Mathematical modelling of microsegregation in eutectic and peritectic binary alloys

M. A. Martorano and J. D. T. Capocchi

A mathematical model of microsegregation for eutectic and peritectic binary alloys was implemented using a finite volume method to solve the differential equations for mass transport. In this model simple ideas are used to handle phase boundaries and coarsening without the need to employ node jumping schemes or any transformation of variables to fix the domain size. Some model results were compared with available analytical solutions, revealing excellent agreement, which proved the approach useful to solve dissolution and diffusion coupled problems as well as microsegregation ones. Furthermore, good agreement was observed between the model result and measurements of eutectic volume fractions published previously for an Al-Cu alloy. The model was also capable of showing some important features of a typical peritectic transformation. Some instability was observed during model calculations, but it was easily handled by a time step refining technique.

The authors are in the Department of Metallurgical and Materials Engineering, Polytechnic School, University of São Paulo, Av. Prof. Mello Moraes, 2463, São Paulo, SP, Brazil, CEP 05508–900. Manuscript received 8 July 1999; accepted 6 January 2000. © 2000 IoM Communications Ltd.
work is an attempt to model a multiphase diffusion problem using equations easily related to the physical phenomenon, without resorting to techniques such as concentration parameters,\textsuperscript{6} node jumping schemes, and domain transformations.\textsuperscript{4} The proposed model was adjusted to simulate some benchmark solutions in order to be validated and was also used to simulate the solidification of a peritectic copper-tin alloy. Although the model is used for a microsegregation problem, it can also be used to simulate other processes that involve multiphase diffusion, such as diffusion couples or precipitate dissolution.

Previous mathematical modelling of microsegregation

FUNDAMENTAL DIFFERENTIAL EQUATIONS

Cylindrical,\textsuperscript{10,11} hexagonal,\textsuperscript{7,12,13} and plateletic\textsuperscript{2,4,10,14} control volumes have been used in numerical models of microsegregation depending on the dendrite structure morphology. After establishing the control volume shape and its position relative to the dendrite skeleton, Fick’s second law is usually solved. Fick’s law and its heat transfer equivalent should be applied to every phase in the system to find a general solution to the microsegregation problem. However, it is usually possible to regard the control volume as isothermal when its size is comparable to the secondary dendrite arm spacing,\textsuperscript{4,15} which eliminates the need to solve the microscopic heat transfer differential equation. Therefore, the following system of differential equations was used by many authors\textsuperscript{2,4,8,14,16,17} to model solute transport during microsegregation formation

$$\frac{\partial C_i}{\partial t} = V_i (D_i V_i C_i) \quad i = 1, 2, \ldots, n \quad (1)$$

where $i$ is a particular phase in the system (such as any of the solid phases or the liquid), $n$ is the total number of phases, $C_i$ is the solute concentration, $i$ is time, and $D_i$ is the diffusion coefficient for phase $i$. The control volume extension is usually assumed to be half the average secondary arm spacing. Many authors have assumed that the solute concentration in the liquid is homogeneous, which makes application of equation (1) to the liquid phase unnecessary.

The usual boundary conditions at phase boundaries for a moving boundary problem are\textsuperscript{19}

$$\frac{dS_{i+1}}{dt} = D_i \frac{\partial C_i}{\partial x} \bigg|_{k_{i+1}} - D_{i+1} \frac{\partial C_{i+1}}{\partial x} \bigg|_{k_{i+1}} \quad (2)$$

$$k_{i+1} C_i^* = m_{i+1} C_{i+1} \quad (3)$$

$$T^* = m_{i+1} C_{i+1}^* \quad (4)$$

where $C_i^*$ and $C_{i+1}^*$ are solute concentrations at each side of the boundary adjacent phases $i$ and $i+1$ respectively, $S_{i+1}$ is the position of that boundary, $k_{i+1}$ is the equilibrium solute partition coefficient between phases $i$ and $i+1$ (which is a function of the boundary temperature according to the phase diagram), $T^*$ is the temperature at the phase boundary, and $m_i$ and $m_{i+1}$ are functions that relate temperature and equilibrium solute concentrations of the $i$ and $i+1$ phases respectively.

PHASE BOUNDARIES

Different methods to handle phase boundaries have been adopted in numerical models of microsegregation. Some authors have forced a predetermined\textsuperscript{2,10,16} movement to the solid/liquid interface, whose position is not found out from the general solution, but is a given function of time. On the other hand, Kirkwood and Evans\textsuperscript{20} determined the phase boundary movement from the heat flow crossing the control volume boundary. It was assumed equal to the sensible heat flow just before the start of solidification, which were determined from experimental cooling curves.\textsuperscript{2,8} Howe\textsuperscript{18} also used a heat balance approach to model a peritectic alloy, but some instability problems were reported in the calculations.

