Phase-field Modeling of Rapid Solidification in Small Alloy Droplets

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(Received on April 14, 2003; accepted in final form on June 2, 2003)

Phase field modeling has been applied first to simulate microstructural evolution during rapid solidification of small Al–0.02 mole fraction Cu alloy droplets. We use a phase-field model with the parameters determined at a finite interface thickness condition. Numerical computation is stable over a wide temperature range because same interface energy and interface thickness are applied during computation by using temperature dependence of phase field parameters. For numerical efficiency, we adopted rather thick interface thickness, large interface energy and small interface kinetics coefficient, compared with reported values. Nevertheless, overall features of microstructural evolution presented in this study show close resemblance with the reported theoretical predictions and experimental results; initial dendrite/plane-front transition when the nucleation undercooling is small, plane-front/cell and cell/dendrite transition in high interface velocity regime, complete disappearance of dendritic structure in high heat transfer coefficient and deflection phenomena in cellular growth direction.

KEY WORDS: phase field modeling; solidification; rapid solidification; microstructure; solute trapping.

1. Introduction

The microstructural evolution in rapid solidification of small alloy droplets have been very attractive subject in experimental and theoretical works because of not only the interesting morphological transitions of solid–liquid interface in a droplet, but also technological importance for development of high strength materials by gas-atomization. The solidification patterns in rapid solidification of alloy droplets are dependent on the heat transfer coefficient between droplet surface and external coolant, $h$ and the undercooling just before onset of nucleation, $\Delta T$. When a large $h$ or high $\Delta T$ is given, the partitionless solidification with complete solute trapping often occurs first and then the interface pattern is developed into cellular and dendritic mode just before onset of nucleation, $\Delta T$. When a large $h$ or high $\Delta T$ is given, the partitionless solidification with complete solute trapping often occurs first and then the interface pattern is developed into cellular and dendritic mode with recalescence. When a small $h$ and low $\Delta T$ are given, on the other hand, the dendritic pattern is dominant.

The pattern selection problem in rapid solidification of alloy droplets under the given conditions have been treated by analytical models where the Ivantsov solutions for thermal and solutal diffusion fields around the needle crystal and the marginal stability criterion are combined to yield a unique solution for dendritic tip radius and tip velocity. The models have been successfully applied to various slow or rapid solidification situations and have been standard tools for quantitative prediction of solidification microstructure, even though the marginal stability criterion has severe limitations concerning the validity of theoretical foundations.

Recently a new computational methodology (phase-field model) for prediction of the microstructural evolution during solidification have been proposed. Phase-field models are very powerful in describing the complex pattern evolution of the interface between mother and new phases in non-equilibrium state. The models are efficient especially in numerical treatment because all the governing equations are written as unified ones in the whole space of system with distinguished interface from the mother and new phase, and direct tracking of the interface position is not needed during numerical calculation. Recently several phase-field models have been developed mainly for the solidification of pure materials and they have been extended to the solidification of binary alloys with a single solid phase or two solid phases. The alloy phase-field model proposed by Wheeler, Boettinger and McFadden (WBM model) have been applied to the two-dimensional (2-D) isothermal solidification and non-isothermal solidification with recalescence effect in a binary alloy which may be regarded as a model for rapid solidification in a droplet. However the computational results in 2-D showed not only dendritic pattern without any cellular or plane-front pattern which may be anticipated in rapid solidification, but also rather negligible changes in dendrite scale in a droplet even with rapid recalescence effect.

