Phase Field Simulation on Directional Solidification of Succinonitrile (SCN)–Acetone Organic Model Alloy

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Phase field simulation on directional solidification of succinonitrile (SCN)–acetone organic model alloy was performed. The development of concentration and phase field profile was calculated in order to clarify the dependences of growth velocity \( V \) and temperature gradient \( G \) on the morphology of growing crystal.

Concerning the primary dendrite arm spacing, \( \Lambda_1 \), the relationship between \( \Lambda_1 G^2 V / k \Delta T_0 \) and \( V \) was examined, where \( k \) and \( \Delta T_0 \) are partition coefficient and temperature difference between liquid and solid phases, respectively. The calculated values of \( \Lambda_1 G^2 V / k \Delta T_0 \) did not show a universal relationship but the trends of the present calculation can be understood by extrapolation from experimental data. The power law index of \( V \) for the \( \Lambda_1 G^2 V / k \Delta T_0 - V \) plot took similar values between the experiments and the present calculation for some cases. The \( \Lambda_1 - V \) relationship did not show dependences on temperature of the low temperature side and nor acetone concentration. For the curvature radius \( R \), the \( R - V \) relationship can be fitted by a simple function regardless the value of \( G \). In addition, the calculated values of \( R \) and the power low indexes of \( V \) for \( R \) were compared to the dendrite growth theory and good accordance was confirmed.

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Keywords: phase field method, succinonitrile (SCN)-acetone organic model alloy, directional solidification, dendrite growth, primary arm spacing, secondary arm spacing

1. Introduction

Phase field method is a newly developed simulation technique for structural formation process of various materials.1–6 It has been attracted much attention among wide range of researchers because it has clear theoretical backgrounds based on non-equilibrium thermodynamics and because it can reproduce non-equilibrium effects in material production processes. In addition, the phase field method has great advantage such that it can calculate dynamic process without tracking interface which often take complicated shape during simulation. Therefore the phase field method has been adopted to study dynamical structural formation process such as pure metal solidification and binary alloy solidification for solid solution and eutectic systems.

Phase field is a field parameter with arbitrary value between 0 and 1, which represents the state of phase as a function of location and time. For example in solidification problem, 0 and 1 represent solid and liquid phase respectively and the intermediate value between 0 and 1 means solid-liquid interface. Free energy of the system is expressed as functionals of phase field, temperature field and/or concentration field, and then the time developing equations for each field can be obtained by variational principles. The obtained time developing partial differential equations are solved numerically under appropriate initial and boundary conditions. Thus the dynamical change of material structure can be obtained as time development of phase field.

The authors performed simulations of isothermal solidification process for Al–Cu7) and Al–Zn8) alloys using phase field method and examined the effects of the difference of concentration and super cooling on the crystal morphology and growth rate. In addition, growth velocity and curvature radius of dendrite arm tip were calculated and compared to the dendrite growth theory based on stability analysis and the validity of phase field model was demonstrated. In the proceeding works, directional solidification process by phase field method was performed for Al–Zn binary alloy.9) The obtained results were visualized and the effects of Zn concentration \( C_0 \), temperature gradient \( G \) and growth velocity \( V \) on crystal morphology and stability of flat interface were studied. It was clarified that the morphology of solid–liquid interface changed from the flat interface through dipped plate to cell-like structure with Zn segregation as increasing \( V \). The interface stability was found to be determined by the values of \( G/V \) and \( C_0 \). Especially the boundary of flat interface at low Zn concentration region was found to be proportional to \( C_0 \). In addition, the temperature gradient \( G \) was lowered and dendrite formation process in directional solidification of Al–Zn system was simulated.10) The time development of Zn concentration and phase field were calculated and the effects of \( V \) and \( G \) on crystal morphology were studied. It was demonstrated that the primary dendrite arm spacing \( \Lambda_1 \) decreased as \( V^{-0.5} \) and that the third power of the secondary dendrite arm spacing \( \Lambda_2^3 \) was proportional to the solidification time \( t \). It was also confirmed that the calculated values of curvature radius \( R \) and the power law index of \( V \) to \( R \) showed good accordance with the dendrite growth theory.

