Numerical Simulation of Peritectic Reaction in Fe–C Alloy Using a Multi-phase-field Model

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1. Introduction

Peritectic reaction during rapid solidification of twin roll cast sometimes causes surface or inner defects due to the difference of physical and chemical properties between austenite and ferrite phases.

In order to investigate the formation process of the second phase from the primary one, the relationship between the cooling rate and the growth rate of the second phase has been theoretically discussed using simplified one-dimensional model.1-4) Two-dimensional simulations, which adapt phase-field model, have successfully reproduced complex microstructure evolution during peritectic solidification.5,6) However, although the effect of solute diffusivity on the peritectic reaction is briefly investigated,5,6) those studies are mainly designed to show the applicability of the phase-field model to the multi-phase system.

The interface energy is one of the important factors in the microstructure formation. The magnitude of the interface energy can be changed by adding small amounts of the alloying elements, for example, δγ interface energy decreases to one fourth of the original value when phosphorous is added only 0.3 mass% into the steel.7) In this study, the effect of interface energy on the rate of peritectic reaction for Fe–C alloy is discussed using a multi-phase-field model. The shape of the interface around the triple junction and the growth of the second phase in an isothermal dendrite are discussed in association with the relative magnitude of interface energy for δ, γ and liquid phases.

We adopt the recently developed phase-field model9) using parabolic potential9) and thin interface limit10) by authors. The conventional quartic potential and/or sharp interface limit model seems not to be the best one for mainly two reasons: the quartic potential shows unnecessary local minimum in the free energy functional at the triple junction point, and the sharp interface limit model requires huge computational time to narrow the gap between zero interface width assumption and actual finite interface condition.

2. Numerical Simulation

2.1. Governing Equations

In the multi-phase-field model for three phase system, total free energy of the system F is defined by,8,11)

\[
F = \int \left[ \sum_{i=1}^{3} \sum_{j=1}^{3} \left( \frac{1}{2} \epsilon_{ij} | \phi_{i} \nabla \phi_{j} - \phi_{j} \nabla \phi_{i} |^{2} + \phi_{i} f_{ij} c_{i} T + W_{ij} \theta \phi_{i} \phi_{j} \right) \right] dV
\]

where subscripts i and j = 1, 2, 3 represent the fraction of δ, γ and liquid phase, respectively, c_i is carbon composition of each phase, \( \epsilon_{ij} \), \( W_{ij} \) are parameters related to the interface energy \( \sigma_{ij} \) and interface width 2\( \lambda \) defined by,8,

\[
\epsilon_{ij} = \frac{4 \sqrt{\lambda \sigma_{ij}}}{\pi}
\]

\[
W_{ij} = \frac{2 \sigma_{ij}}{\lambda}
\]

Note that calculation results do not depend on the interface width. The finite interface width is introduced for the convenience of numerical calculation in the phase-field model.

The parabolic potential has the form,9) and \( g(\phi_{i}, \phi_{j}) = \phi_{i} \phi_{j} \) and \( f(c, T) \) represents the free energy of the bulk phase expressed using dilute solution approximation as follows,

\[
f_{ij}(c_{i}, T) = \left[ \mu_{\delta} (1-c_{i}) + \mu_{\gamma} c_{i} + RT \left( c_{i} \log c_{i} + (1-c_{i}) \log (1-c_{i}) \right) \right] V_{m}
\]

where \( R \) is the universal gas constant, \( T \) is the temperature, \( V_{m} \) is the molar volume and \( \mu_{\delta} \) is chemical potential written as,

\[
\mu_{\delta} = \mu_{\delta}^{0} + RT \ln (1-c_{i}), \mu_{\gamma} = \mu_{\gamma}^{0} + RT \ln c_{i} \ldots(5)
\]

Applying equilibrium conditions between two phases \( i \) and \( j \) (\( \mu_{\delta} = \mu_{\gamma}^{0} + \mu_{\gamma} = \mu_{\gamma}^{0} + RT \ln c_{i} \)) and setting liquid phase as the standard state, \( \mu^{0}_{\delta} \) can be relate to equilibrium compositions as follows,

\[
\mu^{0}_{\delta} = RT \ln \left( \frac{1 - c_{i}^{e}}{1 - c_{j}^{e}} \right)
\]

\[
\mu^{0}_{\delta} = RT \ln \left( \frac{c_{i}^{e}}{c_{j}^{e}} \right) \quad (j = 2, 3)
\]

\[
\ldots(6)
\]

where \( c_{ij}^{e} \) is the equilibrium concentration of i phase contacting with phase j.