In the original WBM model, the parameters in the phase-field equation have been determined at the sharp interface limit condition. The model predicts decreasing partition coefficient with increasing interface velocity, which is inconsistent with experimental results. Thus the
A phase-field model for solute trapping in solidification of alloys have been proposed by Wheeler et al.\(^{30}\) In their model where the concentration gradient energy term, besides of the phase field gradient energy term, is added to the free energy functional. As pointed out in reference,\(^{27,30}\) however, the concentration gradient energy term is not a necessary condition for solute trapping. The finite interface thickness can result in the solute trapping effect, because the relaxation time for partitioning of the solute atoms in the diffuse interface should be finite in that case. In order to describe the solute trapping effect by a simple phase-field model without concentration gradient energy term, therefore, we need the parameters in the phase-field equation determined at finite interface thickness condition, not at sharp interface limit condition. This kind of work for alloy has been done by Kim et al.,\(^{30}\) which is an extension of the idea developed by Karma and Rappel for pure materials.\(^{31}\)

They showed that all parameters in the phase-field equation can be determined at a finite interface thickness condition, not at zero interface thickness (sharp interface) condition, and the chemical potential gradient in the interfacial region introduced by the finite interface thickness results in the solute trapping effect.\(^{30}\)

In spite of some computational phase-field modelings for rapid solidification of alloys in 1-D\(^{27,30}\) or 2-D,\(^{24}\) however, there has not been any computational result which shows the microstructural evolution including the partitionless plane front, cellular and dendritic solidification. In this study we will use the phase-field model\(^{30}\) with the parameters determined at the finite interface thickness condition for the 2-D computation of microstructural evolution during rapid solidification of small alloy droplets, and we will show that the model can reproduce almost all of the characteristic patterns and their transitions observed in experiments.

In gas-atomization process for production of rapidly solidified alloy powders, it has been typically observed in rapidly solidified alloy powders. In this study we will use the phase-field model\(^{30}\) with the parameters determined at the finite interface thickness condition for the 2-D computation of microstructural evolution during rapid solidification of small alloy droplets, and we will show that the model can reproduce almost all of the characteristic patterns and their transitions observed in experiments.

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2. Phase-field Model

2.1. Governing Equations

The free energy density of a solid–liquid mixture may be written as

\[
f(c, \phi) = h(\phi) f^s(c) + (1 - h(\phi)) f^l(c) + \varepsilon g(\phi), \quad (1)
\]

where \(f^s\) and \(f^l\) are the free energy density of the solid and liquid phase, respectively, as a function of the solute mole fraction \(c\). The phase field \(\phi\) is defined as a continuous variable between \(\phi = 1\) at bulk solid and \(\phi = 0\) at bulk liquid phases, and the functions \(h(\phi)\) and \(\varepsilon g(\phi)\) may be chosen as

\[
h(\phi) = \phi(6\phi^2 - 15\phi + 10) \quad (2)
\]

\[
\varepsilon g(\phi) = \varepsilon \phi^2 (1 - \phi)^2 \quad (3)
\]

where \(\varepsilon g(\phi)\) is a double-well potential associated with the phase change and \(\varepsilon\) is the potential height. We do not impose any restriction on the functional forms of the free energy density of the solid and liquid phases, and so any special models or a thermodynamic data for them may be adopted.

Time dependences of the anisotropic phase field and concentration field in 2-D can be described by

\[
\phi_i = M_i \left[ \nabla \cdot \left( \varepsilon(\theta)^2 \nabla \phi \right) + \frac{\partial}{\partial y} \left( \varepsilon(\theta) \delta(\theta) \frac{\partial \phi}{\partial y} \right) - f_\theta \right] \quad (4)
\]

and

\[
c_i = -\nabla \cdot \left( D(\phi) \nabla f_c \right) \quad (5)
\]

where \(\varepsilon(\theta)\) in Eq. (4) is assumed to have a four-fold symmetry;

\[
\varepsilon(\theta) = \varepsilon \delta (1 + \delta \cos 4\theta) \quad (6)
\]

where \(\delta\) and \(\delta\) are constants. Even though one may permit an anisotropy in phase field mobility \(M_\theta\), it will be assumed to be isotropic. \(D(\phi)\) is the chemical diffusivity as a function of phase field. It should be noted that \(\varepsilon\) dependence of diffusivity takes an effect on solute trapping behaviour. Equation (5) guarantees the constant diffusivities in the bulk solid and liquid phases, irrespective of specific free energy density model.