When the control volume is considered isothermal, its temperature may be given directly by experimental measurements or by macroscopic heat transfer models. If that temperature, which is also the interface temperature, is known, the phase diagram gives the solute concentration at phases adjacent to the interface. Those solute contents might be employed in a mass balance that enables the calculation of phase boundary positions.\textsuperscript{11,21}

Voller and Sundarraj\textsuperscript{4} defined a ‘chemical activity’ that allowed the solution of the mass transport equation without explicitly employing equation (2) at a phase boundary. Using a technique called node jumping scheme, the time step was continuously adjusted so that the interface always rested on a node position. The correct time step was found iteratively to make the temperature and solute concentrations at the interface match those given by the phase diagram.

Ueshima et al.\textsuperscript{7} and Matsumiya et al.\textsuperscript{13} proposed a different technique to model microsegregation where the interface was always placed on a volume element face. The phase transformation of a whole volume element was forced, and diffusion was allowed to occur afterwards. In the period after one volume had transformed into another phase and before its adjacent volume changed phase, local equilibrium at the interface was not maintained. However, this would cause no serious errors after refining the mesh size and time step of the numerical calculations.

COARSENING OF SECONDARY DENDRITE ARMS

In microsegregation models, coarsening of secondary dendrite arms is usually simulated by increasing the size of the adopted control volume. Its size may be given by empirical relationships developed from experiments where specimens are frozen during solidification,\textsuperscript{2,10,11,18} and secondary arm spacing measured and related to elapsed time.\textsuperscript{15}

However, Kattamis et al.\textsuperscript{22} have shown that empirical relationships between secondary dendrite arm spacing and local solidification time could be used to describe coarsening. The local solidification time should be replaced by the time elapsed after the beginning of solidification in this case. On the other hand, some authors\textsuperscript{4,14,15,23} have predicted the coarsening rate during each time step by using isothermal coarsening models. Nevertheless, there is still no ultimate conclusion about the most accurate procedure.\textsuperscript{14}

To simulate coarsening, different ways to deal with the expanding control volume have been proposed.\textsuperscript{4,17,23} Kirkwood\textsuperscript{21} and Roosz et al.\textsuperscript{23} added a liquid volume element with average solute content to the control volume after each time step, simulating the dilution effect brought about by coarsening. Voller and Sundarraj\textsuperscript{4} used a transformation of variables to change the real expanding domain into a fixed one, at the expense of introducing convectivelike terms into Fick’s law.

Mathematical model development

A mathematical model of microsegregation for eutectic and peritectic binary alloys is proposed in the present work. The main objective is developing a model based on simple ideas available in the literature and showing that these
ideas can be used for multiphase problems with coarsening and give accurate results.

BASIC ASSUMPTIONS
The basic assumptions in the present work model are summarised below:

(i) a unidimensional platelike control volume was used for some simulations and was placed between secondary dendrite arms, extending for half the average secondary arm spacing from the longitudinal axis of a secondary arm trunk
(ii) in some simulations a spherical control volume was adopted
(iii) coarsening was incorporated in the model by periodically increasing the control volume size
(iv) the temperature in the control volume is assumed uniform
(v) the control volume is a closed system, i.e. it does not exchange matter with its surroundings
(vi) any type of undercooling from curvatures, solute accumulation at dendrite tips and nucleation is neglected
(vii) before solidification starts, the solute concentration in the liquid is homogeneous
(viii) all phase boundaries are planar for a platelike control volume and are spherical for a spherical control volume
(ix) there is thermodynamic equilibrium at every phase boundary
(x) solute transport in the liquid and solid phases occurs by diffusion alone.

FINITE VOLUME EQUATIONS
The mass transport problem of microsegregation was solved by applying equation (1) to each phase within the adopted control volume. The resulting partial differential equations were transformed into a system of algebraic equations by the implicit finite volume method after dividing the control volume into many volume elements. The equation for each volume element is

\[ V \left( C_i^{k+1} - C_i^k \right) = A_w (Q_i^{k+1} - A_w Q_i^{k+1} - A_r Q_r^{k+1} \]  \hspace{1cm} (5)

where \( V \) is the volume of each volume element, \( \Delta t \) is the time step, \( C_i^{k+1} \) and \( C_i^k \) are the solute contents associated with the node within volume \( P \) at time \((k + 1) \Delta t \) and time \( k \Delta t \) respectively, \( A_w \) and \( A_r \) are the area of the left face and right face of the volume element respectively, \( Q_w \) is the solute flux into the volume element through the left face, and \( Q_r \) is the solute flux out of the volume element through the right face. These quantities are described in detail in the Appendix. Equation (5) can be easily adjusted to simulate different volume shapes, such as hexagons and spheres, solely by changing \( V \), \( A_f \), and \( A_w \) accordingly. Equations for platelike and spherical volume elements are also given in the Appendix.

