Microsegregation model including Soret effect: an application for Sn-Bi alloy

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Abstract. We present an application of a microsegregation model that takes into account the Soret effect. This model, summarized here, lies in the context of the evaluation of thermodiffusion influence in alloys solidification. Initially, we deal with the thermodiffusion effect on the microsegregation scale. Subsequently, the Soret effect on macrosegregation shall be analyzed. The present model was conceived with similar considerations compared to the Gulliver-Scheil approach. A dimensionless parameter emerged from the model, which is potentially useful for assessing the Soret effect on the solidification of binary alloys. In the present work, this parameter was applied to an Sn-Bi alloy. The microsegregation model including the Soret effect can be widely used in the study of solute redistribution.

1. Introduction

The Soret effect is the diffusion of chemical species in a mixture driven by thermal gradients. This kind of transport has been systematically neglected on solidification models [1]. This is done based on the typically low value of thermodiffusion coefficient in solid solutions compared to chemical driven diffusion coefficient. A parameter commonly used to show that is the Soret coefficient, $S_T$, defined by $S_T = D_T/D$, where $D_T$ is the thermodiffusion coefficient, $D$ is the diffusion coefficient. However, this parameter does not includes other important phenomena inherent to solidification process, such as thermal conduction or energy and solute supplying due to phase change.

In fact, recent results such as those of references [2] and [3] suggest that thermodiffusion can significantly influence relevant parameters of solidified materials in the cases studied. Accordingly, since the temperature gradient in the liquid is often high, the thermodiffusion may have a considerable or influence on the composition of the liquid and the solidified final product.

The present work is part of an effort to analysis the influence of thermodiffusion in solidification processes [4]. Initially, the objective is to obtain parameters to evaluate the effect of thermodiffusion on the microsegregation scale. The present work fits this context. Subsequently, the Soret effect on macrosegregation will be analyzed.

In this paper, we present an application of the microsegregation model, presented elsewhere, which includes the Soret effect. The present model was conceived from similar considerations made by Gulliver and after by Scheil in their well known microsegregation model [1, 5], hereafter called G-S model in this text. But here the thermodiffusion across the system boundary was taken into account. The development of the mentioned model allowed the definition of a potentially useful dimensionless parameter for evaluating Soret effect on the solidification of binary alloys. In the present work, this parameter was applied to a Sn-35wt%Bi binary alloy. Lack of space, here we will summarize the
development of the model used in this text that is focused on a specific result. A more comprehensive explanation will be done elsewhere [4]. The microsegregation model including Soret effect can be widely used in the study of solute redistribution, with the advantage of being less restrictive than G-S model concerning the physical phenomena inherent to the solidification process.

In the section 2 we summarize the model developed for describe microsegregation on binary alloys including thermodiffusion. This model exposes a potential useful dimensionless parameter, which is presented in the section 3. Some results for several values of the mentioned parameter show the range of influence of thermodiffusion on microsegregation. Finally, a case study is presented for the Sn-35wt%Bi alloy.

2. Summary of microsegregation model including thermodiffusion

The present authors have proposed a solute balance equation to describe microsegregation in a binary alloy where the component can flow through the system boundary, driven by thermal gradient (thermodiffusion) [4]. This flow was taken into account via source term affecting the composition of the whole system over time.

The model was based on the following assumptions: a) an one-dimensional system between secondary dendrite arms, similar to that established for the G-S model [1, 5]; b) the solute diffusion in the solid is null (D_s = 0); c) the solute diffusion in the liquid is fast enough to have a uniform profile in this phase; d) local equilibrium at the solid/liquid interface and C_s(t) = k_0 C_l(t); e) a binary alloy with equal and constant densities for liquid and solid phases, so that the mass and volume solid fractions are coincident; f) no convection in the liquid; g) solute may flow across the system boundary due to the effect of thermodiffusion (Soret effect); h) the secondary arm spacing remains constant over time.

