Numerical Modeling of Microsegregation for Fe-base Multicomponent Alloys with Peritectic Transformation Coupled with Thermodynamic Calculations

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Numerical model was developed to simulate the microsegregation and phase transformation for an Fe-based multicomponent alloy with peritectic transformation. The present model was based on the simplest one-dimensional free boundary problem and assumed the local equilibrium condition at the interface. In addition, the model was coupled with thermodynamic calculation software (ChemAPP) in order to calculate equilibrium concentration at an interface. As the calculation region, the transverse and longitudinal cross section of columnar dendrite was approximated by a star shape, assuming dendrite envelope. The validity of the present model was evaluated by comparing with the analytical models and experimental data.

In the comparison with the analytical models, which are lever rule, Gulliver–Scheil model and Clyne–Kurz model, the calculated results were close to the curve of lever rule for Fe–C binary alloy, and were close to the curve of Gulliver–Scheil model for Fe–Mn binary alloy. For both alloys, the calculated results were in good agreement with the curves of Clyne–Kurz model. The relationship between peritectic temperature range and carbon content was calculated for Fe–C binary alloy and compared with the result of a model by Fredriksson et al. [H. Fredriksson et al.: Metal Science, 16 (1982), 575]. The calculated result was in great agreement with their one. Also, the peritectic temperature range for peritectic content was not always the maximum, and the carbon content slightly shifted to hyper-peritectic side as the cooling rate became higher. For Fe–C–Mn–Si–P–Mo alloy, we calculated microsegregation and peritectic transformation, and compared with the experimental data reported by Ueshima et al. [Y. Ueshima et al.: Tetsu-to-Hagané, 73 (1987), 1551]. Temperatures of δ/γ transformation and γ-solidification decreased by adding to molybdenum, and these results were close to those of Ueshima et al. Also, the distributions of manganese, phosphorus and molybdenum calculated by the present model were in essential agreement with those of their experimental data.

KEY WORDS: numerical simulation; multicomponent alloy; microsegregation; thermodynamic calculation; peritectic transformation; solidification.

1. Introduction

Several models have been proposed to analyze microsegregation for interdendritic region. Analytical models are one-dimensional model for volume element, which considers between the secondary dendrite arms, and give the relationship between the concentration in solid, \( C_s \), and solid fraction, \( f_s \), during solidification. The simplest model is lever rule (equilibrium solidification), which the solute perfectly diffuses in both solid and liquid phases. However, the perfect diffusion in solid and liquid is not realistic. Gulliver\(^{31}\) was first proposed the model where diffusion in the solid is negligible, and the same one was later proposed by Scheil.\(^{21}\) Thus, their model have been called Gulliver–Scheil model. In the Gulliver–Scheil model, a microsegregation profile is given by \( C_s = kC_0(1 - f_s)^{k-1} \), where \( k \) is the partition coefficient and \( C_0 \) is initial concentration. However, this model is not valid for the case where diffusion in the solid is not negligible, \( e.g. \) low cooling rate, high diffusivity in solid and so on. In that case, “back diffusion” to the solid must be considered. Brody and Flemings\(^{31}\) presented the first treatment of this problem by considering a flux balance in the solid, and \( C_s - kC_0[1-(1-2k\alpha)f_s^{k-1}] \) was obtained. This has been called Brody–Flemings model. \( \alpha \) is Fourier number (dimensionless diffusion coefficient), \( \alpha = Dl/\lambda \), \( D \) is diffusivity, \( l \) is solidification time and \( \lambda \) is arm spacing. Substituting \( \alpha = 0 \) (no diffusion in the solid) into their equation reduces it to the Gulliver–Scheil model. One would also anticipate that \( \alpha \to \infty \) would produce the lever rule, however, this is not the case, in fact, setting \( \alpha = 0.5 \) recovers the lever rule. This is because Brody–Flemings model does not conserve solute in the solid. Therefore, numerous models have been developed to expand and improve their model. The first of these was presented by Clyne and Kuczak\(^{41}\) who replaced \( \alpha \) in the Brody–Flemings model by \( \Omega \), based on the Fourier number, \( \Omega = \alpha[1-\exp(-1/\alpha)]-0.5\exp(-1/2\alpha) \), which is close to the lever rule in the limit as \( \alpha \to \infty \). Thanks to its simplicity, this model has been widely used. However, this model does not perfectly improve the problem that the
solute is not conserved in the solid. After this improvement, Ohnaka\textsuperscript{5} extended the Brody–Flemings model by assuming a parabolic form for the solute profile in the solid, and Kobayashi\textsuperscript{6} has developed an exact analytical solution to microsegregation problem and has also provided some higher order approximations. Moreover, Matsumiya \textit{et al.}\textsuperscript{7} have developed a numerical model to analyze microsegregation by using the finite difference method (FDM), and Ueshima \textit{et al.}\textsuperscript{8,9} expanded Matsumiya’s model to microsegregation of a peritectic alloy. In addition, several models, which are the simplest one-dimensional model for volume element, have been developed for peritectic\textsuperscript{10–14} and eutectic alloys.\textsuperscript{14–16}