A piecewise linear profile was used to describe solute concentration between two adjacent nodes, placed inside every volume element. When there are no phase boundaries within a volume element and its neighbouring volumes, flux calculations are straightforward, as indicated in the Appendix.

Node positions do not change within volume elements. When a phase boundary exists within an element, however, its node is assumed to belong to the boundary and flux calculations are made according to the same procedure used for other elements. The boundary position should be known in this case. Moreover, when a volume element contains a phase boundary, calculations of solute fluxes through its right and left faces should employ solute concentrations at the right and left sides of the interface respectively. If the interface temperature is given, solute concentrations of the right and left phases are given by the phase diagram. Figure 1 shows the concentration profile used to calculate fluxes at volume element faces.

According to the finite volume method (Ref. 6), \( \frac{C_i^{k+1}}{C_i^k} \) and \( C_i^k \) from equation (5) are solute contents associated with the node within volume \( P \) and are assumed to prevail across the whole volume element. The solute profiles at both sides of a phase boundary inside a volume element were also considered uniform, though concentrations at each side are obtained from the phase diagram for a given temperature. Therefore, \( C_i^k \) of the volume element with a phase boundary is only the average solute content, which depends on the phase boundary position.

PHASE BOUNDARIES
The algebraic system of equations obtained by writing equation (5) for every volume element was solved by the tridiagonal matrix algorithm after knowing the position of all phase boundaries. The technique used in the present model to predict a phase boundary position assumes that the volume element temperature is given. If only one phase boundary exists within a volume element, the phase to the right of the boundary has a volume fraction calculated as

\[ f_t^{k+1} = \frac{C_{PE}^{k+1} - C_{PW}^{k+1}}{C_{PE}^{k+1} - C_{PW}^{k+1}} \]  \hspace{1cm} (6)

where \( f_t^{k+1} \) is the volume fraction of the phase to the right of the boundary within the volume element at time \((k + 1) \Delta t \), \( C_{PE}^{k+1} \) is the solute content of the phase to the right, and \( C_{PW}^{k+1} \) is the solute content of the phase to the left of the boundary at time \((k + 1) \Delta t \). Both of these concentrations are given by the control volume temperature and the phase diagram. If the volume element geometry is known, \( f_t^{k+1} \) allows one to calculate the phase boundary position at time \((k + 1) \Delta t \).

When a phase boundary is inside a volume element, \( f_t^{k+1} \) is always between 0 and 1 for that element. If \( f_t^{k+1} \) becomes negative or greater than one, the volume element where the phase boundary is located can no longer support the phase boundary. Therefore, the boundary should move to the closest neighbour volume element. If the phase boundary cannot be placed inside the neighbour element, either, it is held at the element 'entrance' until its solute content has decreased to a value giving \( f_t^{k+1} \) between 0 and 1. Sundaraj and Voller used an equation similar to equation (6) to find out the phase boundary position. However, they had to apply the equation to all volume elements, while in the present work model, the equation is
only applied to the volume housing the boundary in the previous time step.

Since an implicit method is used to solve the differential equations, phase boundary positions at the end of each time step are necessary. Thus, one should start with the boundary positions known at the last time step to first calculate a tentative concentration profile for the next step. Afterwards, a new interface position is obtained using the tentative profile. This new position is used to calculate the same concentration profile again and the process continues iteratively until convergence of phase boundary positions is achieved, which usually required about six iterations.

Problems with iterations of the phase boundary position were brought about when the time step was not controlled. The implicit method assumes that solute concentrations and boundary positions at the end of the time step prevail throughout the entire time step period. Therefore, during calculation of solute profiles, phase boundaries are considered fixed. This will give unrealistic solute fluxes and concentrations if the real boundary position changes largely during an excessively long time step. As the calculation of the boundary position will be based on that unreal concentration profile, serious difficulties in convergence might arise. To solve this problem, during each time step the solute concentration of any volume element was never allowed to change by more than 5%. Whenever this limit was exceeded, the profile was calculated again using one quarter of the current time step. This time step refining was repeated until concentration changes were within the limit mentioned above. After obtaining a profile, calculations for the next step always began by using the initial coarsest time step again.