The multi-phase-field and concentration-field equations are derived applying the variational differentiation to Eq. (1) and given by:

\[
\frac{\partial \phi_{i}}{\partial t} = -\frac{2}{n} \sum_{j=1}^{n} M_{ij} \left( \frac{\delta F}{\delta \phi_{j}} - \frac{\delta F}{\delta \phi_{i}} \right) \ldots(7)
\]

\[
\frac{\partial c_{i}}{\partial t} = \nabla \cdot \left( D_{i} \nabla \phi_{i} \right) \ldots(8)
\]

where \( M_{ij} \) is a i/j interface mobility obtained in the same manner as single phase system10)

\[
M_{ij}^{-1} = \epsilon_{ij} \left[ \frac{RT}{V_{m}} \frac{1 - k_{ij}^{2}}{m_{ij}^{2}} \beta_{ij} + \frac{\epsilon_{ij}}{D_{i} \sqrt{2 W_{ij}}} \zeta(c_{i}^{e}, c_{j}^{e}) \right] \ldots(9)
\]
where, \( \zeta(c_i', c_j') = (c_i' - c_j') \int_0^{L} \frac{\phi(1-\phi)}{1-\phi_{L}} d\phi \).

\( k^e \) is the partition coefficient, \( m^i \) is the liquidus, solidus slope or the slope of \( \delta' \gamma, \gamma' \gamma \) phase-boundary, \( D \) is the solute diffusivity in the interface region and \( \beta \) is the inverse of kinetic coefficient;

### 2.2. Numerical Simulation

The peritectic reaction of Fe–1.75mol%C alloy is simulated. The system temperature is uniform and continuously reduced from the liquidus temperature at a cooling rate of 300 K/s. Though the calculation area is set to be 140 \( \mu \)m square, only the quarter region is calculated since the steel dendrite structure shows four-fold symmetry. We assume that the \( \gamma \) phase nucleates at one point when and where the carbon concentration firstly reaches peritectic composition. The physical properties and the calculation condition are shown in Table 1.\(^{12,13}\) The interface energy between \( \delta/L \) is set to be 0.204 J/m\(^2\), and those of \( \delta'/\gamma \) and \( \gamma'/\gamma \) are set to be 0.204, 0.306 or 0.408 J/m\(^2\). There is no experimental report on the value of \( \sigma_{\delta L} \). However, because the interface energy between fcc crystal and liquid phases can be larger than that of bcc/liquid interface,\(^{14,15}\) \( \sigma_{\delta L} \) value is assumed to be the same or larger value than that of \( \sigma_{\delta L} \). On the other hand, since \( \sigma_{\delta} \) is reported as 0.457 J/m\(^2\),\(^{16}\) the values of \( \gamma \)-related interface energies are increased up to twice of \( \sigma_{\delta} \), to investigate the effect of interfacial energy on the microstructure. The governing Eqs. (3) and (4) are solved explicitly using a finite difference scheme.

### 3. Numerical Result and Discussion

Figure 1 shows the effect of the interface energy on the interface shape around triple junction point. The same volume fraction of \( \gamma \) and \( \delta' \) phases are initially put and the system temperature is kept at the peritectic one. All the interface energies are set to be the same in Fig. 1(a), and \( \sigma_{\delta L} \), or/and \( \sigma_{\delta L} \) are larger than that for \( \sigma_{\delta L} \) by 50% in Figs. 1(b–d), respectively. It is clear from the figure that the interface shape at the triple junction point is determined to satisfy the mechanical equilibrium, and when the value of \( \sigma_{\delta} \) is increased, the moving distance of the triple junction point is decreased. These results are derived from the nature of the phase-field equations; minimizing the total system free energy.

Figure 2 shows the microstructure evolution in the peritectic solidification. Firstly the primary \( \delta \) phase grows in the dendritic shape and then \( \gamma \) phase nucleated at the root of the secondary arm. The growth rate of the \( \gamma \) phase is small immediately after the nucleation due to the small undercooling (Fig. 2(a)). When the driving force for the \( \gamma \) phase amount to large enough value, it rapidly crystalline along to the \( \delta \) phase through the peritectic reaction (Fig. 2(b)). The \( \delta \) phase is completely covered with the \( \gamma \) phase (Fig. 2(b)). Because the peritectic transformation is limited by the solute diffusion through \( \gamma \) phase, \( \delta \) phase still exist at a temperature below more than fifteen degrees from the peritectic temperature (Fig. 2(d)).

