Solute redistribution and segregation in solidification processes

Wanqi Jie*

State Key Laboratory of Solidification Processing, Northwestern Polytechnical University, Xi’an 710072, People’s Republic of China

Abstract

In this review paper, research on solute redistribution coefficients for equilibrium, near equilibrium and non-equilibrium solidification processes were first analyzed. Then, different models advanced since the 1950s for solute redistribution during the directional solidification process with a planar interface were summarized. The so-called second-order opposite diffusion compensation method (SODCM) presented by the author was described in detail. Thirdly, solute redistribution in the dendritic solidification process and the segregation were discussed. It is concluded that the problem can be described resulting \( \varphi_S - \varphi_L \) functions. Among the different models, that obtained by the present author in 1994 was explained. Fourthly, the formation of macro-segregation mainly caused by liquid flow in the mushy zone is analyzed. A parameter about the driving force for the liquid flow is described. The parameter is considered to be the controlling parameter for the formation of macro-segregation. The relationship between the parameter and the compositions in steel is also given in the paper as an example. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Solute redistribution; Segregation; Solidification process

Solute redistribution in the solidification process is a vital problem, which determines growth morphologies and phase distribution as well as concentration segregation. In the present paper, the investigations on the problem are reviewed in four aspects, i.e. solute partition and the partition ratio, solute redistribution in directional solidification process with planar interface, solute redistribution in dendritic solidification process and macro-scale segregation and its controlling parameter.

1. Solute partition and the partition ratio in the solidification process

The most important parameter for solute redistribution in the solidification process, the solute partition ratio \( k \), can be discussed at three different levels, i.e. equilibrium partition ratio \( k_0 \) for equilibrium solidification, efficient partition ratio \( k_e \) for near equilibrium solidification and the real partition ratio \( k_z \) for non-equilibrium solidification. The three different situations are shown in Fig. 1.

1. Equilibrium solidification: the solute redistribution near the growth interface in the equilibrium solidification process of a binary alloy is shown in Fig. 1b. The equilibrium partition ratio \( k_0 \) can be determined by the thermodynamic equilibrium condition

\[
k_0 = \frac{w_S}{w_L} = \frac{f_L}{f_S} \exp\left(\frac{\mu_0^L(T) - \mu_0^S(T)}{RT}\right)
\]

(1)

where \( R \) is the gas constant, and \( w, \mu_0^L(T) \) and \( f \) are the solute content, the standard chemical potential and the activity coefficient, respectively. The subscripts \( L \) and \( S \) are for the liquid and the solid, respectively. \( k_0 \) is usually not constant, but changes with chemical composition and temperature. Other factors, such as interface curvature, pressure, etc. will also influence the value of \( k_0 \) [1].

2. Near equilibrium solidification: near equilibrium means that the solute diffusion is not sufficient in the liquid and the solid, but the solute partition at the growth interface is in equilibrium. The efficient partition ratio \( k_e \) can be used for the near equilibrium solidification process:

\[
k_e = \frac{w_S^e}{w_L}
\]

(2)

\( k_e \) depends on \( k_0 \) and the solute diffusion, for which a mathematical model has been deduced by Burton et al. [2]:

\[
k_e = \frac{k_0}{k_0 + (1 - k_0) \exp(-u/D_L \delta)}
\]

(3)

where \( D_L \) is the diffusion coefficient, \( u \) the growth rate, and \( \delta \) the thickness of the solute boundary layer which is determined by the solute transportation conditions.
such as convection, etc. When \( D_L \to \infty \) or \( \delta, u \to 0 \), then \( k_s \to k_0 \).

3. Non equilibrium solidification: the real solute partition ratio for non-equilibrium solidification process \( k_s \) is defined as:

\[
k_s = \frac{w_s}{w_L}
\]

which has be determined through dynamic analysis such as that of Backer [3], Jackson [4] and Aziz [5]. The most popular one is the Aziz’s model, which is written as:

\[
k_s = k_0 + (1 - k_0) \exp \left( -\frac{1}{b} \right)
\]

for a step-wise growth process, and:

\[
k_s = \frac{b + k_0}{b + 1}
\]

for continuous growth, where \( b = \frac{uL}{D_L} \), \( D_L \) is the diffusion coefficient at the growth interface, which can be approximated by that in the liquid, \( u \) is the growth rate, \( \lambda \) is the atomic space. \( k_s \to 1 \) when \( u \to \infty \). and \( k_s \to k_0 \) when \( u \to 0 \).

2. Solute redistribution for directional solidification with a planar interface

Solute redistribution for directional solidification with a planar interface offers the background for all other complicated processes.