2.2. Parameters in Phase-field Equation

In phase-field equation, there are three parameters \(\varepsilon_{e_c}\) and \(M_e\), which are to be matched with the interface thickness, interface energy and interface kinetics coefficient. The parameters can be determined at a finite interface thickness condition,\(^{30}\) as well as at conventional sharp interface limit condition.\(^{16}\) In this section we describe the procedure for determination of parameters at the finite interface thickness condition. The derivation of the relevant equations has been described in reference.\(^{30}\)

2.2.1. Determination of \(\varepsilon_{e_c}\) and \(M_e\)

At first, the parameters \(\varepsilon_{e_c}\) and \(M_e\) are matched with the interface thickness and interface energy at thermodynamic
equilibrium state. Assuming a system with 1-D flat interface, whose normal is parallel to x axis, at thermodynamic equilibrium state, the chemical potential \( f_\phi \) must be constant across the interface and then the concentration profile \( \tilde{c}(\phi) \) as a function of the stationary phase field \( \phi \) is obtained by numerical integration of

\[
\frac{d\tilde{c}(\phi)}{d\phi} = f_o \tilde{c}(\phi) - \frac{f_\phi}{f_o} \tilde{c}(\phi, \phi) \quad \text{(7)}
\]

under the boundary conditions \( \tilde{c}(0) = c^l_0 \) and \( \tilde{c}(1) = c^s_0 \), where \( c^l_0 \) and \( c^s_0 \) are equilibrium concentrations of liquid and solid phases, respectively. The interface energy \( (\sigma_o) \) at the equilibrium state and a measure of the interface thickness (\( \lambda_\phi \)) at the equilibrium state over which the phase field changes from 0.1 to 0.9 are obtained as

\[
\sigma_o = \sqrt{2} e_o \sqrt{\int_0^1 F(\phi_o) - F(0) \, d\phi_o} \quad \text{(8)}
\]

\[
2\lambda_\phi = \frac{\sigma_o}{\sqrt{2} e_o} \int_0^1 \sqrt{Z(\phi_o)} - Z(0) \, d\phi_o \quad \text{(9)}
\]

respectively, where the function \( F(\phi_o) - F(0) \) is given by

\[
F(\phi_o) - F(0) = w(\phi_o^3 - \phi_o^2) + (Z(\phi_o) - Z(0)) \quad \text{(10)}
\]

and the function \( Z(\phi_o) \) is defined as

\[
Z(\phi_o) = h(\phi_o) f^3(\tilde{c}(\phi_o)) + (1 - h(\phi_o)) f^4(\tilde{c}(\phi_o)) - f^4(c^l_0) - f^4(c^s_0) \tilde{c}(\phi_o) \quad \text{(11)}
\]

Note that the second term in right-hand side of Eq. (10) is a fixed potential related with the free energy density of solid and liquid, whereas the first term must be manipulated to give the required interface energy and interface thickness. Thus temperature dependences of two parameter \( e_o \) and \( w \) in phase-field equation can be determined by numerical integration of Eqs. (8) and (9) for given fixed interface energy and thickness. However there exists a limit to the interface thickness that we can use during numerical calculation;

\[
2\lambda_\phi \leq \frac{\sigma_o}{2} \int_0^1 \frac{1}{\sqrt{Z(\phi_o) - Z(0)}} \, d\phi_o \quad \text{(12)}
\]

This inequality comes from the fact that even with \( w = 0 \) in Eqs. (8) and (9) both the interface energy and interface thickness must be finite. Evaluating this limit as a function of temperature by numerical integration, with thermodynamic data given in Table 1 and \( \sigma_o = 0.093 \text{ J/m}^2 \), it results in 2\( \lambda_\phi \leq 7.143 - 18.08 \text{ nm} \) in the temperature range of 840–910 K. This value means that if we simulate the solidification behaviour, for example, in a droplet of 10 \( \mu \text{m} \) in diameter the total grid number should be square of several thousands when the grid size is a quarter of the interface thickness. To circumvent this problem in computational efficiency, it is inevitable to use an increased interface energy.

