

DEVELOPMENT AND APPLICATION OF PHASE-FIELD MODELS
TO STUDY
THE SOLIDIFICATION OF STEELS IN A WELD POOL

THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
AT THE UNIVERSITY OF LEICESTER

BY

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DEC 2012

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**Development and Application of Phase-Field Models to Study
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Abstract

The quality of welded products is largely determined by solidified structures and dendrite is the predominant pattern. However, studying the evolution of morphology during solidification at micrometre scale using experimental techniques is of high cost. Therefore, in this PhD project phase-field (PF) models were developed and applied to simulate the dendritic growth of industrially important steels in a weld pool.

The problem of Ohno and Matsuuras proposal to include solid diffusivity in PF simulations is that a priori unknown term associated with the solute flux needs to be input. In this work, mathematical and numerical analyses indicate that credible results can be obtained by setting that term as zero. The effect of solid diffusivity on the steady-state dendrite under free growth was next investigated, showing that the solid diffusivity of C should be included for Fe-C alloys.

The evolution of side branches under the imposed transient conditions by decreasing the velocity was examined because dendrites do not grow under steady state in a weld pool. It was observed that the remelting of the smaller side branches started from the side branch tips and the necklace width of the surviving side branches increased during the ripening process whether under steady state or transient conditions. However, the final necklace widths of the surviving side branches are finer under the transient conditions, implying that the detachment of side branches is more likely to occur under the transient condition, in agreement with the published experimental reports.

Finally a new quantitative thin-interface PF solidification model for ternary alloys was extended and validated. The proposed model has the advantages: (1) the schemes of thin-interface limit analysis and anti-trapping current are adopted to simultaneously ensure the calculation efficiency and accuracy, and (2) the solid diffusivity can be included for steels.

Acknowledgements

I would like to thank all those who have given me help and advice during my doctoral study, particularly with great appreciation and thanks to

Professor Hongbiao Dong for his excellent supervision; I can obviously feel my progress in every research-related aspect under his supervision and I appreciate every of his suggestions.

Professor Jonathan A. Dantzig at EPFL for his constant help and suggestions in an encouraging and humourous manner.

They both create a relaxing atmosphere during my study and induce my interest in the research field.

Also thanks to

Professor Helen V. Atkinson for her co-supervision and good suggestions.

The European commission, the University of Leicester and the Engineering Department for the financial support.

Professor John Hunt at the University of Oxford and Professor Andrew Mullis at the University of Leeds for their discussions and suggestions.

Dr. Simon Gill at the University of Leicester for his assessing the 1st- and 2nd- year reports and revision suggestions.

MOM group for their informative and entertaining conversations.

Special thanks to my Mum, Dad, my sister, my grandparents, and my uncle's family.

Also those friends in China, including Yongli Wang, Lu Zhang and Jingfeng Yang, for their encouragement and support. As well as friends here, Xiaoxiao Han, Chenlong Shang, Lifeng Ding, Mike Dodge, Scott Simmonds and Tristram Broadbent, for making my life more colorful during studying abroad.

Nomenclature

α_i	Thermal diffusivity in phase i ; $i = l$ for liquid and $i = s$ for solid
Δs	Entropy of fusion
ΔT	Undercooling
ΔT_C	Constitutional undercooling
ΔT_K	Kinetic undercooling
ΔT_R	Curvature undercooling
ϵ_4	4-fold coefficient for the interfacial anisotropy
γ_{sl}^0	Orientation-averaged part of the interfacial energy
Γ_{sl}	Gibbs-Thomson coefficient
γ_{sl}	Solid/Liquid interfacial energy
κ	Curvature
λ	A dimensionless parameter relates w to d_0
λ_1	Primary spacing of the array dendritic/cellular structure
$\lambda_{lower}, \lambda_{upper}$	Lower and upper limit of the primary spacing under certain directional solidification respectively
μ_i^e	Equilibrium chemical potential of solute i at the temperature T

μ_k	Kinetic coefficient
Ω	Supersaturation
ϕ	Phase field variable
ρ	Solid density
τ	Time constant in the PF evolution equation
$\tilde{q}(\phi)$	Interpolation function for diffusivity used in phase-field models
$\vec{n}$	Unit vector
a_1, a_2	Anisotropy coefficients
a_n	Anisotropy expression
C	Solute concentration; for multi-component, it is C_i
C_l^*	Interface composition at the liquid side; also C_l^{*R} and C_l^{*r} , and for multi-component, it is C_{il}^*
C_s^*	Interface composition at the solid side; for multi-component, it is C_{is}^*
C_l^0	Liquidus composition at the temperature T_l^0 ; for multi-component, it is C_{il}^0
C_0	Interpolated equilibrium concentration at the entire solidification domain with the help of the interpolation function $h(\phi)$
C_{i0}	Alloy composition in a multi-component system
C_{il}^e	Equilibrium solidus composition of solute i at the temperature T
C_{is}^e	Equilibrium liquidus composition of solute i at the temperature T
C_l	Solute concentration in liquid phase
C_s	Solute concentration in solid phase

C_s^0	Equilibrium solidus concentration at the temperature T_l^0
D	Diffusivity
d_0	Capillary length scale; for multi-component, it is d_i
D_l	Liquid diffusivity of a solute; for multi-component, it is D_{il} for solute i
D_s	Solid diffusivity of a solute; for multi-component, it is D_{is} for solute i
E_1	Exponential integral function
$erfc$	Complementary error function
F	Phenomenological free energy
f_v^A	Gibbs free energy of pure A at the melting temperature T_m in phase v
G	Gibbs free energy; also f_i in phase i
G, V_p	Thermal gradient and pulling velocity defining the directional solidification
G_l	Gibbs free energy of liquid phase
G_s	Gibbs free energy of solid phase
Iv_{2D}, Iv_{3D}	Ivantsov functions in 2D and 3D respectively
j_{at}	Anti-trapping current
K_ϕ	Kinetic constant for the phase-field evolution
k_e	Equilibrium coefficient; for multi-component, it is k_i^e
m_e	Liquidus slope; for multi-component, it is m_i for solute i
Pe	Peclet number
Q	First cubic harmonic function

R	Radius of a curve; also r
R_{tip}	Tip radius of a dendrite
S	Second cubic harmonic function
s_v	Entropy density of phase v
t	Time
T^*	Temperature at the S/L interface
T_m	Melting point of the pure material
u	Dimensionless variable defined to represent the solute concentration C ; for multi-component, it is u_i for solute i
V_a	Absolute stability limit for planar morphology under directional solidification
V_c	Constitutional undercooling limit for planar morphology under directional solidification
V_n	Growth velocity normal to the interface
V_{tip}	Tip velocity of a dendrite; also V
w	Interface width in phase-field simulation
W_{hf}	Width at the half height of a side branch used to represent the side branch width
W_{nc}	Necklace width for the necklace connecting a side branch to the primary stalk of a dendrite
x, y, z	Cartesian coordinates
Z_r	Stalk width defined as the distance from the side branch root to the central line of a dendrite

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CHAPTER ONE

Solidification during Welding

Solidification occurs in the fusion welding process and the work-pieces are joined together upon solidification. Dendrites are the predominant structure and the quality of the welded products depend strongly on the length scale and segregation pattern. In this chapter, basic solidification theories with an emphasis on the relation between the length scale of the solidified dendrites and the solidification conditions were reviewed, based on which the complexity of solidification during welding was discussed in the final section.

1.1 Governing equations of solid growth

For a pure system, latent heat is released when the solid grows during solidification and there is a flux of heat flow in the system and from the system to the surroundings. For an alloy system, solute transport additionally exists in the system because the equilibrium solute concentration in the solid is normally different from that in the liquid. Generally, the thermal transport is faster than the solutal transport [1, 2] and the latter controls the solidification process to a larger extent. Thus, it reasonably only considers the solutal transport in the alloy solidification system for simplification. Without convection, the evolution equation of solute with time t for binary alloys is [2, 3, 7]

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i \quad (1.1)$$

where $i = l$ is for the liquid and $i = s$ for the solid; C_i is the solute concentration in the phase i ; D_i is the solute diffusivity in the phase i .

At the Solid/Liquid (S/L) interface, the mass of solute is conserved, and the mass conservation equation is [2, 3]

$$(C_l^* - C_s^*) V_n = D_s \frac{\partial C_s}{\partial \vec{n}} - D_l \frac{\partial C_l}{\partial \vec{n}} \quad (1.2)$$

where C_l^* and C_s^* are solute concentrations of the liquid side and the solid side at the S/L interface, respectively; $\vec{n}$ is the unit vector normal to the interface; V_n is the solid growth velocity normal to the interface. For the S/L interface being in local equilibrium during solidification, Gibbs-Thomson equation is satisfied at the interface, considering the constitutional undercooling, curvature undercooling and the kinetic undercooling [2, 3].

1.1.1 Constitutional undercooling

The constitutional undercooling (ΔT_C) is resulted by the presence of solute in the liquid. Figure 1.1 is the simplest equilibrium phase diagram of a binary alloy with constant equilibrium partition coefficient k_e and linear liquidus slope m_e . For an alloy with composition C_l^0 , as indicated in Figure 1.1, the equilibrium liquidus temperature is T_l^0 . If the composition at the liquid side of the S/L interface is C_l^* which is generally different from C_l^0 , there exists a constitutional undercooling expressed as [2, 3]

$$\Delta T_C = m_e (C_l^0 - C_l^*) \quad (1.3)$$

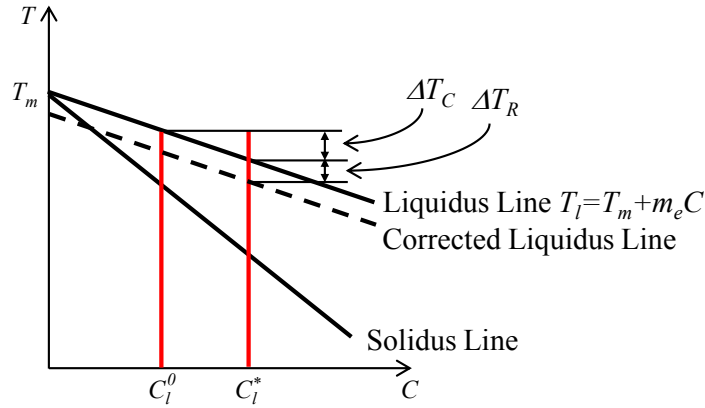


Figure 1.1: A segment of a dilute binary phase diagram, showing the liquidus line corrected for the curvature of a solid particle.

1.1.2 Curvature undercooling

The curvature undercooling is associated with the Gibbs-Thomson effect. When the S/L interface is curved, an excess Gibbs free energy is required to form the interface and leads to the decrease in the liquidus temperature. Figure 1.1 also shows the liquidus line corrected by the curvature effect. The curvature undercooling is [2, 3]

$$\Delta T_R = \Gamma_{sl} \kappa \quad (1.4)$$

where Γ_{sl} is the Gibbs-Thomson coefficient and κ is the curvature. Γ_{sl} is defined as $\frac{\gamma_{sl}}{\rho_s \Delta s}$ where γ_{sl} is the S/L interfacial energy, ρ_s is the solid density and Δs is the entropy of fusion.

Interfacial energy is not isotropic but anisotropic, which is of significance in determining the dendrite morphology by choosing the preferred growth orientation (further discussion below). The interfacial energy is expressed as

$$\gamma_{sl} = \gamma_{sl}^0 a_n \quad (1.5)$$

where γ_{sl}^0 is the orientation-averaged part of the interfacial energy; a_n is the anisotropy expression. a_n can be expressed, for a crystal with cubic symmetry, in terms of cubic harmonics [8]

$$a_n = 1 + a_1 (Q - 3/5) + a_2 (3Q + 66S - 17/7) + \dots \quad (1.6)$$

where $\vec{n}$ is the crystalline direction in the reference frame, a_1 and a_2 are the first two anisotropy coefficients, and the harmonics Q and S are defined in terms of the Cartesian components of $\vec{n}$ as

$$Q = \frac{n_x^4 + n_y^4 + n_z^4}{(n_x^2 + n_y^2 + n_z^2)^2}; \quad S = \frac{n_x^2 n_y^2 n_z^2}{n_x^2 + n_y^2 + n_z^2} \quad (1.7)$$

This anisotropy expression admits several preferred dendrite growth orientations, including $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$. This is by contrast to the more commonly used expression with only one anisotropy coefficient ϵ_4 , displayed as [9]

$$a_n = 1 - 3\epsilon_4 + 4\epsilon_4 Q \quad (1.8)$$

for which only $\langle 100 \rangle$ or $\langle 111 \rangle$ dendrites can appear.

1.1.3 Kinetic undercooling

The kinetic undercooling is associated with the attachment of solute atoms during solidification. To have solidification happened, atoms need to gain enough energy for overcoming the energy barrier of the S/L interface and attaching to the solid surface. The kinetic undercooling providing the driving force of atom attachment is given by [2, 3]

$$\Delta T_K = V_n / \mu_k \quad (1.9)$$

where μ_k is the kinetic coefficient. Unless the solidification occurs at very high speed, ΔT_K is small, meaning that it can be neglected compared to other two contributions of undercooling under most conditions.

Considering those three kinds of undercooling, the temperature at the S/L interface is

$$T^* = T_l^0 - m_e (C_l^0 - C_l^*) - \Gamma_{sl}\kappa - V_n/\mu_k \quad (1.10)$$

When the solid grows under isothermal temperature T_l^0 , $T^* = T_l^0$ and Eq. (1.10) becomes

$$m_e (C_l^0 - C_l^*) = -\Gamma_{sl}\kappa - V_n/\mu_k \quad (1.11)$$

Eq. (1.11) is the Gibbs-Thomson relation at isothermal solidification. It can be seen that driving a solid with an curvature growing the liquid composition at the S/L interface (C_l^*) needs to be less than the equilibrium liquid composition (C_l^0) at the operating temperature. Supersaturation Ω is thus defined to indicate the degree of driving force, expressed as

$$\Omega = \frac{C_l^* - C_l^0}{C_l^* (1 - k_e)} \quad (1.12)$$

If a sphere solid grows with composition C_0 at isothermal temperature T_l^0 where the liquidus composition is C_l^0 , the C_0 should be less than C_l^0 for the solid growing. The supersaturation is $\Omega = \frac{C_l^0 - C_0}{C_l^0 (1 - k_e)}$ in this case. Actually this is a classical problem in solidification study, i.e. an isolated dendrite freely growing under an undercooled melt, as shown in Figure 1.2. The research on this problem would be reviewed in the following section.

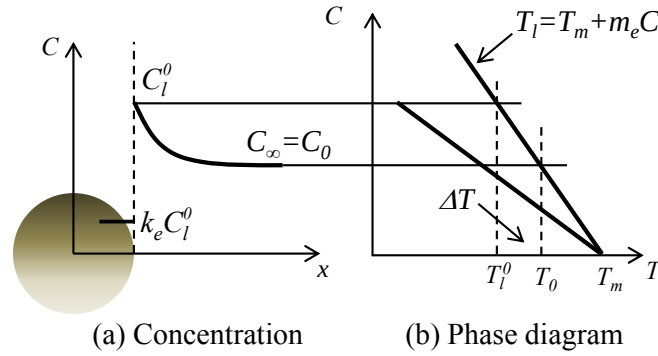


Figure 1.2: Schematic of the isolated dendritic growth.

1.2 An isolated dendrite under free growth

1.2.1 Equiaxed solidification and columnar solidification

There are equiaxed solidification and columnar solidification based on the thermal gradient ahead of S/L interface [1,3]. In equiaxed solidification, the temperature in liquid is lower than that in solid, as shown in Figure 1.3a, and the thermal gradient ahead of S/L interface is negative. Released latent heat flows in the same direction of solid growth and the solid can grow freely in any direction if the undercooling permits. Solidified structure under this condition is equiaxed, for which its name comes. By contrast, the thermal gradient in columnar solidification is positive, as shown in Figure 1.3b, and the released latent heat flows in the direction opposite to that of solid growth. The S/L interface would not advance unless the isotherms around the interface move. Columnar crystals growing in one direction are observed. The growth rate is constrained by the moving of the isotherms (i.e. pulling velocity), for which this solidification is also called as constrained solidification. The directional solidification belongs to the columnar solidification.

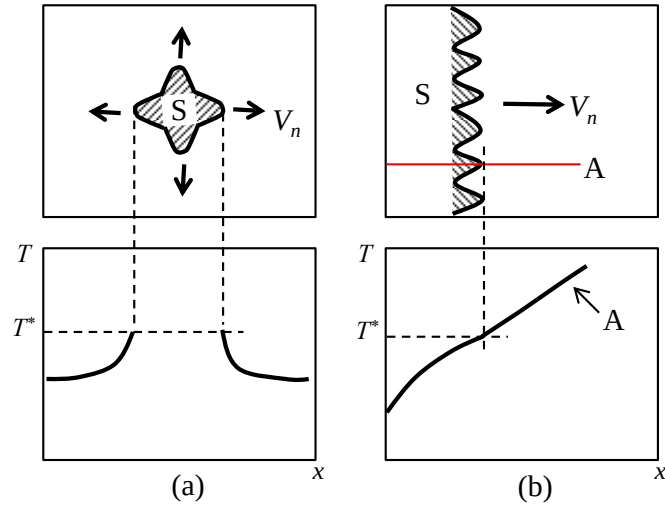


Figure 1.3: Schematic of (a) equiaxed and (b) columnar solidification (figure based on [1]).

Dendrite, i.e. a tree-like form with a primary stalk and side branches, is the main morphology in either solidification. Before going to the more complex dendritic array growth under a directional solidification, an isolated dendrite freely growing into an infinite undercooled melt is firstly discussed, which will help us have a understanding of the effect of solidification condition on the morphology and length scale of a dendrite.

1.2.2 An isolated dendrite under free growth

1.2.2.1 Ivantsov solution without inclusion of the S/L interfacial energy

Solving the governing equations, i.e. Eq. (1.1)-(1.11), to get an analytical solution to this steady-state dendrite is difficult because it is a free-boundary problem. That is because the morphology of S/L interface is not known a priori but must be obtained as a part of the solution. To simplify the problem, a base assumption is made that the obtained dendrite shape is a parabola in two dimensions (2D) or a paraboloid of revolution in three dimensions (3D). The shape of the paraboloid is determined by the tip radius R_{tip} .

Ivantsov solution [10] to the heat diffusion equation was given in 1947. Besides the assumption of the dendrite shape, other assumptions include (1) the dendrite grows in a shape-preserving way at constant tip velocity V_{tip} , which means the analytical solution is for steady-state dendrite, (2) the dendrite grows in an infinite melt, which means the undercooling far way from the dendrite keeps constant as ΔT , and (3) the interfacial energy is not taken into account, which means the dendrite surface is isothermal with the temperature equal to the melting point T_m . The Ivantsov solution is given by

$$\Delta T = Iv_{2D}(Pe) = \sqrt{\pi Pe} \exp(Pe) \operatorname{erfc}(\sqrt{Pe}) \quad 2D \quad (1.13)$$

$$\Delta T = Iv_{3D}(Pe) = Pe \exp(Pe) E_1(Pe) \quad 3D \quad (1.14)$$

In the equations, $Iv_{2D}(Pe)$ and $Iv_{3D}(Pe)$ are Ivantsov functions corresponding to 2D or 3D, respectively. Pe is the Peclet number defined as $Pe = V_{tip}R_{tip}/2\alpha_l$ with α_l the thermal diffusivity in the liquid. $\operatorname{erfc}(\sqrt{Pe})$ and $E_1(Pe)$ are complementary error function and exponential integral functions, respectively.

Under certain undercooling, the Ivantsov solution gives

$$R_{tip}V_{tip} = \text{constant} \quad (1.15)$$

Therefore, Ivantsov solution predicts a continuous range of solution for the 'operating state' (V_{tip}, R_{tip}) at a given ΔT , as shown in Figure 1.4. However, an unique combination of (V_{tip}, R_{tip}) was observed in the dendrites of pure SCN growing into an undercooled melt [11, 12]. One reason for the failure of Ivantsov solution is that it neglects the effect of interfacial energy.

1.2.2.2 Effect of S/L interfacial energy and its anisotropy on dendritic growth

A number of researchers have improved the Ivantsov solution by considering the interfacial energy and some of them considered its anisotropy. Though, to obtain an

unique solution, a selection criterion needs to be imposed in each improved model.

A summary of these improved work are listed in Table 1.1.

Table 1.1: Summary of analytical models for isolated dendritic growth improved based on Ivantsov solution.