As mentioned above, computer experiments was successful to predict the solidified structure, while it is desirable to observe solidification process of real alloy system directly to clarify the mechanism of metal solidification. However, in situ observation of metal solidification process is very difficult because the temperature of specimen is too high and the material is not transparent. So quenched specimen are usually observed at the end of or during the course of
solidification. Such limitation inhibits the thorough study of dynamic structural formation during solidification.

In recent years, transparent organic compounds are used as model alloy and its solidification process is observed in situ and compared to that of the real alloy system. The relationships among thermodynamic driving force, growth velocity and crystal morphology were studied and compared to those of real alloy system. The obtained results were effectively utilized to analyze the crystal growth process. Therefore simulation of solidification of transparent organic model alloy and comparison with experimental and theoretical results will give essential insights to utilize computer simulation for prediction of structural formation of materials. Based on the above mentioned point of view, dendrite growth simulation for prediction of structural formation of materials will give essential insights to utilize computer simulation of succinonitrile–aceton binary model alloy in directional solidification process was performed in the present study. The obtained results were visualized and the change of crystal morphology was studied under various aceton concentration, temperature gradient and crystal growth velocity. In section 2 the calculation method is described and results and discussion are given in section 3.

2. Method of Calculation

2.1 Formulation of phase field method

In the present study, the isothermal solidification model for binary alloy developed by Warren and Boettinger was utilized. Here only brief review of governing equations to be solved is given. Let c be concentration of species B in A of A–B binary alloy and φ be phase field. φ is parameter which takes an arbitrary real value between 0 and 1, while 0 and 1 represent solid and liquid state respectively. c and φ are both functions of location in space and time and their time developments are described by the governing equations as follows.

For concentration field c,
\[
\frac{\partial c}{\partial t} = \nabla D_c \left[ \nabla c + \frac{v_m}{R_g} c (1 - c) (H^B - H^A) \nabla \phi \right]
\] (1)

and for phase field φ in 2 dimensional xy space,
\[
\frac{1}{M_\phi} \frac{\partial \phi}{\partial t} = [\xi^2 \eta^2 \nabla^2 \phi - (1 - c) (H^A - H^B)]
+ \hat{\xi}^2 \eta \left[ \sin(2\theta)(\phi_{yy} - \phi_{xx}) + 2 \cos(2\theta)\phi_{xy} \right]
\]
\[
- \frac{1}{2} \hat{\xi}^2 [\eta^2 + \eta''] \times [2 \sin(2\theta)\phi_{xy}]
- \nabla^2 \phi - \cos(2\theta)(\phi_{yy} - \phi_{xx})].
\] (2)

In eq. (1), Dc is effective diffusion constat of B species at the present location and time and can be calculated as
\[
D_c = D_s + p(\phi)(D_L - D_s)
\] (3)

where Ds and DL are diffusion constant of B species in solid and liquid state respectively, and
\[
p(\phi) = \phi^3 (10 - 15\phi + 6\phi^2)
\] (4)
is a weighted function which takes a value between 0 and 1. \(v_m\) is molar volume and \(R_g\) the gas constant. The functions \(H^A\) and \(H^B\) appeared also in equation (2) can be expressed as
\[
H^A(T, \phi) = W^A \phi^2 + 30gL^A \left( \frac{1}{T} - \frac{1}{T_m^A} \right)
\] (5a)
\[
H^B(T, \phi) = W^B \phi^2 + 30gL^B \left( \frac{1}{T} - \frac{1}{T_m^B} \right)
\] (5b)

where
\[
g(\phi) = \phi^2(1 - \phi)^2, \quad g'(\phi) = \frac{dg}{d\phi}.
\] (5c)

The effects of interfacial energy and supercooling on free energy are taken into account in these functions. The parameters \(W^A\) and \(W^B\) reflect interfacial energy and \(L^A\) and \(L^B\) are latent heat of fusion of A and B species respectively.

