layer at the solid/liquid interface. The general form of the Brody–Flemings model is

\[ f = \frac{1}{1 - \beta k} \left(1 - \frac{C_1}{C_0} \right)^{(1 - \beta k)/(k-1)} \]  

(3)

where \( \beta \) can be considered to be a back-diffusion parameter. In the Brody and Flemings version of this model

\[ \beta = 2\alpha, \]  

(4)

where \( \alpha \) is a Fourier number,

\[ \alpha = \frac{4Dt_f}{\lambda^2}, \]  

(5)

and \( D \) is the solid diffusivity. Note a value of \( D = 0 \) (i.e., \( \alpha = 0 \)) will reduce Eq. (3) to the Gulliver–Scheil equation. As shown by Clyne and Kurz [3], however, this basic Brody–Flemings model becomes unphysical and fails to conserve mass if \( \alpha \) is large (>0.7). Based on the assumption of an exponential solid solute profile Clyne and Kurz [3] devise a modification for the definition of \( \beta \) that addresses the problems in the basic Brody–Flemings model.
model, viz.

\[ \beta = 2\alpha \left[ 1 - \exp \left( -\frac{1}{\alpha} \right) \right] - \exp \left( -\frac{1}{2\alpha} \right) \]  

(6)

Note in this model a value of \( \beta = 0 \) will correspond to the Gulliver–Scheil equation. A value of \( \beta = 1 \) will correspond to complete diffusion in the solid phase and reduces Eq. (3) to the equilibrium lever rule. A similar modification, based on the assumption of a quadratic solid solute profile is presented by Ohnaka [4]. In this case the diffusion parameter is given by the equation

\[ \beta = \frac{2\alpha}{1 + 2\alpha}. \]  

(7)

The above semi-analytical models arrive at an explicit expression for the microsegregation behavior that is essentially an approximate solution of Fick’s second law of diffusion in the solid. An alternative approach is to directly solve – analytically or numerically – Fick’s second law in the solid phase. In the case of a parabolic solid growth Kobayashi [5] presents an exact analytical solution for the microsegregation. When compared with the Kobayashi solution the predictive performance of the semi-analytical models – Eqs. (3)–(7) above – is very poor, particularly if the partition coefficient, \( k \), and Fourier number, \( \alpha \) are small [5]. On comparing with a complete numerical analysis Ganesan and Poirier [6] indicate that in order to provide sound predictions the semi-analytical models need to use a variable value of \( \beta \) and that a constant value (Eqs. (4)–(6) or Eq. (7)) will underestimate the extent of microsegregation.

In this paper an analysis is presented that explicitly identifies the problem of a nonconstant value of \( \beta \) in the Brody–Flemings semi-analytical models. Of far more significance, however, is the finding that – with a constant value of \( \beta \) – these models are valid, consistent and reasonably accurate when used for the analysis of microsegregation in solidifications which are cooled at a constant rate, e.g., in a Bridgeman furnace. In other words, the Brody–Flemings class of microsegregation models [2–4] (Eqs. (3)–(7)) developed for analysis during parabolic solid growth are more applicable to situations in which the arm space is cooled at a constant rate; a condition that will typically not lead to a parabolic growth rate.

2. The model

2.1. Preliminaries

The microsegregation model is based on the solute mass balance in a secondary arm spacing of a binary eutectic alloy. If the arm spacing is cooled at a constant rate, due to the rapid nature of thermal diffusion the temperature in the arm spacing will be uniform at each point in time. Further, since the liquid concentration in the arm spacing is also uniform and the lines in the phase diagram are straight, a constant cooling implies that the rate of change of liquid concentration, \( \frac{dC}{dt} \), is also constant. To simplify the analysis, without loss of generality, the local solidification time and half arm spacing are set to \( t_f = 1 \) and \( \lambda/2 = 1 \), respectively. In this way, the Fourier diffusion number becomes \( \alpha = D \) and, if a eutectic phase forms

\[ \frac{dC}{dt} = C_{eut} - C_0, \]  

(8)

where \( C_{eut} \) is the eutectic composition. For later reference it is noted that, with the settings of \( t_f = 1 \) and \( \lambda/2 = 1 \), parabolic growth is given by

\[ f = (1 - f_{eut})\sqrt{t} \]  

(9)

and the term

\[ f \frac{df}{dt} = \frac{1}{2}(1 - f_{eut})^2 \]  

(10)

is a constant.