Researchers	Anisotropy	Selection criterion	Refs
Temkin	No	Minimum tip radius	[13]
Nash and Glicksman	No	Minimum tip radius	[14]
Oldfield	No	Stability of the per- turbation	[15]
Langer and Muller	No	Marginal stability	[16]
Ben-Jacob and Goldenfeld, <i>et al</i>	Yes	Fastest growing	[17]
Kessler and Levine	Yes	Microscopic solvabil- ity condition	[18, 19]

Among those improved work, the last four listed in Table 1.1 all proposed another expression with same form to limit R_{tip} and V_{tip} given by [15–19]

$$R_{tip}^2 V_{tip} = constant \quad (1.16)$$

The difference lies in the constant value. Thus, Eq. (1.15) and Eq. (1.16) together decide unique value R_{tip} and V_{tip} , as the schematic shown in Figure 1.4.

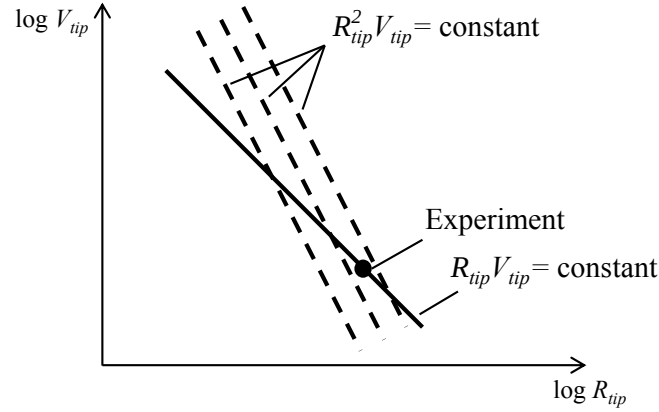


Figure 1.4: A schematic of the various analytical models for determining the 'operating state' of an steady-state isolated dendrite under free growth. The solid line represents the Ivantsov solution and the dash lines represents various stability theories stating $R_{tip}^2 V_{tip} = constant$ (figure based on Ref [2]).

Among these improved work, microscopic solvability theory [18,19] significantly suggests that the S/L interfacial energy has an effect on stabilizing the dendrite which can be simulated by phase-field modelling. Without the consideration of the anisotropy in the interfacial energy, the solidified structure is a hyperbranched structure while it changes to a branched dendrite with preferred orientation decided by the anisotropy with a very small amount of crystalline anisotropy [2]. Figure 1.5 shows the phase-field simulated equiaxed dendrites with various anisotropy coefficient in Eq.(1.7) calculated by our code. The simulated material is pure Fe and the dendritic growth starts with a small sphere seed growing into a undercooled melt with $\Delta T = 0.4$. As can be seen in Figure 1.5, with the various of the values of anisotropy coefficient a_1 and a_2 , structures changed from $\langle 100 \rangle$ preferred with relatively large a_1 to $\langle 100 \rangle$ with relatively large a_2 . In the middle, there is a zone consisting of the highbranched structures due to no a_1 or a_2 can be overwhelming over the another to determine the preferred growth orientation. Similar structure map was obtained when the equiaxed dendritic growth for Al-Zn alloys was simulated [20].

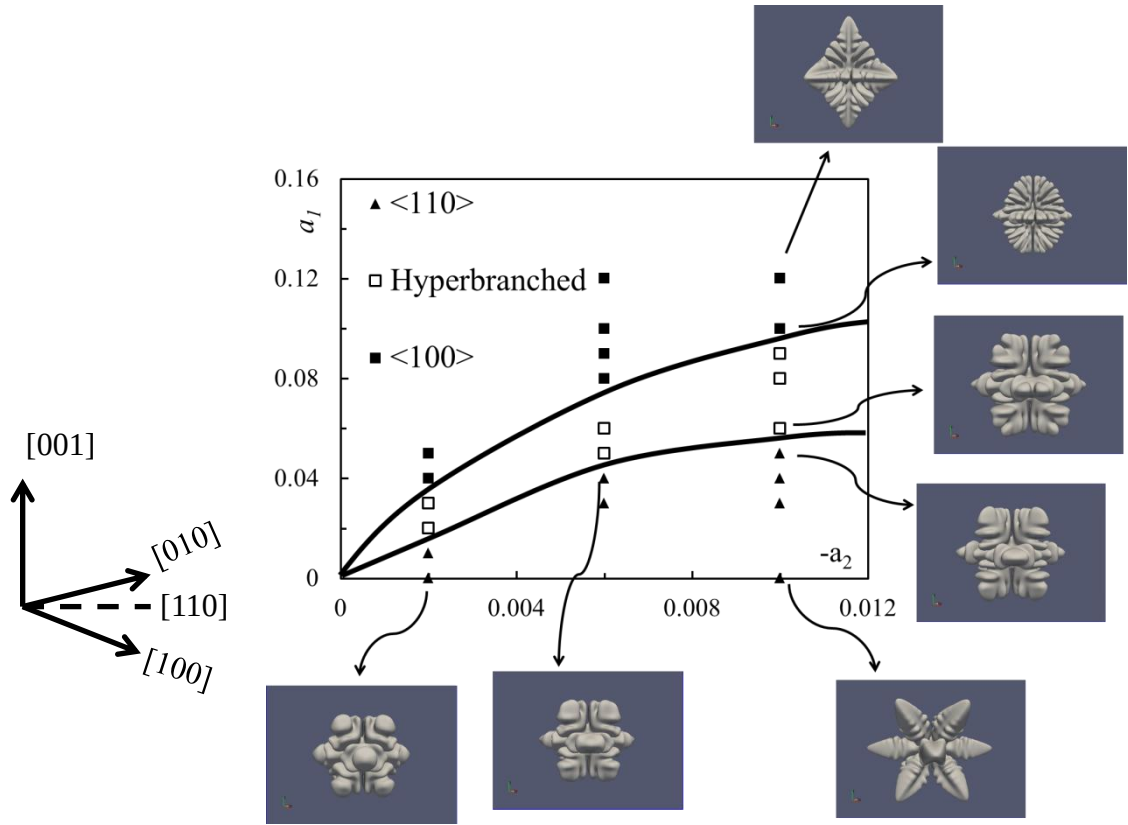


Figure 1.5: Phase-field results of equiaxed dendritic growth for different anisotropy coefficient in Eq. (1.7). Parameters other than anisotropy coefficients are the same for comparison.

The growth rules for the pure material can be extended to the binary alloys straightforwardly. For example, by replacing ΔT with Ω in Eq. (1.13) and Eq. (1.14), the Ivantsov solution to the diffusion equation can be obtained. Meanwhile, the same selection criteria listed in Table 1.1 can be also applied to the dendritic growth in binary alloys. Commonly used analytical models for binary alloys include the LGK model [21] for free growth and KGT model [22] for directional solidification.

As shown by the discussed analytical models, the steady-state isolated dendrite is controlled together by the heat/solute transport and the interfacial energy, of which the anisotropy of the interfacial energy has the effect of stabilizing the dendrite and determining the morphology. A serious shortcoming of those analytical model is that the side branches observed in experiments are not considered, which is however

important to the array dendritic/cell growth under the directional solidification as discussed below.

1.3 Cellular/dendritic array under directional solidification

1.3.1 Cellular/dendritic transition

If a small solid with planar interface grows under a directional solidification with thermal gradient G and pulling velocity V_p , the planar interface may be broken into cellular or dendritic. A stability analysis was done by Mullins and Sekerka [23], and Figure 1.6 is the resultant map showing the relation between growth condition and interface morphology. There are two limits for the stability: (1) constitutional undercooling limit, $V_c = -\frac{k_e D_l}{C_0(1-k_e)m_e}G$. As named, this limit is associated with the constitutional undercooling due to the rich layer of solute, and (2) absolute stability limit, $V_a = -\frac{D_l C_0(1-k_e)m_e}{k_e \Gamma_{sl}}$. At a constant G , when $V_p < V_c$ or $V_p > V_a$, the planar interface is stable, and otherwise it become cellular or dendritic.

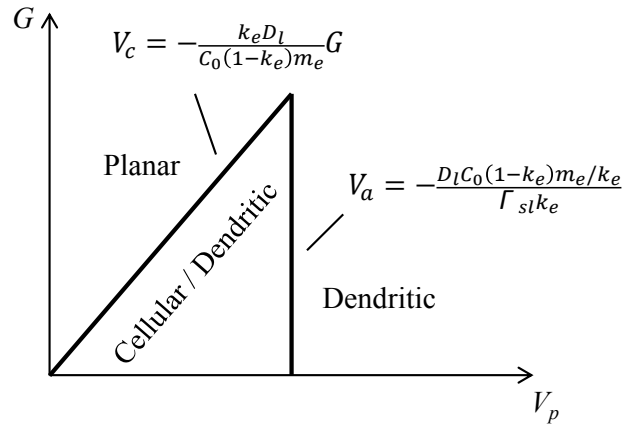


Figure 1.6: Map of stability of planar interface in directional solidification.

When the interface planar is broken, it will grow into cellular or dendritic morphology depending on the G/V_p . Figure 1.7 is an example of experimental obser-

vation showing the morphology varying from cellular to dendritic with the pulling velocity increasing. The differences between a cell and a dendrite are [3]

- (1) Growth direction; A cell tends to grow with their axes parallel to the direction of thermal flow. In contrast, a dendrite tends to grow along the preferred growth direction.
- (2) Side branches; Side branches will not grow out for a cell which they will grow out for a dendrite if the primary spacing permits.
- (3) Interface shape near the tip; Interface shape near the dendrite tip is close to a parabola (2D) or a paraboloid of a revolution (3D) with the smallest radius of curvature at the tip. However, the interface shape near the tip for a cell is more rounded and tends to have the largest radius of curvature at the tip.

For the first two listed differences, it is not always so clear cut; if the G is large enough or the interfacial anisotropy is weaker, a dendrite would be found to grow between the preferred growth direction and the direction of thermal flow; if the primary spacing is not enough, there is not enough space for the side branches growing out in a dendrite. However, the third is much better to be used as the criterion for distinguishing a cell or a dendrite.

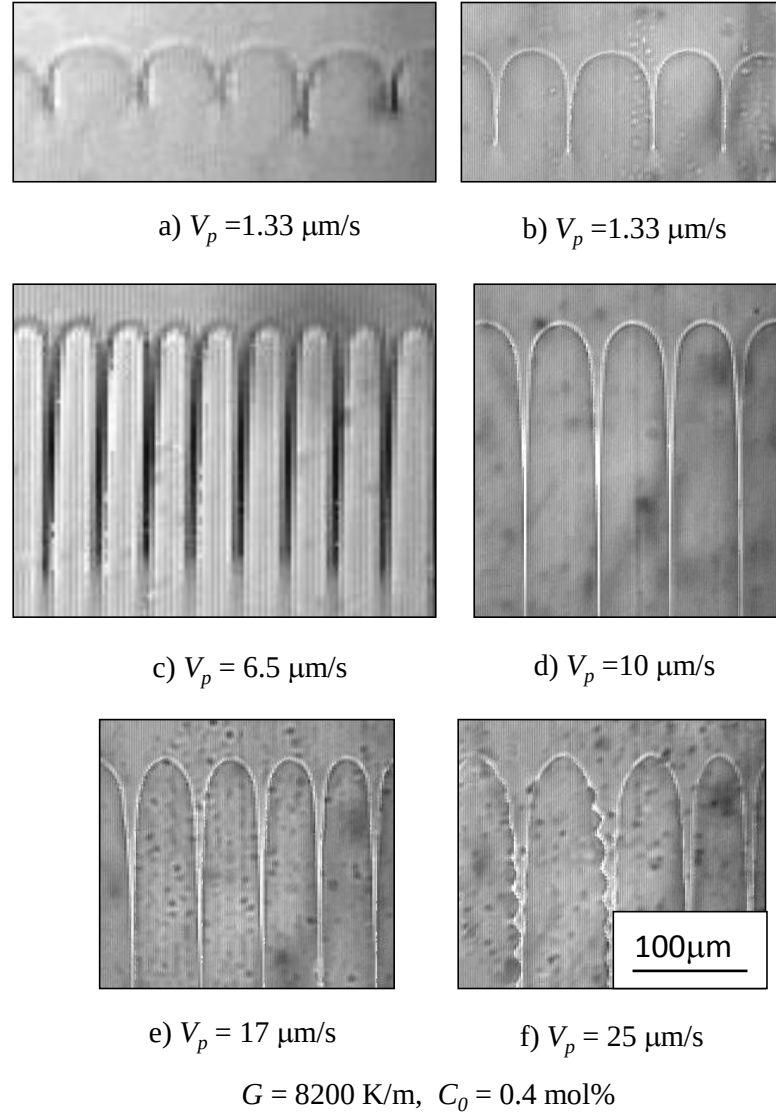


Figure 1.7: An example of experimental observation showing morphology varies from cellular to dendritic with the pulling velocity at a constant thermal gradient. The material is SCN-acetone alloy (microstructures reproduced from Ref. [3]).

In addition, it can be noted in the Figure 1.7 that the solidified structure is not an isolated cell or dendrite but an array consisting of interactive cells or dendrites. This brings an additional length scale, i.e the primary spacing λ_1 . As discussed, for an isolated dendrite under free growth, R_{tip} and V_{tip} are determined only by the solidification condition. Then for dendritic array with an additional length, what is the relation between the scale of the obtained dendrites and the solidification

condition?

1.3.2 Scale of dendrites with primary spacing varying under certain directional solidification condition

1.3.2.1 Freedom of λ_1 under certain condition

Primary spacing λ_1 is not constant under certain directional solidification condition, as generally observed [24, 25]. Hunt *et al* [4, 26–32] proposed that under certain condition, the λ_1 varies in a finite range with a lower limit λ_{lower} and an upper limit λ_{upper} , and the limits can be explained by the primary spacing adjustment mechanism. For the dendritic array, the primary spacing adjustment mechanisms are (1) dendrite submergence defining λ_{lower} , and (2) overgrowth of the tertiary side branch defining λ_{upper} . Figure 1.8 are the schematics of the primary spacing mechanisms for the dendritic array growth. If one dendrite with λ_1 lower than λ_{lower} , then it would be submerged by its neighbouring dendrite with λ_1 higher than λ_{lower} by solute diffusion between these dendrites. By such, Hunt *et al* calculated the solute concentrations varying with different λ_1 and found the λ_{limit} . However, their studies do not take the side branches into account and therefore it is limited to confirm the λ_{upper} .

Later, phase-field modelling was used to confirm the λ_{lower} [33, 34]. In phase-field modelling, only one dendrite is considered and the improvement is the side branches can be considered. Although the occurrence of tertiary side branches were observed when λ_1 was about 2 to 4 times as the obtained λ_{lower} , no overgrowth of tertiary side branches were observed meaning that it is also difficult to confirm λ_{upper} . Although the λ_{upper} has not confirmed yet, Hunt *et al* [4, 26–32] and Wang *et al* [33, 34] provide an information that λ_{upper} is a value that is at least 2 times of λ_{lower} .

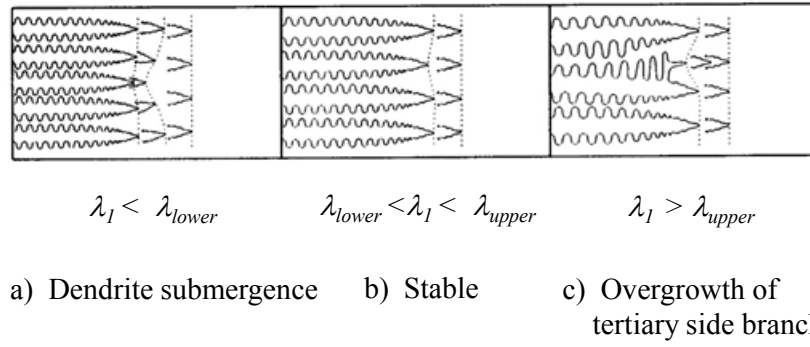


Figure 1.8: Schematics of the primary spacing mechanisms for dendritic array growth (figure reproduced from Ref. [4]).

Because there exists a finite range for the primary spacing under a certain directional solidification, it is reasonable to observe that the average primary spacing is dependent not only on the final solidification condition but also strongly on the middle process [35] during solidification. Regarding the transient growth condition, the average λ_1 in the former growth condition may still in the range for the latter growth condition, meaning that the average λ_1 may keep constant even the growth condition varies during the transient growth condition. This has been observed in a phase-field simulation for transient growth condition [36].

1.3.2.2 Scale of a dendrite

A dendrite basically consists of the primary stalk and the side branches, the question is that how the scale of the dendrite change with the various λ_1 under certain solidification condition is raised. Figure 1.9 is a 2D schematic of a typical dendrite consisting of primary stalk and side branches. Again it should be noted that side branches may not occur due to the limitation of the primary spacing. As mentioned, without the consideration of side branches, the primary stalk is outlined by a parabola in 2D or a paraboloid of revolution in 3D, characterized by the tip radius R_{tip} . When side branches grow out, the S/L interface would be modified and the fitting parabola based on the tip radius will cross over the side branches, as shown in Figure 1.9. Here besides the tip radius R_{tip} , another length scale would

be examined in our study, i.e. the height of the root between the neighbouring side branches indicated as Z_r in Figure 1.9, to investigate the length scale of the primary stalk. Researchers [37] guess the root height would not change too much under the transient growth condition, which is however not be validated because it is difficult to measure in experiments.

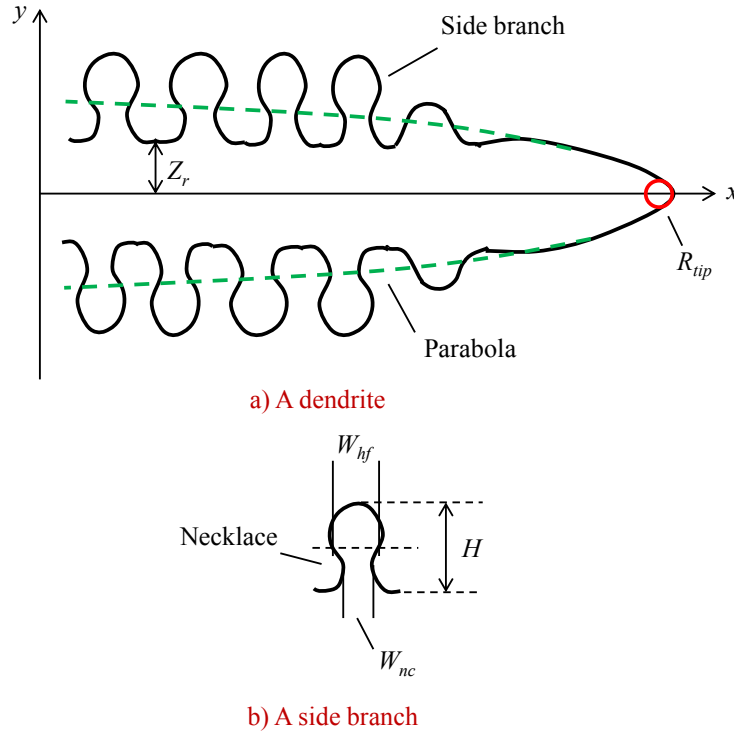


Figure 1.9: Schematic of a dendrite consisting of primary stalk and side branches.

Although the varying primary spacing, it was found that R_{tip} almost kept constant with side branches changing, which means side branches play an important role in scaling a dendrite. Except the side branches initially growing out near the primary stalk (dendrite) tip, the side branches far away from the tip is connected to the primary stalk with a necklace as shown in Figure 1.9. In this study, the width at the half height of the side branch was used to indicate the size of a side branch, symbolized as W_{hf} in Figure 1.9b. The necklace width (radius for 3D), denoted as W_{nc} in Figure 1.9b, is of high interests in this PhD study because it relate to the so-called detachment of side branches.

1.4 Side branches of dendrites under directional solidification

1.4.1 Evolution of side branches

Side branches begin to develop a few tip radii behind the tip and then grow through competitive growth with their neighbouring side branches with different sizes and growth orientations. During this process, some side branches become coarser by eliminating others which dissolve, the process of which is termed as coarsening or ripening.

Figure 1.10 shows a simple model on the competitive growth of two side branches. The side branches are supposed as cylinders with two different radii, R and r with $R > r$. Assuming the temperature is uniform, then the liquidus compositions at the S/L interface have $C_l^{*R} > C_l^{*r}$ based on the Gibbs-Thomson relation. Then solute will diffuse from the larger side branch to the smaller side branch through which the larger side branch will continue to grow while the smaller side branch will gradually dissolve. Although this is a simple model which can not plot the full complex of the evolution of side branches, it explains that the competitive growth is due to the solute distribution in the root between two neighbouring side branches.

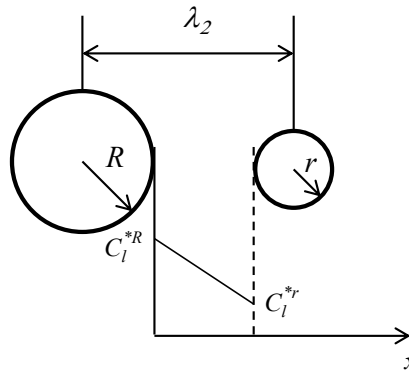


Figure 1.10: A simple model for the coarsening of neighbouring dendrite arms (figure based on Ref. [2]).