COARSENING
As previously mentioned, coarsening might be incorporated into microsegregation models by an increase in the control volume size located between secondary dendrite arms. In the present work, a procedure similar to that presented by Kirkwood and Roosz et al.25 was adopted. A liquid 'slice' with a thickness equal to that of one volume element was added whenever the condition below was fulfilled

\[ S(t) - L(t) > \Delta x \]  

where \( S(t) \) is the actual secondary dendrite arm spacing at time \( t \), \( \Delta x \) is the volume element size, and \( L(t) \) is the control volume size at time \( t \). The liquid volume element added had a solute content equal to the average one.

EUTECTIC AND PERITECTIC TRANSFORMATION
For an alloy that undergoes eutectic transformation, when the control volume temperature reached the eutectic temperature, all the remaining liquid was assumed to change into eutectic instantaneously, replacing the old solid/liquid interface by a solid/eutectic interface. This new interface was handled in exactly the same way as other phase boundaries. However, the average composition of the eutectic layer was assumed to remain constant during cooling.14 Diffusion was considered absent within the eutectic layer, which was motivated by the assumption that each phase of that eutectic is small enough to have a homogeneous solute concentration and therefore, no internal concentration gradient existed. Battle and Pehlke14 used a similar approach.

For an alloy reaching a peritectic temperature, it was assumed that only peritectic transformation occurred, i.e. a very thin layer of a new solid phase was formed instantaneously between the liquid and the primary solid phase. In the numerical method, this was considered by creating two new interfaces, namely a solid/solid and a solid/liquid interface, at the location of the old solid/liquid interface, which disappeared from the system. This could be a problem, because in order to apply equation (6), two interfaces can never be admitted into one volume element. Thus, this volume element was simply divided into two parts exactly at the location of the old solid/liquid interface when the peritectic temperature was reached. Each part of the old volume housed a new phase boundary, and they always moved in opposite directions.

STABILITY ANALYSIS
An analysis was carried out to verify stability conditions for the numerical model described above. Equation (5) was derived for a volume element that houses a phase boundary at a certain time. To derive this equation, it was also assumed that the neighboring volume elements were clear of any phase boundaries. The following expression results for a platelike geometry

\[
\frac{\Delta x}{\Delta t} (C_{W}^{k+1} - C_{E}^{k}) = \frac{D_{W}}{\Delta x_{W}} (C_{W}^{k} - C_{W}^{k+1}) - \frac{D_{E}}{\Delta x_{E}} (C_{E}^{k+1} - C_{E}^{k}) \quad \quad \quad \quad (8)
\]

where \( \Delta x \) is the size of one volume element, \( D_{W} \) and \( D_{E} \) are diffusion coefficients for the left and right side boundary phases respectively, \( \Delta x_{W} \) is the distance between the phase boundary and the left volume node, and \( \Delta x_{E} \) is the distance between the phase boundary and the right volume node. Using equation (6), the following approximation was assumed:

\[
C_{E}^{k} \approx (1 - f_{E}) C_{W}^{k} + f_{E} C_{E}^{k-1} \quad \quad \quad \quad (9)
\]

Rearranging equations (8) and (9) yields

\[
C_{E}^{k+1} = \frac{D_{W}}{\Delta x_{W}} C_{W}^{k+1} + \frac{D_{E}}{\Delta x_{E}} C_{E}^{k+1} + \left( 1 - f_{E} \right) \frac{D_{W}}{\Delta x_{W}} C_{W}^{k} + f_{E}\left( \frac{D_{W}}{\Delta x_{W}} + \frac{D_{E}}{\Delta x_{E}} \right) C_{E}^{k-1} \quad \quad \quad \quad (10)
\]

This equation approximately describes the calculation of the average solute content of a volume element within which a phase boundary is located. The concentrations \( C_{W}^{k+1} \) and \( C_{E}^{k+1} \) are constants given by the phase diagram rather than determined from the system of equations generated by the implicit method. Stability is maintained in the system as long as all coefficients of concentration are positive, which guarantees physical meaningful results.5 Considering that \( \Delta x_{W} \) and \( \Delta x_{E} \) are always equal or greater than \( \Delta x/2 \), the resulting stability conditions might be written as

\[
\frac{D_{W} \Delta t}{\Delta x^{2}} \leq \frac{1}{2} \quad \quad \quad \quad (11)
\]

\[
\frac{D_{E} \Delta t}{\Delta x^{2}} \leq \frac{1}{2} f_{E} \quad \quad \quad \quad (12)
\]

