Microsegregation in multicomponent alloy analysed by quantitative phase-field model

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Abstract. Microsegregation behaviour in a ternary alloy system has been analysed by means of quantitative phase-field (Q-PF) simulations with a particular attention directed at an influence of tie-line shift stemming from different liquid diffusivities of the solute elements. The Q-PF model developed for non-isothermal solidification in multicomponent alloys with non-zero solid diffusivities was applied to analysis of microsegregation in a ternary alloy consisting of fast and slow diffusing solute elements. The accuracy of the Q-PF simulation was first verified by performing the convergence test of segregation ratio with respect to the interface thickness. From one-dimensional analysis, it was found that the microsegregation of slow diffusing element is reduced due to the tie-line shift. In two-dimensional simulations, the refinement of microstructure, viz., the decrease of secondary arms spacing occurs at low cooling rates due to the formation of diffusion layer of slow diffusing element. It yields the reductions of degrees of microsegregation for both the fast and slow diffusing elements. Importantly, in a wide range of cooling rates, the degree of microsegregation of the slow diffusing element is always lower than that of the fast diffusing element, which is entirely ascribable to the influence of tie-line shift.

1. Introduction

Microsegregation is characterized by non-uniform distribution of alloying elements on a scale of dendritic structures [1]. Description and prediction of microsegregation in practical alloys require precise description of multicomponent diffusion during formation process of the solidification microstructure. A number of theoretical and numerical studies on microsegregation have been carried out and they have contributed to understanding of the microsegregation behaviour [2-9]. However, many of the previous works have focused on binary alloy systems and most of the works involve several assumptions and simplifications especially regarding multicomponent diffusion as well as morphology of the growing solid.

Diffusion in the liquid play an important role in solidification when the multicomponent alloy consists of fast and slow diffusing solute elements that are defined in this paper as elements with high and low diffusivities in the liquid, respectively. The diffusivities of fast and slow diffusing elements differ by one order of magnitude in some practical alloys such as carbon steels. In such a case, the
concentrations of both the elements at the solid-liquid interface deviate from the tie-line passing through the average concentrations [10]. For example, when the partition coefficients of both the elements are less than 1, the liquid concentration of the slow (fast) diffusing element at the interface increases (decreases) due to coupled solutal diffusion in the liquid phase. In other words, the tie-line during the solidification shifts from the tie-line associated with the average concentration. This is called the tie-line shift in this study. The amount of tie-line shift depends on the difference in the liquid diffusivity between the fast and slow diffusing elements. Although effects of the tie-line shift on dendritic growth process has been numerically analysed [11], its influence on the microsegregation has been neither elucidated in a systematic manner nor exploited with a view to controlling microsegregation. Importantly, the amount of tie-line shift is dependent on morphology of the growing phase [10]. Therefore, the detailed description of microstructural process is indispensable for analyses of the influence of tie-line shift on microsegregation.

The phase-field model is a powerful tool to describe microstructural evolution processes in solidification [12-15]. The quantitative phase-field (Q-PF) model, which is constructed based on the thin-interface limit, enables us to carry out quantitative simulations of microstructural evolution processes [16-20]. However, the Q-PF models developed in early works can be applied only to alloy systems without diffusion in the solid phase(s) and therefore these models cannot be utilized for analyses of microsegregation. In order to describe microsegregation behaviour, the Q-PF model was recently extended to deal with alloy systems with an arbitrary value of the solid diffusivity in binary alloys [21, 22]. Moreover, one of the present authors recently developed the Q-PF model which is applicable to non-isothermal solidification in multicomponent alloys with diffusion in the solid [23]. This model can be utilized for detailed analyses of microsegregation behaviour in multicomponent alloys. The aim of this study is to shed light on the influence of tie-line shift on microsegregation behaviour in multicomponent alloys by means of the quantitative phase-field simulation.

2. Quantitative phase-field model

We recently developed the Q-PF model which is applicable to non-isothermal solidification in multicomponent alloys with arbitrary values of the solid diffusivities [23]. In this study, the Q-PF model in Ref. [23] was used to describe the formation of microsegregation during continuous cooling process. We focus on a ternary alloy system consisting of solutes 1 and 2. The temperature is assumed spatially uniform and it is cooled from the liquidus temperature at a constant rate $|dT/dt|$. Then, the microstructural evolution process is described by the following time evolution equations,

$$
\rho \frac{\partial u_i}{\partial t} = \nabla \cdot \left[ a_i(\hat{n}) \nabla \phi + W \nabla \left( \frac{\nabla \phi}{\partial (\nabla \phi)} \right) \right] + \phi - \phi^* - \lambda (1 - \phi^*)^2 \left[ \theta + u_i + \left( \frac{d}{d_j} u_j \right) \right],
$$