2.1. One-dimensional solute balance

The solute balance in a control volume defined in accordance to the constraints a), e), f) and g) listed above may be expressed as follows:

\[
\int_{0}^{x^*} C_s(x, t) \, dx + \int_{0}^{x^*} C_l(x, t) \, dx = X(t) \bar{C}(t)
\]  

(1)

In the present text, the subscript \( l \) refers to the liquid phase, while \( s \) indicates the solid phase. \( X \) is the whole length of the system (half the secondary arm spacing); \( C \) is the total solute composition for the entire control volume, \( 0 \leq x \leq X(t) \); the integration limit \( x^* \) is the location of the solid-liquid interface measured from the center of dendrite arm (the amount of solid in our one-dimensional analysis).

Applying the simplifications c) and d) to equation (1), dividing the result by \( X \), making \( (X - x^*) = x_1^* \) and recognizing that \( g_l = x_1^*/X \), we have

\[
\frac{1}{X} \int_{0}^{x^*} C_s \, dx + g_l C_1^* = \bar{C}
\]  

(2)

where \( C_1^* = C_1^*(x, t) \). We have omitted \((x, t)\) function notation to simplify the writing. Differentiating the previous equation with respect to time, using Leibniz’s rule for the first term,

\[
\left( \int_{0}^{x^*} C_s \, dg_l \right) \frac{1}{X} \frac{dX}{dt} + \int_{0}^{x^*} \frac{1}{X} \, dC_s \, \frac{dg_l}{dt} + g_l \frac{dC_1^*}{dt} + (1 - k_0)C_1^* \frac{dg_l}{dt} = \dot{\bar{C}}
\]  

(3)

where \( \dot{\bar{C}} = d\bar{C}/dt \). In the last result we have also used the partition coefficient defined as \( k_0 = C_1^*/C_s^* \), along with \( g_s = 1 - g_l \), resulting in \( C_s^* \, dg_s/dt = -k_0 C_1^* \, dg_l/dt \). In addition, \( X \) does not depend directly on \( x \), allowing changing variables: \( x/X = d \). 

Equation (3) express the solute balance in a one-dimensional control volume, where the total amount of solute can change. In the present work we deal with a particular case of (3) by applying simplifications...
b) (no diffusion in the solid phase) and h) (constant secondary arm spacing). That is, \( dX/dt = dC_s/dt = 0 \), and equation (3) reduces to
\[
g_l \frac{dC_l^s}{dt} + (1 - k_0)C_l^s \frac{dg_l}{dt} = \dot{C}
\]

(4)

2.2. Thermodiffusion across the boundary as a source term

The total mass of solute crossing the boundary S surrounding V, per unit of time, is
\[
F_p = -\int_S \dot{j} \cdot \hat{n} \, dS
\]
where the flux of solute \( \dot{j} \) due to thermodiffusion is given by [6],
\[
\dot{j} = -\frac{L_{1q}}{T^2} \nabla T = -\rho \alpha \bar{C}_A \bar{C}_B \nabla T
\]
(6)
\( C_A \) and \( C_B \) are the solvent and solute mass fraction, respectively. \( D^T \) is the thermodiffusion coefficient \( ([D^T] = m^2 K^{-1} s^{-1}) \), \( L_{1q} \) is the Onsager’s phenomenological cross coefficient and T is the temperature.

To consider solute flux crossing the boundary as a source term acting at each point in the volume,
\[
\dot{\bar{C}} = \frac{1}{\rho V} F_p = -\frac{1}{\rho V} \int_S \dot{j} \cdot \hat{n} \, dS = \frac{1}{\rho V} \int_S \frac{L_{1q}}{T^2} \nabla T \cdot \hat{n} \, dS
\]
(7)

Note that \( V \) is the total volume (solid plus liquid), since \( \bar{C} \) is the average concentration over the entire volume. However, we consider that all thermodiffusion occurs only through the liquid boundary, \( S_l \). Here, it should be noted that the control volume \( V \) is small enough so that the integrand can exit the above integral. However, for convenience, \( \nabla T \) will be left in the operator. In fact, the is not computed within \( V \), but occurs between \( V \) and the neighborhood via \( S_l \).