Recently, a phase-field model (PFM) has been often used as an effective tool to simulate a microstructural evolution during the solidification. The PFMs for pure materials,\textsuperscript{17,18} binary alloy,\textsuperscript{19,20} multicomponent alloy,\textsuperscript{21} and multiphase alloy,\textsuperscript{22,23} have been developed, and a model for an alloy is applicable to not only the simulation of dendrite morphology but also the simulation of microsegregation pattern. However, the PFM has a disadvantage that the computational grid size is quite small, and considering the accuracy of quantitative calculations, the grid size of less than 1 \textmu m should be used in the PFM. Thus, owing to the long computational time, at present, it is hard to simulate solidification processes for the conditions like low cooling rate at multicomponent alloys by using PFM.

In the present work, we developed a numerical model to be able to simulate microsegregation profiles and phase transformation at practical solidification conditions in Fe-based multicomponent alloys with peritectic transformation. Our model is based on the simplest one-dimensional free-boundary problem and satisfies local equilibrium condition at an interface. In order to give local equilibrium condition at an interface for practical alloys, which are multicomponents, we were coupling this model and ChemAPP,\textsuperscript{24} which is thermodynamic calculation software. Thanks to the use of one-dimensional FDM, the computational time will be very short in the present model.

2. Model

2.1. Assumptions

As shown in Fig. 1, the transverse and longitudinal cross section of columnar dendrite is approximated by a star shape, assuming dendrite envelope, in a regular square. Heat transfer is assumed to be longitudinal along solidification direction, while diffusion of solutes for solid and liquid phases is in radial direction on the transverse cross section, that is, the diffusion in solid and liquid phases to the solidification direction is neglected. One-eighth transverse cross section, that is, the triangle area shown in Fig. 1, is considered as the calculation domain because of symmetry, and this domain is divided into segments for the FDM.

The S/L interface (or \(\delta/\gamma\) interface) exists in a segment, and the position is determined by the solid fraction (or the \(\gamma\)-phase fraction) of the segment including the interface (Details are given in Sec. 2.3). At the S/L interface and the \(\delta/\gamma\) interface, the solutes are distributed by the condition of local equilibrium. Solidification, \(\delta/\gamma\) transformation and melting proceed with planar interface morphology as a dendrite envelope. As shown in Fig. 2, the \(\gamma\)-phase develops from the interface between the \(\delta\)-phase and the liquid phase. As the other assumptions, we do not consider mass flow, undercooling and density change on solidification and \(\delta/\gamma\) transformation in the model.

2.2. Solute Distribution

Based on assumptions as described in Sec. 2.1, the diffusion and distribution of solutes in the \(\delta\), \(\gamma\) and liquid phases are calculated by the FDM. The calculation domain is divided into some nodal areas as shown in Fig. 3. The nodal points are set on the line segment joining the points O and A. The length of the line segment OA corresponds the half of the primary dendrite arm, \(\lambda_1/2\), and the interval between the nodal points, \(\Delta x\), is constant except the one between the interface and the neighboring nodal point as shown in Fig. 2. In order to consider the dendrite envelope of star shape, the different shapes of a nodal area in a triangle OBC (Area
diffusivity of the solute element \( j \) for phase \( p \), respectively. \( A_i \) and \( L_i \) for the Area 1 and Area 2 are given as follows:

\[
A_i = \frac{(2i-1)\lambda_i \Delta x}{4n_d}\]

\[
L_i = \left( \frac{i \Delta x}{\sqrt{2}} \right)^2 \left( \frac{i \lambda_i}{n_d \sqrt{2}} \right)^2 \]  