If the solute diffusion in the solid is ignored, the solute distribution along the growth length will be:

\[
w_S = k_0 w_L(x, x')_{x'=0} = k_0 w^*_L
\]

where \( x \) and \( x' \) are shown in Fig. 1. The main problem is to determine \( w_L(x, x') \). For a process with complete mixture in the liquid the following ‘Pfaan’ model can be used [6]:

\[
w_S = k_0 w^*_L \left( 1 - \frac{x}{L} \right)^{(1-k)}
\]

For the diffusion control process, the solute distribution along the specimen is divided into three sections, i.e. initial transient section, stable section and final transient section.

(a) The models for the initial transient process include the following:

(i) Smith’s model [7], which can be simplified to:

\[
w_S = \frac{w_0}{2} \left\{ 1 + \text{erf} \left( \frac{1}{2} \left( \frac{ux}{D_L} \right)^{1/2} \right) \right. \\
+ (2k - 1) \exp \left[ -k(1 - k) \frac{ux}{D_L} \right] \\
\times \text{erfc} \left( \frac{2k - 1}{2} \left( \frac{ux}{D_L} \right)^{1/2} \right) \right\}
\]

where \( \text{erf}(\cdot) \) is the error function, and \( \text{erfc}(\cdot) \) is the anti-error function.

(ii) Tiller’s model [8]:

\[
w_S = w_0 \left[ 1 - (1 - k) \exp \left( -\frac{uk}{D_L} \frac{x}{L} \right) \right]
\]

(iii) Pohl’s model [9]:

\[
w_S = k w_L |_{x'=0} \\
= k w_0 \left[ 1 + \frac{1 - k}{k} \left( 1 - \exp \left( -\frac{(1 - k) k u}{D_L} \frac{x}{L} \right) \right) \right]
\]

(b) Stable section: in the stable section, \( w_S = w_0 \). The only important thing is to determine the solute distribution in the liquid in front of the growth interface, which

![Fig. 1. Solute redistribution around a solid/liquid interface: (a) phase diagram; (b) equilibrium distribution; (c) near equilibrium distribution; (d) non-equilibrium distribution.](image-url)
diffusion field \( w_L \) (see Fig. 2). Thus, the diffusion field \( w_{LB}' \) is obtained by the addition of \( w_L'' \) to \( w_{LB} \). Then, suppose that an opposite diffusion field \( w_{LB}'' \) is symmetrical with \( w_{LB}' \) about the cross-section \( x' = l - x_0 \). Adding \( w_L'' \) to \( w_{LB}' \), the approximate value \( w_{LB} \) of the actual diffusion field is obtained as:

\[
w_{LB} = w_{LB}' + w_{LB}'' = w_L + w_L'' + w_{LB}''
\]  
(13)

Letting \( x' = 0 \), it is found that:

\[
w_S = k w_0 \left\{ 1 + \frac{1-k}{k} \left[ 1 + \exp \left( - \frac{4u}{D_L} (L-x) \right) \right] \right. \]
\[
+ \exp \left( - \frac{2u}{D_L} (L-x) \right)
\]  
\[
- \left( 1 + \exp \left( - 4(1-k) \frac{u}{D_L} (L-x) \right) \right)
\]  
\[
+ 2 \exp \left( - 2(1-k) \frac{u}{D_L} (L-x) \right)
\]  
\[
\times \exp \left( - (1-k) \frac{u}{D_L} ut \right) \}
\]  
(14)

Eq. (14) is suitable for a system where \( k_0 \) is small. For any specimen with limited length, Eq. (14) can be used until the remaining liquid length \( l - x_0 \) is decreased to less than \( \delta/4 \). After that, a large error will be introduced. \( \delta \) is the thickness of the solute concentrated region in front of the growth interface. Some calculation examples are given in Fig. 3.

3. Solute redistribution during dendritic solidification and the micro-segregation

Micro-scale segregation is a common phenomenon in dendritic solidification, which is usually considered as a solidification defect. However, it offers the background for semi-solid casting technologies.

The following parameters can be used for the evaluation of micro-segregation [1]:

1. segregation ratio \( q \):

\[
q = \frac{w_{\text{max}}}{w_{\text{min}}}
\]  
(15)

where \( w_{\text{max}} \) and \( w_{\text{min}} \) are the maximum and minimum values of the solute concentrations in the micro-structure, respectively.

2. segregation rate \( \eta \):

\[
\eta = \frac{w - w_0}{w_0}
\]  
(16)
where \( w \) is the solute concentration at the specified position, and \( w_0 \) is the average solute concentration in the alloy.

3. The volume fractions of non-equilibrium eutectic \( \varphi_E \) or the second phases \( \varphi_H \):

\[
\varphi_E = \frac{V_E}{V} \tag{17}
\]

\[
\varphi_H = \frac{V_H}{V} \tag{18}
\]

where \( V \) is the total volume of the alloy, \( V_E \) is the volume of the eutectic phase and \( V_H \) is that of the second phase.