During the occurrence and the coarsening of side branches, the morphology and the sizes of side branches evolve. Self-similarity was found in the evolution of steady-state dendrites [38] in the region close to the stalk tip. If the points at the tip of the side branches are connected together, then it forms an enveloped shape. This enveloped shape can be scaled by the tip radius, meaning that the side branches in this region are still strongly controlled by the tip where the R_{tip} is constant during the steady-state evolution. Although those studies, the investigation on the morphology of the side branches, the length scales of Z_r , W_{nc} and W_{hf} are relatively rarely reported due to the high requirements of the experimental techniques. Only a few papers will be summarized in the following in terms of the detachment of side branches.

1.4.2 Detachment of side branches

Detachment of side branches, the so-called fragmentation, has been proposed as one feasible mechanism for columnar-to-equiaxed (CET) transition [39–41], grain refinement [42] and the appearance of stray crystals [1, 43] in commercial casting.

Both mechanical breakdown and remelting of side branches have been the cause of the detachments. As seen, during the evolution of side branches, some of the branches would be remelted. The key issue related to the detachment is: how do the side branches remelt during this process. If the remelting starts at the tip of the side branch, no detachment would happen. If the remelting starts at the necklace of the side branch, the side branches would happen.

The detachment of the tertiary side branches were observed by the expensive in situ synchrotron X-ray radiation for Al-Cu alloys [41, 44–47] under the steady-state directional solidification. The necklace of the tertiary side branches becomes finer leading to the detachment of side branches, and they attributed it to the piling up of the solute between the side branches. Note: the detachment of the secondary side branches is not observed.

Another recognized observation is that detachment of the secondary side branches is seldom except for a long time but however, it is largely increased under the transient directional solidification [37, 48]. Phase-field study on the dendrite growth under the varying isothermal solidification also observed the detachment of the side branches [49]. Based on this study it seems that the detachment is more likely to happen under the transient growth condition rather than steady-state condition. Then a curious question is: what happened for the dendritic evolution under the steady state and the transient growth condition? Whether the remelting of side branches or the mechanical fragmentation, evolution of side branches during dendritic growth and its correction to the solute distribution in the liquid around the side branches should be importantly concerned to answer the question.

1.5 Solidification in a weld pool

1.5.1 Solidification during welding

We focus on conventional fusion welding that involves melting and solidification of work-pieces because it is widely used to join the industrial alloys with high melting-point, such as Ni-based and Fe-based alloys. The heat sources that heat the work-pieces to the melting temperature in a short time have evolved from electric arc to high-intensity electron beams and lasers [5, 50]. During welding, work-pieces near the heat source and the filler materials are heated and melted to form a weld pool (fusion zone) which forms welded joint upon solidification. The parts in the vicinity of the weld pool are also affected by heat sources but no melting process involves and only experience solid-phase transformation. This region is defined as heat-affected zone and the remaining region that experiences no change in welding is called base metal. The schematic diagram of these three zones, i.e. fusion zone, heat-affected zone and base metal, in welding is shown in Figure 1.11a. Depending on the heat source, the cooling rates during solidification change from 100°C to several million

degrees Celsius per second. Even in the weld pool, temperature, composition and cooling rate are varied because of the distance from the heat source. Thus, buoyancy resulted from the spatial variation of liquid metal density, together with the variation of surface tension, drives the metal to undergo vigorous recirculatory motion in weld pool. Figure 1.11b schematically shows the recirculatory motion within the weld pool. The recirculatory motion, in turn, increases the spatial variation in temperature, composition and cooling rates.

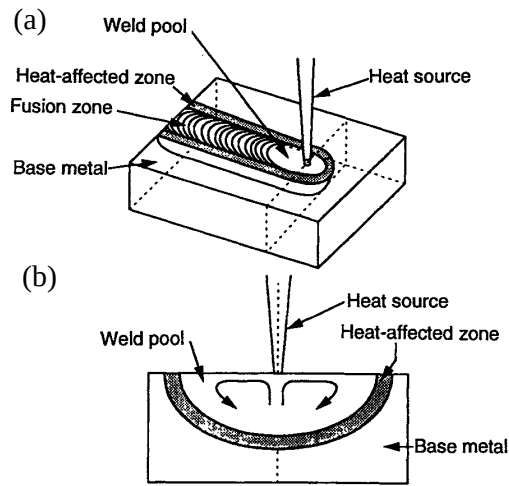


Figure 1.11: (a) Three distinct regions in welding: the fusion zone, the heat-affected zone and the base metal, and (b) the recirculatory motion within the weld pool (figure reproduced from [5])

Due to the complex conditions in the weld pool, it is not easy to measure the solidification condition using the experimental tools. CFD modelling has been widely used to simulate the solidification conditions [51–53]. The results show that the thermal gradient G and the growth velocities V varied largely across the weld pool. Our project partner at University College Dublin National University of Ireland, Ireland (UCD) used a front-tracking model to simulate the solidification conditions in the weld pool. The details of the method could be found in Ref. [54–56]. Figure 1.12 shows the simulated G and V in the weld pool for a Fe-C alloy. The results are in the same magnitude of those published data [53] and large variations can be ob-

served in this figure. In Chapter 5, their results of solidification condition was used to investigate the dendritic growth under the steady-state directional solidification condition.

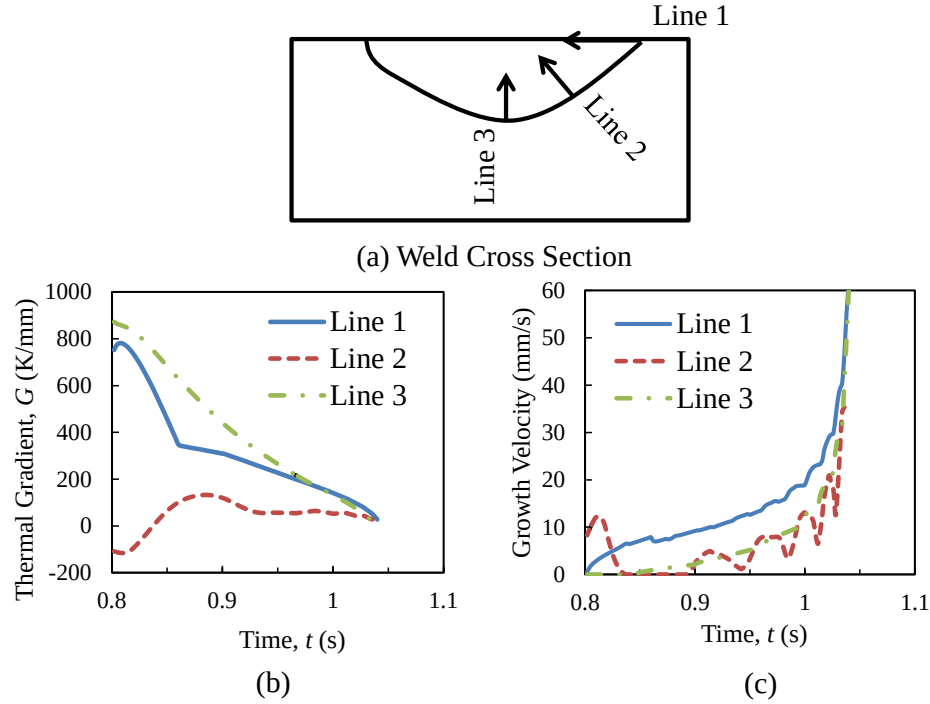


Figure 1.12: Solidification condition in a weld pool calculated using front-tracking modelling by our UCD partner in MintWeld Project. (a) Location of the three lines of interest in the weld pool, (b) the calculated thermal gradients, and (c) growth velocities along the three lines.

1.5.2 Challenges of studying solidification in a weld pool: transient growth condition

The solidification process happening in a weld pool is characterized by its varied conditions through the weld pool, which will lead to the variation in microstructure and solute microsegregations, as discussed above. The transition from planar to cellular and dendritic crystals have been observed a weld pool for Ni-based alloys [50]. As an earlier cooperated work, we have simulated variations in microstructures and solute microsegregations within the MintWeld project [57] using the phase-field modelling and however the dendrites were grown under the steady-state condition.

However, in the weld pool a dendrite actually grow in the transient condition, i.e. the conditions changes when it grows. As discussed, an important phenomenon associated with this kind of growth condition is the occurrence of the detachment largely related to the morphology evolution of the side branches and the solute distribution between the roots of the side branches. In this PhD work, it aims to use the developed phase-field models to study the dendritic growth under the steady-state and the transient conditions. The morphology and solute distribution related to the side branches of dendrites will be focused.

CHAPTER TWO

An Existing Code for Further Development

Phase-field modelling was selected to simulate the dendritic growth occurring in a weld pool in the PhD project because of its overwhelmingly power to deal with the free boundary problem. Developing PF models was part of the work, which involved (1) the derivation or evaluation of a new model and (2) the coding for the new model. Coding involved in the project was not from the scratch, but instead was based on an existing code provided by Prof. Jon Dantzig at the University of Illinois at Urbana-Champaign, USA. In this chapter, the model and the numerical algorithms related to the available code was reviewed.

2.1 Concept of PF modelling

There are two kinds of modelling, i.e. sharp-interface modelling and PF modelling, for simulating the dendritic growth during solidification, and they are distinguished by the width of the S/L interface. In the sharp-interface modelling, the interface width is zero and the solute profile discontinues at the S/L interface, as shown in Figure 2.1a; C_l^* and C_s^* are governed by the Gibbs-Thomson equation expressed as Eq. (1.11). Due to the complex evolution of S/L interface, it is numerically difficult for the sharp-interface modelling to locate the S/L interface.

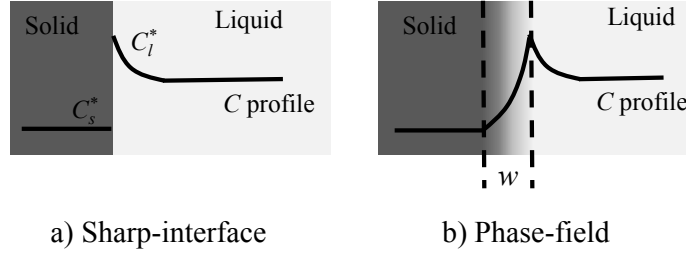


Figure 2.1: Schematic of (a) sharp-interface modelling and (b) phase-field modelling showing the difference in interface width and the solute profile between these two kinds of modelling.

Advantageously, the PF modelling circumvents the direct tracking the S/L interface by introducing a new variable ϕ . This new variable is termed as phase field because it is designed to distinguish different phase fields [58]: $\phi = +1$ in solid, $\phi = -1$ in liquid, and intermediate values correspond to the S/L interface. Thus, the S/L interface is treated as a diffuse field with a non-zero width (w) as shown in Figure 2.1b, which is different from the sharp-interface modelling. The phase field variable satisfied Eq. (2.1) which ensures the total free energy of the system thermodynamically decreases with time during solidification.

$$\frac{\partial \phi}{\partial t} = -K_\phi \frac{\delta F}{\delta \phi} \quad (2.1)$$

where F is the phenomenological free energy of a system and K_ϕ is a kinetic constant that is generally temperature-dependent.

However, quantitative predictions using real physical length remain a major challenge because the diffuse interface width w is a few angstroms of nanometre scale [59,60]. By contrast, diffusive solute transport in bulk phases occurs on microscopic length, which are several orders of magnitude larger than w . Spanning from nano-scale to micro-scale length/time scale in PF simulations is computationally impractical.

To improve the calculation efficiency, an interface that is wider than the physical

one of nanometre scale needs to be constructed in PF simulations and the key is how to maintain the Gibbs-Thomson relation and the mass conservation at the extended interface. Karma and Rappel [61–64] presented a thin-interface asymptotic analysis for pure systems to recover the Gibbs-Thomson relation and the mass conservation at the extended interface. This analysis applies to the case where the diffusivities in the solid and liquid phases are equal. In alloys, where the ratio of diffusivities is usually very small, the interface with finite width artificially traps solute, leading to erroneous results. Karma [65] showed that this artificial solute trapping can be canceled by introducing an anti-trapping current to the solute diffusion equation. Since then, PF models [66–73] pursuing the combination of calculation efficiency and calculation accuracy have developed by applying the thin-interface limit analysis and the anti-trapping current on deriving the PF models.

2.2 Karma’s thin-interface PF model with anti-trapping term excluding solid diffusivity

The PhD project begun with an existing code for a PF model of binary alloys proposed by Karma *et al* [65, 66]. In this section, the model is summarized, of which the full mathematics derivation can be found in Ref. [65, 66]. Note the solid diffusivity is excluded in this model.

2.2.1 Governing equations

For a dilute binary alloy with solvent A and solute B under directional solidification, the governing equations of PF model consist of solute diffusion equation and phase field equation. The solute diffusion equation without convection is based on Fick’s law, expressed as

$$\frac{\partial C}{\partial t} = \nabla \cdot [\tilde{q}(\phi) D_l \nabla C] \quad (2.2)$$

where $\tilde{q}(\phi) D_l$ is the diffusivity in the entire solidification domain; $\tilde{q}(+1) = D_s/D_l$ in solid, $\tilde{q}(-1) = D_l$ in liquid, and varies across the interface field. The dimensionless variable u were next defined as

$$u = \ln \frac{C}{[(C_l^0 + C_s^0)/2 + h(\phi)(C_s^0 - C_l^0)/2]} \quad (2.3)$$

where C_l^0, C_s^0 is the equilibrium solute concentration at the reference temperature T_l^0 having $C_s^0 = k_e C_l^0$. The equilibrium composition C^0 across the entire solidification domain is $(C_l^0 + C_s^0)/2 + h(\phi)(C_s^0 - C_l^0)/2$ with the interpolation function $h(\phi)$ defined below. Eq. (2.3) indicates that u is a measure of the deviation of solute concentration C from the equilibrium concentration C^0 . Then, Eq. (2.2) becomes

$$\frac{\partial C}{\partial t} = \nabla \cdot \left[\tilde{q}(\phi) D_l e^u \frac{C_l^0 [1 + k_e - (1 - k_e) h(\phi)]}{2} \nabla u \right] \quad (2.4)$$

During solidification, the solute is rejected from solid to liquid through the S/L interface when the equilibrium coefficient is smaller than 1 ($k_e < 1$). When the growth velocity of the solid growth is large enough that there is no enough time for the solute to diffuse from the interface, solute will be trapped in solid and this physical phenomenon is called solute trapping [1,2]. When it happens the effective partition coefficient k_{eff} is larger than the equilibrium one, i.e. $k_{eff} > k_e$. In the thin-interface PF model, the interface width used in a simulation is generally larger than the real physical width, $w \gg w^*$. It means that solutes need more time to diffuse across the extended interface and the solute would be trapped in the extended interface even under a relatively low growth velocity. Therefore, in PF simulation, solute trapping consists of the real solute trapping and the artificial solute trapping [65, 70, 74, 75], of the latter will adversely bring wrong simulation results.

To reduce the artificial solute trapping, an additional anti-trapping current was

added to the diffusion equation [65, 66] and Eq. (2.4) becomes

$$\frac{\partial C}{\partial t} = \nabla \cdot \left[\tilde{q}(\phi) D_l e^u \frac{C_l^0 [1 + k_e - (1 - k_e) h(\phi)]}{2} \nabla u \right] - \nabla \cdot j_{at} \quad (2.5)$$

with the anti-trapping current term expressed as

$$j_{at} = -a(\phi) w (1 - k_e) C_l^0 e^u \frac{\partial \phi}{\partial t} \frac{\nabla \phi}{|\nabla \phi|} \quad (2.6)$$

with $a(\phi)$ described further below. The anti-trapping current is proportional to the interface width w and $\partial \phi / \partial t$ that implies the velocity of every point within the calculation domain, and is related to the equilibrium partition coefficient k_e . When $k_e < 1$, the anti-trapping current is from solid to liquid during solidification, opposite to the direction of the artificial solute trapping.

The phase field equation is given as [66]

$$\tau \frac{\partial \phi}{\partial t} = w^2 \nabla^2 \phi + (\phi - \phi^3) - \frac{\lambda}{(1 - k_e)} (1 - \phi^2)^2 (e^u - 1) \quad (2.7)$$

where τ is the time constant and λ is a dimensionless parameter that relates the phase-field length scale (w) to the physical length scale (i.e. capillary length scale: $d_0 = \Gamma_{sl} / (|m_e| C_l^0 (1 - k_e))$). To correctly describe the S/L interfacial energy, $\lambda = \alpha_1 w / d_0$ is established, where α_1 is a constant with the value dependent on the definition of the interpolation function $h(\phi)$ in Eq. (2.3) and Eq. (2.5).

2.2.2 Thin-interface limit analysis

In Karma's model, the thin-interface limit analysis is used to evaluate the phase field parameters, e.g. τ in Eq. (2.7) and $a(\phi)$ in Eq. (2.6). This analysis is based on the matching of the outer range and the inner range defined across the calculation domain. The inner range is the diffuse interface; otherwise the outer range. The concentration is symbolized as C in the inner range and $\tilde{C}$ in the outer range

respectively, as indicated in Figure 2.2a. Compared to the outer range, the inner range is very narrow and therefore the inner solutions can be solved order by order based on a small expansion parameter during the thin-interface limit analysis. In Karma's paper [66], this expansion parameter is $\epsilon = w/d_0$. Suppose the solution of the outer range at the interface are symbolized as $\tilde{C}^+$ in the liquid side and $\tilde{C}^-$. It can be seen that $\tilde{C}^+$ and $\tilde{C}^-$ are boundary condition of the inner solution C , based on which matching conditions among $\tilde{C}^+$, $\tilde{C}^-$ and C can be established. Then, imposing the Gibbs-Thomson relation and mass conservation equation for $\tilde{C}^+$, $\tilde{C}^-$, the PF parameters are defined. Figure 2.2 shows the steps of the thin-interface limit analysis.

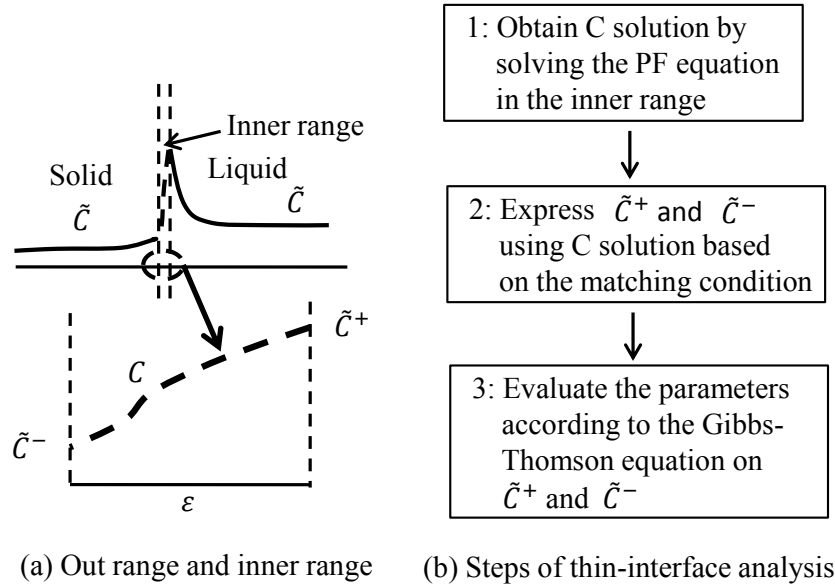


Figure 2.2: Schematic for the thin-interface limit analysis; (a) definition of the inner range and the outer range and (b) steps of the thin-interface limit analysis.

To satisfy the Gibbs-Thomson relation, for the isothermal solidification it should satisfy

$$\beta = \alpha_1 \left(1 - \alpha_2 \frac{\lambda w^2}{\tau D_l} \right) \quad (2.8)$$

where $\beta = \mu_k/(|m_e|C_l^0(1 - k_e))$ and α_2 is a constant with value dependent on $h(\phi)$.

To maintain the mass conservation equation at the interface, it has the restricted equation

$$a(\phi) = \frac{[h(\phi) - 1][1 - q(\phi)]}{\sqrt{2}(\phi^2 - 1)} \quad (2.9)$$

It should be noted that Eq. (2.8) and Eq. (2.9) were obtained when the solid diffusivity is assumed to be zero, i.e. $D_s = 0$. If $h(\phi) = \phi$, then $\tilde{q}(\phi) = \frac{1-\phi}{1+k_e-(1-k_e)\phi}$, and then $a(\phi) = \frac{1}{2\sqrt{2}}$.