(2) 

where \( n_d \) is the number of nodal area in the Area 1

\[
A_i = \frac{\lambda_i \Delta x}{4}\]

\[
L_i = \left( \frac{i \Delta x}{\sqrt{2}} \right)^2 \left( \frac{\lambda_i - i \Delta x}{n_d \sqrt{2}} \right)^2 \]  

(3) 

At the nodal area of \( N \), including the \( \delta/\gamma \) interfaces, the solute concentrations of each phase, which are \( C_{\delta}^{N} \) and \( C_{\gamma}^{N} \), are determined by the phase diagram of Fig. 4. In a similar manner, \( C_{\delta}^{N} \) and \( C_{\gamma}^{N} \) become the solute concentrations of \( \gamma \) - and liquid phases at the nodal area of \( N \) including the \( \gamma/L \) interface, respectively. The concentration of solute element \( j \) at these interface areas is calculated as follows:

\[
C_{i,j}^{N} = C_{i,j}^{N} + \frac{\Delta t}{A_i} \left[ D_{j,i} L_{N_i} (C_{i,j}^{N} - C_{i,j}^{N}) \right] \Delta x_{\delta} + D_{\gamma,j} L_{N_\gamma} (C_{i,j}^{N} - C_{i,j}^{\gamma}) \Delta x_{\gamma} \]  

(4) 

\[
C_{i,j}^{N} = C_{i,j}^{N} + \frac{\Delta t}{A_i} \left[ D_{j,i} L_{N_i} (C_{i,j}^{N} - C_{i,j}^{N}) \right] \Delta x_{\delta} + D_{\gamma,j} L_{N_\gamma} (C_{i,j}^{N} - C_{i,j}^{N}) \Delta x_{\gamma} \]  

(5) 

where \( \Delta x_{\delta}, \Delta x_{\gamma}, \Delta x_{\gamma} \) and \( \Delta x_{L} \) are intervals between the interface and the neighboring nodal point as shown in Fig. 2. Due to the condition of local equilibrium at the interface, the disruption of a mass balance in the system occurs when the above equations are solved numerically. Thus, we carry out the following correction of mass balance in the model. The increase or decrease of concentration for each step of numerical computation are added to the concentration of liquid phase after averaged by the number of nodal area of liquid phase.

2.3. Determination of the Interface Position

Considering the mass balance at the interface areas, the concentrations of the solute element \( j \) of \( N_1 \) and \( N_2 \) are also given as follows:

\[
C_{i,j}^{N_1} = f_{i,j}^{N_1} + f_{i,j}^{N_1} + f_{i,j}^{N_1} + f_{i,j}^{N_1} \]  

(6) 

\[
C_{i,j}^{N_2} = f_{i,j}^{N_2} + f_{i,j}^{N_2} + f_{i,j}^{N_2} + f_{i,j}^{N_2} \]  

(7) 

where \( f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} \) are the fractions of each phase at the interface areas \( (f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1} f_{i,j}^{N_1}) \). These fractions for the solute element \( j \) can be determined by
using the values of $C_{\gamma 1}$ and $C_{\gamma 2}$ obtained by solving Eqs. (4) and (5). In the multicomponent alloy, although the multiple values of fraction for each phase are obtained by solving Eqs. (6) and (7) for each solute element, the only one value of fraction for each phase must be determined. Thus, the average values of fraction for each phase are determined by the following equation.

$$f_{p}^{i+\Delta t} = \frac{1}{n} \sum_{m=1}^{n} f_{p,m}^{i+\Delta t} \quad (p = \delta, \gamma 1, \gamma 2, L) .......(8)$$

where $n$ is the number of solute element. From the average fractions, the intervals between the interface and the neighboring nodal point are calculated by Eq. (9), and the position of the interface is determined in the interface area.