$$
\frac{1}{2} \left( 1 + k_i - (1 - k_i) \phi \right) \frac{\partial}{\partial t} u_i = \nabla \left[ \frac{1}{2} \left( k_i D_{i,j} + D_{i,j} + (k_i D_{i,j} - D_{j,i}) \phi \right) \nabla u_i \right] - \frac{1}{2} \left( 1 + k_i \right) \frac{\partial}{\partial t} u_i \nabla \phi \cdot \nabla \cdot J_{\text{cap}} + \frac{1}{2} \left( \frac{k_i}{D_{i,j}} \right) \left( 1 + (1 - k_i) \right) W \frac{\partial}{\partial \phi} \frac{\partial}{\partial \phi} \left( \phi \nabla \phi \right),
$$

where $\phi$ is the phase-field which takes $+1$ in the solid and $-1$ in the liquid and continuously changes from $+1$ to $-1$ inside the solid-liquid interface. $u_i$ is the dimensionless diffusion field of solute $i$ and it is defined by $u_i = (c_{i,\text{avg}} - c_{i,0})/[(1 - k_i)c_{i,0}]$ with the liquid concentration, $c_{i,\text{avg}}$ average concentration, $c_{i,0}$ and the partition coefficient, $k_i$ of solute $i$. $W$ is the interface thickness, $\tau_0$ is the relaxation time and $\zeta(u_1, u_2)$ is given by $\zeta(u_1, u_2) = 1 + (1 - k_1)u_1 + (1 + (1 - k_2)u_2)D_{i,j}d_i/(d_2D_{2,2})$ where $d_i$ is the chemical capillary length of solute $i$ and $D_{i,j}$ is the liquid diffusivity of solute $i$. $a_i(\hat{n})$, where $\hat{n} = -\nabla \phi/|\nabla \phi|$, is a function describing the anisotropy of the solid-liquid interfacial energy. We focus on the fourfold crystalline anisotropy and its strength is determined by a parameter $\varepsilon_t$. The specific form of $a_i(\hat{n})$ is found in Ref.
$\theta$ is given by $\theta = (T - T_l)/(m_1(1-k_1)c_{0,1}/k_1)$ where $T_l$ is the liquidus temperature of the alloy and $m_1$ is the liquidus slope of solute 1. $\lambda$ is the coupling constant and the relation $\tau_0 = \alpha_2W^2/D_{s,1}$ holds with a constant $\alpha_2 (= 0.6267\ldots)$ when the kinetic coefficient is negligibly small. $D_{s,i}$ is the solid diffusivity of solute $i$. The last term in equation (2) is the noise term expressing fluctuation of solute diffusion fields which is necessary to simulate the side branching [24,25]. The details of equations (1) and (2) can be found in Ref. [23].

The main concern of this paper is the influence of tie-line shift on the microsegregation behaviour in a ternary alloy. In order to highlight this phenomenon, we focus on a model alloy system rather than practical alloy systems. We employed $k_1 = k_2 = 0.2$ and $m_1 = m_2 = 500$ K/mol. Then, if $c_{0,1}$ is equal to $c_{0,2}$, there is no distinction between the solutes 1 and 2 in terms of the phase equilibria. We chose $c_{0,1} = c_{0,2} = 0.0008$ which yields the solidification range of $\Delta T = 3.2$ K. We focused on this small $\Delta T$ to save the computational time but it is sufficient for the present purpose. The capillary lengths were set to $d_0 = d_1 = d_2 = 6.25 \times 10^{-8}$ m and $\epsilon_4 = 0.02$ was employed as a typical value in metallic alloy systems. Also, for the sake of simplicity, we chose $D_{s,1} = D_{s,2} = 1 \times 10^{-11}$ m$^2$/s. The difference between the parameters for the solutes 1 and 2 appears only in the liquid diffusivity. We employed $D_{l,2} = 0.1 D_{l,1}$ with $D_{l,1} = 1 \times 10^{-9}$ m$^2$/s. Therefore, the solute 1 corresponds to the fast diffusing element, while the solute 2 is the slow diffusing element. We also carried out the simulation for $D_{l,2} = D_{l,1}$. For convenience, the simulations for $D_{l,2} = 0.1 D_{l,1}$ and $D_{l,2} = D_{l,1}$ are called cases A and B, respectively.

We employed a two-dimensional system shown in Figure 1(a) where the lengths of $x$- and $y$-axes were set to 100 and 25 $\mu$m, respectively. The periodic boundary condition was used at $x = 0$ and 100 $\mu$m, while the mirror boundary condition was applied at $y = 0$ and 25 $\mu$m. The plate-shape solid phase was initially put on the edge of $y$-axis and the initial thickness of this plate was set to 1 $\mu$m. As the cooling proceeds, the thickness gradually increases, i.e., the planar interface moves in $y$ direction. Then, depending on the cooling rate, the instability of planar interface occurs and the dendrite arms
develop. The dendrite arms developing in y direction are called the secondary arm in this paper. This system was chosen because it is convenient to investigate a response of the microstructural process to different cooling condition and the resulting microsegregation behaviour. We changed the cooling rate \(|dT/dt|\) from 1 to 40 K/s and carried out simulations for each cooling condition three times using different seeds for the noise term in equation (2). In addition to the two-dimensional simulation, one-dimensional simulations were conducted.