The description of micro-segregation means to determine the relationship between the solute concentration at the growth interface \( w_S^* \) and the solid fraction \( \varphi_S \). In the dendritic solidification process, solute diffusion in the liquid is usually sufficient, i.e. \( w_L = w_L^* \).
$w_S^*$ is therefore determined by $w_L$. The problem is the determination of the $w_L - \varphi_S$ function.

Solute diffusion in the solid is usually ignored in the conventional model. However, this actually depends on the value of the following diffusion parameter:

$$a = \frac{D \tau}{L^2}$$  \hspace{1cm} (19)

where $D$ is the diffusion coefficient, $\tau$ is the diffusion time and $L$ is the diffusion distance.

If $a \gg 1$, the diffusion is supposed to be sufficient and the equilibrium model can be used to describe the solute redistribution, i.e.:

$$w_S = k w_L = \frac{k w_0}{1 - (1 - k) \varphi_S}$$  \hspace{1cm} (20)

If $a \ll 1$, the diffusion can be ignored and the Scheil equation can be used, i.e.:

$$w_S = k w_0 (1 - \varphi_S)^{(1 - k)}$$  \hspace{1cm} (21)

All of the other models reviewed by Clyne and Kurz [11] neglected the diffusion in the solid. A method for the evaluation of solute diffusion into the solid is suggested by the present author, and the solute redistribution functions of $\omega_L - \varphi_S$ were deduced for different growth processes [13] with the considerations of the growth morphologies and the growth rates. A linear growth process, i.e. $d\varphi_S/d\tau = K$, is for the Bridgman growth process and parabolic growth, i.e. $d\varphi_S/d\tau = K_1 \tau^{-1/2}$, is for the normal casting process.

(a) Plate-like dendrites, linear growth rate:

$$\varphi_S = \left(1 + \frac{ak}{1 - \beta^2}\right) \left[1 - \left(\frac{w_L}{w_0}\right)^{(1 - \beta^2)(1 - k)}\right]$$  \hspace{1cm} (22)

(b) Plate-like dendrites, parabolic growth rate:

$$\varphi_S = \frac{1}{1 - \frac{2ak}{1 - \beta^2}} \left[1 - \left(\frac{w_L}{w_0}\right)^{(1 - \beta^2)(1 - k)(1 - (2ak/1 - \beta^2))}\right]$$  \hspace{1cm} (23)

(c) Needle-like dendrites, linear growth rate:

$$\varphi_S = \frac{1}{1 - \frac{\pi ak}{1 - \beta^2}} \left[1 - \left(\frac{w_L}{w_0}\right)^{(1 - \beta^2)(1 - k)(1 - (\pi ak/1 - \beta^2))}\right]$$  \hspace{1cm} (24)

(d) Needle-like dendrites, parabolic growth rate:

$$\varphi_S = \frac{B_1 \left[1 - \left(\frac{w_0}{w_1}\right)^{A \sqrt{B^2 - 2B}}\right]}{1 + \left(\frac{B_1}{B_2}\right) \left(\frac{w_0}{w_1}\right)^{A \sqrt{B^2 - 2B}}}$$  \hspace{1cm} (25)

where $A = 2\pi ak/1 - k$, $B = (1 - \beta^2)/2\pi ak$, $B_1 = B - \sqrt{B^2 - 2B}$, $B_2 = B + \sqrt{B^2 - 2B}$, $a = D_s \tau_i/L^2$, $\beta$ the shrinkage rate, $D_s$ the diffusion coefficient in the solid, $\tau_i$ the local solidification time and $L$ is the half dendrite spacing. The calculation results and their

![Fig. 4. Comparison of the evaluated non-equilibrium $\theta$ phase in Al–4.8%Cu.](image-url)
comparison with experimental results are shown in Fig. 4.

4. Macro-segregation and the controlling parameter

The formation of macro-segregation mainly depends on the liquid flow in the mushy zone as well as the solute partition at the interface and the diffusion in the liquid and the solid. The liquid flow can be promoted by the solidification shrinkage and the natural convection caused by the different density of the liquid because of the inhomogeneous solute concentration and temperature. The natural convection in the mushy zone can be described by Darcy’s law and has been discussed by many researches [15–20]. A controlling parameter $B$ for the macro-segregation formation was presented by the present author [21]:

$$B = \frac{d\rho_L}{dT_L} = \frac{\partial \rho_L}{\partial T_L} + \frac{1}{m} \frac{\partial \rho_L}{\partial w_L} \tag{26}$$

Since $T_L$ is a function of $\varphi_L$, the parameter $B$ can be substituted for $B' = \partial \rho_L/\partial \varphi_L$. When $B < 0$ or $B' < 0$, the liquid in the mushy zone will flow up and the positive segregation will be formed on the top part of the cast for the elements with $k_i < 1$. Otherwise, when $B < 0$ or $B' < 0$, the liquid in the mushy zone will flow down and positive segregation will be formed on the bottom of the cast. The liquid flow in the mushy zone is also the reason for the formation of channel segregation. If $B \rightarrow 0$ or $B' \rightarrow 0$, the natural convection in the mushy zone and therefore the macro segregation will be eliminated.