$$\Delta x_{p}^{i+\Delta t} = \left( \frac{1}{2} + f_{p}^{i+\Delta t} \right) \Delta x \quad (p = \delta, \gamma 1, \gamma 2, L) .......(9)$$

The intervals obtained by Eq. (9) will correspond to the interface position in the case of square-shaped nodal area. As shown in Fig. 3, however, the shape of nodal area is not square in our model. Thus, the fractions have to be modified to obtain the correct interface position. The fraction obtained by Eq. (8) is equal to the area ratio $A_{\delta}/A_{\gamma}$, where $A_{\delta}$ is the area of gray part in the interface area as shown in Fig. 2. From the area ratio, the modified fraction, $f_{p,mod}$ is given as follows:

$$f_{p,mod}^{i+\Delta t} = \frac{-L_{i-1} + \sqrt{L_{i}^{2} - L_{i-1}^{2} \left(1 - f_{p}^{i+\Delta t} \right)} + L_{i}^{2} f_{p}^{i+\Delta t}}{L_{i} - L_{i-1}} \quad (p = \delta, \gamma 1, \gamma 2, L) \quad .............(10)$$

$$f_{p,mod}^{i+\Delta t} = f_{p}^{i+\Delta t} \quad (p = \delta, \gamma 1, \gamma 2, L) \quad (at \ Area \ 2) \quad .............(11)$$

Replacing $f_{p}$ in Eq. (9) with $f_{p,mod}$ the correct position of the interface can be calculated for each phase.

### 2.4. Thermodynamic Calculation

The concentrations at the interface are always set the equilibrium concentrations, which are $C_{\delta}, C_{\gamma 1}, C_{\gamma 2}$ and $C_{L}$ as shown in Fig. 2, because the condition of local equilibrium is assumed in the present model. For a binary alloy, it is relatively easy to obtain them from a phase diagram. For a multicomponent alloy, however, they vary depending both on temperature and composition, and must be determined for each step of numerical computation. In the present model, we used ChemAPP software to calculate them. ChemAPP software is the engine for calculating thermodynamic equilibrium, and in order to calculate the thermodynamic equilibrium, ChemAPP reads ChemSage Thermochemical (CST) data files, which can be generated by the FactSage Equilib module. There is many sort of FactSage database for alloy, oxide and so on, in this work, we used FactSage SGTE2007 alloy database. Coupling with thermodynamic calculations by ChemAPP is performed during the time stepping scheme, and thus the equilibrium concentrations at the interface are renewed every time step. The renewed concentrations are used to determine the fractions in the Eqs. (6) and (7).

#### 2.5. Peritectic Transformation ($\delta$-\(\gamma\) Transformation)

The following assumptions are made for the calculation of peritectic transformation.

First, the $\gamma$-phase forms at the interface between the liquid phase and $\delta$-phase as shown in Fig. 2 when the amount of $\gamma$-phase at the $\delta$-L interface becomes more than zero by the thermodynamic calculation. After this, in order not to be existed two interfaces in the same nodal area, new interface is set the neighboring nodal area including the $\delta$-L interface. It is decided by the following rule. In the case of $f_{\delta} < 0.5$, the $\delta$-\(\gamma\) interface forms in the nodal area of the $\delta$-phase side, and the $\delta$-L interface replaces the $\gamma$-L interface, while, in the case of $f_{\gamma} > 0.5$, the $\gamma$-L interface forms in the nodal area of the liquid phase side and the $\delta$-L interface replaces the $\delta$-\(\gamma\) interface.

Second, the transformation is governed by a diffusion controlled mechanism. On the basis of these assumptions, Eqs. (4) and (5) are solved as mass balance equations at the interface during peritectic transformation.

### 3. Numerical Results and Discussion

In this section, the present model is subjected to the numerical tests in order to investigate the computational performance by comparisons of the analytical models and experimental data.