3. Results and discussion

3.1. Convergence test
The accuracy of the phase-field simulation can generally be improved by decreasing \(W\). However, it leads to increment of the computational cost. Therefore, a value of \(W\) should be determined in the light of balance between the accuracy and the computational cost by checking the convergence behaviour of results with decreasing \(W\). It was demonstrated in our previous study [23] that the Q-PF model described in the previous section shows excellent convergence regarding steady-state dendritic growth in ternary alloys. However, our focus in this paper is not steady-state growth and it is thus necessary to check convergence behaviour of simulation results of the microsegregation.

Figure 1(b) shows the segregation ratio, \(r_i\), obtained from the phase-field simulations for different values of \(W\). The segregation ratio, \(r_i\), is defined as \(r_i = c_{i,max}/c_{i,min}\) where \(c_{i,max}\) (\(c_{i,min}\)) is the maximum (minimum) value of concentration of solute \(i\) in the microstructure just after the completion of solidification. The simulations were performed for \(|dT/dt| = 30\) K/s and \(D_{22} = 0.1\ D_{11}\) (case A). It is noted that the secondary arms develop in this cooling condition as shown in Figure 1(a) and hence the microstructure is not exactly the same in each run due to the difference in the noise term. The square plots indicate the results of Q-PF model explained in the previous section, while the circle plots represent those of Q-PF model without the antitrapping (AT) current which corresponds to the term multiplied by \(\partial \phi\) on the right-hand side of equation (2). It is noted that the result of Q-PF model with AT term does not significantly depend on \(W\), indicating the excellent performance of the present model. However, both \(r_1\) and \(r_2\) gradually decrease with increase in \(W\) in the case of Q-PF model without AT term. This comparison clearly demonstrates an importance of the AT term. In this study, we chose \(W/d_0 = 2.0\) in the light of balance between the accuracy and the computational cost.

In Figure 1(b), \(r_2\) is lower than \(r_1\). In other words, the microsegregation of slow diffusing element is not significant compared to that of fast diffusing element. This is an important consequence of the tie-line shift as explained in detail below.

3.2. One-dimensional analysis
One-dimensional analysis, in which solidification proceeds merely by motion of the planar interface, should facilitate understanding of important aspects of the tie-line shift. Hence, we first discuss results of one-dimensional simulations in which the system length was set to 25 \(\mu\)m.\n
Figure 2(a) shows the liquid concentrations at the solid-liquid interface, \(c_i^*\), at each solid fraction calculated for \(|dT/dt| = 6\) K/s. For comparison, results of the Brody-Flemings [3], Clyne-Kurz [4] and Ohnaka’s models [5] as well as the lever rule and the Scheil model [2] are shown in Figure 2 (a). The solidification time \(t_f\) obtained from the Q-PF simulation for the case B was employed to calculate the analytical models. The result of case B coincides with those of three analytical models. In the case A, on the other hand, such agreement was not obtained although not shown here. \(c_1^*\) in the case A (open square) is very close to the one in the case B (open circle), while \(c_2^*\) (filled square) exhibits quite different behaviour. The high values of \(c_2^*\) for \(f_s^* < 0.7\) are associated with the formation of diffusion layer of this slow diffusing element. The concentration of slow diffusing element in the solid is accordingly high compared to the one of fast diffusing element up to \(f_s = 0.7\). Then, \(c_2^*\) takes slightly lower value than \(c_1^*\) in the late stage of solidification. This behaviour is ascribable to the influence of tie-line shift. Figure 2(b) demonstrates the solidification paths at different cooling rates. The average concentrations in the liquid are plotted. The dotted line indicates the relation \(c_1 = c_2\) and it is called the...
normal path in that the lever rule, Scheil model, Brody-Flemings, Clyne-Kurz and Ohnaka’s models follow this path. The solidification path in the case A gradually deviates from the normal path with increasing cooling rate, which indicates the occurrence of tie-line shift.

Figure 2(c) represents the dependences of $c_{i,\text{max}}$ and $r_i$ on the cooling rate in the case A. The results of case B are not shown here because those are almost identical to the results of fast diffusing element in the case A. It is seen that when the cooling rate is higher than about 6 K/s, $c_{2,\text{max}}$ is always lower than $c_{1,\text{max}}$ and also $r_2$ is always lower than $r_1$. In other words, the degree of microsegregation of slow diffusing element is lower than that of fast diffusing element. Furthermore, although $c_{1,\text{max}}$ and $r_1$ gradually increases with increase in the cooling rate, $c_{2,\text{max}}$ and $r_2$ take almost constant values in the region of high cooling rates.