For what follows it will be useful to remember that, for a single phase region of volume \( V \), subjected only to heat conduction, we have that,
\[
\frac{1}{\alpha} \int_V \frac{\partial T}{\partial t} \, dV = \int_S \nabla T \cdot \hat{n} \, dS
\]
(8)
where the divergence theorem was applied, with \( S \) being the surface containing the arbitrary volume \( V \), and the thermal diffusivity \( \alpha \) was considered a constant.

Extracting \( \frac{L_{1q}}{T^2} \) from the integral in equation (7) and using equation (8) with \( V = V_l \) and \( S = S_l \),
\[
\dot{\bar{C}} = \frac{1}{\rho V} \int_{V_l} \frac{1}{\alpha} \frac{\partial T}{\partial t} \, dV = \frac{L_{1q}}{\rho T^2 \alpha} \frac{g_l}{dT} \dot{d}T
\]
(9)

For the last result, both time derivative of temperature, \( \partial T/\partial t \) \( (=dT/dt) \), and thermal diffusivity \( \alpha \) were considered uniform in \( V \). In addition, it was made \( V_l/\alpha = g_l \).

2.3. Solute balance including thermodiffusion

Replacing from equation (9) in the equation (4),
\[
\frac{dC_l^s}{dt} + \frac{dg_l}{dt} = \frac{L_{1q}}{\rho \alpha T^2} \frac{g_l}{dT} \dot{d}T
\]
(10)

Assuming that the liquidus curve can be approximated locally by a linear coefficient line \( m_l \), the liquidus slope, we obtain \( T - T_f = m_l C_l^s \) and \( dC_l^s/dt = (1/m_l) \dot{d}T/\dot{d}t \). Here, \( T_f \) is a reference temperature for which the solute composition is null (the melting temperature of pure solvent). Using this linearization of the liquidus line and some rearrangement, we rewrite (10) as follows.
\[
\frac{1}{g_l} \frac{dg_l}{dt} = \frac{1}{k_0 - 1} \left[ \frac{1}{T - T_j} - \frac{m_l L_{1q}}{\rho \alpha T^2(T - T_j)} \right] dT dt
\]

(11)

The expression (11) is a separable first order ordinary differential equation subject to the following boundary conditions:

\[
g_l = 1 \iff T = T_0
\]

(12)

where \(T_0\) is the liquidus temperature corresponding to the nominal (initial) concentration of the alloy, \(C_0\). That is, \(T_0 = m_l C_0 + T_f\).

The resolution of the above boundary value problem (11) and (12) provided the main result for the microsegregation model in a binary alloy including Soret effect [4]:

\[
g_l = \left( \frac{T - T_f}{T_0 - T_f} \right)^\Theta \left( \frac{T_0}{T} \right)^\Lambda \left[ \exp \left( \frac{T_0}{T} - 1 \right) \right]^\Phi
\]

(13)

with

\[
\Theta = -\frac{1}{1 - k_0} + \frac{C_{A_0} C_{B_0} m_l D^T}{(1 - k_0) \alpha}; \quad \Lambda = \frac{C_{A_0} C_{B_0} m_l D^{T_f}}{(1 - k_0) \alpha}; \quad \Phi = \frac{C_{A_0} C_{B_0} m_l D^{T_r}}{(1 - k_0) \alpha}
\]

(14)

where \(T_j = \sqrt{T_f T_r}\) is the geometric mean between \(T_f\) and \(T_r\). The phenomenological coefficient \(L_{1q}\) is not directly available. To get around this fact, the exponents (14) were written in terms of thermodiffusion coefficient, \(D^T\), evaluated for each temperature \(T_f\) and \(T_r\):

\[
D^T_f = \frac{L_{1q}}{\rho C_{A_0} C_{B_0} T_f^2} \quad \text{and} \quad D^T_r = \frac{L_{1q}}{\rho C_{A_0} C_{B_0} T_r^2}
\]

(15)

where \(C_{A_0}\) and \(C_{B_0}\) are the initial mass fraction of the alloy components.