#### 3.1. Comparison with Analytical Models

As mentioned in Chap. 1, some analytical models for microsegregation have been developed. As the first test, the calculations of $\delta$-solidification were carried out for Fe-0.07wt%C and Fe-5.0wt%Mn binary alloys, and the calculated results by the present model were compared with three analytical models, which are lever rule, Gulliver–Scheil model and Brody–Flemings model modified by Clyne and Kurz (Clyne–Kurz model). The diffusion coefficients for each element used in the numerical and analytical calculations are shown in Table 1. Also, in order to compare with the analytical models, we employed the system of one-dimensional direction without the length and area of the nodal area, that is, the conditions of $L_{i} = L_{i-1} = 1$, $A_{\gamma 1} = 1$ in Eq. (1), $L_{\gamma i} = L_{\gamma i-1} = 1$, $A_{\gamma i} = 1$ in Eq. (4) and $L_{\gamma i} = L_{\gamma i-1} = 1$, $A_{\gamma i} = 1$ in Eq. (5). The calculated condition were

| Element | Diffusivity in $\delta$-phase, $D_{\delta}$(m$^{2}$/s) |
|---------|-----------------------------------------------|
| C       | 1.27X10$^{-8}$ exp(-8.14X10$^{3}$/K)          |
| Mn      | 7.6X10$^{-8}$ exp(-2.24X10$^{3}$/K)          |
| Si      | 8.0X10$^{-8}$ exp(-2.49X10$^{3}$/K)          |
| P       | 2.9X10$^{-8}$ exp(-2.33X10$^{3}$/K)          |
| Mo      | 6.3X10$^{-8}$ exp(-2.24X10$^{3}$/K)          |

| Element | Diffusivity in $\gamma$-phase, $D_{\gamma}$(m$^{2}$/s) |
|---------|------------------------------------------------------|
| C       | 7.6X10$^{-8}$ exp(-1.35X10$^{3}$/K)                  |
| Mn      | 5.5X10$^{-8}$ exp(-2.49X10$^{3}$/K)                  |
| Si      | 3.0X10$^{-8}$ exp(-2.49X10$^{3}$/K)                  |
| P       | 1.0X10$^{-8}$ exp(-1.83X10$^{3}$/K)                  |
| Mo      | 3.5X10$^{-9}$ exp(-2.49X10$^{3}$/K)                  |

| Element | Diffusivity in Liquid phase, $D_{L}$(m$^{2}$/s) |
|---------|-----------------------------------------------|
| C, Mn, Si | 2.0X10$^{-8}$                             |

Gas constant, R=8.314 (J/mol K)
used that the dendrite arm spacing, $\lambda_1$, was 250 $\mu$m, the interval of nodal point, $\Delta x$, was 2.5 $\mu$m and the cooling rate, $R_c$, was 0.1 and 5 K/s.

In the case of Fe–0.07wt% C alloy, the calculated carbon distributions, $C_{C}/C_{C0}$, which was normalized by the initial content, $C_{C0}$, were close to the curve obtained by lever rule because of high diffusivity in solid (Fig. 5(a)). The calculated result for $R_c=0.1$ K/s corresponded the curve of lever rule, and that for $R_c=5$ K/s was in agreement with that obtained by the Clyne–Kurz model. The value of $\Omega$ in the Clyne–Kurz model was determined by the condition of $\alpha=4D_{C}t_{g}/\lambda_1$ and the value of $\alpha$ was 2.77, which was calculated by using $D_{C}=6.0\times10^{-9}$ m$^2$/s, $t_{g}=7.21$ s and $\lambda_1=250$ $\mu$m. On the other hand, in the case of Fe–5.0wt% Mn alloy, the calculated manganese distributions, $C_{Mn}/C_{0,Mn}$, were approached to the curve obtained by Gulliver–Scheil model because of low diffusivity in solid (Fig. 5(b)). The calculated results for both $R_c=0.1$ K/s and $R_c=5$ K/s were in agreement with those obtained by the Clyne–Kurz model. The values of $\alpha$ for $R_c=0.1$ K/s and $R_c=5.0$ K/s were 0.18 ($D_{C}=1.8\times10^{-11}$ m$^2$/s, $t_{g}=154.5$ s, $\lambda_1=250$ $\mu$m) and 0.008 ($D_{C}=1.8\times10^{-11}$ m$^2$/s, $t_{g}=6.75$ s, $\lambda_1=250$ $\mu$m), respectively. From these results, therefore, it was found that the present model can simulate the microsegregation distributions for the volume element as used in the analytical models. In addition, comparing with the analytical models, the present model has the advantages that it can deal with a sequence of calculation from $\delta$-solidification to $\delta$–$\gamma$ transformation and the dendrite envelope is assumed as the calculation region.