Now move our eyes on eq. (2) which describes time change of phase field \(\phi\). \(M_\phi\) is a parameter which represents “inertia” against time change of phase field and can be expressed as weighted average of pure substance parameters \(M^A\) and \(M^B\) by concentration,
\[
M_\phi = (1 - c)M^A + cM^B.
\] (6)

\(\bar{\varepsilon}\) and \(\eta\) constitute a function which represents anisotropy of interfacial energy as
\[
\varepsilon(\theta) = \bar{\varepsilon} \eta(\theta) = \bar{\varepsilon}(1 + \gamma \cos(k\theta)).
\] (7)

\(\eta\) is called as anisotropy factor and a function of angle between normal to the interface and a reference direction (here we take x-direction in x–y plane), \(\theta\). Note that primes on \(\eta\) in eq. (2) mean derivatives by \(\theta\) as
\[
\eta' = \frac{d\eta}{d\theta}, \quad \eta'' = \frac{d^2\eta}{d\theta^2}.
\] (8)

Suffixes on \(\phi\) mean partial derivatives along suffixed direction as
\[
\phi_{xx} = \frac{\partial^2 \phi}{\partial x^2}, \quad \phi_{yy} = \frac{\partial^2 \phi}{\partial y^2}.
\] (9)

In the governing equations of concentration field (1) and phase field (2), the values of parameters \(T_m^A, M^B, W^A, W^B, \bar{\varepsilon}\) are to be determined. They can be determined by comparison of conventional theory as
\[
M^A = \frac{(T_m^A)^2}{6\sqrt{2L^A\delta^A}}, \quad M^B = \frac{(T_m^B)^2}{6\sqrt{2L^B\delta^B}}
\] (10a)
\[
W^A = \frac{3\sigma^A}{\sqrt{2T_m^A\delta^A}}, \quad W^B = \frac{3\sigma^B}{\sqrt{2T_m^B\delta^B}}
\] (10b)
\[
\bar{\varepsilon} = \frac{6\sqrt{2\sigma^A\delta^A}}{T_m^A} = \frac{6\sqrt{2\sigma^B\delta^B}}{T_m^B}
\] (10c)

where \(\beta^A (\beta^B)\) is kinetic coefficient, \(\delta^A (\delta^B)\) is interface thickness, \(\sigma^A (\sigma^B)\) interfacial energy, \(T_m^A (T_m^B)\) melting point, and \(L^A (L^B)\) latent heat of fusion of pure material A(B). For the parameters \(\gamma\) and \(k\) in anisotropy factor \(\eta(\theta)\) [eq. (7)], the value of \(\gamma\) is empirically given as the strength of anisotropy and that of \(k\) is determined which reflects symmetry of the crystal (4 for 4-fold symmetry).

As stated above, the phase field parameters can be determined from the data of pure substances A and B, then the eqs. (1) and (2) for A–B binary alloy are now to be
solved. Using explicit difference method, the eqs. (1) and (2) are solved numerically by a finite time step

$$\Delta t = \frac{\Delta x^2}{\tau D_L},$$

where $\Delta x$ is one grid size in descretized space and $\tau$ is a parameter which guarantee the stability of numerical solution and is taken to be usually more than 5. The imposed boundary condition is Neumann type, what we call mirror condition. In difference scheme, care must be taken so as to keep mass conservation law at each grid point.

The existance of noise is found to be essential for dendrite crystal to grow. Here the noise term

$$\sigma r(16g(\phi))(1 - c)H^A + H^B)$$

was added to the right hand side of eq. (2) which govern the development of phase field, where $\sigma$ in (12) is a parameter which represents the strength of noise, of which value was set to be 0.3 here, and $r$ is a uniformly distributed random number between $-1$ and 1.