It is easy to see that if the above conditions are fulfilled for \( D_{E} = D_{W} \), the following is a necessary requirement

\[
\frac{D \Delta t}{\Delta x^{2}} \leq \frac{1}{4} \quad \quad \quad \quad (13)
\]

Notice that, even though an implicit method has been used, there is a stability condition for a volume element containing a phase boundary. That condition is very similar to the classical condition for explicit methods. This might be the reason why some unstable values were observed in the solute profiles during some simulations. However, the time refining technique mentioned before managed to keep the system stable.
2 Tin concentration profiles as function of distance across control volume: comparison shown between the results of proposed model and analytical solutions, Scheil\(^{24}\) plate-like and sphere, Kobayashi\(^{25}\) plate-like, and Nastac and Stefanescu\(^{26}\) for which a means radial coordinate in spherical control volume; solid lines are always analytical solutions, which are behind model results represented by different symbols

Although some conditions should be obeyed to maintain stability in the volume elements where phase boundaries are located, all other volume elements are unconditionally stable. This is owing to the fact that, for those volume elements, one has a problem with a Dirichlet boundary condition, i.e., the concentration at the phase boundary is given, which can be easily solved by implicit methods. Consequently, when just one phase boundary exists, only one volume element might generate instability. The solution to a simple diffusion problem with Dirichlet boundary conditions by an explicit method was examined. It is known that, for this case, a stability requirement similar to equation (13) exists for all the volume elements, except that \( \frac{\Delta \xi}{\Delta \xi} \) is replaced by \( \frac{1}{\Delta \xi} \). Nevertheless, when all the elements but one obey the stability condition, the Fourier number given by the left side equation (13) might be as great as 0.85 for that element without unstable values propagating through the calculation domain. However, when two phase boundaries are present, which is the case during a peritectic transformation, two volume elements should obey stability conditions. In this case, the Fourier number for these elements had to be smaller than 0.65 for the system to be stable. Therefore, the time step should be controlled carefully when the peritectic transformation is simulated.

Instability problems can also be interpreted on a physical basis. An increase in time step should originate a larger displacement of the actual phase boundary during this interval. Both the explicit and implicit methods assume that the phase boundary remains at the same position during the whole time step. Thus, gross errors might arise in the flux calculations involving the phase boundary if an unduly large time step is defined. These unreal fluxes are likely to generate unreal average concentration variations in the volume containing the phase boundary.

### Results and discussion

**COMPARISON WITH ANALYTICAL SOLUTIONS**

The mathematical model of microsegregation proposed in the present work was adjusted to simulate some situations for which an analytical solution is available in the literature. Important parameters used in the model for some of the comparisons are shown in Table 1. The solute partition coefficient was 0.19, the average solute concentration was 8.0 wt-%, and the control volume size was 20 \( \mu \text{m} \), except for the last comparison. Some of the analytical solutions assume a growth law for the solid/liquid interface, which had to be forced in the proposed model. Two morphologies were studied, plate-like \( (p) \) and spherical \( (s) \). Interface velocities for the parabolic and linear growth laws could be calculated from the control volume size and local solidification time, which is also given in Table 1. Except for the steady state solution, where 200 volumes were used, all simulations employed a space mesh of 100 volumes and the coarsest time step was \( 1.2 \times 10^{-3} \, \text{s} \).

Figure 2 shows a comparison between the concentration profile in the solid given by the model and that given by Kobayashi's exact solution\(^{25}\) for the liquid phase was used to check how accurately the model treated liquid diffusion. Figure 3 shows results of the solute profile in the liquid and solid phases. The interface was forced to move at a constant velocity of 2 \( \mu \text{m} \, \text{s}^{-1} \) and the liquid solute profile naturally reached steady state at the end of the computation. No local solidification time was necessary. It can be seen in Fig. 3 that good agreement was obtained. The last test shown in Table 1 is a comparison with Mortensen's\(^{28}\) analytical solution for a plate-like control volume where diffusion in the solid was neglected and a homogeneous liquid was assumed. A special feature about Mortensen's\(^{28}\) analytical solution is that secondary arm spacing \( S_0 \) undergoes coarsening according to the following law

\[
S_0 = B t^b \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad
\]

where \( B = 6 \) and \( b = \frac{1}{2} \) for the comparison, and \( t \) is the time elapsed since the beginning of solidification. A constant cooling rate of 1 K s\(^{-1}\) was adopted and the final control volume size after 193 s was 17.5 \( \mu \text{m} \).