### 3.2. Peritectic Transformation of Fe–C and Fe–C–Mn Alloys

As the second test, the calculations of peritectic transformation for Fe–C binary and Fe–C–Mn ternary alloys were carried out. For the Fe–C binary alloy, the relationships between peritectic temperature range and initial carbon content,$C_{C0}$, were calculated and the results compared with the ones of a model reported by Fredriksson et al.\cite{Fredriksson2010} for Fe–C binary alloy.

Figure 6 shows the relationship between peritectic temperature range, $\Delta T_p$, and the initial carbon content, $C_{C0}$, at Fe–C binary alloys. The peritectic temperature range is defined as the difference between peritectic temperature (1763 K) and a temperature when peritectic reaction finished. The calculations were carried out for three cooling rates of 0.1, 0.5 and 5.0 K/s under a condition of a fixed dendrite arm spacing of 250 $\mu$m, and for comparison, simultaneously with our results plotted the ones for the cooling rates of 0.5 K/s reported by Fredriksson et al.\cite{Fredriksson2010}. The peritectic temperature ranges were different in each carbon content and cooling rate. Comparing with the results of Fredriksson et al., the result of $R_c=0.5$ K/s in the present model was in good agreement with their one. However, they assumed that the carbon concentration in $\gamma$-phase is linearly decreasing from the $\gamma/L$ interface to the $\delta/\gamma$ interface, and the carbon concentration in liquid and $\delta$-phases are uniform. Actually, the solute diffuses in every phases and the solute distribution will be affected by the cooling rate and so on. Thus, their model might not obtain the correct result when the cooling rate is high. As an effect of cooling rate, in our results, the peritectic temperature range for peritectic content was not always the maximum, and the carbon content slightly shifted to hyper-peritectic side as the cooling rate became higher.

Figure 7 shows the relationship between initial carbon content, $C_{C0}$, and peritectic temperature, $T_p$, at Fe–C–2wt% Mn ternary alloys. For comparison, simultaneously with our results plotted a calculated phase diagram of Fe–C–2wt% Mn pseudo-binary system. In more than 0.2wt% C, peritectic temperatures for all cooling rates corresponded well to peritectic temperature on the phase diagram. On the other hand, in less than 0.2wt% C, they were different in three cooling rates and were lower than that of the phase diagram in the cooling rates of 1.0 and 5.0 K/s. This is because a tie-line at $\delta/L$ interface shifted to high manganese side. In the low carbon content, the $\delta$-phase fraction becomes high when a system temperature reaches peritectic temperature. In addition, the microsegregation of manganese occurs in $\delta$-phase due to the low diffusion velocity of manganese in $\delta$-phase. The distribution of manganese becomes higher from the center of dendrite to the interdendritic region. Considering the mass balance in a
3.3. Microsegregation and Phase Transformation of 
\textit{Fe-C-Mn-Si-P-Mo} Alloys

As the third test, the calculations of microsegregation and peritectic transformation for \textit{Fe-C-Mn-Si-P-Mo} alloys were carried out. As the calculated conditions, $\lambda_i = 200 \mu m$, $\Delta x = 2 \mu m$ and $R_s = 0.45 K/s$ were used.

Figure 9 shows change in fraction of phase during solidification at Fe–0.16 wt%C–1 wt%Mn–0.2 wt%Si–0.01 wt%P–1 wt%Mo alloys ($X=0, 1$). Solid line is the calculated result of the alloy without molybdenum, and broken line is the one with molybdenum. First, explaining about the change in phase fractions of the alloy without molybdenum (solid line in Fig. 9), $\delta$-solidification started at 1790 K, and the $\delta$-phase fraction increased by 1759 K. Then $\delta/\gamma$ transformation occurred at 1759 K, and $\delta$-phase decreased and $\gamma$-phase increased rapidly. At 1750 K, peritectic transformation finished and $\delta$-phase vanished. After that, at 1736 K, liquid phase vanished and $\gamma$-solidification finished.