In present numerical calculation, we chose \( \sigma_o = 4.5 \times 0.093 \text{ J/m}^2 \). In this case inequality (12) yields 2\( \lambda_\phi \leq 32.14 - 81.36 \text{ nm} \) in the temperature range of 840–910 K and so we took 2\( \lambda_\phi = 30 \text{ nm} \) irrespective of temperature. Using thermodynamic data on \( \alpha \text{-FCC solid solution and liquid phases in Al-Cu alloy, given in Table 1, the corresponding values of the parameters } e_o \text{ and } w \text{ were determined by using following procedures: After calculating the equilibrium chemical potential and concentrations of solid and liquid at a given temperature, } \tilde{c}(\phi_o) \text{ was obtained as a power series of phase field } \phi \text{ to seventh order from Eq. (7). Then } e_o \text{ and } w \text{ could be determined by an iterative method from Eqs. (8) and (9). These procedure were repeated at eight different temperatures in the range of 840–910 K. The variations of } e_o \text{ and } w \text{ values with temperature were very well-fitted with parabolic curves of}

\[
e_o = (53.022 - 0.10184 T + 6.3450 \times 10^{-5} T^2) \times 10^{-5} \quad \text{(J/m)}^{1/2}
\]

and

\[
w = (150.57 - 0.35785 T + 2.1278 \times 10^{-4} T^2) \times 10^{3} \quad \text{J/m}^3
\]

2.2.2. Determination of \( M_c \)

At the finite interface thickness condition, we can get a relationship between the phase-field mobility \( M_c \) and the interface kinetics coefficient \( \mu_c^L \)

\[
\frac{\sigma_o}{M_c e_o^2} + \frac{e_o}{2 \sqrt{2}} \frac{RT}{V_m} \frac{1 - k^2}{\mu_c^L m^2} \quad \text{(15)}
\]

where \( T \) is the system temperature, \( m^2 \) is the equilibrium liquids slope in the phase diagram, \( V_m \) is molar volume, \( R \) is the gas constant, \( k^2 = c^l_0 c^s_0 \) and a temperature dependent
constant $\xi$ is given by

$$
\xi = \int_{0}^{\phi_{f}} \int_{0}^{\phi_{i}} \left( \frac{f_{x}(\tilde{c}_{x}, \phi_{i})}{D(\phi_{i})} \left( \tilde{c}_{x}(\phi_{i}) - \tilde{c}_{x} \right) d\phi_{i} \right) \\
\times \left( \frac{f_{x}(\tilde{c}_{x}, \phi_{f})}{f_{x}(\tilde{c}_{x}, \phi_{f})} d\phi_{f} \right)
$$

From Eq. (15), we can determine $M$, as a function of temperature for given $\phi_{i}$ and $\phi_{f}$ values by evaluating numerically the integral in Eq. (16). In doing this, how we define the diffusivity at the interfacial region is not a trivial problem because the solute trapping effect in our phase-field model is governed by the interface Péclet number $2\lambda_{fi}/D_{i}$, where $D_{i}$ is the average interfacial diffusivity. In the aforementioned procedure for the determination of $\xi$, $\phi_{i}$, we have used $2\lambda_{fi}=30$ nm and $\sigma_{f}=4.5 \times 0.093$ J/m$^{2}$. Considering that the real interface thickness is only a factor of 0.1 nm, the assumed interface thickness is unrealistically large, which leads to exaggerated solute trapping effect. One way to make a compromise with a large interface thickness is to use high $D_{i}$. We therefore assumed that the diffusivity throughout the interface is equal to the diffusivity in liquid phase $D_{l}$, that is $D(\phi)=D_{l}$ for $\phi<0.9$ and $D(\phi)=D_{i}$ for $\phi>0.9$, where $D_{i}$ is diffusivity in solid phase.

