

## A model for the numerical computation of microsegregation in alloys

A.J.W. OGILVY<sup>1</sup> & D.H. KIRKWOOD<sup>2</sup>

<sup>1</sup> Osprey Metals Ltd., Neath, South Wales, UK; <sup>2</sup> Department of Metallurgy, Sheffield University, Sheffield, UK

**Abstract.** A development of the Brody-Flemings model for the prediction of dendritic microsegregation in alloys is proposed. The original model considered one-dimensional back diffusion into thickening platelike dendrite arms of fixed spacing. The present modification allows for the dendrite arm coarsening which is observed to occur during solidification and considers microsegregation in both binary and multi-component alloy systems. It is shown that numerical calculations of microsegregation using finite difference techniques based on this model give good agreement with experiment.

### Nomenclature

$B = (1-f)/(1-(1-k)f)$ , correction factor for fast diffusing species  
 $c$  concentration in solid, wt.%  
 $c^0$  average concentration, wt.%  
 $c^l$  concentration in liquid, wt.%  
 $D$  diffusion coefficient in solid  
 $f$  fraction solid ( $= X/L$ )  
 $k$  equilibrium partition coefficient  
 $L$  half dendrite arm spacing  
 $t$  time  
 $W$  cooling rate  
 $x$  direction coordinate normal to dendrite plate  
 $X$  distance solidified  
 $\beta$  liquidus gradient  
subscript  $i$  refers to the  $i$ th solute element

### Introduction

The first attempts to predict microsegregation quantitatively [1,2] assumed that within a characteristic volume element, related to a dendrite spacing or the grain size, the liquid region during solidification is completely mixed, whereas negligible diffusion occurs in the solid and local thermodynamic equilibrium is maintained at the moving interface described by a constant equilibrium partition coefficient. This model gives rise to the so-called Scheil equation:  $c = kc^0(1-f)^{k-1}$ .

With the introduction of microprobe analysis it soon became apparent that the assumption of negligible solid-state diffusion was untenable and Brody and Flemings [3] proposed a model involving one-dimensional back diffusion into growing dendrites of plate-like morphology. Apart from this modification, the previous assumptions of interface equilibrium and complete solute mixing in the liquid are maintained.

An analytical solution of the differential equation was derived from the model by assuming the dendrite growth rate and approximating for the composition gradient at the solid interface. This has been criticised however [4] as being an invalid approximation when diffusion is important. A general disadvantage of analytical treatments of microsegregation is their inability to deal with the complexity of real systems in which partition coefficients, diffusion coefficients and dendrite spacings all change with time or temperature during solidification. These problems are readily overcome using numerical techniques to solve the basic differential equations.

The partial differential equation derived from the Brody-Flemings model of one-dimensional back diffusion into plate-like dendrites in a binary alloy system is:

$$c'(1 - k) \, dX/dt = D(\partial c/\partial x)_X + dc'/dt(L - X)$$

where  $L$  is half the appropriate dendrite arm spacing (see Fig. 1). Using an explicit finite difference method to calculate diffusion and the above equation to control the interface movement, Brody and Flemings were able to compute the solute distribution throughout the solidification process, and compare their predictions with measurements of microsegregation in Al-Cu alloys solidified under a range of conditions [5]. In order to obtain agreement with experiment it was necessary to employ dendrite arm spacings approximately one third of the measured value. This large discrepancy has been attributed later by Flemings [6] to the simple geometries assumed, to the use of inaccurate diffusion data or to coarsening effects. It is believed that diffusion data in the Al-Cu system is now well enough established not to be considered a source of significant error [7]. It is clear however that dendrite morphologies can be extremely complex and change during growth, particularly in highly alloyed systems [8] and under conditions of rapid growth and low temperature gradient. It would not be expected that the model proposed in this paper could be satisfactorily applied under these conditions.

The observation that the spacing of secondary (and higher order) arms increases during solidification was made by Kattamis et al. [9], who proposed that this coarsening occurred by smaller arms melting away at the expense of their larger neighbours by a diffusion process driven by surface tension. It has also been shown that coalescence of adjacent arms to form a single larger arm can occur driven by the same surface tension forces [10,11]. These coarsening processes have a important effect on the calculation of dendritic microsegregation as will be shown.

A fuller discussion of the assumptions involved in different microsegregation models has been published recently [12].