Second, comparing with the change in phase fractions with molybdenum (broken line in Fig. 9), by adding molybdenum of 1 wt%, the $\delta$-phase fraction increased from 0.79 to 0.83 and then $\delta/\gamma$ transformation temperature decreased from 1759 to 1747 K. These results were close to those of a model reported by Ueshima et al.\textsuperscript{9} which are 1765 K without molybdenum and 1753 K with molybdenum. Also, adding molybdenum to the alloy lowered finishing temperature of peritectic transformation from 1750 to 1729 K because molybdenum is one of the ferrite ($\delta$-phase) former at a carbon steel.

Figure 10 shows the relationship between a distance from center of dendrite, $l_{PDAS}$, and concentration ratio of each solute during peritectic transformation (1741 K) and just after $\gamma$-solidification (1719 K) at Fe–0.16 wt%C–1 wt%Mn–0.2 wt%Si–0.01 wt%P–1 wt%Mo alloy. The distance was divided by half of the primary dendrite arm spacing, and $l_{PDAS}=0$ means the center of dendrite. The concentrations were normalized by the initial content for each solute. The states of phase, which are $\delta$, $\gamma$- and $L$ phases, during $\delta/\gamma$ transformation were distinguished by broken lines in Fig. 10. At 1741 K, all elements were enriched in liquid phase in the interdendritic region and the solutes were redistributed in the solid due to $\delta/\gamma$ transformation. Table 2 shows equilibrium partition coefficients for each element during $\delta/\gamma$ transformation at 1741 K obtained by the calculated results. The $k^{\delta/\gamma}$ and $k^{\gamma/L}$ are equilibrium partition coefficients from $\gamma$-phase to $\delta$-phase ($k^{\delta/\gamma}=C_\delta/C_\gamma$) and from $\gamma$-phase to liquid phase ($k^{\gamma/L}=C_\gamma/C_L$), respectively. The distributions of manganese and silicon in solid were nearly equal during $\delta/\gamma$ transformation because the $k^{\delta/\gamma}$ was nearly equal to unity as shown in Table 2. On the other hand, the $k^{\gamma/L}$ of phosphorus and molybdenum were far smaller than unity. As a result, just after $\gamma$-solidification (1719 K), phosphorus and molybdenum were enriched in the center of dendrite, and four elements except carbon were enriched in the interdendritic region. As carbon has a high diffusion velocity in both solid and liquid, the concen-
tration of carbon in all phases was always nearly equal to the equilibrium concentration.

Figure 11 shows the relationship between a distance from the center of dendrite and concentration ratio of manganese (Fig. 11(a)), phosphorus (Fig. 11(b)) and molybdenum (Fig. 11(c)) at 1 573 K. In order to compare with the experimental data by Ueshima et al., we carried out the calculation of diffusion in δ-phase after γ-solidification as well as the calculation of δ-solidification and γ-solidification. The experimental results show that the segregations of manganese and phosphorus in the dendrite were reduced by adding to molybdenum. The calculated results were similar to the behaviors obtained by the experiment. But, for manganese and phosphorus, the calculated distributions around the interdendritic region disagreed with the experimental ones. The reasons for the higher calculated distributions of manganese would be as follows: it is to assume no diffusion of solutes along the solidification direction in the present model. In the experimental, the solute elements of the interdendritic region will diffuse along solidification direction. As a result, the solutal concentration of the interdendritic region would be lower than that of the limited diffusion as used in the model. Also, small MnS particles might be formed at the grain boundary. According to Ref. 9), the experimental samples were including sulfur of about 0.002%, and the MnS particles might be formed at the grain boundary although they have not been reported in Ref. 9), resulting in the lower manganese concentrations in the experimental samples. Next, the reason for the flat calculated distributions of phosphorus might be due to the diffusion coefficient for phosphorus used by the model. In the present model, the diffusion coefficients for binary alloy, e.g. Fe–P alloy, were used and the coupled diffusion was not considered. Since phosphorus is the type of the interstitial diffusion for iron, the diffusion velocity of phosphorus in iron is high. In this calculation, for example, the diffusion coefficient of phosphorus is about 28 times than that of manganese at 1 573 K. As a result, the distribution of phosphorus became more flat than that of manganese. Therefore, in the type of the interstitial diffusion such as the phosphorus, the coupled diffusion including the effect of cross-interaction among the whole elements might have to be considered. This will be confirmed in order to evaluate exactly the microsegregation of a multi-component alloy in near future.