2.3 Numerical algorithms

Adaptive meshing algorithm [6, 76–79] was used in the PF simulations to further improve the calculation efficiency. It can be used because the variables, i.e. ϕ and C , changes rapidly only in the narrow region close to the interface scaled by the interface width w . For numerical convergence, fine grids with spacing Δx that can be comparable with w are needed in this region. However, much coarser grids can be used far away from the interface.

Coding was to solve the above two partial differential equations (PDEs), and finite element method (FEM) was used to solve the PDEs in the existing three-dimensional code provided by Prof. Jon Dantzig at the University of Illinois at Urbana-Champaign, USA. The code is based on the element structured data. Besides storing the arrays for connectivity and neighbour by pointer data, the element also consists of the refinement level and the element error for judging if this element is needed to be refined or coarsened, as shown in Figure 2.3. The element is restricted to cubic and thus only one form of the shape function was needed. When the adaptive algorithm is switched on, the determinant of the Jacobian varies with the the element sizes. For convenience, the determinants of the Jacobian of different element sizes were calculated and stored before calling the solvers of PDE in the code.

```

type element
  integer          :: num_element      !! Element number
  integer          :: level            !! Refinement level
  integer          :: lneigh           !! Number of neighbor elements
  type(connectivity), pointer :: connect !! Pointer of connectivity
  type(connectivity), pointer :: connect_mid !! Pointer of connectivity for disconnected nodes
  integer          :: midindex(6)      !! Index to check for discontinuous nodes
  type(neighbor_elements), pointer:: neighbor !! Pointer to neighbor elements
  integer          :: num_parent(LimitLevel) !! Parent element numbers
  integer          :: num_history(LimitLevel) !! Time step number
  integer          :: merge            !! Index to check if the element should be merged
  real*8           :: error            !! Error estimator value at time step n
  integer          :: nver             !! Vertex node number for disconnected edge node
  integer          :: ntype            !! Element type (liquid/solid/interface)
  !! If phi = -1      , ntype = 1(liquid)
  !! If phi = 1      , ntype = 2(solid)
  !! If -1 < phi < 1 , ntype = 3(interface)
  real*8           :: pe              !! Element pressure
  type(element), pointer :: previous   !! Previous element in linked list
  type(element), pointer :: next       !! Next element in linked list
end type element

```

Figure 2.3: Element structure defined in the code.

Due to the movement of the S/L interface during solid growth, refinement and coarsening of grids were carried on during calculation. Here, we will give a basic introduction of the adaptive meshing algorithm used in our code and further details could be found in Ref. [6]. Four criteria were used to evaluate whether a grid needs to be refined or coarsen, listed as

- (1) If an element includes a node where

$$-0.99 \leq \phi \leq 0.9 \quad (2.10)$$

the element should be refined.

- (2) For an element which does not satisfy condition as Eq. (2.10), the element error estimate will be used, defined as

$$E_e = \int_{\Omega} \nabla \theta \cdot \nabla \theta d\Omega \quad (2.11)$$

where θ is C , ϕ , or both.

If a sub-element is divided from a parent element or the opposite process, the

error estimate E_{sub} for the sub-element and E_p for the parent element has the relationship expressed as

$$E_{sub} = \left(\frac{h_{sub}}{h_{parent}} \right)^2 E_p = 0.25E_p \quad (2.12)$$

When $E_e > E_{max}$, the element should be divided and when $E_e < E_{min}$, the element should be coarsened.

- (3) The absolute difference in refinement level of two neighbours is at most one. When it exceeds one, an element should be refined or coarsened.
- (4) The refinement level should not exceed the max level we set.

Based on the four criteria, the refinement procedure can be described as follows [6]:

- (1) A set of $\{E_0\}$ is created that satisfies the refinement rules. These elements will be refined after the neighboring elements have been refined to satisfy the single-level rule after the coming refinement process.
- (2) A recursive search is then performed to find the outermost elements which need to be refined to satisfy the single-level rule. We do this by first defining a new set $\{E_f\}$ whose initial value is $\{E_0\}$. The neighbouring elements to each element in $\{E_f\}$ are then examined, and any neighbouring element that does not satisfy the single-level rule is added to a new set $\{E_{faf}\}$ and the neighbour satisfying the single-level rule is in the set $\{E_{fa}\}$, as shown in Figure 2.4a. If $\{E_{faf}\}$ is not a null set, then $\{E_f\}$ is replaced by $\{E_{faf}\}$ (Figure 2.4b) and then the $\{E_{faf}\}$ of the new valued $\{E_f\}$ is searched. This procedure is repeated until $\{E_{faf}\}$ becomes a null set. At this point, the set $\{E_f\}$ contains the outermost elements which need to be refined to satisfy the single-level rule, and these elements are then divided into eight sub-elements by bisection of

each face (Figure 2.4c). At this point, the set $\{E_f\}$ is again set equal to $\{E_0\}$, and the search begins anew. This process is repeated until the search for elements to fill set $\{E_{faf}\}$ of the initial $\{E_0\}$ yields a null set. Then, the elements in set $\{E_0\}$ are refined (Figure 2.4d), and the refinement process is completed.

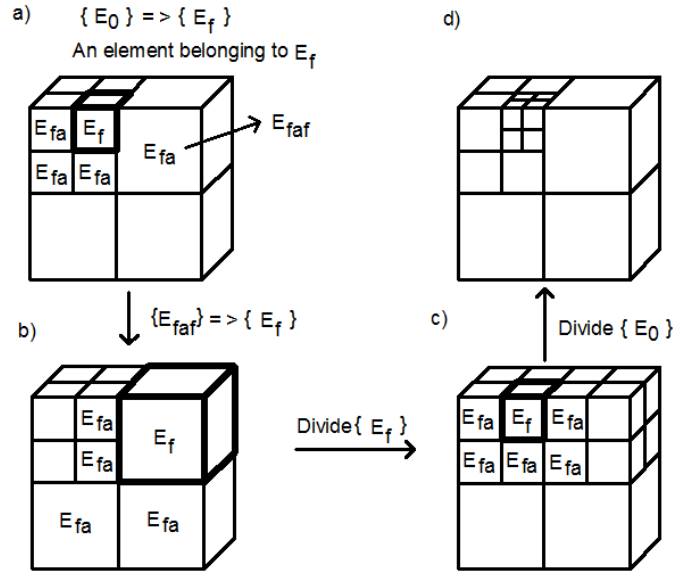


Figure 2.4: Schematic of dividing procedure in the adaptive meshing algorithm (figure based on Ref. [6]).

2.4 Further development of the existing code

Phase-field modelling has been a powerful tool to simulate the solidification structures at micrometre scale. Most published study have focused on (1) the orientation selection influenced by the anisotropy in the interfacial energy (e. g. Refs. [20, 80–82]), (2) the spacing selection (e. g. Refs. [34, 36, 81, 83–85]), (3) the (primary stalk) tip radius and tip velocity compared to the analytical models (e. g. Refs. [6, 63, 86]), (4) solute microsegregation within the primary stalks (e. g. Ref. [87]), and (5) cell to dendrite transient with the varying solidification

condition (e.g. Refs. [88, 89]). So far, rare work investigates the morphologies of the side branches and the solute distribution around the side branches even by the experimental techniques due to the high experiment cost and great difficulty in quantitative measurement. However, as reviewed in the previous chapter, investigating the evolution of side branches by PF modelling is specially important, which is therefore one of objective in the project.

Fe-C based alloys (steels) is one of the most alloy systems in the welding industry. Different from most of the atoms, the C solute locates in the interstitial vacancy in the $\delta - Fe$. Therefore, the solid diffusivity of C atom is as large as being comparable to the liquid diffusivity and should not be neglected when the dendritic growth of Fe-C alloys is simulated. Karma's model and the existing code is not enough due to its exclusion of the solid diffusivity.

The industrial steels are multi-component to further improve the properties of steels. Solid phase transformation from the austenite phase to martensite phase improves the hardness of the steels and the alloying elements such as Mn, Cr, Si, Mo are added to strengthen the transition from the austenite to martensite [90, 91]. By contrast, Ni element increases the difficulty in the transition which benefits the toughness of the steels [90]. In welding steels, C-Mn steel is one kind of the commonly used steels [91] and it is necessary to use a tertiary PF model to investigate the effect of Mn on the solidification of Fe-C alloys.

Therefore, in this PhD project, the PF models were developed and applied in simulating the dendritic growth in a weld pool for steels. The following aspects were carried out:

- (1) to evaluate an extension for including the finite solid diffusivity;
- (2) to extend Karma's binary thin-interface PF model to ternary alloys with the solid diffusion included;
- (3) to investigate the effect of finite D_s on a dendrite under free growth;

- (4) to study the morphology evolution under the steady-state and transient directional solidification conditions, focusing on the evolution of side branches.

CHAPTER THREE

Evaluating an extension of Karma's PF Model to Include the Solid Diffusivity

As discussed in the previous chapter, the existing code based on PF models [65, 66] can not be used to simulate the solidification with the solid diffusivity (D_s) included, which probably be not applicable to the interested Fe-C alloys. Recently, Ohno and Matsuura (OM) [92] extended Karma's PF models to include the D_s . In OM extension, a solute flux term associated to the solute diffusion in the solid needs to be input and however it is an output of a simulation. In this chapter, we proposed to use the OM extension for including D_s by assuming that priori-unknown term to be zero, and it was validated that credible simulation results can be obtained under such assumption in both mathematical and numerical manners.

3.1 OM extension for finite D_s and the remaining challenges

In Karma's thin-interface PF models [65, 66] for binary solidification with anti-trapping term, as introduced in Chapter 2, the solute diffusion in solid is neglected due to the assumption of $D_s = 0$ during the thin-interface limit analysis. It is limited in simulating the solidification process for Fe-C alloys since in Fe-C systems $D_s/D_l \sim 10^{-1}$ (D_l : the liquid diffusivity) [93]. For the industrial important Fe-C alloys, it is necessary to develop a PF model including the solid diffusivity.

To include the solid diffusivity in PF model, Ohno and Matsuura [92] (OM extension) extended Karma's thin-interface model by removing the assumption of $D_s = 0$ during the thin-interface limit analysis. Then the extension scheme was

used in the two-solid phase PF model and a multi-component PF model. In OM scheme, expressions for the PF parameters and the anti-trapping term were modified to include D_s . For the sake of the comparison, Karma's expressions are redisplayed as

$$\beta = \alpha_1 \left(1 - \alpha_2 \frac{\lambda w^2}{\tau D_l} \right) \quad (3.1)$$

$$a(\phi) = \frac{[h(\phi) - 1][1 - q(\phi)]}{\sqrt{2}(\phi^2 - 1)} \quad (3.2)$$

where the definition of $q(\phi)$ depends on the definition of $\tilde{q}$; $D_l \tilde{q}(\phi)$ is the diffusivity (D) across the whole calculation domain. $\tilde{q}(\phi) = \frac{1-\phi}{1+k_e-(1-k_e)\phi}$ is defined in Karma's model where $D = 0$ in the solid and then $q(\phi) = (1 - \phi)/2$.

When D_s is included, in OM extension [92] those above equations are modified into

$$\beta = \alpha_1 \left\{ 1 - \alpha_2 \left[1 - \frac{1}{2} \left(1 - k_e \frac{D_s}{D_l} \right) \chi(s) \right] \frac{\lambda w^2}{\tau D_l} \right\} \quad (3.3)$$

$$a(\phi) = \frac{[h(\phi) - 1][1 - q(\phi)] - \chi(s)[k_e \frac{D_s}{D_l} - q(\phi)][1 - q(\phi)]}{\sqrt{2}(\phi^2 - 1)} \quad (3.4)$$

Compared to Karma's expression, a term $\chi(s)$ associated to the solute flux defined during the thin-interface analysis [92] in the solid is added; in this term, s is the arclength along the interface. As can be seen from Eq. (3.3) and Eq. (3.4), the priori knowledge of solute flux in solid ($\chi(s)$) is needed to use as input in a simulation, and however $\chi(s)$ is an output of the simulation. This brings the challenges on the application of the OM extension in simulations listed in the following

- (1) Actually in their numerical tests, $\chi(s) = 0$ was used for non-zero solid diffusivity ($D_s \neq 0$). Naturally a question that whether $\chi(s) = 0$ for D_s can give an accurate result is raised. If $\chi(s) = 0$ is associated with a correction that vanishes when the used w is close to zero in simulations, this assumption is feasible. However, it was found that the definition of $\chi(s)$ during the

thin-interface analysis hides the connection between $\chi(s)$ and w .

- (2) Although it was proved in their numerical test that the anti-trapping term obtained when $\chi(s) = 0$ can reduced the artificial solute trapping, and however a more rigorous comparison between the PF results and analytical models or experiment data was needed.

We supposed to assume $\chi(s) = 0$ when OM extension is used to include the D_s and we will valid that the credible results can still be obtained mathematically and numerically. The convergence behaviour of the extension was analysed.

3.2 Mathematical validation for using $\chi(s) = 0$

Thin-interface limit analysis is a complex mathematic derivation which has been presented with full details in Ref. [66,92]. Here, we just presented the key parts that is important and related to our concern.

According to the derivation in Ref. [92], the mass equation expressing the solute flow through the thin interface considering the solid diffusivity is

$$\begin{aligned} \left[1 + (1 - k_e) \tilde{U} \right]^+ v_n &= k_e \frac{D_s}{D_l} \partial_r \tilde{U}^- - \partial_r \tilde{U}^+ \\ &+ \varepsilon \left\{ \frac{\tilde{\kappa} v_n}{2} (H^+ - H^-) + \partial_{ss}^2 \tilde{U}_0 (Q^+ - Q^-) \right. \\ &\left. + \frac{k_e v_n^2}{2} (F'^+ - F'^-) \right\} \end{aligned} \quad (3.5)$$

with

$$H^\pm = \int_0^{\pm\infty} [h(\phi_0) - h(\mp 1)] d\eta \quad (3.6)$$

$$Q^\pm = \int_0^{\pm\infty} [q(\phi_0) - q(\mp 1)] d\eta \quad (3.7)$$

$$F'^\pm = \int_0^{\pm\infty} \left[\frac{h(\phi_0) - 1 - 2a(\phi_0) \partial_\eta \phi_0 - k_e \frac{D_s}{D_l} \chi(s)}{q(\phi_0)} - \frac{h(\mp 1) - 1 - 2a(\mp 1) (\partial_\eta \phi_0)^{\mp 1} - k_e \frac{D_s}{D_l} \chi(s)}{q(\mp 1)} \right] d\eta \quad (3.8)$$

where $\tilde{U}$ is the supersaturation at the outer range with $\tilde{U}|^+$ and $\tilde{U}|^-$ are the supersaturation at the interface. In the used notation system, $|^+$ means the liquid side and $|^-$ the solid side. v_n is the growth velocity normal to the interface and $\epsilon = w/d_0$. ϕ_0 is the phase field solution at the stationary equilibrium, and $\phi_0 = (\eta) = -\tanh\left(\frac{\eta}{\sqrt{2}}\right)$ where η is the length normal to the S/L interface.

Then to sustain the mass conservation equation at the thin interface, $H^+ - H^- = 0$, $Q^+ - Q^- = 0$, and $F'^+ - F'^- = 0$ should be satisfied, leading to the expression of the anti-trapping term shown as Eq. (3.4).

Let us do the following transformation. Define

$$G^\pm = \int_0^{\pm\infty} \left[\frac{1}{q(\phi_0)} - \frac{1}{q(\mp 1)} \right] \quad (3.9)$$

$$F^\pm = \int_0^{\pm\infty} \left[\frac{h(\phi_0) - 1 - 2a(\phi_0) \partial_\eta \phi_0}{q(\phi_0)} - \frac{h(\mp 1) - 1 - 2a(\mp 1) (\partial_\eta \phi_0)^{\mp 1}}{q(\mp 1)} \right] d\eta \quad (3.10)$$

Then Eq. (3.5) becomes

$$\begin{aligned} \left[1 + (1 - k_e) \tilde{U} \right]^+ v_n &= k_e \frac{D_s}{D_l} \partial_r \tilde{U}^- - \partial_r \tilde{U}^+ \\ &+ \varepsilon \left\{ \frac{\tilde{\kappa} v_n}{2} (H^+ - H^-) + \partial_{ss}^2 \tilde{U}_0 (Q^+ - Q^-) \right. \\ &\left. + \frac{k_e v_n^2}{2} (F^+ - F^-) \right\} - \varepsilon \frac{k_e v_n^2}{2} k_e \frac{D_s}{D_l} \chi(s) (G^+ - G^-) \end{aligned} \quad (3.11)$$

Regarding the Gibbs-Thomson equation at the interface, we transformed Eq. (3.3) into

$$\beta = \alpha_1 \left(1 - \alpha_2 \frac{\lambda w^2}{\tau D_l} \right) + \frac{\alpha_1 \alpha_2}{2} \left(1 - k_e \frac{D_s}{D_l} \right) \frac{\lambda w^2}{\tau D_l} \chi(s) \quad (3.12)$$

As can be clearly seen from Eq. (3.11) and Eq. (3.12), the inclusion of the solid diffusivity would add solute flux item in solid, i.e. $\chi(s)$, into the Gibbs-Thomson relation and mass conservation equation.

As supposed, we assume $\chi(s) = 0$ when the D_s is included. The assumption is established when the D_s is zero and not when $D_s \neq 0$. Then the simulation error coming from the assumption is the last terms associated to $\chi(s)$ in Eq. (3.11) and Eq. (3.12). However, it could be noted that $\chi(s)$ is always associated with the interface width $\varepsilon(w)$, meaning that the effects of this assumption is dependent on the thin interface width used in the PF simulation. When the simulation interface width used is small enough, the error coming from the assumption can be neglected and credible results can be also obtained. The convergence behaviour respect to the interface width will be investigated by the numerical tests, in which the effect of the D_s on the convergence behavior will be discussed.

We define

$$\tilde{q}(\phi) = \frac{(1 - \phi) + k_e (1 + \phi) \frac{D_s}{D_l}}{1 + k_e - (1 - k_e) \phi} \quad (3.13)$$

Recalling $D = D_l \tilde{q}(\phi)$, then $D(+1) = D_s$ in the solid. Setting $\chi(s) = 0$ in Eq. (3.4), then it has

$$a(\phi) = \frac{1}{2\sqrt{2}} \left[1 - k_e \frac{D_s}{D_l} \right] \quad (3.14)$$

3.3 Numerical implementation

According to the modified expressions shown as Eq. (3.13) and Eq. (3.14), the original code was updated for the numerical evaluation of the extension with the assumption $\chi(s) = 0$. Equi-axed dendritic growth under isothermal condition was carried out, and the equilibrium partition coefficient of the alloy was 0.15, i.e. $k_e = 0.15$, and four-fold anisotropy coefficient $\varepsilon_4 = 0.02$ was used in the simulations with different solid diffusivities (D_s/D_l).

The simulations started with an initial seed with radius $r_0 = 22d_0$ and thickness $h = 25d_0$, growing in a supersaturated melt with supersaturation of 0.55, i.e. $U = (C_l^0 - C_\infty) / [C_l^0 (1 - k_e)] = 0.55$. The calculation domain is $L_x \times L_y \times h$ with $L_x = L_y = 1600d_0$. It could be seen that $L_x = L_y \gg h$ and the initial seed was full in the direction of z-axis, and therefore the dendrite grew in two dimension. Zero flux boundary condition was used, which was naturally imposed by the finite element method employed to solve the evolution equations. In the calculations, time interval was $\Delta t = 0.01\tau$, where $\tau = a_1 a_2 \lambda w^2 / D_l$ with vanished kinetics according to Eq. (3.12).

Adaptive meshing algorithm was used in simulations to improve the calculation efficiency; the maximum grid spacing $(\Delta x)_{\max}$ equated h and the minimum grid spacing $(\Delta x)_{\min}$ was in the range of $(0.4 \sim 1)w$ to assure numerical convergence. Concentration gradient was used to calculate the error estimation for adaptive criterion, i.e. θ in Eq.(2.11) is the concentration variable C . Figure 3.1 provides an example of the adaptive meshing used in a numerical simulation. In the figure, the maximum grid spacing $(\Delta x)_{\max} = 5w$, the finest grid spacing $(\Delta x)_{\min} = 0.625w$, and the refinement level is 3. As shown in Figure 3.1, the field of the finest grids is about $15w$ in width, which is not a broad region. A comparison was made between the results using adaptive grids and those using fixed grids in which $\Delta x = (\Delta x)_{\min} = 0.625w$. At time $t = 400\tau$, the tip radius using adaptive grids is $21d_0$, within 2% of $R_{tip} = 20.7d_0$ obtained using fixed grids, indicating that the adaptive meshing algorithm in sim-

ulations could lead to creditable simulation results even when the finest grids are only in a narrow region. The narrow region of the finest grids in this case was due to the use of high Ω in the simulation which lead to the high growth velocity meaning the concentration varied in a narrow region based on D_l/V_{tip} . The adaptive algorithm can save much time; for the comparing case, it costed about 4 hours using the adaptive grids and however about 66 hours using the fixed grids.