The variation of $\xi$ with temperature, calculated with thermodynamic data given in Table 1 and $w$ by Eq. (20) for $F(\phi)$, appears to be well-fitted with a parabolic curve

$$
\xi=(446.58-0.944237^{+}4.9948\times10^{-4}T^{2})\times10^{12} \ \ J^{2}/m^{7/2}
$$

In this stage, we should note that there exists a limit on the magnitude of $\mu_{b}^\omega$ available in numerical calculation, which is due to non-zero interface thickness. If we take an infinitely thin interface thickness, that is sharp interface limit, maintaining a finite interface energy in Eqs. (13) and (14), $\xi_{o}$ should be very small, whereas $w \rightarrow 2^{30}$ and then the interface kinetics coefficient is given by

$$
(\mu_{b})_{\text{sharp}} = \frac{RT(1-k^\epsilon)M_{o}c_{x}^{2}}{V_{m}m^{2}^{7/2} \sigma_{m}^{2}}
$$

In this case, we can impose any value for $\mu_{b}$ by adjusting $M_{o}$ to the corresponding value. When the interface thickness is finite, on the other hand, we can see from Eq. (15) that there is a maximum allowable value for $\mu_{b}$ (where $M_{o}$ is infinite),

$$
(\mu_{b})_{\text{max}} = \frac{\sqrt{2}RT(1-k^\epsilon)}{V_{m}m^{2}^{7/2} \sigma_{m}^{2} \xi_{o}}
$$

This maximum values calculated were tabulated in Table 2, which must be a function of temperature because $\xi_{o}$ is dependent on the temperature. As shown later, the temperature of the system in this study does not reach below 850 K where $(\mu_{b})_{\text{max}}=0.00214$ m/s K. We therefore fixed $\mu_{b}$ as 0.002 m/s K in all numerical calculations, which is significantly small compared with the estimated value in metallic systems.\(^{32}\) The corresponding phase field mobility $M_{o}$ then can be determined from the relationship (15).

Note that the relationship (15) can hold true only when the interfacial Péclet number is small because a linear relationship between thermodynamic driving force and interface velocity is derived at this limit condition.\(^{30}\) When the interfacial Péclet number is large, the interface velocity is non-linear with thermodynamic driving force and so the linear interface kinetics coefficient cannot be defined.\(^{30}\) Therefore we will use the phase-field mobility estimated from Eq. (15) for full range of the interfacial Péclet number of this study.

3. Numerical Methods

Even though the temperature can be treated as a function of time and position in a droplet during rapid solidification, we adopt a first approximation where the temperature is uniform within a droplet and varies only with time. In this case, the temperature of droplet in every time step can be determined by a simple energy balance associated with the heat extraction rate by cooling gas and the latent heat release rate from moving interface. However, an expression for energy balance condition and the resultant thermal behaviour depends on the geometry of solidifying system; During rapid solidification of a liquid droplet, thermal behaviour is largely dependent on the ratio of the total solid–liquid interface area to the droplet surface area, especially just after onset of a nucleation on droplet surface. Total interface area is proportional to square of length scale of solid in 3-D, whereas it is linear in 2-D. Therefore, at initial stage of solidification, there should be a large difference in thermal behaviour between 2-D and 3-D model. We thus used an energy balance condition in 3-D which is more realistic;

$$
C_{v}(\pi \chi_{l}^{2}) \frac{dT}{dt} = L \frac{d\phi}{dx} \int_{V} \phi(x,y,t)dV - h(T-T_{p})(2\pi x_{f}^{2} + 2\pi x_{f}^{2}) \quad ...(20)
$$

where $C_{v}$ and $L$ are specific heat and latent heat per unit volume, respectively, $V$ is the volume of a droplet and $h$ is the heat transfer coefficient between droplet surface and cooling gas. In this equation the shape of liquid droplet was approximated to a cylinder with a radius $x_{c}$ and a height $l$, only for convenience in treatment of boundary conditions on the droplet surface. It is assumed that a nucleation event
occurs at the top center of the cylinder.