The effect of the interface energy on the peritectic microstructure is shown in Fig. 3: all the values of interface energy is set to be equal in Fig. 3(a); \( \sigma_{\delta L} \) and \( \sigma_{\delta L} \) are increased by 50% than that of \( \sigma_{\delta L} \) in Fig. 3(b); \( \sigma_{\delta L} \) or \( \sigma_{\delta L} \) is increased 50% in Fig. 3(c); \( \sigma_{\delta L} \) and \( \sigma_{\delta L} \) are increased by 100% than that of \( \sigma_{\delta L} \) in Fig. 3(d). The moving velocity of the triple junction is decreased with increase of \( \gamma \)-related interface energy. The moving distance of triple junction shown in Fig. 3(b–2) is about half of that is shown in Fig. 3(a–2). Because there is little difference in the distance

### Table 1. Physical properties of Fe–C alloy.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solute diffusivity</td>
<td>( 6.0 \times 10^{-10} )</td>
</tr>
<tr>
<td>( \delta ) phase</td>
<td>( 1.0 \times 10^{-10} )</td>
</tr>
<tr>
<td>( \gamma ) phase</td>
<td>( 2.0 \times 10^{-10} )</td>
</tr>
<tr>
<td>Liquidus slope</td>
<td>(-1769.6)</td>
</tr>
<tr>
<td>( \delta / \gamma )</td>
<td>(-1406)</td>
</tr>
<tr>
<td>Partition coefficient</td>
<td>( 0.165 )</td>
</tr>
<tr>
<td>( \delta / \gamma )</td>
<td>( 0.304 )</td>
</tr>
<tr>
<td>Melting point</td>
<td>( 1809 )</td>
</tr>
<tr>
<td>( \delta / \gamma )</td>
<td>( 0.543 )</td>
</tr>
</tbody>
</table>

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between Fig. 3(c-1) and Fig. 3(c-2), not the interface shape at the triple junction but the increase of total free energy due to γ phase formation affects the junction velocity. When the γ-phase related interface energies are increased to twice of the σ_{gl} value, the distance decreases to the one-fourth (Fig. 3(d)).

Assuming that γ/L and δ/γ interface areas equally increase by peritectic reaction, the moving distance varies in inverse proportion to the relative ratio between σ_{gl} and γ-phase related interface energies. Table 2 shows the ratio of γ-phase related interface energy to σ_{gl} and inverse of the product of those energies. The ratio of moving distance agree well with the third column of the Table2. This fact also support that the increase of total interface energy restricts the movement of the triple junction.

Figure 4 shows the relationship between the moving velocity of the triple junction and undercooling from the peritectic temperature. The moving velocity is reported by the direct experimental observation. In the literature the velocity change from 1 600 to 3 700 μm/s when the system undercooled 5 K for Fe–0.65mol%C system. Considering the velocity dependence on the interface energy, the calculated velocity is about three times as large as actual state. Hence, It could be said that these results show good agreement with the experimental data. In this way the effect of the interface energy on the peritectic reaction is quantitatively investigate using the multi-phase-field model.

4. Summary

The effect of interface energy on the peritectic reaction is studied using the multi-phase-field model at thin interface limit. The value of interface energy affects the interface shape at the triple junction and moving distance of the junction. However, the moving distance, namely the velocity, of the triple junction only is affected by the increase of the total interface energy. The calculated junction velocity shows good agreement with experimental data.

Table 2. Ratio between interface energies: \( \sigma_{g\delta} / \sigma_{gL} \) and \( \sigma_{gL} / \sigma_{g\delta} \), and the inverse of those product.

<table>
<thead>
<tr>
<th>Fig.</th>
<th>( \sigma_{g\delta} )</th>
<th>( \sigma_{gL} )</th>
<th>( \sigma_{gL} / \sigma_{g\delta} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>3(a-2)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3(b-2)</td>
<td>1.5</td>
<td>1.5</td>
<td>0.44</td>
</tr>
<tr>
<td>3(c-1)</td>
<td>1</td>
<td>1.5</td>
<td>0.67</td>
</tr>
<tr>
<td>3(c-2)</td>
<td>1.5</td>
<td>1</td>
<td>0.67</td>
</tr>
<tr>
<td>3(d)</td>
<td>2</td>
<td>2</td>
<td>0.25</td>
</tr>
</tbody>
</table>

Fig. 4. Velocity of triple junction vs. undercooling.

REFERENCES