**Microsegregation in binary alloys involving arm coarsening**

The present model makes the same assumptions as Brody and Flemings, except that the average dendrite arm spacing is allowed to increase with time during solidification according to some given relationship. Two adjacent dendrite plates are considered as in Fig. 1, in which the centre to centre spacing is  $2L$ . Within this we select an element bounded by a plate centre (at  $x = 0$ ) and the centre of the liquid region (at  $x = L$ ) for the calculation on solute redistribution. A schematic diagram of solute distribution within the element is given in Fig. 2, representing a point in time during the solidification process. The solute rejected by the interface movement must be absorbed partly by back diffusion into the solid, and partly absorbed into the liquid raising its uniform composition. This distribution is expressed in the first two terms of the right-hand side of the solute balance equation:

$$c^l(1 - k) \, dX/dt = D(\partial c/\partial x)_X + dc^l/dt(L - X) + (c^l - c^0) \, dL/dt. \quad (1)$$

The end term represents the increase in the size of the element due to arm coarsening, which brings in liquid of average composition that requires to be raised to the composition of the existing liquid. It is necessary that liquid of average composition be added to conserve the overall composition in the element: the physical meaning of this is that somewhere in the system a dendrite arm is melting and part of this solid together with its associated liquid is transferred at average composition to the element. This dilution effect is responsible for a reduction in microsegregation.

If we can assume that the cooling rate and the liquidus slope of the alloy system are constants, then we may substitute  $dc^l/dt = W/\beta$  into eqn. 1 to obtain:

$$dX/dt = \frac{\beta D(\partial c/\partial x)_X + W(L - X) + \beta(c^l - c^0) \, dL/dt}{c^l(1 - k)}. \quad (2)$$

Back diffusion of solute into the solid dendrite plate may be calculated using a finite difference formulation of the diffusion equation:  $\partial c/\partial t = D \, \partial^2 c/\partial x^2$ , and employing the boundary condition  $\partial c/\partial x = 0$  at  $x = 0$ . The movement of the interface  $\delta X$  in the time step  $\delta t$  is obtained from the finite difference formulation of eqn. 2, in which  $(\partial c/\partial x)_X$  is approximates from compositions in the solid near the interface at unequally spaced nodes by a method due to Crank [13]. The increase in  $\delta L$  during the time step is obtained from the given functional relationship referred to above. The increase in liquid composition  $\delta c^l$  is now obtained by back substitution in eqn. 1, from which the interface composition of the solid is in turn calculated. These calculations can be repeated, adjusting the diffusion and partition coefficients as appropriate for

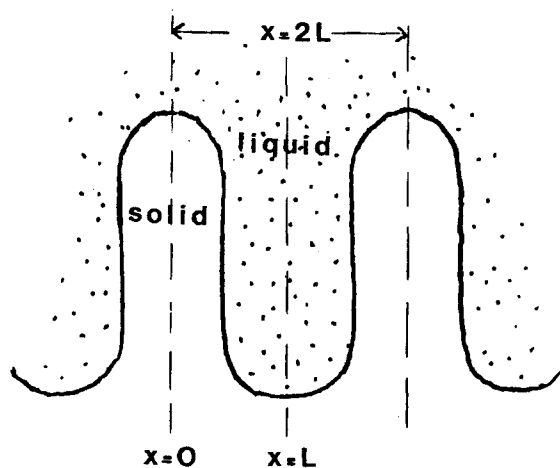


Fig. 1.

the temperature at each step until complete solidification is achieved, that is when either the liquid disappears or it attains eutectic composition. An earlier paper [14] provides further details on the finite difference computation.

In many situations the use of a constant cooling rate during solidification may not be appropriate and a reformulation of eqn. 2 in terms of constant heat extraction given by Howe [15] may be more realistic.

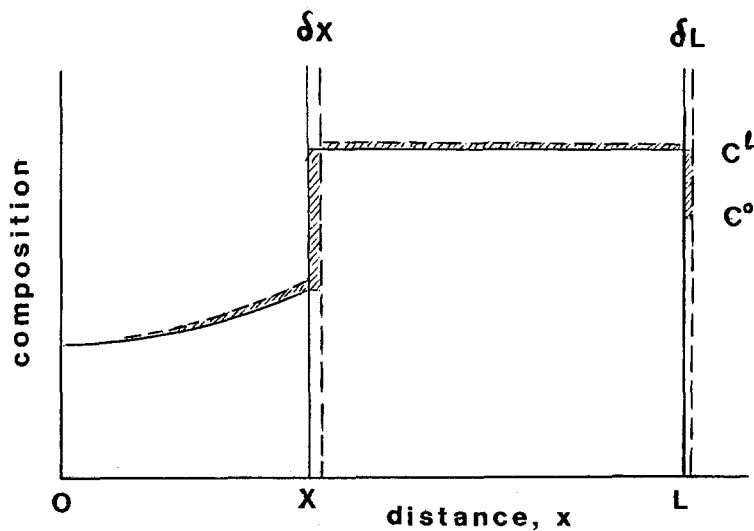


Fig. 2.