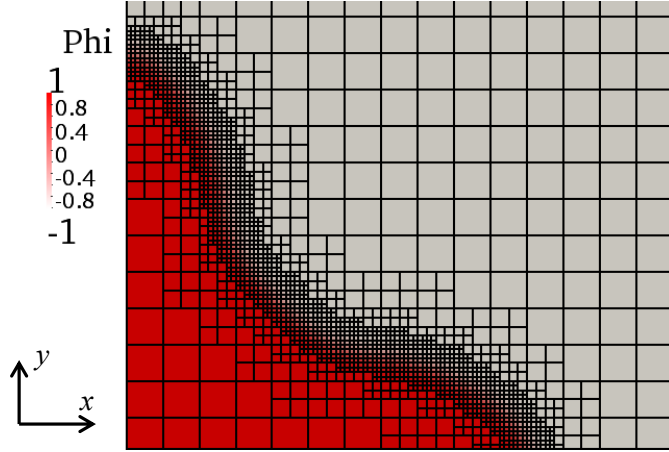


Figure 3.1: Adaptive meshes in the growing dendrite; red region represent the solid, grey region the liquid and otherwise the interface.

Figure 3.2 shows the typical evolution of the tip radius and tip velocity with time. In the example case, $D_s/D_l = 0$. As shown in Figure 3.2, the tip radius increased with time while the tip velocity decreased with time until the steady state was achieved. The selection constant $\theta^* = \sqrt{(d_0 D_l / (R_{tip}^2 V_{tip}))}$ was calculated from the values of R_{tip} and V_{tip} . The result is shown in Figure 3.2c, where we see that reaches a constant value well before the tip velocity and radius reach their steady state values as is commonly observed and indicated by Eq. (1.16). We use the steady-state tip radius and tip velocity to examine the convergence behaviour as a function of the simulation parameters.

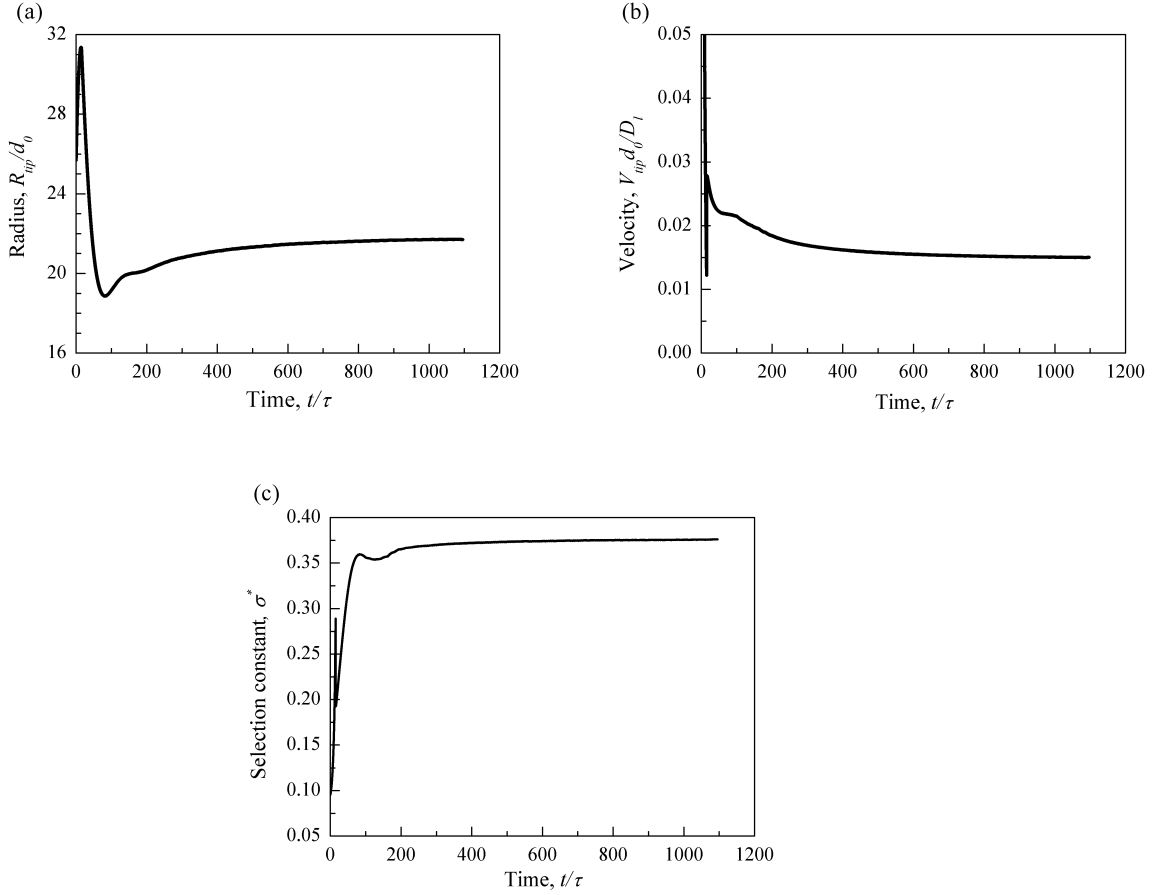


Figure 3.2: Evolution of (a) tip radius, (b) tip velocity and (c) selection constant with time. The supersaturation is 0.55 and the interface width $w = 5d_0$ in the simulation.

3.4 Comparison of the results from the extension and the Gibbs-Thomson relation

The OM extension using $\chi(s) = 0$ will be evaluated by comparing the solute profile calculated from the extension with that from Gibbs-Thomson relation. The solid diffusivity equal to one tenth of the liquid diffusivity was used, i.e. $D_s/D_l = 0.1$, for case study and it is selected because the typical value of D_s/D_l in Fe-C alloy is 0.1 [93]. The tip concentration of the dendrite (C_{tip}) with time along x-axis were considered. Gibbs-Thomson relation relates the tip curvature (R_{tip}) to the tip

concentration (C_{tip}) in solid, expressed as $C_{tip}/C_l^0 = k_e[1 - (1 - k_e)d_0/R_{tip}]$ with the kinetics vanishing. The evolution of C_{tip} calculated by the Gibbs-Thomson relation is shown in dash line in Figure. 3.3. The C_{tip} plot calculated by the OM extension is shown in the line with solid square. In the simulation, $w = 4d_0$ was used. Tip position and tip concentration were obtained at time $t = 50\tau_0 - 600\tau_0$ with the time interval $\Delta t = 50\tau_0$ and the tip position was located when $\phi = 0.999$. As can be observed in Figure 3.3, the plot calculated by OM extension agrees well with that obtained by the Gibbs-Thomson relation, strongly indicate that the proposed extension could recover the Gibbs-Thomson at the thin interface even when use $\chi(s) = 0$.

The tip concentrations calculated by the model without anti-trapping term was also plotted in Figure 3.3, shown as the line with blank square. The same interface width $w = 4d_0$ was used, and however, the tip concentrations are obvious higher than those obtained by our extension and far away from the Gibbs-Thomson relation. The gap between the plots obtained by the models with and without anti-trapping term is attributed to the artificial solute trapping due to the thin-interface width. Therefore, the case study in $D_s/D_l = 0.1$ shows that the proposed use of $\chi(s) = 0$ in OM extension can correctly describe the solid growth with a much reduced artificial solute trapping for D_s included and thus it can recover the Gibbs-Thomson relation in the selection with thin interface width.

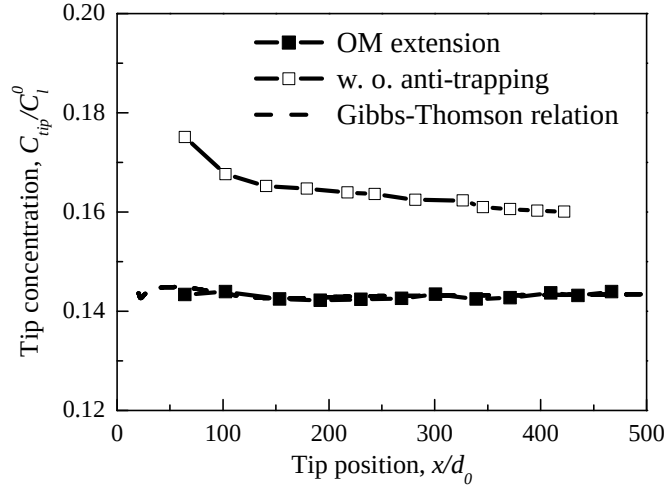


Figure 3.3: Tip concentrations calculated by OM extension with anti-trapping term and the model without anti-trapping term, compared with that predicted by the Gibbs-Thomson relation. The PF simulations were performed at $D_s/D_l = 0.1$ with the interface width $w = 4d_0$, and the tip concentrations were the concentration at tip positions with $\phi = 0.999$ at the time period $t = 50\tau_0 - 600\tau_0$ with the time interval $\Delta t = 50\tau_0$.

3.5 Convergence behaviour of the extension

As discussed, the solution of the PF models was obtained based on a small expansion parameter $\epsilon = w/d_0$ in Karma's model [65,66] and also in the OM extension [92]. During the thin-interface analysis, the thin-interface analysis corrects for dependencies within the solution that is linear in the expansion parameter. Second and higher order dependencies remain, which implies there is an upper limit of interface width, beyond which the simulation results are not convergent to the accurate results which can be gradually approached by considering higher orders. Usually, the upper limit is evaluated by the convergence analysis and therefore we also analysed the convergence behavior of the extension. The convergence behaviour with respect to w was investigated for the extension with anti-trapping term in terms of the solute profile, tip velocity and the tip radius of the steady-state dendrite.

Figure 3.4 shows the the steady-state solute profiles in solid with respect to

interface width. At each plot with certain interface width, shown in Figure 3.4, the concentration abruptly increases because it goes into the thin interface region ($-1 < \phi < 1$) where the concentration gradient is large. Figure 3.4a shows the profiles calculated by the OM extension using different interface widths from $w/d_0 = 3.5$ to $w/d_0 = 10$, together with the steady-state tip concentrations predicted by the Gibbs-Thomson relation at the tip for comparison. As shown in Figure 3.4a, generally the concentration in solid slowly increases with the increasing w except the one at $w/d_0 = 7.2$ located below the one at $w/d_0 = 6.25$ and close to the one at $w/d_0 = 5.5$. Before w is increased to $5.5d_0$, the obtained profiles are close to each other, showing good convergence behavior. The points in Figure 3.4a were predicted by the Gibbs-Thomson relation, where R_{tip} used is simulation results. As respect to the comparison between the PF predictions and the Gibbs-Thomson predictions, the disagreement is within 3 percent surprisingly even when $w/d_0 = 10$. This probably is attributed to the use of the anti-trapping current which effectively removes the artificial solute trapping.

The results calculated by the model without the anti-trapping term are shown in Figure 3.4b. The plots shown are at the interface width from $w/d_0 = 3.5$ to $w/d_0 = 6.25$ and those at larger interface width ($w \geq 7.2d_0$) were not plotted because the stable results could not be obtained by the model without anti-trapping term. With the increase in interface width, the solid concentration increase obviously, showing poor convergence behavior. As can be seen that the solid concentration increases with the increase in the interface width, demonstrating that the artificial solute trapping was more serious with the interface width increasing as also indicated by the anti-trapping term (Eq. 2.6). It should be noted that even when w/d_0 is as small as 3.5, the tip concentration is larger than the equilibrium partition coefficient ($k_e = 0.15$) and the result obviously deviated from the Gibbs-Thomson relation; with the concentration should be lower than k_e corresponding to a finite tip radius.

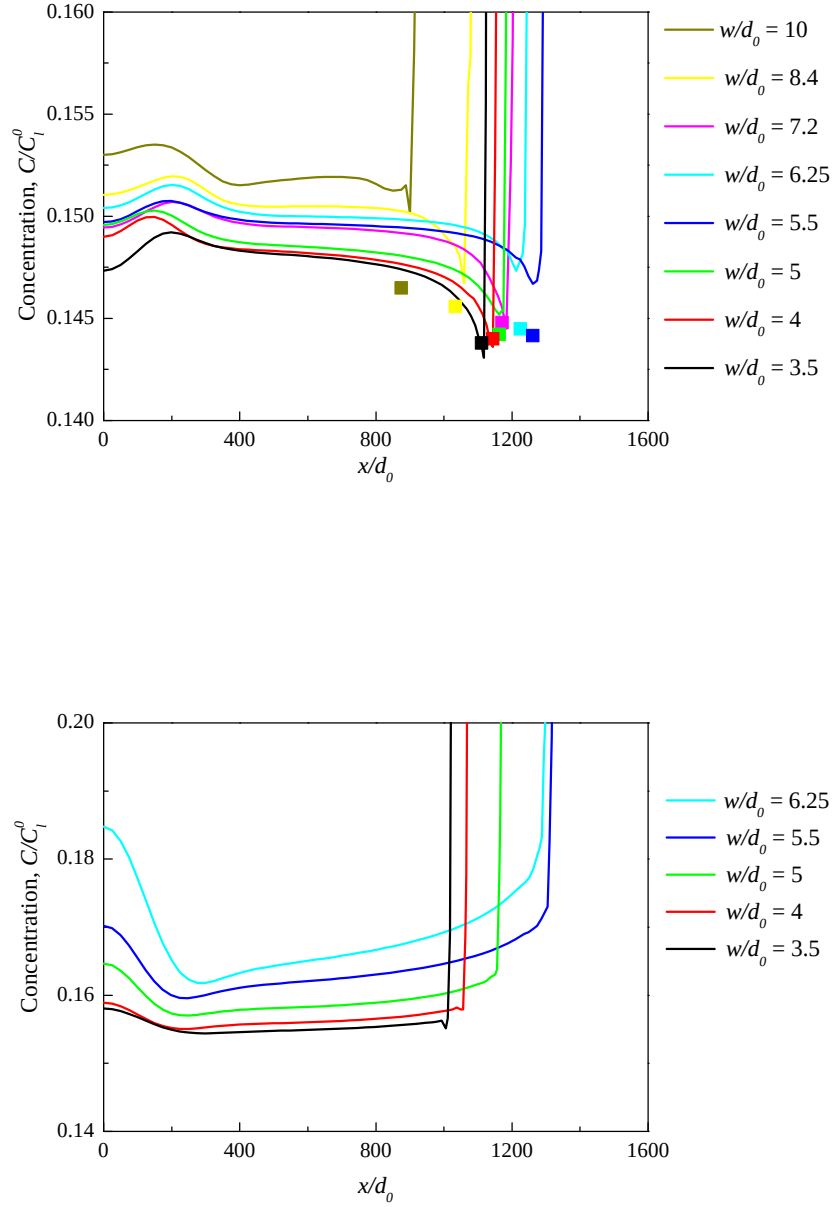


Figure 3.4: Steady-state solute profiles at different interface width, calculated by (a) the extension with anti-trapping term and (b) the model without anti-trapping term. In (a), the steady-state tip concentrations predicted by the Gibbs-Thomson relation (points) are added for comparison. The ratio of diffusivities used is $D_s/D_l = 0.1$.

The steady-state dendrite tip radius with respect to the interface width is plotted in Figure 3.5, calculated by the extension with anti-trapping term (line with solid squares) and the model without anti-trapping term (line with blank squares).

The results calculated by the extension converges well when the interface width is as large as $6.25d_0$ and then it increases significantly with the continuous increase in interface width. For the results calculated without anti-trapping term, the results converges when the interface width is smaller than $5d_0$, and however, the calculated results are smaller than those calculated by the extension. As referred, the model without the anti-trapping term could not provide accurate solid concentration and therefore the calculated results about tip radius are not accurate and gaps exist between the plots calculated by the extension with anti-trapping term and the model without anti-trapping term.

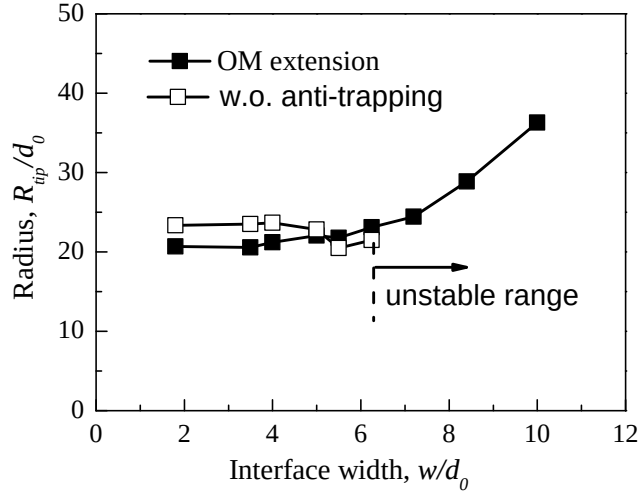


Figure 3.5: Steady-state tip radius with respect to interface width w , calculated by the extension with anti-trapping term and the model without anti-trapping term; $D_s/D_l = 0.1$ in the simulation.

The steady-state tip velocity calculated by the extension with the anti-trapping term using different interface width is shown in Figure 3.6 (line with the solid square). The results with respect to w converges well until the interface width is increased to $w/d_0 = 5.5$ and then it significantly increases. The steady-state tip velocity with respect to w calculated by the model without interface width is also plotted in Figure 3.6 for comparison. It could be seen that the velocity begin to significantly increase when the interface width is larger than 3.5, showing smaller convergence

range than the extension with anti-trapping term. Therefore, in terms of the convergence behavior (Figure 3.4-Figure 3.6), the extension shows better convergence behavior than the model without anti-trapping term.

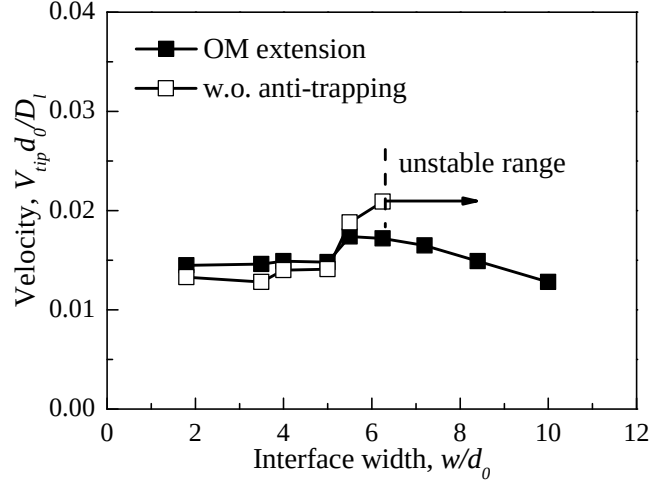


Figure 3.6: Steady-state tip velocity with respect to interface width w , calculated by the extension with anti-trapping term and the model without anti-trapping term; $D_s/D_l = 0.1$ in the simulation.

In sum, the accuracy of the proposed extension is evaluated under the case study with $D_s/D_l = 0.1$. It shows that the extension could accurately simulate the dendrite growth with a much reduced artificial solute trapping to recover the Gibbs-Thomson relation at the thin interface width. The examination of the convergence behavior of this extension shows that the calculation accuracy is still maintained when the interface width is selected as large as $5d_0$ for the case $D_s/D_l = 0.1$.

3.6 Effect of D_s on the maximum interface width

3.6.1 Maximum interface widths for various D_s

As could be seen above, the steady-state tip velocity is sensitive to the PF interface width than the tip radius and therefore the steady-state tip velocity would be used as an indicator to examine the convergence behavior for different solid

diffusivity (D_s/D_l). The investigated range of D_s/D_l is from the lowest 0 to the highest 1 and other calculation parameters are the same as those in the case study with $D_s/D_l = 1.0$.

Figure 3.7 shows the plots of steady-state tip velocity with respect to the interface width at different D_s/D_l . It could be seen that at each PF interface width, the obtained steady-state tip velocity decreases with the increase in D_s/D_l , demonstrating that the dendrite growth velocity is lower in the higher solid diffusivity. For each D_s/D_l , the plot of the tip velocity has the similar trend with the PF interface width increasing; it converges in a range of interface width and then significantly increases, as described above for the case study $D_s/D_l = 0.1$. For the $D_s/D_l = 0$, $D_s/D_l = 0.1$, and $D_s/D_l = 0.5$, the selection of the interface width is $w/d_0 \leq 5$, and however, this range could be enlarged into $w/d_0 \leq 5.5$ for $D_s = D_l$. A magenta line is drawn to distinguish the convergence zone and the unconvergence zone; the left is the convergence zone. It could be seen that this line is not vertical to the x-axis, demonstrating that the selection range of the interface width is enlarged if the interface width is scaled in the capillary length scale d_0 .