2.2 Experimental condition

Table 1 shows the values of parameters for the present study where A is succinonitrile and B aceton. The schematic diagram of the calculated system is shown in Fig. 1. The mesh used for calculation is a 800 × 800 square lattice, of which the left side region was set to be solid phase ($\phi = 0$) as seed crystal and the other was set to be liquid phase ($\phi = 1$). The temperature of the left side, i.e. solid phase side, was kept to be $T_{\text{low}}$ and the region with temperature gradient $G$ was moved from the left side toward the right side at constant velocity $V$. Figure 2 represents the succinonitrile–aceton binary phase diagram. The two kinds of system, the succinonitrile–2.66 mol% aceton and the succinonitrile–4.59 mol% aceton were selected for the present study and their directional solidification process was simulated under the condition listed in Table 2. In this table, it should be noted that the values of $V$ and $G$ are represented in the unit of length $\Delta x (= \Delta y)$ and the unit of time $\Delta t$, i.e., the units of $V$ and $G$ are $\Delta x/\Delta t (= 1.30 \text{ m/s})$ and $K/\Delta x (= 2.00 \times 10^8 \text{ K/m})$, respectively. The values of $V$ and $G$ are rather high compared to the real experiments because of computational limitation both in space and time scale. Using scaling plot, however, the comparison between the present calculation and the real experiments is possible as in the following discussion.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>$D_A$</td>
<td>$1.27 \times 10^{-5}$ (cm$^2$/s)</td>
</tr>
<tr>
<td>$D_B$</td>
<td>$1.27 \times 10^{-6}$ (cm$^2$/s)</td>
</tr>
<tr>
<td>$v_m$</td>
<td>73.4 (cm$^2$)</td>
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<tr>
<td>$L_A$</td>
<td>47.8 (J/cm$^3$)</td>
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<tr>
<td>$T_m^A$</td>
<td>331 (K)</td>
</tr>
<tr>
<td>$\beta^A$</td>
<td>2.05 (cm/(Ks))</td>
</tr>
<tr>
<td>$\sigma^A$</td>
<td>$89.4 \times 10^{-7}$ (J/cm$^2$)</td>
</tr>
<tr>
<td>$L_B$</td>
<td>103 (J/cm$^3$)</td>
</tr>
<tr>
<td>$T_m^B$</td>
<td>179 (K)</td>
</tr>
<tr>
<td>$\beta^B$</td>
<td>2.04 (cm/(Ks))</td>
</tr>
<tr>
<td>$\sigma^B$</td>
<td>$3.58 \times 10^{-6}$ (J/cm$^2$)</td>
</tr>
<tr>
<td>$\Delta x$</td>
<td>5.0 \times 10^{-3} (cm)</td>
</tr>
<tr>
<td>$\delta_A$</td>
<td>$\Delta x/0.94$ (cm)</td>
</tr>
<tr>
<td>$\Delta t$</td>
<td>$\Delta x^2/(5D_L) = 3.85 \times 10^{-3}$ (s)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0.04</td>
</tr>
<tr>
<td>$k$</td>
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<tr>
<td>$\alpha$</td>
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Table 2  The conditions for simulation.

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<tr>
<th>$C_0$</th>
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<th>$G$</th>
<th>$V$</th>
<th>$\Delta x$/step</th>
</tr>
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<tr>
<td>(at%)</td>
<td>(K)</td>
<td>(K/\Delta x)</td>
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<td>293</td>
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Now the dependences of $\lambda_1$ and $R$ on $V$ are examined quantitatively. The estimation procedure of $R$ is as follows. In the calculated phase field $\phi (i, j)$, the solid-liquid interface was defined as the location $(i, j)$ of which the value of $\phi (i, j)$ is between 0.45 and 0.55. The all sets of interface location including tip of growing crystal was fitted by quadratic function, of which the second coefficients are averaged to obtain $R$. Before the estimation of $R$, the stational crystal growth, which means that the growth velocity of the tips of solid-liquid interface was almost constat, was confirmed by a series of concentration profiles obtained during the course of simulation. The significant figure of obtained by the present method is at best 2 order.