In order to calculate the energy source term (the first term in right-hand side) in Eq. (21), in principle, the phase-field Eq. (4) and solute diffusion Eq. (5) should be solved in 3-D. However it is a formidable task because of limits in computational speed and resources. As a first approximation, therefore, we assumed rotational symmetry about with cylinder axis in dendrite shape. Being compared with the real 3-D dendritic shape, the assumed dendrite shape overestimates the volume change of solid, resulting in rapid recalescence at initial stage of solidification. In this way we solved Eqs. (4) and (5) in a 2-D rectangular coordinate and at every time step calculated the source term by rotating the system about the cylinder axis.

The functions \( f_s, f_o, \) and \( f_l \) were obtained by direct differentiation of Eq. (1) combined with free energy data of solid and liquid phases given in Table 1. Equations (4) and (5) are discritized on uniform grids by a second-order differencing scheme for spacial derivatives and a simple explicit differentiation of Eq. (1) combined with free energy data of solid and liquid phases given in Table 1. Equations (4) and (5) should be solved in entire solid region and in the boundary layer respectively. The droplet started to solidify after changing the undercooling of 50K under the liquidus temperature. The liquidus and solidus temperature calculated from free energy densities given in Table 1 were 920K and 834K, respectively. The droplet started to solidify after changing the phase field in a small diamond-shaped area at the top center of the cylindrical droplet from zero to one.

4. Results and Discussion

4.1. Isothermal Solidification

Figure 1 shows the calculated microstructure during isothermal solidification at a temperature of 865K. The calculation domain was right-half and it was reflected about the center line axis. The grey scale in the figure represents the concentration profiles in solid and liquid phases. The white correspond to the initial concentration, \( c = 0.03 \). With increasing darkness, liquid concentration increases toward \( c = 0.03 \) mole fraction. In the solid region of \( c > 0.03 \) and liquid region of \( c > 0.1 \), the darkness was kept constant with that of \( c = 0.03 \) and \( c = 0.1 \) in solid and liquid phases respectively. The black line is the contour of 0.1 < \( \phi < 0.9 \) which may be regarded as the solid–liquid interface. In this figure, the dendrite grows with well-developed side branches, and rapid coalescence occurs behind the dendrite tip, leaving arrays of small liquid droplets between side branches. Along the center line of primary arm or side branch, as in Warren and Boettinger,\(^{18}\) there exist a spine with lower concentration between side branches is very weak compared with Fig. 1. The growth velocity of dendrite at steady state was 0.18 m/s.

Figure 2 shows the dendrite morphology calculated during isothermal solidification at a temperature of 880K. The coalescence of liquid films between side branches is very weak compared with Fig. 1. The growth velocity of dendrite at steady state was estimated to be 0.05 m/s, which is about a fourth of that in Fig. 1. Being compared with Fig. 1, tip radius of the dendrite, width of main centerline spine...
and side branch spacing near the tip are approximately scaled by a same ratio of about two, which is given by root square of tip velocity ratio. This scaling is consistent with the previously reported experimental results and theoretical predictions. Further quantitative test of scaling laws concerning with isothermal dendritic growth will be discussed in a separated article.