Table 2. Equilibrium partition coefficients during δ/γ transformation at 1 741 K obtained by the calculation.

| Element | $k_\delta$ | $k_\gamma$ |
|---------|------------|------------|
| C       | 2.05       | 0.28       |
| Mn      | 1.08       | 0.72       |
| Si      | 0.96       | 0.61       |
| P       | 0.53       | 0.14       |
| Mo      | 0.84       | 0.53       |

Fig. 10. Distributions of (a) C, (b) Mn, (c) Si, (d) P and (e) Mo during δ/γ transformation (1 741 K) and just after γ-solidification (1 719 K) calculated by the present model for Fe–C–Mn–Si–P–Mo alloy.

Fig. 11. Distributions of (a) Mn, (b) P and (c) Mo at 1 573 K calculated by the present model and reported by experiments of Ueshima et al.9) for Fe–C–Mn–Si–P–Mo alloy.
model, since the calculation results are depended on thermodynamic data and will vary according to the database. In this work, we used the SGTE 2007 alloy database as thermodynamic data, if we use a different thermodynamic database, the calculated results might be closer to the experimental data. In near future, this must also be confirmed in order to evaluate the present model.

4. Conclusions

In this work, we developed a numerical model to simulate a microsegregation and phase transformation for Fe-based multicomponent alloy with peritectic transformation and evaluated the performance of present model by three numerical tests.

In the first test, we calculated microsegregation of the \( \delta \)-solidification for Fe–C and Fe–Mn binary alloys and compared the results of the present model with those of three analytical models, which are lever rule, Gulliver–Scheil model and Clyne–Kurz model. In high diffusivity in solid (Fe–C alloy), the calculated results were close to the curve of lever rule, and in low diffusivity in solid (Fe–Mn alloy), they were close to the one of Gulliver–Scheil model. For both case of diffusivity in solid, the calculated results were in agreement with the curves of Clyne–Kurz model, which used the values of \( \alpha \) obtained from the calculated results of the present model.

In the second test, we calculated the peritectic transformation for Fe–C binary and Fe–C–Mn ternary alloys. In Fe–C binary alloy, the relationship between peritectic temperature range and carbon content was calculated and the calculated results compared with the results of a model reported by Fredriksson et al.\(^\text{25}^\text{) The result of } R_c=0.5 \text{ K/s in the present model was in good agreement with their one, and the carbon content when the peritectic temperature range became the maximum slightly shifted to hyper-peritectic side as the cooling rate becomes higher. In Fe–C–Mn ternary alloy, peritectic temperatures at low carbon content were varied by cooling rate and decreased as the cooling rate becomes higher because a tie-line at \( \delta/L \) interface shifted to high manganese side.

In the third test, we calculated microsegregation and peritectic transformation for Fe–C–Mn–Si–P–Mo alloys, and compared with the experimental data reported by Ueshima et al. Temperatures of \( \delta/\gamma \) transformation and \( \gamma \)-solidification decreased by adding to molybdenum, and these results were close to those of Ueshima et al. Also, the distributions of manganese, phosphorus and molybdenum by the present model were in essential agreement with those of their experimental data.

The results of these tests show the validity of the present model for predicting the microsegregation and phase transformation, and moreover, these calculations could be carried out in the practical computational time. For example, in the calculation of Fe–C binary alloy, the computational time was about 10 min and in the calculation of Fe–C–Mn–Si–P–Mo alloy, it was about 5 h (PC with Intel Core2 Quad 3 GHz CPU). Hence the present model can be utilized for predicting microsegregation of solidification with peritectic transformation for a multicomponent practical alloy. For a multicomponent alloy, however, since the determination of a tie-line depends on the thermodynamic database, it should be also remarked that an accurate thermodynamic database must be used to obtain a good simulated result even if there are some assumptions in the model.

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