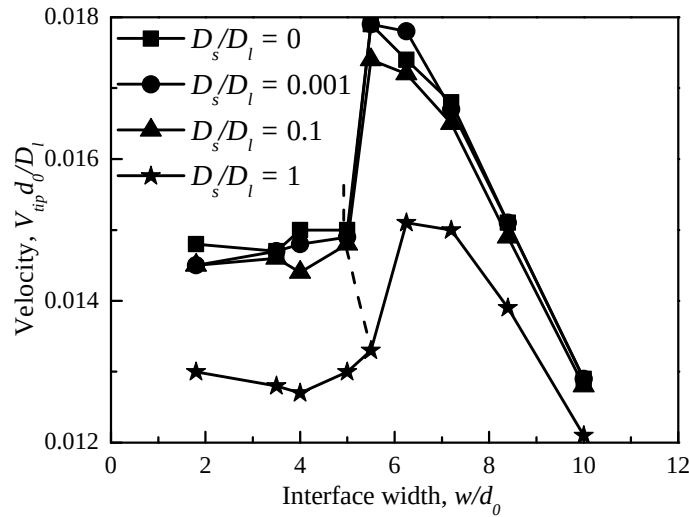


Figure 3.7: Calculated steady-state tip velocity with respect to the interface width by the proposed extension at different solid diffusivities (D_s/D_l)

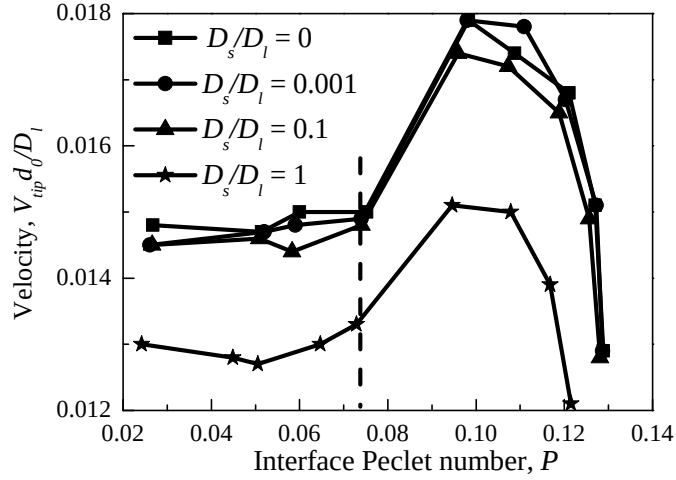


Figure 3.8: Convergence map for different solid diffusivities (D_s/D_l) in terms of the P ($P = w/(D_l/V_{tip})$) parameter.

3.6.2 Interface Peclet number at the maximum interface width

In the thin-interface limit analysis [66], w/d_0 is the expansion parameter and therefore w/d_0 is used as a criterion to select the interface width for a simulation. However, it could be seen that w/d_0 is larger than one, which goes beyond the range for an expansion parameter. Echebarria *et al* [66] also suggested the possibility to use the interface Peclet number $P = w/(D_l/V_p)$ as a small expansion parameter. If P as the expansion parameter, it means there is an upper limit of P to value w that ensures the results convergent to the correct results. Then we will investigate whether the inclusion of D_s will have an effect on the convergence behaviour by examining if the upper limit of P would be changed with varying D_s .

Figure 3.7 was plotted in terms of P . A dash line is drawn to distinguish the convergence zone and the inconvergence zone according to the data of tip velocity. It could be seen that this line is vertical to the x-axis, showing that the P limitation is the same for different D_s/D_l . It implies that the inclusion of D_s has little effect on the convergence behavior of the model with the assumption $\chi(s) = 0$ for finite D_s .

3.7 Conclusions

Ohno and Matsuura (OM) [92] extended Karma's thin-interface PF models [65, 66] with anti-trapping term to alloy solidification involving solute diffusion in solid. The issue of this model is that the solute flux term in solid $\chi(s)$ needs to be input as a parameter for PF simulation and however it is an output of a simulation. Possibility of using $\chi(s) = 0$ was mathematically and numerically validated in this chapter.

Mathematical validation is achieved. It can be used because $\chi(s)$ contributes a correction which vanishes as the interface width tends to zero. In numerical tests, the predicted results using the PF model and those from Gibbs-Thomson relation for alloys with non-zero solid diffusivity were compared. A good agreement was obtained indicating that the developed model with the anti-trapping term can improve the simulation accuracy with much reduced artificial solute trapping. Convergence behaviour of this extension model shows that the results converge well in a finite range of w and it is shown that the effect of D_s has little influence on the convergence zone because the upper limit of the interface Peclet number at the maximum interface width of convergence zone are almost the same.

CHAPTER FOUR

Effect of Finite Solid Diffusivity on Free-Growth Dendrite

The aim of this chapter is to answer under which condition the solid diffusivity can be negligible by investigating the effect of finite solid diffusivity on the steady-state dendrite under free growth in terms of the microsegregation, the steady-state tip radius and the steady-state tip velocity. Due to the equilibrium partition coefficient indicates the amount of solute to be transported during the solidification through diffusion, the effect of equilibrium partition coefficient on the influence of solid diffusivity was also discussed. Based on the results, a map indicating the error resulting from the exclusion of solid diffusivity will be given in this chapter.

4.1 Simulation parameters

The steady-state dendrite freely growing under the isothermal solidification was concerned. The supersaturation keeps constant as 0.55, i.e. $\Omega = 0.55$. The simulations started with an initial seed with radius $r_0 = 22d_0$ and thickness $h = 25d_0$, growing in a supersaturated melt with initial concentration C_∞ . The calculation domain is $L_x \times L_y \times h$ with $L_x = L_y = 1600d_0$. It could be seen that $L_x = L_y \gg h$ and the initial seed was full in the direction of z-axis, and therefore the dendrite grew in two dimensions. In all simulations, the interface widths were set as $w = 5d_0$. D_s/D_l varies from 0, 0.0001, 0.001, 0.01, 0.1 to 1.0, and the equilibrium coefficient k_e varies from 0.15, 0.3, 0.5 to 0.8.

To characterize the effect of D_s on the obtained steady-state dendrite, the fol-

lowing aspects were examined: (1) Solute microsegregation in solid, $S = C_{max}/C_{min}$ where C_{max} is the maximum concentration in the steady-state dendrite, C_{min} is the minimum concentration; (2) Steady-state tip radius, R_{tip} ; and (3) Steady-state tip growth velocity, V_{tip}

4.2 Effect of D_s on steady-state dendrites

4.2.1 Solute microsegregation

Figure 4.1 shows the solute profile evolution along x-axis at different D_s/D_l varying from 0 to 1. In each case, the equilibrium partition coefficient $k_e = 0.15$ was used, and the solute profiles at time $t = 40\tau_0$, $t = 80\tau_0$, $t = 160\tau_0$, $t = 320\tau_0$, $t = 640\tau_0$, and $t = 1000\tau_0$ were plotted from the left and the right. It could be seen that the typical solute profile displays the similar trend; the concentration increases along the x-axis to the peak and then decreases from the peak position to the dendrite tip. Therefore, the direction of the solute flow in the solid is from the peak position to other two ends in terms of one dimension when $D_s \neq 0$, resulting in the increase in solid concentration with the time evolution.

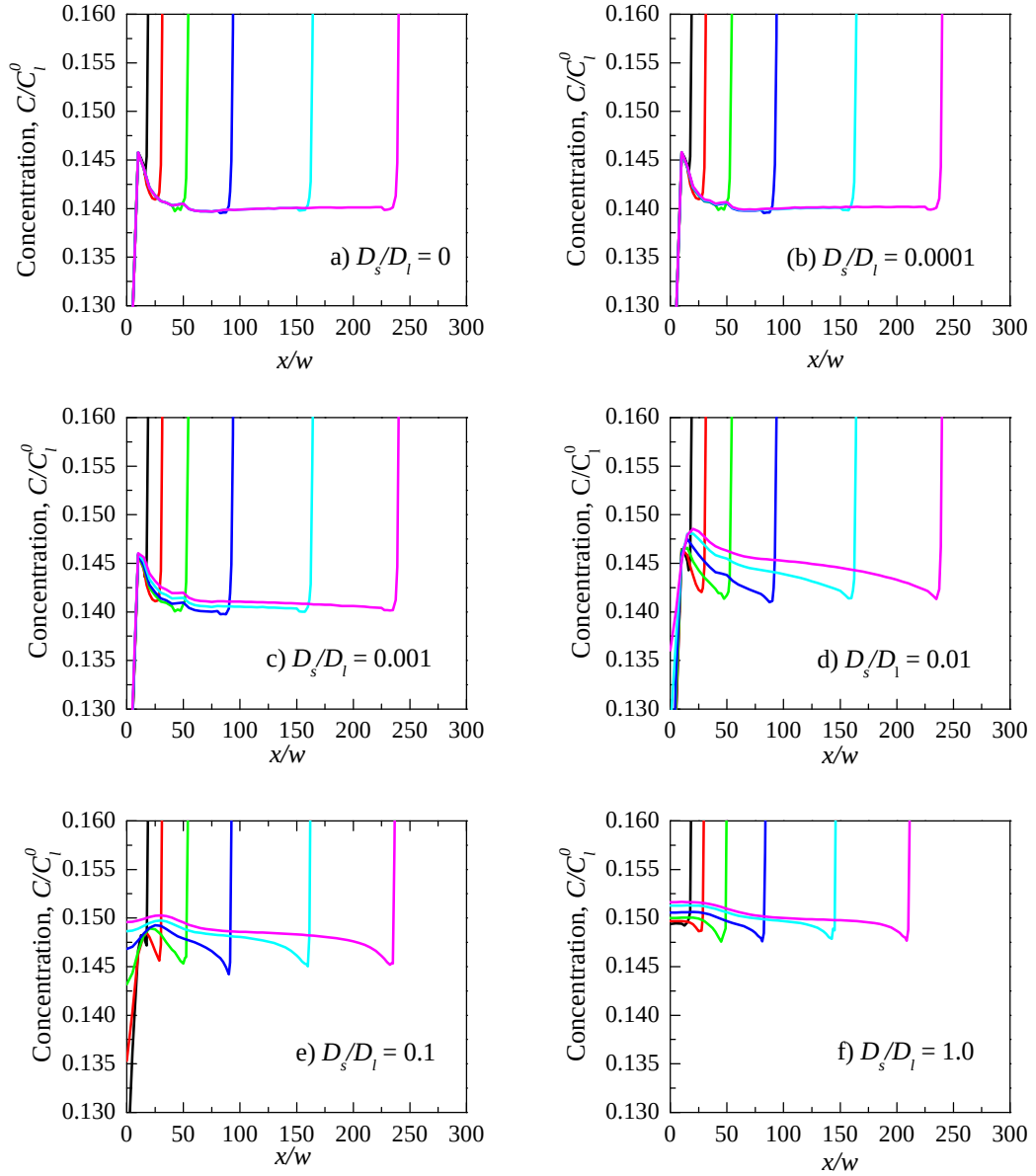


Figure 4.1: Solute profile evolution along x -axis at different D_s/D_l when $k_e = 0.15$; at each sub-figure, solute profile is at time $t = 40\tau_0$, $t = 80\tau_0$, $t = 160\tau_0$, $t = 320\tau_0$, $t = 640\tau_0$, and $t = 1000\tau_0$ from the left to the right.

When $D_s = 0$, it is obviously observed that the concentration in the solid would not change with time due to the zero solid diffusivity. When D_s/D_l is as small as 0.0001, the change in the concentration in the solid with time still can not be observed. When D_s/D_l is increased to 0.001, the concentration in the solid part beyond the peak position increases with time whereas there is no change in the solid part before the peak position. With the continuous increase in D_s/D_l , $D_s/D_l = 0.01$

for example, the concentration in both solid parts (one from the origin to the peak position and one from the peak position to the dendrite tip) obviously increase with time and the concentration gradient in the solid become gentler with time due to the solute flow in the solid. It could be noted that when D_s is as high as D_l , i.e. $D_s = D_l$, the solute distribution in the solid part from the origin to the peak position is almost uniform even at the early stage with time $t = 40\tau_0$. Therefore, this figure clearly shows that the existence of the solid diffusivity, $D_s \neq 0$, leads to the increase in solid concentration with time and results in a more uniform solute distribution in solid.

Figure 4.2 is the steady-state solute profile along x-axis with different D_s/D_l when the equilibrium partition coefficient k_e is fixed as 0.15. It could be seen that with the increase in D_s , from $D_s/D_l = 0$ to $D_s/D_l = 1$, the solid concentration increases and the solute distribution becomes more uniform. When D_s/D_l is as small as 0.0001, the solute profile overlaps that when $D_s/D_l = 0$, indicating that the effect of D_s on the solute distribution could be neglected in this case. When D_s/D_l is as large as 1.0, the solute profile is close to that when $D_s = D_l$, demonstrating that the solute flow is already relatively large in solid compared that in liquid even when the solid diffusivity D_s is only as large as the one tenth of the liquid diffusivity D_l .

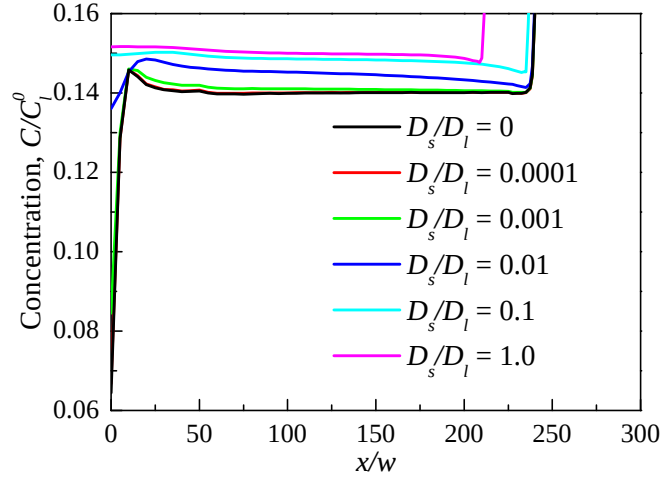


Figure 4.2: Comparison of solute profiles along x -axis at $t = 1000\tau_0$ with different D_s/D_l when $k_e = 0.15$; $t = 1000\tau_0$ is selected because the dendrite growth has been into steady state.

Define a factor $S = C_{max}/C_{min}$, where C_{max} and C_{min} are the maximum and minimum concentration in the solid, to indicate the solute microsegregation. The values of C_{max} , C_{min} and S are summarized in in Table 4.1. It could be seen that with the increase in D_s , the C_{max}/C_{min} decreases largely from 2.364 at $D_s = 0$ to 1.027 at $D_s/D_l = 1.0$, meaning that D_s has an significant influence on the solute microsegregation in the solidified dendrite. According to the Gibbs-Thomson relation, this would effect the shape of the dendrite on curvature of the morphology. Because the side branches are not obvious in the obtained structures, we will only concern the tip radius R_{tip} and the tip velocity V_{tip} presented as follows.

4.2.2 Operating state (R_{tip}, V_{tip})

The steady-state R_{tip} and V_{tip} for different D_s when $k_e = 0.15$ were summarized and also listed in Table 4.1. Generally, the R_{tip} increases while V_{tip} decreases with the increase in D_s . However, it can be seen that the change in tip radius and the tip growth velocity is not obvious until the D_s/D_l is increased as large as 0.01.

To more clearly display the effect of D_s , comparisons were performed by the

Table 4.1: Calculated properties at different D_s/D_l when $k_e = 0.15$ examined in 2D.

k_e	D_s/D_l	C_{max}/C_l^0	C_{min}/C_l^0	S	R_{tip}/d_0	$V_{tip}/(D_l/d_0)$
0.15	0	0.152	0.064	2.364	21.72	0.0151
	0.0001	0.152	0.067	2.269	21.72	0.0151
	0.001	0.152	0.085	1.795	21.72	0.0150
	0.01	0.152	0.136	1.115	21.74	0.0150
	0.1	0.152	0.145	1.045	22.07	0.0148
	1.0	0.152	0.148	1.027	25.39	0.0129

ratios of the properties at each D_s/D_l to those at $D_s = 0$. The following symbols are used: $S' = S(D_s)/S(D_s = 0)$, $R'_{tip} = R_{tip}(D_s)/R_{tip}(D_s = 0)$, $V'_{tip} = V_{tip}(D_s)/V_{tip}(D_s = 0)$. Then these symbols indicate the deviation of the corresponding property at a finite D_s from that at $D_s = 0$. The further away from one of the values means the large deviation and thus means D_s make a larger difference in dendritic growth. The three parameters versus D_s/D_l when $k_e = 0.15$ were plotted in the Figure 4.3. The dash line was drawn with the baseline of the value one. It clearly seen that it is the solute microsegregation S is strongest influenced by D_s , compared to R_{tip} and V_{tip} . When D_s/D_l is as small as 0.0001, the deviation from one is within 5%, whether examined in C_{max}/C_{min} , R_{tip} or V_{tip} , meaning that the effect of solid diffusivity in this case can be negligible.

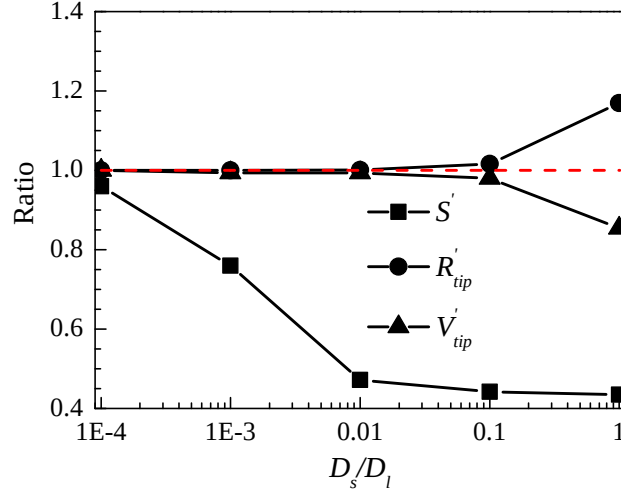


Figure 4.3: Comparison of the properties at steady state with different D_s/D_l when $k_e = 0.15$.

4.3 Value of k_e on the D_s influence

In this section, the value of the equilibrium coefficient k_e was investigated in that the amount of the solute that needs to be transported during solidification was determined by the partition coefficient. Figure 4.4 shows the S for various D_s and k_e . It could be seen that at a constant D_s , the S decreases with k_e increases, meaning that the increase in k_e decreases the degree of microsegregation. As discussed, D_s decreases the microsegregation, as can be seen in Figure 4.4, the effect of D_s on the microsegregation (indicated by S') become milder with the increase in k_e . When k_e is as small as 0.15, the deviation of S' from one is as high as 25% even when D_s/D_l is as small as 0.001. By contrast, when k_e is as high as 0.8, the deviation of S' from one is within 12% even when D_s/D_l is as large as 1.0.

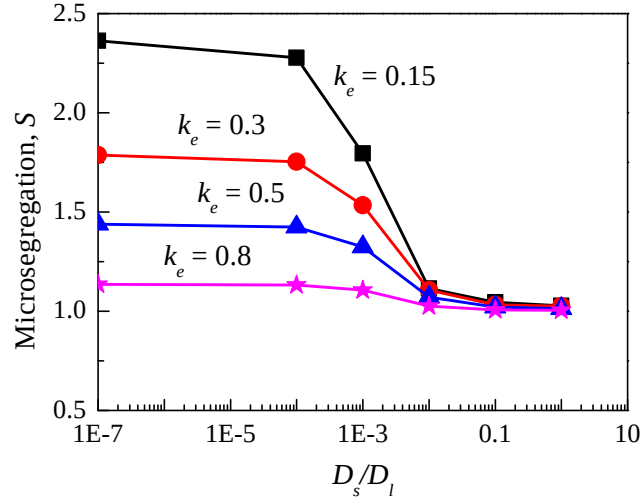


Figure 4.4: Influence of D_s/D_l on the dendrite growth at different k_e in terms of solute microsegregation.

Figure 4.5aa shows the R_{tip} for various D_s and k_e . To compare the tip radius at different equilibrium partition coefficient, the radius was scaled by $d_0(1 - k_e)$ rather than by d_0 as used in the previous chapter. It could be seen that at a constant D_s , the R_{tip} increases with k_e increasing. At constant k_e , the increase in D_s increases in R_{tip} and this kind of increase is furthermore strengthened by the increasing slopes of each plot in Figure 4.5a. This is different from that on microsegregation. Figure 4.5ab shows the V_{tip} for various D_s and k_e . At constant k_e , the V_{tip} decreases with the D_s increasing. When D_s is constant, the increase in k_e leads to lower growth velocity as shown in Figure 4.5ab.