4.2. Non-isothermal Solidification

Figure 3 shows thermal histories of droplets during non-isothermal solidification with four different heat transfer coefficients, (a) $h=1 \times 10^4$, (b) 2 $\times 10^4$, (c) $4 \times 10^4$ and (d) $8 \times 10^4$ W/m², where the downward and topward arrows, respectively, indicate the time at which side arms of each dendrite impinge with side wall and primary arm reaches to the bottom side of the droplet. In curve (a), calculation was stopped before the primary arm reaches to the bottom side and in curve (b) the calculation was stopped before complete solidification occurs. In curve (c) and (d), we can see rapid temperature decrease after complete solidification. In all cases, droplet temperature decreases rapidly from the given nucleation temperature (870 K), reaches a minimum point and then increases rapidly with increasing time at initial stage after nucleation. This is due to the competition between the heat extraction rate by cooling gas and the latent heat release rate from moving interface, that is, the change in the ratio of the total solid-liquid interface area $A_{Sl}$ to the droplet surface area $A_d$; just after a nucleation at 870 K, the dendrite grows slowly because of low initial undercooling. In this stage, moreover, $A_{Sl}/A_d$ is very low, and so the heat extraction rate by cooling gas is higher than the latent heat release rate, which leads to decrease in droplet temperature and therefore increase in dendrite growth velocity. As the dendrite grows, both $A_{Sl}/A_d$ and growth velocity increase, heat extraction rate becomes lower than the heat release rate, which leads to increase in droplet temperature. With increasing heat transfer coefficients, minimum droplet temperature decreases and more rapid change in temperature appeared as expected. If the nucleation temperature is much lower than 870 K, the temperature may start to increase just from the initial stage. The curves in Fig. 3 show other bumps which are resulted from sudden changes in latent heat release rate due to the impingement of interface with side wall or bottom side of the droplets. In curve (d), however, there exist another bumps originated from hysteresis in self-adjustment of interface velocity to temperature change. Due to the temperature variation during nonisothermal solidification, it is expected that solidification microstructure in droplet will vary with time.

Figure 4 shows the calculated solidification microstructure with $h=1 \times 10^4$ W/m². In this figure there exist only a dendritic morphology with continuous changes in concentration of solid as well as in scale of the dendrite. These changes are not monotonic with time, as can be seen clearly in the concentration change in the spine of main stem; the concentration increases toward the bulk composition at initial stage of solidification, and starts to decrease before reaching the bulk composition. The compositional variation corresponds to the temperature changes shown in Fig. 3(a).

The dramatic change in growth patterns appears with a higher $h$. Figure 5 shows a rather complex structural evolution, calculated during solidification with $h=2 \times 10^4$ W/m². After a nucleation on the top center of droplet, a dendrite starts to grow with accelerating velocity and then the dendrite pattern changed into a plane front pattern, leaving a
solid with a composition very close to the bulk composition. Thus partitionless solidification occurs with the advance of the plane front interface. After the transition, however, the plane front interface starts to be decelerated because of the increased latent release rate which is due to the large $A_S/A_d$ and high interface velocity. At a critical velocity (about 0.3 m/s) or a critical temperature (about 860 K), the plane front interface ceases to grow and transformed into arrays of cellular pattern. Note that cells grow into the direction close to that with the maximum concentration gradient and growth direction of the cells deflects continuously from the crystallographically preferred growth direction ($x$ or $y$ axis direction in Fig. 5). This is a well-known phenomena in cellular growth.34) After sufficient recalescence due to large $A_S/A_d$ in this stage, cellular pattern is replaced by well-developed dendritic structure. Cell/dendrite transition preferentially occurs in the cells which are not constrained by their neighbors. Note that the well-developed dendrite with side branches grows only into the preferred growth direction, which has also been observed in experiments.34) The overall pattern transitions in Fig. 5, from the partitionless plane-front, fine cell to dendrite with decreasing interface velocity or increasing interface temperature have not only been predicted theoretically for rapid solidification condition, 1) but also observed frequently in gas atomized alloy powders.2,3)

We will examine in detail the initial dendrite/plane front transition and plane front/cell transition procedures shown in Fig. 5. Figure 6 shows a series of microstructural evolution, corresponding to the dendrite/plane front transition just after a nucleation, calculated with $h=2\times10^4\text{W/m}^2$. At early stage the dendrite grow with a normal parabolic tip (Fig. 6(a)) and droplet temperature decreases as mentioned previously. Once the temperature reaches a critical value under which the dendrite with solute partitioning can not grow, the solute trapping occurs around three dendrite tips where the growth velocity is maximum (Fig. 6(b)). These regions solidifying with negligible solute partitioning expand rapidly and enclose the concave part of the dendrite (Figs. 6(c), 6(d)). Their interfaces eventually meet each other and change into a plane front interface, leaving liquid pockets behind the advancing interface (Figs. 6(e), 6(f)).