Table 1

<table>
<thead>
<tr>
<th>Analytical solution</th>
<th>( D_L ) ( 10^{-26} \text{m}^2\text{s}^{-1} )</th>
<th>( D_S ) ( 10^{-9} \text{m}^2\text{s}^{-1} )</th>
<th>Growth law</th>
<th>Denudate morphology</th>
<th>( t_c ) ( \text{s} )</th>
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3 Tin concentration profiles as function of distance across plate-like control volume, comparison shown between results of proposed model and exact solution due to Tiller et al.\textsuperscript{27} which gives solute profile in liquid ahead of solid/liquid interface

4 Comparison between tin concentration profile given by model and that obtained by Mortensen's\textsuperscript{26} analytical solution for plate-like control volume: \(x/L\) distance along control volume of final size \(L\)

5 Profile of tin concentration as function of distance across plate-like control volume with three different phase layers: comparison shown between results of proposed model and exact solution given by Mei et al.\textsuperscript{25} abrupt concentration variations indicate positions of phase boundaries

A test was devised to assess the ability of the proposed model to deal with the peritectic transformation. If the peritectic transformation is assumed to occur at a constant temperature, it becomes similar to a multiphase diffusion problem. One has a diffusion couple of a primary solid and a liquid phase with the formation of a third solid phase between them. The layer thickness of all phases changes with time depending, for instance, on the solute diffusion coefficients. An exact solution given by Mei et al.\textsuperscript{25} was employed to calculate solute profiles and interface positions for the multiphase diffusion problem. In this case, shown by Fig. 5, it was assumed that thermodynamic equilibrium existed at phase boundaries, the right and left phases were semi-infinite with diffusion coefficients of \(10^{-12}\) m\(^2\) s\(^{-1}\), the central phase had a diffusion coefficient of \(10^{-11}\) m\(^2\) s\(^{-1}\), and the left and right phases had an initial concentration of 1 and 0 respectively. The plate-like control volume length was 20 \(\mu\)m and the initial position of the phase boundaries was the reference origin, located in the middle of the control volume. A third phase layer was created at this position and, after 5 s, had its thickness increased naturally by the proposed model, as presented in Fig. 5. It is possible to see that the model gave virtually the same concentration profile as that of the exact analytical solution, proving itself to be adequate for the multiphase problem in hand. A final comparison was made between the model and experimental results of microsegregation in an Al–4.9 wt.%Cu alloy,\textsuperscript{30} which undergoes eutectic reaction. The calculated and measured eutectic fractions just after solidification and their corresponding cooling rates and local solidification times are given in Table 2. An empirical equation was employed to calculate the control volume size increase due to coarsening. The solidus and liquidus lines were divided into some linear segments, whose equations were used to calculate the solid and liquid phase solute contents for a given temperature. All this data is presented by Sundarraj and Vollcr\textsuperscript{15} and will not be repeated here. Good agreement between measured and calculated volumes of eutectic is observed, though the calculated results are always smaller than the measured ones. Furthermore, Table 2 shows that the agreement between calculated and measured volumes of eutectic is as good as that observed for the results obtained by Sundarraj and Vollcr.\textsuperscript{15} They used the same empirical equation for coarsening but employed a change of variables to handle the expanding domain.

### SIMULATION OF THE PERTECTIC TRANSFORMATION

The model described above was employed to simulate the microsegregation development in a Cu–8 wt.%Sn alloy, which might undergo a peritectic transformation at 799°C. The peritectic reaction for this alloy can be represented as\textsuperscript{31}

\[ \alpha + \beta \rightarrow \gamma \]

where \(\alpha\) is an fcc copper rich phase and \(\beta\) is a bcc phase with 22 wt.%Sn at the peritectic temperature. The equilibrium liquidus and solidus temperatures are 1028 and 858°C respectively, and the initial simulation temperature was equal to the liquidus temperature. The solidus and liquidus lines, as well as the boundaries between \(\alpha\) and \((\alpha + \beta)\) and between \((\alpha + \beta)\) and \(\beta\) fields of the phase diagram were described by linear segments between temperature intervals of 25°C (Ref. 32). The linear segments were

| Table 2. Eutectic volume fraction measured by Sarreal and Abbasschian,\textsuperscript{30} calculated by proposed model, and calculated by Sundarraj and Vollcr\textsuperscript{15} for different cooling rates \(R\) and local solidification times \(t_s\). |
|---|---|---|---|---|
| \(R, \text{ K s}^{-1}\) | \(t_s, \text{s}\) | Sarreal and Abbasschian\textsuperscript{30} | Sundarraj and Vollcr\textsuperscript{15} | Present model |
| 0.1 | 980 | 5.92 | 4.73 | 4.68 |
| 11.25 | 8.72 | 6.76 | 6.45 | 6.45 |
| 187 | 0.52 | 7.44 | 6.77 | 7.13 |
employed to define tin concentrations at every interface for a certain temperature.

