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# Numerical Study of the Influence of Diffusion-Governed Growth Kinetics of Ternary Alloy on Macrosegregation

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**Abstract.** This article is to assess the modeling treatment of the growth kinetics (finite or infinite diffusion in liquid and solid phases) during solidification and its influence on the calculation of macrosegregation. A model of diffusion-governed growth kinetic for ternary alloy is developed and used for this assessment. Solidification of a 2D casting (50 x 50 mm<sup>2</sup>) of a ternary alloy (Fe-0.45 wt.% C- 1.06 wt.%Mn) is considered. The result shows that finite diffusion in liquid, important for the initial stage of solidification, plays very important role in the formation of macrosegregation. Moreover, the role of the finite diffusion kinetics in the formation of macrosegregation shows differently in the two extreme cases of solidification structures (columnar or equiaxed).

### Introduction

Macrosegregation depends on the flow and sedimentation on the one hand, and on the concentration difference between the interdendritic (or inter-granular) liquid and the solidifying crystals on the other hand. This concentration difference originates from the solute partitioning at the liquid/solid interface, but it depends strongly on the diffusion kinetics around the growing crystal as well. Fig. 1 schematically shows the initial stage of solidification, and here the crystal morphology is assumed to be globular (equiaxed) or cellular (columnar). The phases, likely being transported by flow/sedimentation, have concentrations of  $c_{\ell,i}$  and  $c_{e,i}$ . These concentrations, representing the average concentrations of the phases  $\bar{c}_{\ell,i}$  and  $\bar{c}_{e,i}$ , are different from the interface concentrations,  $c_{\ell,i}^*$  and  $c_{e,i}^*$ . However, many recent solidification models applicable for macrosegregation [1-5] are based on the assumption of lever rule  $(c_{\ell,i}^* = c_{\ell,i}, c_{e,i}^* = c_{e,i}, c_{e,i}^* = kc_{\ell,i}^*$ , thermodynamic equilibrium at the interface and infinite mixing in each phase) or Gulliver-Scheil ( $c_{\ell,i}^* = c_{\ell,i}, c_{e,i}^* = kc_{\ell,i}^*$ , thermodynamic equilibrium at the interface and infinite fixing in liquid and no diffusion in solid). These assumptions lead to error estimation of macrosegregation [6].



Fig. 1. Schematic of a globular equiaxed crystal which grows in a volume (sphere) of radius  $R_{\rm f}$ .

We recently developed a method incorporating the diffusion-governed growth kinetics and the ternary phase diagram into a multiphase volume average solidification model [7-9]. The influence of the diffusion-governed kinetics on the formation of microsegregation and solidification path was investigated previously [7]. Here we use the same model to investigate the influence of the diffusion kinetics on the formation of macrosegregation.

	Grain structure	Growth kinetics	$\frac{GMI_{c}}{GMI_{Mn}}$ *	LMI <sub>i</sub> *		
				LMI <sub>c,min</sub> LMI <sub>Mn,min</sub>	LMI <sub>c,max</sub> LMI <sub>Mn,max</sub>	$\frac{LMI_{c,max} - LMI_{c,min}}{LMI_{Mn,max} - LMI_{Mn,min}}$
Col-I	Columnar	Diffusion-governed	$\frac{0.26}{0.076} = 3.42$	$\frac{-0.94}{-0.3}$	$\frac{0.85}{0.29}$	$\frac{1.79}{0.59}$
Col-II	Columnar	Gulliver-Scheil	$\frac{0.19}{0.066} = 2.83$	$\frac{-0.7}{-0.25}$	$\frac{0.75}{0.27}$	$\frac{1.45}{0.52}$
Col-III	Columnar	Lever rule	$\frac{0.39}{0.134} = 2.91$	<u>-0.17</u> -0.61	$\frac{5.5}{1.95}$	$\frac{7.2}{2.56}$
Eqx-I	Equiaxed	Diffusion-governed	$\frac{4.1}{0.34} = 12.1$	$\frac{-13.8}{-1.64}$	$\frac{43}{1.97}$	$\frac{56.8}{3.61}$
Eqx-II	Equiaxed	Gulliver-Scheil	$\frac{10}{3.5} = 2.85$	$\frac{-23.9}{-9.0}$	$\frac{85.8}{23.1}$	$\frac{109.7}{32.1}$
Eqx-III	Equiaxed	Lever rule	$\frac{12}{4} = 3$	$\frac{-22.8}{-8.4}$	$\frac{228}{46.4}$	$\frac{250.8}{54.8}$

Table 1. Case definition and simulation results

\* Definition of LMI<sub>i</sub> and GMI<sub>i</sub> refers to Eq. (6) and Eq. (7).