As an example, the formation of macro-segregation in a steel ingot was analyzed based on the following assumptions:

(a) The local equilibrium solute partition at the growth interface is reached and the solute partition ratio $k$ can be approximated by that in Fe–x binary alloy.
(b) The variation of the solid fraction with temperature can be described with that for Fe-C binary alloy.
(c) The diffusion in the interendritic liquid is sufficient for all elements.
(d) For the elements (named element $i$) which diffuse sufficiently in the solid, equilibrium equation will be used for the solute redistribution, and for those with ignorable diffusion in the solid (named element $j$). The Scheil equation can be used.

Based on the above analysis, the following result is obtained:

$$\frac{d\rho_L}{d\varphi_L} = \frac{\partial \rho_L}{\partial T} \frac{\partial T}{\partial \varphi_L} + \sum_i \frac{\partial \rho_L}{\partial w_L} \frac{\partial w_L}{\partial \varphi_L} + \sum_j \frac{\partial \rho_L}{\partial w_L} \frac{\partial w_L}{\partial \varphi_L} \tag{27}$$

where $w_{Li}$ and $w_{Lj}$ are the concentrations of elements $i$ and $j$, respectively, and can be written as:

$$w_{Li} = \frac{w_{Lj}^0}{k_i + (1 - k_i)\varphi_L} \tag{28}$$

$$w_{Lj} = w_{Lj}^0 (\varphi_L)^{k_j - 1} \tag{29}$$

where $w_{Lj}^0$ and $w_{Lj}^0$ are average concentrations of elements $i$ and elements $j$. $k_i$ and $k_j$ are the solute partition ratio for elements $i$ and elements $j$. It is found from Eqs. (27)–(29) that:

$$\frac{d\rho_L}{\partial \varphi_L} = \frac{\partial \rho_L}{\partial T} \frac{(1 - k_C)(T_f - T_L)}{[k_C + (1 - k_C)\varphi_L]^{2} w_{Lj}^0}$$

$$+ \sum_i \frac{\partial \rho_L}{\partial w_{Li}} \frac{1 - k_i}{\partial w_{Lj}} \frac{1 - (1 - k_i)\varphi_L}{\partial w_{Lj}}$$

$$+ \sum_j \frac{\partial \rho_L}{\partial w_{Lj}} (k_j - 1)(\varphi_L)^{k_j - 2} w_{Lj}^0 \tag{30}$$

where $k_C$ is the partition ratio for carbon.

Eq. (30) shows that $d\rho_L/d\varphi_L$ is the function of the liquid fraction $\theta_L$. Suppose $\varphi_L^* = \varphi_L$ is the lowest value under which the liquid will be unable to flow, the average value for $B'$ in the region of $\varphi_L < \varphi_L^* < 1$ will be:

$$B' = \frac{d\rho_L}{d\varphi_L} = \frac{1}{1 - \varphi_L^*} \int_{1}^{\varphi_L^*} \frac{d\rho_L}{d\varphi_L} \frac{d\varphi_L}{

For the alloyed steel, it is evaluated that C, S, P and Ni can be classified to elements $i$ and Mn, Si, Cr, Cu, V, Mo and W can be classified to be elements $j$. Substituting the parameters into Eq. (31), the dependence of $B'$ on the compositions of the steel is found to be as follows:

$$B' = -0.02429 + 0.0629w_C + 0.1347w_S + 0.1222w_P$$

$$+ 0.0562w_S + 0.0017w_Mn - 0.38 \times 10^{-5}w_Ni$$

$$- 0.0043w_Cr - 0.0033w_Cu - 0.0033w_V - 0.0069w_Mo$$

$$- 0.0213w_W \tag{32}$$

5. Summary

Solute redistribution is one of the most important phenomena in the solidification process of multi-component alloys, which determines segregation in the resulting solid materials and applies strong influences on the crystal growth morphology and the microstructures. In this review paper, the problems have been discussed in the following four aspects: (1) the solute partition and the partition ratio at the growth interface; (2) the solute redistribution in directional solidification process with planar interface; (3) the solute redistribution in the dendritic solidification process
and the resulting micro-segregation; and (4) the formation of macro-segregation and the controlling parameter.

Acknowledgements

This research was funded by the National Natural Science Foundation of China.

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