As discussed in chapter 1 and also shown by Figure 3.2, the selection parameter $R_{tip}^2 * V_{tip}$ was calculated for each case, shown in Figure 4.5ac. As can be seen, when k_e is constant, the selection parameter increases with the D_s increasing, which agrees with the prediction of Langer and Muller [16].

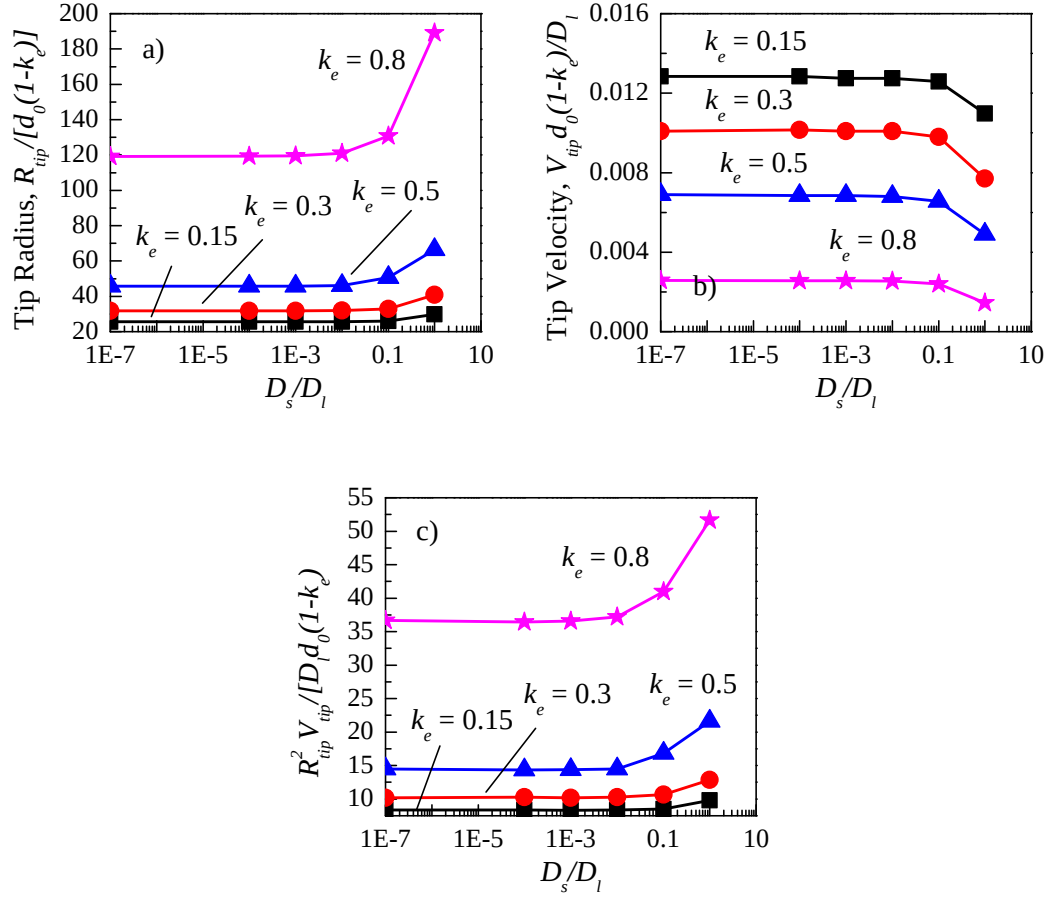


Figure 4.5: Influence of D_s/D_l on the dendrite growth at different k_e in terms of (a) R_{tip} , (b) V_{tip} , and (c) the selection parameter $R_{tip}^2 * V_{tip}$

To answer the question, when D_s needs to be considered, we compared the properties of a finite D_s with their corresponding with zero D_s , which can be indicated by S' , V'_{tip} and R'_{tip} as discussed before. Then the difference can be expressed as by the maximum value among $|S' - 1|$, $|R'_{tip} - 1|$, and $|V'_{tip} - 1|$, symbolized as E . Its value indicates how much of error will be produced if the finite D_s is not considered. Figure 4.6 is a map showing the effect of D_s on the dendrite growth for various k_e based on the E value. If D_s can be negligible when E is within 5%, there are two regions: (1) the commonly recognized range with $D_s < 0.0001$ and (2) high $k_e > 0.8$ and medium $0.0001 < D_s < 0.01$. The point for C solute in Fe-C alloys is plot in the figure, which is in the high error zone. To simulate the dendrite growth

for Fe-C alloys, the consideration of solid diffusivity is necessary.

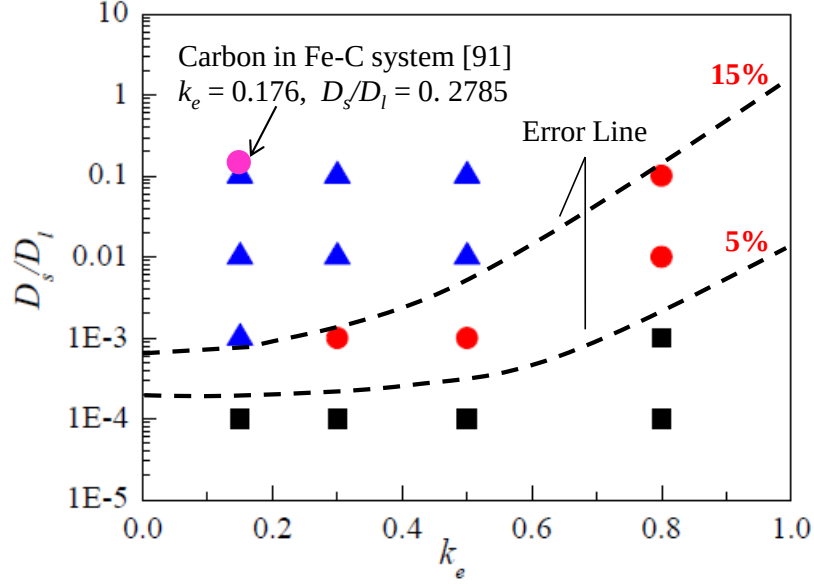


Figure 4.6: Influence of D_s/D_l on the dendrite growth at different k_e in terms of (a) C_{max}/C_{min} , (b) R_{tip} , and (c) V_{tip} .

4.4 Conclusions

The effect of D_s on the steady-state dendrite under free growth was investigated in terms of the microsegregation, the steady-state tip radius R_{tip} and the steady-state tip velocity V_{tip} . The results show that with the D_s increasing, the degree of microsegregation decreases in solid. The R_{tip} increases while V_{tip} decreases with the increase in D_s . Furthermore, the effect of D_s was found to be influenced by the value of k_e . A map was given based on the error coming from the exclusion of the finite D_s for various D_s and k_e . The D_s can be negligible in simulations when (1) $D_s < 0.0001$ or (2) $k_e > 0.8$ and $0.0001 < D_s < 0.01$.

CHAPTER FIVE

Dendritic Growth under Directional Solidification

The outgrowth and the evolution of side branches of a dendrite have rarely been observed at the micrometre scale due to the high experimental cost. However, the outgrowth of the side branches would modify the scaling of a dendrite and furthermore the so-called detachment of side branches happened under the transient growth rather than the steady-state growth. Therefore, dendritic growth under the steady-state directional solidification and transient solidification were investigated using the evaluated PF model (see Chapter 3) in this chapter and the next chapter, respectively. Emphases were given on the evolution of the morphology of side branches and the solute distribution in the liquid around the side branches.

5.1 Introduction

A dendrite consists of a primary stalk and side branches growing out on the primary stalk at a distance from the dendrite (stalk) tip. A lot of volumes of study on the primary stalk have been reported in the literature. When a dendrite freely grows in certain undercooled/supersaturated melt, a determined operating state (V_{tip}, R_{tip}) was observed in the pure SCN [11, 12] when the steady state was achieved. Analytical models [10, 13–17, 21] were proposed to relate the steady-state (V_{tip}, R_{tip}) to the solidification condition for the free-growth dendrite. For example, the LGK model [21] relates the (V_{tip}, R_{tip}) to the gradients of solute concentration and temperature ahead of the stalk tip. Then, Kurz *et al* proposed the so-called KGT model [22] to relate the R_{tip} to the directional solidification condition defined by the thermal gradient G and the pulling velocity V_p . Those above models are

for the isolated dendrite based on the assumption that the shape of the dendrite is a parabola (2D) or the revolution of a paraboloid (3D). The side branches were not taken into account and however the side branches are of significance during the dendritic growth, especially for the dendritic growth under directional solidification.

The outgrowth of the side branches will modify the shape of the primary stalk with a new introduced length scale, i.e. the stalk width Z_r as indicated in Figure 1.9, and measurement in Z_r is difficult through experiments [37]. Under the directional solidification, the solidified structure is not an isolated dendrite but the dendritic array with another additional length scale, i.e. primary spacing λ_1 . Experimental measurements [35] showed that the λ_1 was not a determined value under a certain G and V_p and instead varies in a finite range which also has been numerically modelled by Hunt *et al* [4, 26–32]. However, the steady-state R_{tip} does not change although the various λ_1 [4, 30, 35, 48], which thus implies that side branches largely contribute to the adjustment of the primary spacing.

A side branch is basically connected to the primary stalk with a fine necklace. The occurrence of side-branch detachment (fragmentation) is one mechanism for columnar-to-equiaxed (CET) transition [39–41], grain refinement [42] and the appearance of stray crystals [1, 43]. The detachment is attributed to the remelting of side branches at the necklace or the mechanical failure due to the stress at the necklace. For any of the reasons, the evolution of the side branches on a dendrite is the interest.

In the following part, results of some key papers on the side-branch detachment were reviewed.

- (1) Secondary side-branch fragmentation was observed in Al-Cu alloys under the superheated condition by Wesner *et al* [49] using the PF modelling;

Isolated dendrite grew under the isothermal or the continuous undercooling condition and then a superheated condition with elevated temperature was imposed on the growing dendrite. As a result, the side branches begun to

remelt throughout the entirely side branches when the elevated temperature is higher than the melting point of the side branches. Because the solute concentration at the necklace was higher than those of other parts of a side branch, the remelting speed was higher at the necklace and in itself the necklace was the finest part, the detachment of side branch happened at the necklace due to the remelting at around 0.03 s. In this paper, the detachment of side branch happened because the temperature was elevated on purpose to be higher than the melting point during the dendritic growth, which is not applicable to the directional solidification in which the temperature decreases with time.

- (2) Tertiary side-branch fragmentation was observed in Al-Cu alloys under steady-state directional solidification by Mathiesen *et al* [40,41,44–47] using the X-ray radiography observations;

In those papers, the detachment of the tertiary side branches was observed under the steady-state directional solidification. They attributed them to the accumulation of the solute at the root of the tertiary side branches which led to the melting point was lower than the temperature there. The detachment of the secondary side branches was not observed because of the relatively lower solute concentration around the root of the secondary side branches. The occurrence of the secondary side branches are more common in the casting compared to the occurrence of the tertiary side branches. However, these studies again indicate that the occurrence of detachment is related to the solute distribution and the local temperatures.

- (3) Detachment of the secondary side branches under the transient growth conditions observed by Lu *et al* [37,48].

Competitive growth of the neighbouring side branches undergoes behind the growth front, leading to the so-called ripening. During ripening, the side

branches of large size reject solutes to their neighbouring side branches of smaller size. Then the side branches of large size continue to grow while the smaller ones remelt during which the secondary arm spacing λ_2 increases according to a $t^{1/3}$ relationship under the steady-state evolution. Lu *et al* observed that the ripening process under steady-state growth does not involve significant detachment of side branches except for a very long time (> 1 h). However, a much more obvious detachment was observed during which the velocity began to decrease after the steady state was achieved for the initial condition. It should be noted that the detachment does not start until the dendrite grew upon steady state for about 250 s.

Secondary side branches are commonly a constituent in every dendritic structure and its detachment is more deserved to be studied compared to the tertiary side branches. Thus, the side branches below refer to the secondary side branches without an exceptional explanation. From the above reviews, the detachment is more likely to happen under the transient growth condition, indicating that the evolution of side branches is different from that under steady-state. Therefore, in this study we investigated the dendritic growth under the steady-state and the transient growth conditions to explain why detachment of side branch is more obvious under transient growth condition.

5.2 Simulation parameters

The evaluated PF model (see Chapter 3) that can include C diffusion in solid was used. The nominal composition of the model Fe-C alloy is $C_0 = 0.3$ wt.%, and the material properties fed into PF model are shown in Table 5.1. Note that the input S/L interfacial energy and its anisotropy were obtained from the MD modelling provided by Dr. Jun Liu at University of Leicester, UK. Regarding the value of anisotropy, there is no report on the experimental measurement for Fe-C

alloys and usually the four-fold anisotropy expression (see Eq. 1.8) was used with the coefficient of 0.02 [94]. As discussed in Chapter 1, this one anisotropy coefficient permits only $\langle 100 \rangle$ or $\langle 111 \rangle$ dendrites, and the addition of the second anisotropy coefficient permits more preferred orientations under the equi-axed dendritic growth.

In simulations, we use $G = 150$ K/mm and $V_p = 8$ mm/s which is the condition at one point of the weld pool obtained by the front-tracking modelling carried out by the MintWeld project partners at University College Dublin National University of Ireland, Ireland. Adaptive grids were used in simulations; the minimum grid spacing is equal to the selected interface width in simulations, i.e. $(\Delta x)_{min} = w$, to eliminate the deviations because of different $(\Delta x)_{min}$. Due to limitation of cubic grids in simulations, the selection of $(\Delta x)_{min} = w$ means calculation domain can only be magnified or narrowed by a factor of 2 if w is constant. Therefore, two different values of $w = 0.06$ μm and $w = 0.08$ μm were used to realize more variations in calculation domain. The calculation accuracy was not be affected because both interface widths were in the convergence zone.

Table 5.1: Material properties of the modelled Fe-0.3 wt.% C alloy.

Properties	Values	Sources
Equilibrium partition coefficient, k_e	0.176	Thermodynamic calculation
Liquidus slope, m_e (K/wt.%)	-80	Thermodynamic calculation
Liquid diffusivity, D_l (m^2/s)	2×10^{-8}	Ref. [93]
Solid diffusivity, D_s (m^2/s)	5.57×10^{-9}	Ref. [93]
Interfacial energy, γ_{sl} (J/m^2)	0.164	MD calculation
Anisotropy, a_1	0.0288	MD calculation
Anisotropy, a_2	-0.000612	MD calculation

One dendrite/cell growth was simulated in a x-y rectilinear frame, in which the thermal gradient and the pulling velocity were imposed along the x-axis. Because of

the cubic symmetry, only 1/4 sphere seed of radius $r_0 = 4 w$ was placed at the origin and directionally grew along the x-axis. The length of y-axis was $L_y = 1/2\lambda_1$ where λ_1 was the primary spacing of the dendrite/cell array. Because the λ_1 varies in a finite range under a certain directional solidification [4,27,29–32,35], we assumed different values for the concerned solidification condition. Symmetry boundary conditions were imposed on the x-y face and x-axis was long enough to keep free boundary condition during the dendritic growth.

Steady state is expected in this study and it achieves when the dendrite/cell tip velocity is equal to the pulling velocity, i.e. $V_{tip} = V_p$. If the sphere seed starts with the equilibrium temperature corresponding to alloy composition $C_0 = 0.3 \text{ wt.}\%$, the initial velocity of solid growth is low and far away from the pulling velocity, meaning that a long solidification time (t) is required for the achievement of the steady state. Due to the finite length of x-axis set in the simulations, the steady state may not be allowed before the free boundary condition is broken. To overcome this problem, a supersaturation $\Omega = \frac{C_l^0 - C_0}{C_l^0(1 - k_e)}$ is imposed to force the initial growth velocity to be closer to the pulling velocity. In simulations, the initial concentration field was defined as

$$C = \begin{cases} k_e C_l^0 & r < r_0 \\ C_l^0 (1 - \Omega (1 - k_e)) + C_l^0 \Omega (1 - k_e) \frac{r_0}{r} & r \geq r_0 \end{cases} \quad (5.1)$$

5.3 Achieving steady state

Figure 5.1 shows V_{tip} VS. t for varying Ω . In these simulations, $L_x = 2048 w$ with $w = 0.08 \text{ }\mu\text{m}$ and $\lambda_1 = 40.96 \text{ }\mu\text{m}$. As can be seen, the growth velocity at each Ω has the trend to get closer to the pulling velocity shown as dash line. As expected, solidification time needed to approach the steady state is the least at the highest Ω . When Ω is as small as 0.3, the steady state is not achieved at the current calculation domain and longer x axis is needed which will largely increase

the calculation cost. On the other hand, higher initial V_{tip} at higher Ω means the solidified dendrite is longer at the same t . Thus, the free boundary condition may be also broken before the steady state is achieved. Because we aim to analyse the evolution of dendrite after steady state, we favoured such kind of Ω under which the steady state is achieved and furthermore sufficient evolution time is allowed for the ripening process after the steady state whilst the maintenance of free boundary condition along the growth direction. As shown in Figure 5.1, $\Omega = 0.45$ and longer $L_x = 4096 w$ were used, under which the steady state arrived at time $t = 0.009$ s.

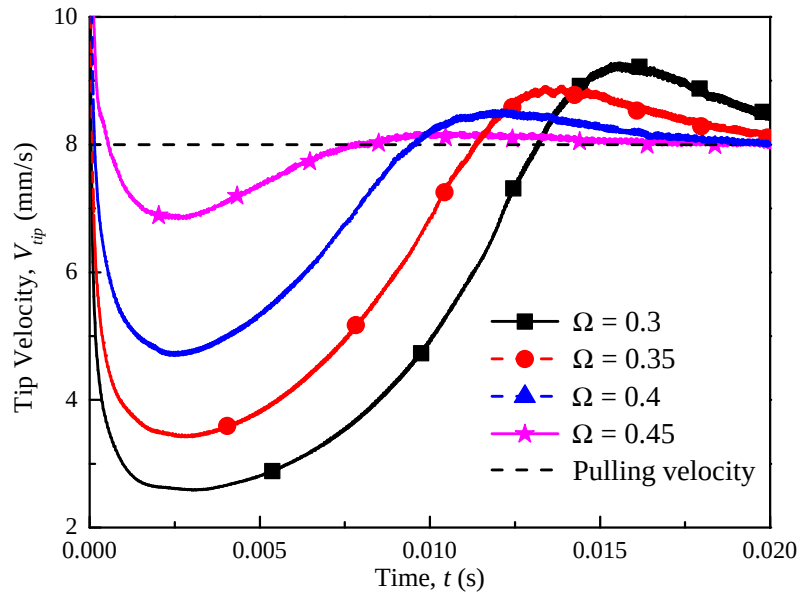


Figure 5.1: Evolution of V_{tip} for different Ω set in the initial condition; $\lambda_1 = 40.96 \mu\text{m}$ in the simulation.

Figure 5.2 shows the morphology visualized by the solute concentration when the steady state just arrived at time $t = 0.009$ s. In the simulation, $\Omega = 0.45$ and the assumed λ_1 is $40.96 \mu\text{m}$. The morphology indicates that the obtained solidified structure under the concerned solidification condition is dendritic rather than cellular according to the sharp shape near the stalk tip. Clearly, the assumed λ_1 is large enough to permit the occurrence of the side branches. Different values of λ_1 were assumed and the side branches were suppressed when λ_1 was as small

as $15.36 \mu\text{m}$. Because $40.96 \mu\text{m}$ permits the outgrowth of the side branches and thus fits the purpose on studying the evolution of the side branches, we select the dendrite with $\lambda_1 = 40.96 \mu\text{m}$ for the analysis. As observed in the morphology shown in Figure 5.2, side branches are connected to the primary stalk with a necklace which evolved through the ripening process during the later solidification. It can be seen that solutes are richer in the liquid near the roots between the neighbouring side branches than other parts around the dendrite.