### Numerical model and simulation settings

The numerical model was presented previously [7-11]. Key features are:

- 1. Three phases are considered: liquid ( $\ell$ ), equiaxed (e), columnar (c). They are quantified by their volume fraction:  $f_{\ell}$ ,  $f_{\rm e}$ ,  $f_{\rm c}$ .
- 2. Ideal crystal morphologies are assumed: spheres for equiaxed (globular) grains, and cylinders for columnar (cellular) dendrite trunks.
- 3. Velocity fields,  $\vec{u}_{\ell}$  and  $\vec{u}_{e}$ , of two moving phases are solved.
- 4. Origin of equiaxed grains is modeled according to a continuous heterogeneous nucleation law.
- 5. Volume-averaged concentrations  $(c_{\ell,i}, c_{e,i}, c_{c,i})$  of different phases are solved, where i = A or B, indicating different solute elements. At the liquid/solid interface, thermodynamic equilibrium concentrations  $(c_{\ell,i}^*, c_{e,i}^*, c_{c,i}^*)$  are assumed. Solute partitioning at the interface occurs.
- 6. The concentration differences  $(c_{\ell,i}^* c_{\ell,i})$ ,  $(c_{e,i}^* c_{e,i})$  and  $(c_{e,i}^* c_{e,i})$  are driving forces for the diffusions, hence driving forces for crystal growth. For the condition of a very high cooling rate, a simple approach is introduced to consider 'solute trapping'.

The diffusion-governed growth, an example of a globular equiaxed crystal, is schematically shown in Fig. 1. The crystal growth is governed by diffusion in both liquid and solid [7]:

$$v_{R_{\rm e}} = \frac{D_{\ell,\rm i}}{l_{\ell,\rm e}} \cdot \frac{\left(c_{\ell,\rm i}^* - c_{\ell,\rm i}\right)}{\left(c_{\ell,\rm i}^* - c_{\rm e,\rm i}^*\right)} + \frac{D_{\rm s,\rm i}}{l_{\rm s,\rm e}} \cdot \frac{\left(c_{\rm e,\rm i}^* - c_{\rm e,\rm i}\right)}{\left(c_{\ell,\rm i}^* - c_{\rm e,\rm i}^*\right)},\tag{1}$$

where  $D_{\ell,i}$  and  $D_{s,i}$  are diffusion coefficients of the solute element i (A or B) in liquid and solid,  $l_{\ell,e}$  and  $l_{s,e}$  are diffusion lengths. For the growth of columnar trunk, the same formulation applies, but the subscript 'e' is replaced by 'c'. For a ternary alloy, the growth velocities derived according to solute element A and B must fulfill a consistent condition, i.e.  $v_{R_e}\Big|_{i=A} = v_{R_e}\Big|_{i=B}$ ,

$$\frac{D_{\ell,A}}{l_{\ell,e}} \cdot \frac{\left(c_{\ell,A}^{*} - c_{\ell,A}\right)}{\left(c_{\ell,A}^{*} - c_{e,A}^{*}\right)} + \frac{D_{s,A}}{l_{s,e}} \cdot \frac{\left(c_{e,A}^{*} - c_{e,A}\right)}{\left(c_{\ell,A}^{*} - c_{e,A}^{*}\right)} = \frac{D_{\ell,B}}{l_{\ell,e}} \cdot \frac{\left(c_{\ell,B}^{*} - c_{\ell,B}\right)}{\left(c_{\ell,B}^{*} - c_{e,B}^{*}\right)} + \frac{D_{s,B}}{l_{s,e}} \cdot \frac{\left(c_{e,B}^{*} - c_{e,B}\right)}{\left(c_{\ell,B}^{*} - c_{e,B}^{*}\right)}.$$
(2)