A plate like control volume was located between two adjacent secondary dendrite arms and a cooling rate of 0.87 K s⁻¹ was chosen. The control volume extension was half the average secondary dendrite arm spacing and its origin was placed at the arm centre. The secondary dendrite arm spacing adopted was 42 µm and no coarsening was considered for these simulations.

Diffusion coefficients for the z, β, and liquid phases are given in the Appendix. The control volume was discretised by a mesh of 100 nodes, each at the centre of one volume element. The coarsest time step used, which is the one with no refinement, was 1.2 × 10⁻⁷ s. Solute concentration profiles were obtained until the control volume temperature decreased to 587°C. Calculations lasted for approximately 20 min on a personal computer with a Pentium II 330 MHz microprocessor and 64 Mb of RAM.

Figure 6 shows the tin concentration as a function of the fractional distance along the control volume at specific temperatures. At the temperature of 902°C, a characteristic solute profile is displayed, where a homogenous liquid and a solute concentration gradient in the solid can be seen. The position of the solid(α)/liquid interface is indicated by the abrupt solute concentration change. At 801°C, a greater fraction of solid is present and it is clearly seen that the solute content of the solid and particularly its minimum concentration increased due to solid diffusion. At the temperature of 978°C, just below the peritectic temperature (799°C), the solid(α)/solid(β) and solid(β)/liquid phase boundaries are both present in the control volume, showing that there is still liquid left due to the hindered peritectic reaction. The two new phase boundaries (α/β and β/liquid) were seen to move at opposite directions, causing both an increase in the β phase layer thickness and a decrease in liquid fraction. The peritectic transformation was finished, i.e. the liquid phase completely disappeared, within ~1 K below the peritectic temperature. Shortly after the end of that transformation, i.e. after the solid(β)/liquid boundary had disappeared through the control volume boundary, the solid(α)/solid(β) interface reversed its movement direction causing the start of β phase dissolution. This can be seen by comparing the profiles for 978°C and 757°C. At 587°C, the β phase had dissolved completely and the concentration profile showed a sinusoidal appearance.

The proposed model seems to correctly simulate some fundamental features of the peritectic transformation and phase dissolution process. At the cooling rate of 0.87 K s⁻¹, the peritectic transformation was nearly complete very close to the peritectic temperature, although the new solid phase β, prevents the direct contact between α and liquid phases. Furthermore, the β phase was totally dissolved before the control volume reached room temperature, resulting in a structure of only one phase.

Conclusions

A model of microsegregation for eutectic and peritectic binary alloys was presented. It employs simple ideas proposed by other authors, but never put together before to handle the solidification of alloys undergoing eutectic and peritectic transformations. After examining the model behaviour, the following conclusions could be drawn:

1. The mathematical model of microsegregation proposed in the present work was able to give concentration profiles in excellent agreement with these analytical solutions: Scheil's solution, Kobayashi's exact solution for a plate like morphology, Nastac and Stefancescu's solution for a spherical morphology, the steady state solution of Tiller et al. and Mortensen's solution considering coarsening in a plate like morphology, and the exact solution by Mei et al. for a multiphase diffusion problem.

2. The volume of eutectic obtained from the present mathematical model was in good agreement with some experimental results published by Sarreal and Abbaschian for an Al-4.9 wt-%Cu alloy subject to different cooling rates.

3. The model correctly simulated the basic features of a peritectic transformation and the phase dissolution that followed.

4. Some stability requirements seem to exist for the volume elements that contain a phase boundary. Those requirements appear to be more severe when more than one volume element houses a phase boundary.