Note that if \(D^T = 0\) (no thermodiffusion), equation (13) reduces to the Gulliver-Scheil microsegregation model given by

\[
g_l = \left( \frac{T - T_f}{T_0 - T_f} \right)^{-\frac{1}{(1 - k_0)}}
\]

(16)

3. A dimensionless parameter for Soret effect on solidification

Observing the exponents of equation (13) presented at equations (14), we recognize the following dimensionless parameter [4]:

\[
\mathcal{H} = \frac{C_{A_0} C_{B_0} m_l D^T}{(1 - k_0) \alpha}
\]

(17)

This parameter relates thermodiffusion, heat transfer and the amount of solute segregated due to solidification.

Applied to (13), \(\mathcal{H}\) shall be evaluated for \(T_f\) and \(T_r\), using equations (15), so that

\[
g_s = 1 - \left( \frac{T - T_f}{T_0 - T_f} \right)^{-\frac{1}{(1 - k_0)}} + \mathcal{H}_f \left( \frac{T_0}{T} \right)^\mathcal{H}_r \left[ \exp \left( \frac{T_0}{T} - 1 \right) \right]^\mathcal{H}_r
\]

(18)

where, for convenience, we have used the solid fraction \(g_s\) with \(g_s = 1 - g_l\). Note that if \(\mathcal{H}\) vanishes, we have the G-S equation from the above expression.
4. Results and discussion

4.1. Preliminary results

We have generated some results from equation (18) using values $\mathcal{H} = \{10^{-4}, 10^{-3}, 10^{-2}, 10^{-1}\}$ and $\mathcal{H} = \{-10^{-4}, -10^{-3}, -10^{-2}, -10^{-1}\}$, considering data of table 1. These results are shown in the figures 1 and 2, plotted along with both G-S and lever-rule (LR) equations. The values in these figures are arbitrary, but table 1 are valid for Sn-35wt%Bi. For the case $\mathcal{H} > 0$ (figure 1), the curves from equation (18) lie below that of G-S model. For $\mathcal{H} < 0$ (figure 2), the curves from equation (18) are above the G-S curve. In our case, the figures 1 and 2 show that for $|\mathcal{H}| < 10^{-2}$ the contribution of Soret effect for $(g_s, T)$ profile is negligible. Thermodiffusion gets relevance around $|\mathcal{H}| \sim 10^{-1}$, when the curve for the present model is quite different from that of G-S model.

![Figure 1](image1.png)

**Figure 1:** Solidification path for some values of $\mathcal{H} > 0$.  

![Figure 2](image2.png)

**Figure 2:** Solidification path for some values of $\mathcal{H} < 0$.

4.2. An application of microsegregation model with Soret effect

We present here an application of the microsegregation model including the Soret effect. We have based our calculation on the data from Jafar-Salehi [3] (see table 1).
Considering the Sn-Bi phase diagram from reference [7], the liquidus and solidus lines have been locally fitted by linear approximations. For values of (C, T) around $C_0 = 35\text{wt}\%\text{Bi}$, this approximation would be as follows

\[
T = -1.6314C_t + 513.34 \tag{19}
\]
\[
T = -4.4280C_s + 505.14 \tag{20}
\]
\[m_t = -1.6314 \tag{21}\]
\[m_s = -4.4280 \tag{22}\]
\[k_0 = \frac{m_t}{m_s} = 0.368 \tag{23}\]