**Microsegregation in ternary and higher component systems**

In a ternary system a solute balance at the moving interface may be written for both diffusing solute species, 1 and 2:

$$c_1^l(1 - k_1) \, dX/dt = D_1(\partial c_1/\partial x)_X + dc_1^l/dt(L - X) + (c_1^l - c_1^0) \, dL/dt$$

$$c_2^l(1 - k_2) \, dX/dt = D_2(\partial c_2/\partial x)_X + dc_2^l/dt(L - X) + (c_2^l - c_2^0) \, dL/dt.$$

We may also write for the cooling rate:  $W = \beta_1 \, dc_1^l/dt + \beta_2 \, dc_2^l/dt$ . Multiplying the two upper equations by the appropriate  $\beta$  and adding to eliminate  $dc^l/dt$  from each, we have:

$$dX/dt = \left[ \beta_1 D_1(\partial c_1/\partial x)_X + \beta_2 D_2(\partial c_2/\partial x)_X + R(L - X) + \left\{ \beta_1(c_1^l - c_1^0) + \beta_2(c_2^l - c_2^0) \right\} dL/dt \right] \left[ \beta_1 c_1^l(1 - k_1) + \beta_2 c_2^l(1 - k_2) \right]^{-1}.$$

It is clear from the form of this equation that it may be generalised for higher component alloys:

$$dX/dt = \frac{\sum \beta_i D_i(\partial c_i/\partial x)_X + R(L - X) + \sum \beta_i(c_i^l - c_i^0) \, dL/dt}{\sum \beta_i c_i^l(1 - k_i)}.$$

The finite difference procedure is carried out exactly as in the binary case; having determined  $\delta X$  for a given time step,  $\delta c^l$  may be obtained for each solute element by back substitution in the first equations.

**Microsegregation in an alloy containing a fast diffusing solute element**

When explicit finite difference equations are used to solve the diffusion equation, a condition for the mathematical stability of the solution is that we must choose a time step  $\delta t$  such that  $D\delta t/\delta x^2 \leq 1/2$  [16]. This requires that where we have a fast diffusing species, the time step will be determined by it and will necessarily be small. Therefore a large number of computer calculations are needed to complete the solidification and the time taken for the overall microsegregation calculation can be unacceptable.

In many practical situations one (or more) elements may diffuse so fast as to establish partial equilibrium between the solid and liquid phases, for example interstitial elements such as carbon in steels. In such cases the compositional gradients of the solute in each phase is negligible, and we may write for the solute balance at the moving interface:

$$c_i^l(1 - k_i) \, dX/dt = k_i X \, d\frac{c_i^l}{dt}/dt + dc_i^l/dt(L - X) + (c_i^l - c_i^0) \, dL/dt.$$

Eliminating  $dc_i^l/dt$  in all the solute balance equations as before, we have:

$$dX/dt = \frac{\sum \beta_i D_i(\partial c_i/\partial x)_X + R(L - X) + \sum \beta_i(c_i^l - c_i^0) B_i \, dL/dt}{\sum \beta_i c_i(1 - k_i) B_i}.$$

Table 1. Predicted effect of back diffusion on microsegregation in Al-5wt.%Cu alloy solidified at a cooling rate of 1 K/s.

Assumptions	C <sub>min.</sub> /C <sub>0</sub>
Fixed dendrite arm spacing	0.25
Dendrite coarsening	0.34
Dendrite coarsening Constant <i>D</i> (liquidus value)	0.46

where  $B_i = 1$  for slow diffusing solute elements (e.g. in substitutional solution), and  $B_i = (1 - f)/(1 - (1 - k_i)f)$  for fast diffusing solute elements (e.g. in interstitial solution).

This equation may also be recast in an alternative form where the assumption of a constant rate of heat extraction is more appropriate (see Howe [15]).

## Discussion

Table 1 shows the results of numerical calculations using the present model to predict microsegregation in Al-5wt%Cu alloys. They are expressed as the ratio of the minimum concentration at the centre of the dendrite arm to the average concentration, which was measured by Bower et al. [5] to be  $\sim 0.30$  and by Bennett [17] to be  $\sim 0.35$  under a variety of solidification conditions. Using a fixed arm spacing (the final spacing measured after solidification) clearly results in an overestimation of the degree of microsegregation as previously shown by Brody and Flemings [3]. Using the coarsening relationship:  $L = 8t^{0.31}$  (where  $L$  is in  $\mu\text{m}$ . and  $t$  in seconds) obtained from experimental measurements of secondary arm spacings during solidification in this alloy [11], the prediction of the model is in good agreement with the measured values of microsegregation. The third computation demonstrates the sensitivity of the calculation to the choice of diffusion coefficient. A constant value has been used, calculated at the liquidus temperature of the alloy, and this clearly predicts too low an amount of microsegregation.

The use of this model for predicting microsegregation in more complex alloys has been made by Howe and is reported in this volume [15].

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