With this consistent condition, together with other three thermodynamic correlations,

$$T = T_{\rm f} + m_{\rm L,A} c_{\ell,A}^* + m_{\rm L,B} c_{\ell,B}^* , \qquad (3)$$

$$c_{\mathrm{e,A}}^* = k_{\mathrm{A}} \cdot c_{\ell,\mathrm{A}}^* \,, \tag{4}$$

$$c_{e,B}^* = k_B \cdot c_{\ell,B}^*$$
, (5)

four unknowns,  $c_{\ell,A}^*$ ,  $c_{\ell,B}^*$ ,  $c_{e,A}^*$  and  $c_{e,A}^*$ , can be solved analytically [7], as the volume averaged concentration,  $c_{\ell,A}$ ,  $c_{\ell,B}$ ,  $c_{e,A}$  and  $c_{e,A}$ , are known from the solution of the global transport equations. Here,  $m_{L,A}$  and  $m_{L,B}$  are the slope of the equilibrium liquidus surface in respect to the corresponding solute element.  $T_f$  is the melting point of matrix element.  $k_A$  and  $k_B$  are the partition coefficients.

Solidification of a 2D casting (50 x 50 mm<sup>2</sup>) of a ternary alloy (Fe-0.45 wt.% C- 1.06 wt.%Mn) with two different solidification structures (columnar or equiaxed) is calculated. The casting is cooled from an initial temperature of 1777 K in a die of 373 K, and the heat transfer coefficient between the casting and the die is 300 Wm<sup>-2</sup>K<sup>-1</sup>. All the thermo-physical and thermodynamic data refer to a previous publication [7]. 6 Cases were calculated, Table 1.

#### Results

The severity of macrosegregation is assessed by two quantities: the local macrosegregation index (LMI<sub>i</sub>) and the global macrosegregation intensity (GMI<sub>i</sub>). They are defined as:

$$LMI_{i} = \frac{c_{mix,i} - c_{0,i}}{c_{0,i}} \times 100,$$
(6)

$$GMI_{i} = \frac{100}{V_{domain}} \cdot \iiint_{V_{domain}} \left| \frac{c_{mix,i} - c_{0,i}}{c_{0,i}} \right| dV.$$

$$\tag{7}$$

Distributions of the predicted  $LMI_i$  of different simulation cases are shown in Fig. 2-3. The predicted  $GMI_i$  and extremes of  $LMI_{i,min}$  and  $LMI_{i,max}$  are summarized in Table 1.

For the cases of columnar solidification (Fig. 2 and Table 1):

- Macrosegregation patterns of 3 cases are quite different. Both LMI<sub>i</sub> distribution range (LMI<sub>i,max</sub> – LMI<sub>i,min</sub>) and GMI<sub>i</sub> increase in an order of Col-II, Col-II, Col-III. Gulliver-Scheil slightly underestimates macrosegregation, while lever-rule overestimates macrosegregation.
- Meso-segregation (small channel) would be predicted by Gulliver-Scheil and lever rule kinetics, while the diffusion governed kinetic did not predict such meso-segregation. Both Gulliver-Scheil and lever rule kinetics overestimate meso-segregation.
- 3) C is more prone to macrosegregation than Mn. GMI<sub>c</sub> is about 3 times of GMI<sub>Mn</sub>. Segregation distribution patterns of both elements are very similar, although they are not identical.



Fig. 2. Predicted LMI<sub>i</sub> (local macrosegregation index) for columnar solidification. Upper row is for C, Bottom for Mn. The color scale and the segregation range are given for each figure individually. Different growth kinetics are compared: a) Col-I for diffusion-governed; b) Col-II for Gulliver-Scheil; c) Col-III for lever rule.



Fig. 3. Predicted LMI<sub>i</sub> (local macrosegregation index) for equiaxed solidification. Upper row is for C, Bottom for Mn. The color scale and the segregation range are given for each figure individually. Different growth kinetics are compared: a) Col-I for diffusiongoverned; b) Col-II for Gulliver-Scheil; c) Col-III for lever rule

For the cases of equiaxed solidification (Fig. 3 and Table 1):

- Macrosegregation patterns of 3 cases show some similarity, but huge difference in segregation intensity is found. Both LMI<sub>i</sub> distribution range (LMI<sub>i,max</sub> – LMI<sub>i,min</sub>) and GMI<sub>i</sub> increases significantly in an order of Eqx-I, Eqx-II, Eqx-III. Both Gulliver-Scheil and lever rule kinetics dramatically overestimate macrosegregation.
- 2) C is more prone to macrosegregation than Mn. GMI<sub>c</sub> is about 3 times of GMI<sub>Mn</sub> for cases of Eqx-II and Eqx-III. Distribution patterns of both elements for cases of Eqx-II and Eqx-III are very similar, while for Eqx-I distribution patterns of both elements is quite different.