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Appendix

Equations for solute fluxes, areas, and volumes

The relationships for the quantities used in equation (5) are better explained with the help of Fig. 1. Volume element P has a contact area $A_W$ with volume element W, and a contact area $A_E$ with volume element E. A plate like control volume has unity contact area, whereas a spherical control volume with a reference system placed at the centre has contact areas defined as

$$A_W = 4\pi (x_p - \delta x_W)^2$$

(16)

$$A_E = 4\pi (x_p + \delta x_E)^2$$

(17)

where $x_p$ is the node position within volume element $P$ and $\delta x_W$ and $\delta x_E$ are shown in Fig. 1. The volume $V$ of volume elements is given by the following equations for plate like and spherical morphologies respectively

$$V = (\delta x_E + \delta x_W)$$

(18)

$$V = \frac{4}{3} \pi [(x_p + \delta x_E)^3 - (x_p - \delta x_W)^3]$$

(19)

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Solute flux equations are based on the assumption of a piecewise linear concentration profile between two adjacent nodes and are given by

\[ Q_{i}^{k+1} = 0 \quad \text{for volume element } P = 0 \quad \ldots \quad (20) \]

\[ Q_{i}^{k+1} = (C_{w}^{k+1} - C_{w}^{k+1}) \left( \frac{\delta x_{w}}{D_{w}} + \frac{\delta x_{w}}{D_{p}} \right) \quad \text{for volume element } P \neq 0 \quad \ldots \quad (21) \]

\[ Q_{i}^{k+1} = 0 \quad \text{for volume element } P = (N - 1) \quad \ldots \quad (22) \]

\[ Q_{i}^{k+1} = (C_{w}^{k+1} - C_{w}^{k+1}) \left( \frac{\delta x_{w}}{D_{w}} + \frac{\delta x_{w}}{D_{p}} \right) \quad \text{for volume element } P \neq (N - 1) \quad \ldots \quad (23) \]

where \( D_{w} \), \( D_{p} \), and \( D_{p} \) are the diffusion coefficients calculated at the concentrations of volume elements \( E, W, \) and \( P \) respectively, and \( N \) is the number of volume elements used to discretise the domain and these are indexed from 0 to \( N - 1 \).

**Diffusion coefficients**

The diffusion coefficient of tin in the liquid alloy Cu-8 wt.-%Sn at 1028 °C was calculated, for example, by Roy and Chhabra. The interdiffusion coefficient \( D_{Cu-Sn} \) in the solid \( z \) phase of the Cu-Sn system was measured by Oikawa and Hosoi, who gave the following in units of m² s⁻¹

\[ D_{Cu-Sn} \approx 2 \times 10^{-6} \times 10^{13} N_{Sn} \exp \left( \frac{-156000}{83147 T} \right) \quad (24) \]

where \( N_{Sn} \) is the tin molar fraction and \( T \) is the absolute temperature.

To the present authors' knowledge, there are no measurements of the diffusion coefficient in the \( \beta \) phase of the Cu-Sn system. However, an estimate was attempted based on this system similarity to the Cu-Zn one. Phases \( z \) and \( \beta \) of the Cu-Sn system have similar crystal structures to \( z \) and \( \beta \) of the Cu-Zn system. While \( z \) phase has an fcc structure, \( \beta \) phase has a bcc structure that is not ordered. The copper rich side of phase diagrams for the Cu-Sn and Cu-Zn systems can be made very similar if temperature and solute concentration are properly scaled. Moreover, Philibert has presented some recommendations to help the estimate of self-diffusion coefficients when no other information is at hand. Self-diffusion coefficients at the melting point and the ratio between activation energy for diffusion and melting temperature have comparable values for materials of similar crystalline structures. The ratio between the interdiffusion coefficient in the \( z \) phase of the Cu-Sn system and that in the Cu-Zn system was calculated at the peritectic temperature at the maximum solute solubility. This ratio was assumed equal to the ratio between the interdiffusion coefficients in the \( \beta \) phases of both systems and is given by

\[ \frac{D_{Cu-Sn}}{D_{Cu-Zn}} \approx 0.15 \quad \ldots \quad (25) \]

Thus, it was possible to use the available interdiffusion coefficient in the \( \beta \) phase of the Cu-Zn system to estimate that for the \( \beta \) phase of the Cu-Sn system. Therefore, for a corrected absolute temperature \( T' \), defined as

\[ T' = T \left( \frac{T_{Cu-Zn}}{T_{Cu-Sn}} \right) \quad \ldots \quad (26) \]

where \( T_{Cu-Zn} \) and \( T_{Cu-Sn} \) are the peritectic temperatures of the Cu-Zn and Cu-Sn systems, hence in units of m² s⁻¹

\[ \frac{D_{Cu-Sn}}{D_{Cu-Zn}} \approx 0.15 \left( \frac{T_{Cu-Zn}}{T_{Cu-Sn}} \right) = 0.15 \left( \frac{T_{Cu-Zn}}{T_{Cu-Sn}} \right) \quad \ldots \quad (27) \]

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