2.2. The solute balance

The solute balance in the arm spacing can be written as

\[ \int_0^f C_1 \, dx + (1 - f)C_1 = C_0 \]  

(11)

or, on differentiating with respect to time,

\[ \frac{df}{dt} (k - 1)C_1 + \int_0^f \frac{dC}{dt} \, dx + (1 - f) \frac{dC_1}{dt} = 0. \]  

(12)
In deriving this equation the Leibniz rule has been used and the condition of equilibrium at the interface, \( C^\text{int}_s = kC_s \), has been invoked. The second term on the left-hand side of Eq. (12) represents the back diffusion into the solid phase,

\[
\int_0^f \frac{\partial C_s}{\partial t} \, dx = \frac{\partial C_s}{\partial x} \bigg|_{\text{int}}
\]

and, as such, an alternative form of Eq. (12) is

\[
df{f}{dt} (k - 1)C_1 + \frac{\partial C_s}{\partial x} \bigg|_{\text{int}} + (1 - f) \frac{dC_1}{dt} = 0. \tag{14}
\]

Progress is made on setting

\[
\frac{\partial C_s}{\partial x} \bigg|_{\text{int}} = \beta k \frac{dC_1}{df}. \tag{15}
\]

This substitution should be viewed as an approximation with its validity resting on the definition of the diffusion parameter \( \beta \). If \( \beta \) is constant — an assumption justified below — then Eq. (10) can be integrated to give

\[
f = \frac{1}{1 - \beta k} \left( 1 - \left[ \frac{C_1}{C_0} \right]^{(1 - \beta k)/(k - 1)} \right) \tag{16}
\]

which is the Brody–Flemings form of the microsegregation model (see Eq. (3) above). In this case, however, it is of key importance to recognize that no explicit assumption has been made on the nature of the solidification, in particular the parabolic growth rate used in the Brody and Flemings model [2] has not been invoked.

2.3. Calculating the diffusion parameter

Valid use of Eq. (16) requires a constant for the value of \( \beta \). Following Ohnaka [4] one suitable approach for finding \( \beta \) is to, at each point in time, approximate the solute distribution in each solid half of the arm spacing, by the quadratic

\[
C_s(x) = kC_1 + c[x^2 - f^2], \quad 0 \leq x \leq f, \tag{17}
\]

where \( c \) is a constant. From this assumed distribution it follows that

\[
\frac{\partial C_s}{\partial x} \bigg|_{\text{int}} = 2cf, \tag{18}
\]

and

\[
\int_0^f \frac{\partial C_s}{\partial t} \, dx = k \frac{dC_1}{dt} f - 2cf^2 \frac{df}{dt}. \tag{19}
\]

Substitution in Eq. (13) leads to the following equation in \( c \):

\[
2xcf - k \frac{dC_1}{dt} f - 2cf^2 \frac{df}{dt} = 0 \tag{20}
\]

from which

\[
c = \frac{(k/2)(dC_1/dt)}{f(df/dt) + \alpha}. \tag{21}
\]

A value of \( \beta \) can be obtained through Eqs. (15) and (18). This step will only be appropriate, however, if the value of \( c \) defined by Eq. (22) is a constant. This will be true if both the conditions

\[
\frac{dC_1}{dt} = \text{constant} \tag{23}
\]

and

\[
\frac{df}{dt} = \text{constant} \tag{24}
\]

hold. The first of these conditions holds if a constant cooling rate is imposed. The second holds if parabolic growth is assumed (see Eq. (10)). As noted previously, however, in general situations it is unlikely that both constant cooling and parabolic growth will hold simultaneously. This suggests that the Ohnaka parabolic growth model [4], which relies on a constant value of \( c \) in Eq. (17), is inconsistent. For this model, and by association, the model suggested by Clyne and Kurz [3], to be consistent a variable value of \( c \) and hence a variable value of the diffusion parameter \( \beta \) is required, a situation that will require a numerical solution.