3.3. Two-dimensional analysis
As mentioned in the introduction, the amount of tie-line shift is dependent on morphology of the growing phase [10]. To be more specific, the amount of tie-line shift increases when the curvature radius of solid-liquid interface decreases. Hence, one may expect that refinement of the solidification microstructure should enhance the influence of the tie-line shift on the microsegregation.

Figure 3 (a) shows results of two-dimensional simulations for the case B. The planar interface is stable in the whole solidification process up to about 12 K/s and, thereby, the dependences of $c_{i,\text{max}}$ and $r_i$ are almost identical to those of the one-dimensional simulations. However, the instability of planar interface takes place and secondary arms well develop during the cooling process at $|dT/dt| > 15$ K/s. Then, $c_{i,\text{max}}$ slightly decreases with increase in the cooling rate, which is due to the reduction of the arm spacing. $r_i$ takes almost the constant value when the cooling rate is higher than 15 K/s. These results represent effects of microstructural change on the microsegregation in the present system without the tie-line shift.
Figure 3(b) shows $c_{1,max}$ and $c_{2,max}$ in the case A. They drastically decrease when the cooling rate becomes higher than about 6 K/s. This is because the secondary arms start to develop even at 6 K/s.

Figure 3. Results of two-dimensional simulations. (a) Maximum concentration and segregation ratio calculated for different cooling rates in case B. (b) Maximum concentrations and (c) segregation ratios calculated for different cooling rates in case A.

Figure 4. Snapshots of microstructures at $t_s = 0.85$ calculated for different cooling rates in case A. The snapshots on the left and right-hand sides represent concentration maps of fast and slow diffusing elements, respectively.

Figure 3(b) shows $c_{1,max}$ and $c_{2,max}$ in the case A. They drastically decrease when the cooling rate becomes higher than about 6 K/s. This is because the secondary arms start to develop even at 6 K/s.
due to the formation of diffusion layer of the slow diffusing element and the microstructure accordingly becomes fine, which facilitates back diffusion in the solid. At $|dT/dt| > 15$ K/s, $c_{1,\text{max}}$ slightly increases, while $c_{2,\text{max}}$ is almost constant. In Figure 2 (c), also, $r_2$ takes a constant value when $|dT/dt|$ is higher than 6 K/s. The difference between $r_1$ and $r_2$ gradually increases with increase in the cooling rate. Hence, the microsegregation of slow diffusing element is less significant.

It is also noted that the segregation ratio of the fast diffusing element in the case A ($r_1$ in Figure 3(c)) is lower than that of the case B above $|dT/dt| = 6$ K/s. This is because the refinement of the microstructure (viz., growth of the secondary arm) starts to occur even at low cooling rates in the case A.

Distribution of solute concentrations immediately after the completion of the solidification can be understood in Figure 5 which shows relative frequencies of the solute concentrations in the microstructure in the case A. There are two peaks at each cooling rate in both the figures. The first peak in the low concentration region is related to the redistribution of solutes during motion of the planar interface. The second peak in the high concentration region is associated with the growth of secondary arms. In Figures 5(a) and (b), the height of the first peak gradually decreases and the one of the second peak increases as the cooling rate increases. Importantly, the positions of the first and second peaks for $c_2$ are closer to the average value $c_{0,1}$ (i.e., $c/c_{0,1} = 1$) than those for $c_1$ at each cooling rate. It indicates that the tie-line shift influences the redistributions of the slow diffusing element during both the planar interface motion and the growth of the secondary arms. As compared to $c_1$, $c_2$ is more uniformly distributed near the average value at each cooling rate.

4. Conclusions

Quantitative phase-field (Q-PF) simulations were carried out to investigate the influence of tie-line shift on the microsegregation behaviour in a ternary alloy consisting of fast and slow diffusing elements. We first verified the accuracy of the Q-PF simulation by performing the convergence test of the segregation ratios with respect to the interface thickness. The Q-PF simulations showed the excellent convergence behaviour. Then we carried out one-dimensional analysis. It was found that the microsegregation of slow diffusing element is reduced due to the tie-line shift. The difference between the segregation ratios of the fast and slow diffusing elements gradually increases with increase in the cooling rate. In two-dimensional simulations, the refinement of microstructure, viz., the decrease of the secondary arms spacing occurs at relatively slow cooling rates due to the formation of diffusion layer of the slow diffusing element. It yields reduction of degrees of microsegregation for both the fast
and slow diffusing elements. Importantly, in a wide range of cooling rates, the degree of microsegregation for the slow diffusing element is always lower than that of the fast diffusing element, which is entirely ascribable to the influence of tie-line shift.

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