Figure 7 shows a series of microstructural evolution, corresponding to plane front/cell transition procedure, calculated with $h=2\times10^4\text{W/m}^2$. As the plane front interface moves into liquid (Fig. 7(a)), the system approaches the situation...
where the release rate of latent heat becomes more dominant than heat extraction rate. Therefore, droplet temperature begins to increase and the interface velocity decreases as solidification continues. Once the temperature reaches a critical value over which the solute partitioning should occur, the plane front interface becomes unstable and the plane front interface changes into a cellular pattern. This transition starts at the interface with preferred orientation (Fig. 7(b)) and propagate into the remaining parts of the interface (Fig. 7(c)). Eventually, the plane front interface is completely transformed into well-developed cellular arrays, leaving arrays of liquid pocket in the intercellular region (Fig. 7(d)). Note that a dendrite-like pattern has already formed at the interface, where cellular growth is unfavourable from the point of crystallographic orientation. The cells in other region grows further and becomes the well-developed dendrite with side branches as in Fig. 5.

**Figure 8** shows calculated microstructural evolution during solidification with \( h = 4 \times 10^4 \text{ W/m}^2 \). Compared with the case with \( h = 2 \times 10^4 \text{ W/m}^2 \), the volume fraction of the region solidified with plane front and cellular interface increased. Also we can see that microstructural scale becomes finer due to higher solidification velocity, especially at late stage of the solidification. One interesting phenomena is that there exists several coupled cellular pattern. This kind of pattern, known as ‘cellular doublets’ \(^{35}\), have been observed in directional solidification of thin organic film, and reported to have a close relationship with the role of grain boundary on the onset of the instability of plane front interface. In our system, however, there exist no grain boundary. The mechanism and condition for the formation of cellular doublet remain unclear in our case.

**Figure 9** shows calculated microstructural evolution during solidification with \( h = 8 \times 10^4 \text{ W/m}^2 \). The microstructure are mainly composed of array of fine cells. Note the presence of faint solute bands perpendicular to growth direction.
the wall of right and left sides. The microstructure with fine cells, without dendrite, also have been reported in small alloy droplets. \(^3\) In this figure we can see solute-bands parallel to the advancing interface on macroscopic view, which are related with the bumps in curve (d) of Fig. 3.

In this study we used the WBM model to model microstructural evolution during rapid solidification in an alloy droplet. For the numerical simulation, the phase field parameters were determined at a finite interface thickness condition as mentioned in Sec. 2. The parameters guarantee constant solid-liquid interface energy independent of temperature during numerical calculation. This may be the reason we obtained very consistent structural change with increasing heat transfer coefficient, which may indicate the effectiveness of the finite thickness phase field model. \(^3\)

From our best knowledge this is the first work presenting so variety of structural evolution during non-isothermal solidification by phase field modeling.

5. Conclusions

For numerical simulation of microstructural evolution during rapid solidification of small Al–0.02 mole fraction Cu alloy droplets, we used the phase-field model with the parameters determined at a finite interface thickness condition. For numerical efficiency, we adopted rather thick interface width, large interface energy and small interface kinetic coefficient, compared with reported values. Nevertheless, overall features of microstructural evolutions presented in this study show close resemblance with reported theoretical predictions and experimental results; initial dendrite/plane-front transition when the nucleation undercooling is small, plane-front/cell and cell/dendrite transition in high interface velocity regime, complete disappearance of dendritic structure at rapid solidification with a high heat transfer coefficient and deflection phenomena in cellular growth direction.

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