Figure 4(a) shows the relationship between $\lambda_1$ and $V$ of the succinonitrile–4.59 mol% acetone system ($G = 0.001 \sim 0.1$, $T_{low} = 293$) with the data obtained from real experiments. As can be seen from this figure, the power law index of $V$ for $G = 0.1$ was $-0.42$ which is as same as that of the real experiment by Miyata et al.,12) $-0.48$. In the cases of $G = 0.01$, 0.001, the $\lambda_1$ was almost constant against $V$ because of supercooling. In Fig. 4(b) the $\lambda_1$–$V$ relationships for $G = 0.05$–0.3 is given. The power law index of $V$ for $G = 0.05$–0.1 decreased from that of $G = 0.2$, while that for $G = 0.2$, 0.3 saturated. It is worth to note that the value of the index of $V$ for $G = 0.05$ and $G = 0.3$ were almost same as those of the real experiment by Somboonsuk et al. (−0.35),11) Shinomiya (−0.39)13,14) and Miyata et al. (−0.48),12) respectively. Figure 5 shows the $\lambda_1$–$V$ relationships were compared for the succinonitrile–4.59 mol% acetone system with $G = 0.1$, $T_{low} = 293$ and for the succinonitrile–2.66 mol% acetone system with $G = 0.1$, $T_{low} = 305$. This figure shows that the similar trend was obtained for $\lambda_1$ within these temperature and concentration region.

It was proved by the theory that $\lambda_1^4G^2V = \text{const.}$.20) This relationship was examined for the previous published experimental data and for the present calculation. Figure 6 shows the relationship between $\lambda_1^4G^2V/k\Delta T_0$ and $V$, where $k$ is partition coefficient and $\Delta T_0$ the difference of temperature of liquid and solid phases. Trivedi pointed out that $\lambda_1^4G^2V/k\Delta T_0$ does not stay constant but obeys power law of $V$, which contradicts against the theory.11) Figure 6 supports this relationship, i.e. $\lambda_1^4G^2V/k\Delta T_0$ obtained from experiments and the present calculation obeys power law of $V$. While the power law indexes of $V$ were different case by case, i.e., $\lambda_1^4G^2V/k\Delta T_0$ does not obey the unique scaling relationship. However, the $\lambda_1^4G^2V/k\Delta T_0$–$V$ curve obtained from the present calculation may be understood by the extrapolation of that obtained from experiments. Especially, it is interesting that the almost same power law index obtained from experiment by Somboonsuk et al. was obtained from the calculation for $G = 0.05$.

Figure 7 shows the $R$–$V$ relationship for the succinonitrile–4.59 mol% acetone system ($G = 0.05$–0.3, $T_{low} = 293$). The power law index showed variation depending on the value of $G$, however, the $R$–$V$ curve obtained for the present calculation can be seen as the extrapolation of that obtained from experiments. Moreover, the $R$–$V$ relationship can be globally fitted by a simple function regardless the value of $G$.  

3. Results and Discussion

3.1 Crystal morphology

Figure 3 shows the acetone concentration profiles obtained under the condition such that $T_{low} = 293$ [K], $G = 0.3$, 0.1, 0.01 and $V = 0.01$, 0.025, 0.05, 0.1 for the succinonitrile–4.59 mol% acetone system. From the results for $G = 0.3$, 0.1, it was clarified that the curvature radius $R$ of the tip of the prime dendrite arm decreased and the number of the prime dendrite arm increased (i.e., the prime dendrite arm spacing $\lambda_1$ decreased) with increasing growth velocity $V$. The dependence of crystal morphology on growth velocity was lost for $G = 0.01$ because super cooled solidification occurred under this temperature gradient condition. In addition, the dependence of crystal morphology on acetone concentration was found to be slight from the results of the succinonitrile–2.66 mol% acetone system.
The coincidence of $R$–$V$ relationship between the calculation and experiment is much better than the case of $\lambda_1$–$V$ relationships. This is attributed to the fact that there is almost no dependence of $R$ on $G$, as experimentally shown by Somboonsuk et al.\textsuperscript{11})