\[
{\mathcal{H}} = -1.053 \times 10^{-3} \tag{24}
\]

| Property                                      | Symbol | Value         |
|-----------------------------------------------|--------|---------------|
| Nominal solute mass fraction (wt % Bi)        | $C_0$  | 35            |
| Thermal diffusivity ($m^2\text{s}^{-1}$)      | $\alpha$ | $2.622 \times 10^{-5}$ |
| Eutectic mass fraction (wt % Bi)              | $C_{eut}$ | 57           |
| Diffusion coefficient ($m^2\text{s}^{-1}$)    | $D$ | $1.89 \times 10^{-9}$ |
| Thermal diffusion coefficient ($m^2\text{s}^{-1}\text{K}^{-1}$) | $D_T$ | $4.697 \times 10^{-10}$ |

Figure 3: Solidification path of Sn-35\%wtBi. Comparison between G-S model, the present model and the lever rule (LR). An enlarged detail of the present model and the G-S model curves is shown.

To employ the microsegregation model, we must calculate the dimensionless number $\mathcal{H}$. According to the physical properties listed in the table 1, the equation (17) results in

\[\mathcal{H} = -1.053 \times 10^{-3}\]
This result allows us to calculate $g_s(T)$ from equation (18). However, based on the analysis made in the previous section, we can expect that thermodiffusion can be neglected in this case. To verify this, we calculate the solidification path $g_s(T)$ to compare it with G-S results.

Figure 3 shows the results of equation (18) for the present case. The curve of G-S and that of the present model are indistinguishable on the scale of the whole path. This fact is confirmed in figure 4, which shows the difference between the models. The maximum difference found was $3.24 \times 10^{-4}$, confirming the previous conclusion made only by evaluating the parameter.

![Figure 4: Difference between the curves ‘present model’ and ‘G-S model’ from the figure 3.](image)

Despite the seemingly negligible influence of thermodiffusion on microsegregation (for the present alloy), it does not mean that it has no effect on other phenomena present in solidification. On this subject Platten and Legros [8, p. 576] stated: “The mass fraction gradient established under the effect of thermal diffusion is very small (…), but our theme is that such a small concentration gradient disproportionately influences hydrodynamics relative to its contribution to the buoyancy of the fluid. Therefore thermal diffusion cannot be ignored”. Convection is not taken into account in the present model. However, microsegregation models can be coupled in multi-scale solidification modeling, where convection can be a major player.

The solidification paths presented in figures 1 and 2 were calculated for a specific alloy. For now, we cannot conclude that parameter $\mathcal{H}$ is better than the Soret coefficient to evaluate the thermodiffusion influence on solidification. However, this parameter groups all relevant transport properties presented at solidification process. This prevents us that it can be more suitable for evaluation of the thermodiffusion on solidification than Soret coefficient is.

5. Conclusions

In this text we have summarized an analytical model for microsegregation during the solidification of a binary alloy, including thermodiffusion effect. A new parameter emerges naturally from the model, which correlates thermodiffusion, heat transfer, and the amount of solute segregated due to solidification. Equation (17) suggests that, in addition to thermodiffusion coefficient itself, the solute content, the liquidus slope and the partition coefficient are also parameters indicating the thermodiffusion relevance in solidification phenomena.

Depending on the value of the parameter $\mathcal{H}$, we can attempt a non-negligible difference between the solidification paths calculated using the present model and those from G-S equation. The present model was applied to calculate the solidification path of an Sn-35wt%Bi alloy. The results were compared with those from G-S equation. The calculation shown no significant difference between the two models,
indicating that thermodiffusion is not a relevant phenomenon for solid fraction path in the case studied. This conclusion could also be made inspecting the parameter $\mathcal{H} \sim 10^{-3}$ for the case considered.

More studies are necessary to verify the usefulness of $\mathcal{H}$ as a similarity parameter. In addition, a simplified version of the result (18) may be possible without major losses.

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