## Discussions

During pure columnar solidification, only thermal-solutal convections are involved. It is the interdendritic flow which induces the macrosegregation [12]. For the current alloy,  $\beta_{\rm T} = 1.43 \times 10^{-4} \text{ K}^{-1}$ , the cooled melt is heavier;  $\beta_{\rm c,C} = 1.1 \times 10^{-2} \text{ wt.}\%$ C,  $\beta_{\rm c,Mn} = 0.2 \times 10^{-2} \text{ wt.}\%$ Mn, the solute enriched melt is lighter. At the initial stage of solidification the thermal convection dominates, the cooled melt sinks along the side wall. With the progress of solidification, the solute enriched melt in the mush becomes lighter, tends to rise. At a certain moment, the solutal convection overtakes the thermal convection, the flow direction in the mush near the columnar tip front will reverse (Fig. 4(d)). The moment and location of the reversion of flow direction depend on (1) the intensity of the solute enrichment in the mushy zone; (2) the thickness and (3) the permeability of the mushy zone. For the finite diffusion-governed kinetic (Col-I), the solute in the mushy zone is less enriched than for the other two cases of infinite-mixing kinetics (Col-II and Col-III), but the thickness of the mushy zone in cases Col-I and Col-II is larger than in the case Col-III. The predicted columnar tip front of the case Col-I moves much faster than Col-II and Col-III. How the diffusion kinetics influences the mushy zone was investigated by Zaloznik and Combeau [6], will not be repeated here. The reason why the segregation in Col-I is more severe than in Col-II is due to the larger moving velocity of the columnar tip front, hence the larger mush zone thickness and larger mush permeability. The predicted largest segregation intensity of Col-III is mainly due to the interdendritic melt

solute enrichment, and the formation of meso-segregation. Formation of meso-segregation (channel segregation) was investigated previously [13]. The liquid solute mixing promotes the formation of channel segregation. The reason why C is more prone to macrosegregation than Mn is mainly due to the difference in the partition coefficients of the elements ( $k_c$ =0.36,  $k_{Mn}$ =0.75).



Fig. 4. Transient solidification process, macrosegregation and liquid velocity field during columnar solidification (at 35 s): a)-c). Distributions of LMI<sub>c</sub> are shown in color scale. Figure d) plots  $f_c$ distributions and y-component of liquid velocity along Path A-A

During equiaxed solidification, crystal sedimentation and the sedimentation-induced flow dominates over the thermo-solutal convection. Independent of growth kinetics, flow patterns and flow intensities are quite similar for all cases, hence the final segregation patterns look similar. However, the difference in the segregation intensity of the three cases is huge. Microsegregation caused by diffusion kinetics was studied previously [7]. Due to the finite diffusion in liquid of the case Eqx-I, the enrichment rate of solute surrounding the growing equiaxed grains is smaller, hence the macrosegregation intensity in this case is much smaller than other two cases. For cases Eqx-II and Eqx-III,  $GMI_e$  is about 3 times of  $GMI_{Mn}$ . The same reason as for the columnar solidification: it is mainly due to the difference in the partition coefficients. For the case Eqx-I,  $GMI_e$  is about 12 times of  $GMI_{Mn}$ . This dramatic difference is due to the different partition mechanisms. As diffusion coefficient of Mn in liquid is very small and the partition coefficient is close to 1, and the initial cooling rate of the casting is high, 'solute trapping' mechanism operates occasionally at the liquid/solid interface, therefore, the segregation of Mn is much less pronounced than C for which thermodynamic equilibrium solute partition mechanism operates [7].

Grid size sensitive study was performed. Results presented in the current article are based on a grid size of 0.625 mm, and the time step is as smaller as  $10^{-4}$  s to ensure that the strictly-defined convergence criteria are fulfilled. For columnar solidification, a grid independent result for the case Col-I was easily obtained; but in the cases of infinite-mixing kinetics (Col-II and Col-III), results are very sensitive to grid resolution. Even the grid is as fine as 0.625 mm, the final segregation pattern is still not sufficiently convergent. For equiaxed solidification, all cases are sensitive to the grid size due to the enhanced flow instability caused by crystal sedimentation, but obviously the case of finite diffusion kinetic (Eqx-I) is less sensitive to the grid resolution than infinite-mixing cases (Eqx-II and Eqx-III).

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