An alternative approach to arrive at a consistent model is to define an average value of the diffusion parameter. For parabolic growth, Ganesan and
Poirier [6] achieve this by using a statistical package to match a best fit to numerical solutions of the solute balance. In the case of constant cooling, however, a more analytical approach for obtaining an averaged value of $c$ can be adopted. First an averaged value of $c$ is defined as the value that satisfies the weighted residual form of Eq. (21). That is the value of $c$ that satisfies the equation

$$
\int_0^1 w \left[ 2xcf - k \frac{dC}{dt}f - 2c \frac{df}{dt} \right] dt = 0,
$$

where the integration is taken over the solidification time, $0 < t < 1$ ($= t_f$) and $w$ is a weighting function. Clearly the constant value of $c$ derived from this equation will depend on the choice of weight $w$. In general $w$ can be any arbitrary function. In a practical sense, however, a value with a physical meaning would be more appropriate. One convenient and interesting choice is

$$
w = \frac{1}{f}.
$$

This choice is convenient because, if a constant cooling rate is assumed, Eq. (25) can be readily integrated to give

$$
c = \frac{(k/2)(dC/dt)}{\frac{1}{2}(1 - f_{eut})^2 + x}.
$$

The choice is interesting because use of the expression for $c$ in Eqs. (15) and (18) leads to the following form for the diffusion parameter

$$
\beta = \frac{2x}{(1 - f_{eut})^2 + 2x},
$$

which, if no eutectic forms (i.e., $f_{eut} = 0$), will reduce to the form for $\beta$ previously suggested by Ohnaka (see Eq. (7) above). Note in this case, however, this form is derived under the assumption of a constant cooling rate and not a parabolic growth rate. Use of Eq. (28) with the general Brody–Flemings model (Eq. (16)) is straightforward. If no eutectics forms then the value of $\beta$ can be used directly in Eq. (16). If eutectic forms, iterations are required to determine the eutectic fraction, $f_{eut}$. Typically, simple successive substitution over a handful of iterations is sufficient to converge.

### 2.4. Discussion

The key step in arriving at the averaged value of $c$ in Eq. (27) and the diffusion parameter, $\beta$, rests is the choice of $w = 1/f$ as the weighting function in the weighted residual, Eq. (26). In this work no direct attempt has been made to choose an optimum weighting factor. The choice in Eq. (26) is driven by the need to arrive at an explicit form for $c$ via a consistent route. This choice does, however, result in the Ohnaka [4] version of the Brody–Flemings model. The original Ohnaka version was developed and applied under the assumption of a parabolic growth rate. Not only is this development inconsistent – see arguments above – but previous workers [5,6] have demonstrated that, when applied to parabolic growth problems, the Ohnaka [4] and similar versions of the Brody–Flemings model perform poorly at low values of Fourier number $x$ and partition ratio $k$.

The above suggests that, if the choice of weight function in Eq. (26) is reasonable, the Ohnaka version of the Brody–Flemings model, Eqs. (16) and (28), may be more suitable for cases of constant cooling rate. This statement will be tested below by investigating the performance of the Ohnaka model in predicting microsegregation in a constant cooling regime.

### 3. Results

In testing the proposed microsegregation model for constant cooling regimes the focus will be placed on its ability to predict (1) the maximum solute concentration – the ratio of the solid concentration at the end of solidification to the nominal composition – in noneutectic binary alloys, and (2) the fraction of eutectic that forms in a binary eutectic alloy. The first set of these predictions matches the work done by Kobayashi [5] when testing the parabolic growth microsegregation models. The second set of predictions represents an important microsegregation parameter. The performance of the microsegregation model is measured on comparing its predictions with those obtained with a numerical model.
3.1. Brief description of the numerical model

Eq. (12) – given above – represents the solute balance in an arm spacing. Recall that (1) the second term on the left-hand side represents the back-diffusion into the solid phase, and (2) under the assumption of a constant cooling rate the derivative in the third term is constant. If, at any given point in time, the value of the back-diffusion is known Eq. (12) can be solved in terms of \( C \). In this work a simple one-step Euler scheme in time is used. The old time values of the back-diffusion required for this calculation are determined by solving a finite-difference form of the diffusion equation in the solid fraction. This solution is implemented on a continuously deforming grid – with a fixed number of node points – that grows throughout the calculation to match the growth of the solid fraction. This calculation technology is based on a previously developed general deforming grid approach [7] and its application in solving microsegregation diffusion problems has been validated in Ref. [8]. In reporting results from this numerical model every effort has been made to insure that the choice of time steps in the Euler solution and space steps in the finite difference solution provide grid independent solutions. Typically 10 000 time steps are used in the Euler solution and 200 space steps in the finite difference solution. This choice does not place an excessive burden on computation time, usually computations times of less than 1 min are required on a low end PC.