3.2 Comparison with the dendrite growth theory

Mullins and Sekerka\textsuperscript{21}) studied the stability of flat solidified interface in dilute binary alloy which moves at growth velocity $V$. In their study sinusoidal perturbation with period $A$ was given to flat solidified interface and the growth/ extinction of the perturbation was analyzed by solving the governing equation for concentration and temperature fields under appropriate boundary condition. Trivedi and Kurz\textsuperscript{22}) extended their treatment to the case of high Peclet number, i.e., the case that the values of $V$ are large compared to the thermal and diffusion lengths of solute atom, and obtained the condition for stationary and stable growth of flat solidified interface. The validity of the perturbation theory for stability of flat solidified interface was confirmed by various experiments such as growth of ice from solution,\textsuperscript{23}) directional solidification of Al–Cu,\textsuperscript{24}) Al–Ti and Al–Cr dilute binary alloy.\textsuperscript{25}) In the dendrite growth theory, tip of the sinusoidal perturbation at marginal stability of flat solidified interface is considered to be tip of growing dendrite. According to this theory, if the shape of the tip of an isolated dendrite is parabola, the relationship between $R$ and $V$ can be obtained as\textsuperscript{26–28}:

$$V \left( \frac{k_v \Delta T_0^v}{D} \right) \left( \frac{1}{1 - (1 - k_v) \nu(P_c)} \right) \xi_t - 0.5G = \frac{\Gamma}{\sigma^* R^2}, \quad (13)$$

where $k_v$ is solute partition coefficient with the fast growth velocity correction, $\Delta T_0^v$ is temperature difference between liquid and solid states at concentration $c_0$, $\nu(P)$ is Ivantsov function which describe stable growth of parabola (paraboloid in 3 dimension) shaped solid-liquid interface, $\xi_t$ is a correction function describing the influence of solute diffusion on stability, $P_c$ the Peclet number of solute diffusion, $\Gamma$ the Gibbs–Tomson coefficient, $\sigma^*$ the structure factor.\textsuperscript{29})

The comparison between this Trivedi–Kurz theory (abreviated as TK model below) and the present simulation is shown in Table 3. In addition, $\lambda_1$ was evaluated from $R$ using the relationship\textsuperscript{30,31}:

$$\lambda_1 = \left( \frac{3 \Delta T_0 R}{G} \right)^{1/2}, \quad (14)$$

where $\Delta T_0$ is temperature difference between the liquidus temperature and the solidus temperature at a fixed concentration. The obtained results were also shown in Table 3.

The values of $R$ obtained by TK model and the phase field method showed good accordance, although the value of the phase field method was a little bit smaller than that of TK model. In addition, the values of power law index of $V$ for $V$–$R$ relationship showed good accordance between TK model and the phase field model except the case of $G = 0.01$. In that case, large difference between the two models was found,
which can be considered as the result of super cooling occurred in the phase field simulation. The trends of $A_1$ were similar to those of $R$, while the values of power law index of $V$ for $V = A_1$ relationship showed large difference between the two models. It should be noted that the accordance of the power law index by the phase field simulation with real experiments ($-0.35 \sim -0.48$) was much better than that by the TK model.

4. Summary

Phase field simulation on directional solidification of succinonitrile (SCN)–acetone organic model alloy was performed. The development of concentration and phase filed profile was calculated in order to clarify the dependences of growth velocity $V$ and temperature gradient $G$ on the morphology of growing crystal. The obtained results can be summarized as follows.

(1) Concerning the primary dendrite arm spacing, $A_1$, $A_1 = G^2 V / \Delta T_0$ obtained from experiments and the present calculation obey power law of $V$. The power law indexes of $V$ were different case by case, i.e., $A_1 = G^2 V / \Delta T_0$ does not obey the unique scaling relationship. However, the $A_1 = G^2 V / \Delta T_0$ curve obtained from the present calculation may be understood by the extrapolation of that obtained from experiments.
The curvature radius $R-V$ relationship did not show dependences on temperature of the low temperature side and nor acetone concentration.

The $d_1-V$ relationship can be fitted by a simple function regardless the value of $G$.

The calculated values of $R$ and the power low indexes of $V$ for $R$ were compared to the dendrite growth theory and good accordance was confirmed.

**REFERENCES**


Appendix of Ref. 9) gives detail explanation.