3.2. Prediction of the maximum solute concentration

In a binary alloy that solidifies without an eutectic reaction the maximum solute concentration is defined as

\[
C_{\text{max}} = \frac{C_{\text{final}}}{C_0},
\]

where \( C_{\text{final}} \) is the concentration of the solute in the last part of the spacing to solidify. This quantity can be calculated on setting \( f_{\text{eut}} = 0 \) and rewriting Eq. (16) as

\[
c_{\text{max}} = [\beta k]^{(k-1)/(1-\beta k)},
\]

Following Kobayashi – Table 2 in Ref. [5] – predictions of maximum concentration – across a range of values of \( k \) and \( \alpha \) – are compared with numerical predictions in Fig. 2. As an additional comparison point the maximum concentration predicted with the Kobayashi analytical parabolic model are also shown in this figure. The following observations are made:

1. The performance of the Ohnaka model [4] under constant cooling conditions is significantly better than its performance under parabolic growth conditions.
2. At values \( a \geq 0.1 \) the performance of the Ohnaka model is sound.
3. At small values of \( a \) the performance deteriorates.

This last point indicates that at small Fourier number the back-diffusion controlled by the value of \( \beta \), Eq. (28), is not large enough. In this respect the following ad hoc modification for the calculation of \( \beta \) is suggested:

\[
\beta = \frac{2a}{V(1 - f_{\text{eut}})^2 + 2a}, \quad (31)
\]

where \( V \leq 1 \) will be a function of \( a \) and \( k \) and will approach a value of 1 as \( a \) increases. Using spreadsheet tools to fit the model in Eq. (31) to a range of numerically predicted data a suitable general form for \( V \) – which also accounts for cases where eutectic forms and \( f_{\text{eut}} > 0 \) – is

\[
V = \frac{2a}{V^*(1 - f_{\text{eut}})^2}, \quad (13 - 12(1 - f_{\text{eut}}) + 2a)
\]

\[
V^* = 0.05 - 0.01 \frac{1 + \log(k)}{\log(2)}. \quad (32)
\]

On reference to the open triangles in Fig. 2 it is seen that, across the range of practical values of \( k \) and \( \beta \), the performance of this modification of the Ohnaka model is excellent.

3.2.1. Prediction of eutectic fraction

The ability of the Ohnaka model to predict eutectic fractions in constantly cooled binary eutectic alloys is tested by using representative data for an aluminum copper system,

\( k = 0.16, C_0 = 4.9 \) and \( C_{\text{eut}} = 33.2. \)

Model predictions of the eutectic fraction against the Fourier number \( a \) are shown in Fig. 3. These predictions are compared with predictions obtained from a constant cooled and parabolic growth rate versions of the numerical model. The following observations are made.

1. The performance of the Ohnaka model [4] (Eqs. (16) and (28)) under constant cooling conditions is significantly better than its performance under parabolic growth conditions.
2. In the case of predicting eutectic fractions the results are bound by the Gulliver–Scheil and lever limits. This constraints the variations in predictions obtained with the Ohnaka model and its performance is reasonable across the full range of \( a \).
3. Nevertheless, at small values of \( a \) the performance does deteriorate slightly. Use of the modified form for the parameter \( \beta \) (Eq. (31) and (Eq. (32))) however, improves the performance in this regime, see the open triangles in Fig. 3.
4. Testing of other alloys with different values of \( k \), etc., shows the performance of the Ohnaka model and it suggested modification to be at the same level.

4. Conclusions

As process models of solidification systems become more complex requiring coupling across many length scales the need for an easy to use single expression, explicit model for prediction of microsegregation parameters increases in importance. One potentially useful class of microsegregation models is based on the Brody–Flemings [2] form developed for dealing with situations controlled by parabolic growth. In particular the version suggested by Ohnaka [4], Kobayashi [5], and Ganesan and Poirier [6] have demonstrated, however, that
this class of models has poor performance at low values of $k$ and $a$. This paper has made two contributions in this regard.

1. An analytical treatment has clearly identified the inconsistency in the development of the Ohnaka model.

2. A consistent development of the Ohnaka model (Eqs. (16) and (28)) has been achieved but under the assumption of a constant cooling rate for the arm spacing and not parabolic growth.

Results, based on testing the ability of the Ohnaka model in predicting microsegregation parameters, clearly indicate that the performance of the Ohnaka model is significantly superior in predicting in a constant cooling regime. Further, a modification has been suggested, Eqs. (31) and (32), that extend the range of applicability of the Ohnaka model.

The bottom line is that in predicting microsegregation in constantly cooled regimes the Ohnaka version [4] of the Brody-Flemings [2] model is a sound tool. If the problem of interest is controlled by parabolic growth of the solid then this model should not be used. In this case the recent model of Wang and Beckermann is recommended [9].

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**References**