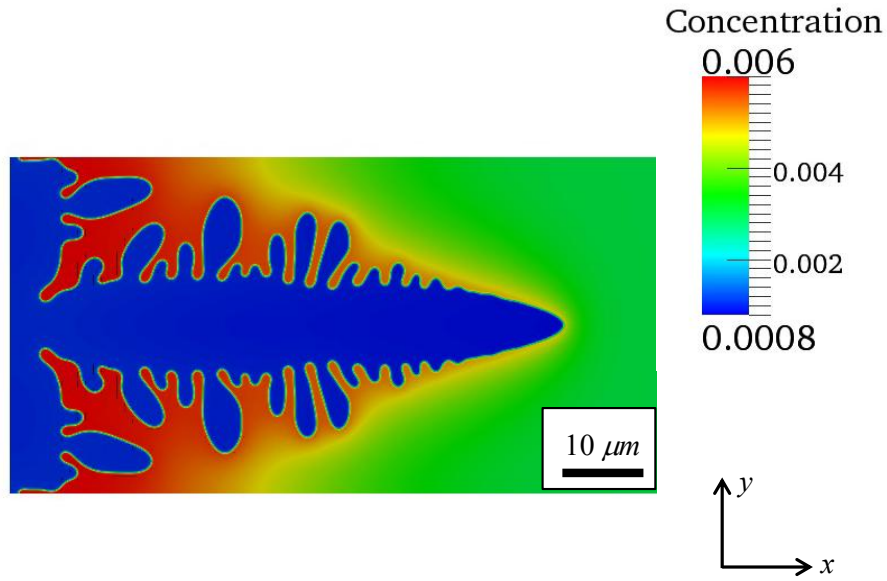


Figure 5.2: Dendritic morphology visualized by solute concentration when steady state just arrived at time $t = 0.009 \text{ s}$; $\lambda_1 = 40.96 \mu\text{m}$ was assumed.

Figure 5.3 shows the interfacial morphologies ($\phi = 0$) at different t upon steady state, including $t = 0.009 \text{ s}$, $t = 0.012 \text{ s}$ and $t = 0.015 \text{ s}$. With the time going, the dendrite tip advanced, new side branches grew out on the newly formed primary stalk and the old side branches located relatively further from the stalk tip underwent the ripening process through the competitive growth between the neighbouring side branches. As shown in Figure 5.3, some of the side branches became coarser while some became smaller on the evolution, during which the necklace changed. Then

the below presentations will answer how the shapes (morphologies) and the sizes (length scales) of the primary stalk and side branches evolves upon the steady state. The possibility of detachment of the side branches is then discussed based on the results.

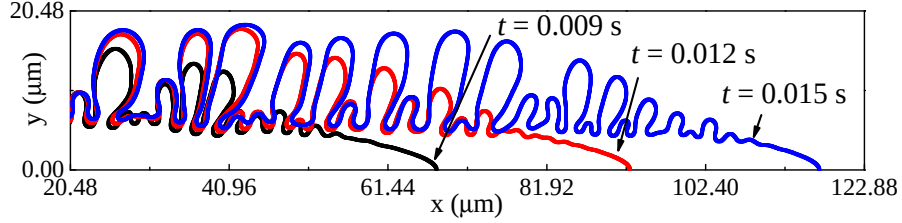


Figure 5.3: Morphology evolution of the dendrite with time.

5.4 Evolution of the primary stalk upon steady state

The morphologies of the dendrite at different times shown in Figure 5.3 were redrawn with the tips overlapping at the origin (0, 0), shown as Figure 5.4. As such the absolute of the x coordinate in the figure is the distance from the tip, notated as x_{tip} . At steady state, $V_{tip} = V_p$ and then by calculation the tip advanced about $24 \mu\text{m}$ in a time interval 0.003 s . It means that the dendrite part with $x_{tip} \leq 24 \mu\text{m}$ in the figure was newly formed at the time interval (0.003 s) .

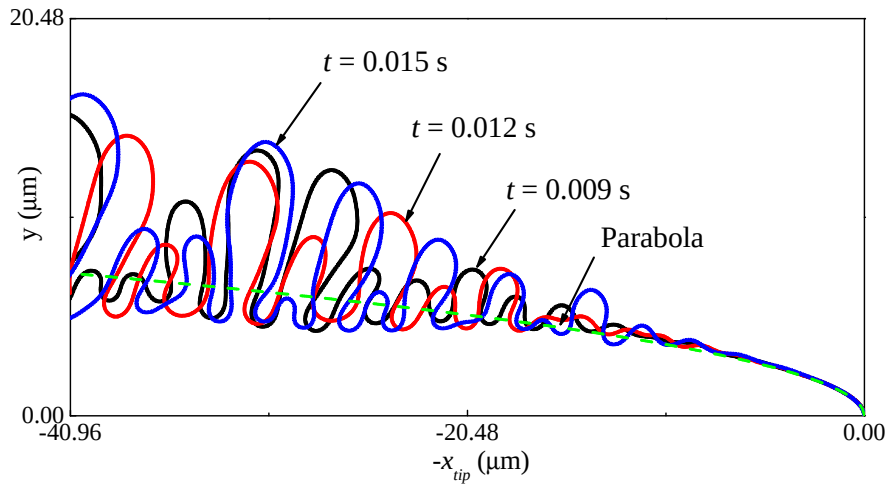


Figure 5.4: The re-plotting of the Figure 5.3 with the stalk tips overlapping at the origin; x_{tip} represents the distance from the tip.

As can be seen in Figure 5.4, the regions around the dendrite tips well overlap until the outgrowth of the first side branch at a distance from the tip. The steady-state shape of the primary stalk was commonly considered as a parabola in two dimensions which is characterized by the tip radius R_{tip} [10, 13–17, 21]. The tip radius R_{tip} of the dendrite was $0.66\text{ }\mu\text{m}$ by measurement and a parabola, expressed as $y = \sqrt{-2x_{tip}R_{tip}}$, was then plotted in Figure 5.4 as the dash line. As can be observed, the parabola fits well with the the primary stalk without side branches.

The shape of the primary stalk connected with the side branches were modified and deviated from the parabola as shown in Figure 5.4; the tips of the side branches are generally higher than the parabola while the roots formed due to the side branches with negative curvature are lower. Because of this modification, additional length scale is needed to outline the morphology of the primary stalk. It is the width of the primary stalk Z_r , as indicated in Figure 1.9, measuring the vertical distance from the root of the side branch to the central line of the dendrite along the growth direction. For 3D, it is the radius of the primary stalk, as referred in Ref. [37].

As shown in Figure 5.3, the Z_r changed with x-axis and with time t in a narrow variation within $0.3\mu\text{m}$ and the measurement showed that Z_r is around $4.5\mu\text{m}$. The variation of Z_r is attributed to the solute variation at the side branch root during the ripening process with further discussion below. It can be noted that the height of the side branches far away from the tip is over 2 times as Z_r , indicating the primary spacing in this case is largely occupied by the side branches.

If the primary stalk of a dendrite was accounted by (1) the part without side branches connected, and (2) the part with the side branches connected. According to the above analysis, the primary stalk of a dendrite can be characterized by two length scales:

- (1) The tip radius R_{tip} outlining a parabola (2D) or a revolution of paraboloid;
- (2) The primary stalk with Z_r (2D) or radius of the stalk (3D).

As the evolution of the dendrite upon the steady state, R_{tip} keeps constant and Z_{tip} slightly increases with time during the ripening process, and then it can be concluded that the primary stalk evolves in a shape-conserved manner upon steady state evolution.

5.5 Evolution of side branches upon steady state

5.5.1 Outgrowth of the side branches

As the primary stalk evolved in a shape-conserved way, new side branches grew out in the newly formed part of the primary stalk. The steady-state morphologies of $x_{tip} \leq 81.92 \mu\text{m}$ from $t = 0.009 \text{ s}$ to $t = 0.027 \text{ s}$ with a time interval 0.006 s are shown in Figure 5.5. Looking at any one of the morphologies, the first side branch grew out at around $x_{tip} = 10 \mu\text{m}$. The side branches within $x_{tip} \leq 20.48 \mu\text{m}$, as shown in Figure 5.5, just grew out, and thus the shape and the growth orientation of these side branches are not obvious. By contrast, the shape and growth orientation of the side branches with x_{tip} larger than $20.48 \mu\text{m}$ became obvious. Importantly, the side branches shown in Figure 5.5 'independently' evolved since its formation and the ripening process had not seriously influenced the outgrowing side branches. Therefore, observing the side branches relatively close to the stalk tip, particularly the ones with $x_{tip} \leq 50 \mu\text{m}$, could have an idea on the growth orientation of the outgrowing side branches.

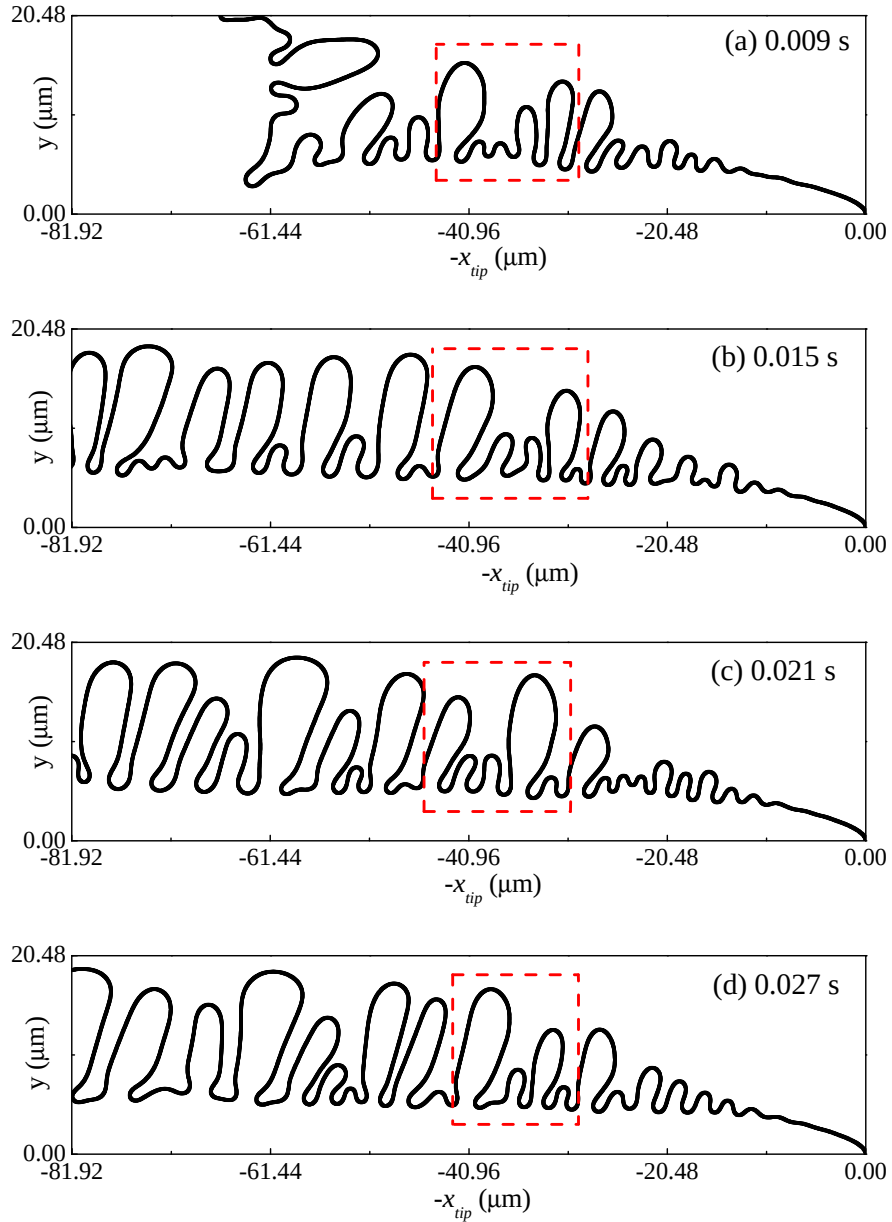


Figure 5.5: Morphologies of the dendrite showing the side branches close to the stalk tip from solidification time 0.009 s to 0.027 s with the time interval 0.006 s.

At each morphology, the formed side branches (see the region outlined by the box of dash line) grew in different growth orientations with respect to the primary stalk around the preferred orientation that is determined by the anisotropy in interfacial energy as discussed in Chapter 1. These side branches showing different orientations should grow in different growth velocities, and thus side branches of different sizes are observed in Figure 5.5. The side branches with larger sizes are

in the preferred orientation which is not vertical to the primary stalk but is tilted. This is due to the accounting of the anisotropy coefficient a_2 which permits $\langle 110 \rangle$ preferred besides $\langle 100 \rangle$. It can be seen that the side branches of small sizes are always located between two large side branches, which remelted during the ripening process as further discussed below.

An interesting observation is that the outgrowth of the side branches seems in a periodic manner. If we observed the side branches in the boxes of dash line at different times, the group of side branches are similar in shape and orientation. Furthermore, they have the similar distance from the stalk tip. This probably indicates that the formed side branches grew out in a periodic group consisting of side branches with different orientations around the preferred orientation.

5.5.2 Coarsening and remelting of the side branches during initial ripening process

5.5.2.1 Coarsening

In this part, we examine the coarsening and remelting of the side branches during the initial ripening process involving the side branches relatively further from the stalk tip (or closer to the dendrite bottom). Figure 5.6 shows the morphologies involving the side branches close to the dendrite bottom at time $t = 0.012$ s and $t = 0.030$ s. 6 surviving side branches after the competitive growth were marked by numbers in the morphologies. At earlier time $t = 0.012$ s, there are side branches of small sizes in the numbered side branches which was almost remelted and disappeared after the competitive growth as shown in the morphology at $t = 0.030$ s. The surviving side branches are almost in the same orientation which should be the preferred orientation determined by the anisotropy in interfacial energy, except the Side-branch 2. Therefore, the happening of the 'initial ripening process' referred here is due to the different orientations of the outgrowing side branches discussed

above and spanned the time until the side branches deviated from the preferred orientation remelted through the competitive growth of side branches.

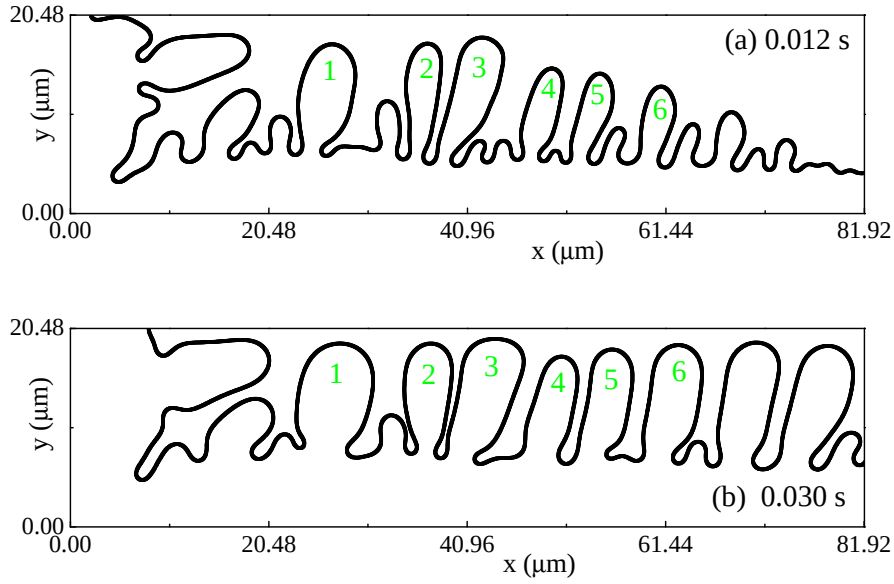


Figure 5.6: Morphologies showing the side branches relatively further from the stalk tip at solidification time 0.012 s and 0.030 s.

As shown in these figures, each side branch has different widths at different height along y-axis and then the width at the half height of the side branch is used to indicate the side branch width, symbolized by W_{hf} . A side branch was connected to the primary stalk by a fine necklace and the necklace width W_{nc} is important to the detachment of side branches because detachment generally happened at the necklace whether due to the remelting [40, 41, 44–47, 49] or the mechanical failure. The indications of W_{hf} and W_{nc} have been shown in Figure 1.9 in Chapter 1. If it is due to the mechanical failure by the stress related to the weight of the side branches, then the absolute value of the W_{nc} is not sufficient to indicate how fine the necklace is. The ratio of W_{hf} to W_{nc} was then used; the larger the ratio is, the finer the necklace width.

Figure 5.7a shows the necklace widths of the side branches marked in Figure 5.6. It can be seen that at earlier time, the necklace widths of the side branches are around $1.5 \mu\text{m}$ while this value is increased to $3.5 \mu\text{m}$ through the ripening process. The side

branched widths (W_{hf}) are shown in Figure 5.7b. There are large fluctuation in the side-branch width, ranging from about $3.12 \mu m$ to about $5.6 \mu m$ at time $t = 0.009 s$. After the competitive growth of the side branches, the side branches became coarser with larger W_{hf} as shown in Figure 5.7b. The ratio of W_{hf}/W_{nc} in Figure 5.7c shows that the ratio becomes smaller through the competitive growth, indicating that the detachment due to mechanical failure will become harder after the ripening process. Then, whether the detachment happened through the remelting of the side branches led to the investigation on the remelting process of side branches.

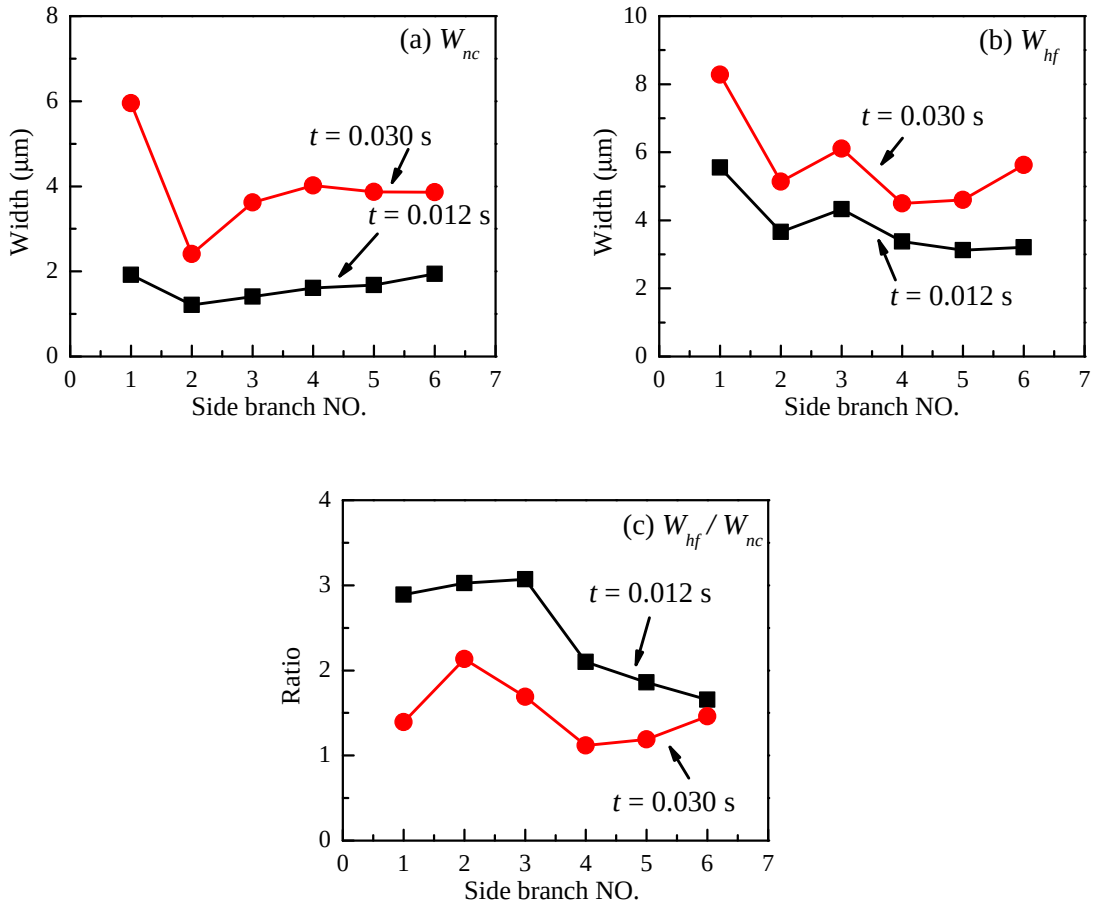


Figure 5.7: Necklace width W_{nc} , side branch width W_{hf} and W_{hf}/W_{nc} at time 0.012 s and time 0.030 s.

5.5.2.2 Remelting

To examine how a side branch remelted during the initial ripening process, the remelting process of the side branches between Side-branch 1 and 2 were tracked. The morphologies with $x = 20.48\text{--}40.96\mu\text{m}$ which includes the concerned side branches for various times are shown in Figure 5.9. It can be noted that those side branches consist of the periodic group mentioned above. In this group, there are three small side branches; two with smaller size and the other with relatively bigger. The two small sizes had entirely dissolved at the time $t = 0.012\text{ s}$ whilst the relatively larger one continued to grow. After that, the relatively larger one began to remelt when grew competitively with the Side-branch 1 and 2. It can be seen that the remelting of all the side branches started from the tip with decreased height while the necklace width became coarser. When it was totally remelted, the coarser necklace became part of the primary stalk and the stalk width was slightly increased as has been discussed. Figure 5.9 shows the remelting process of the side branches between the Side-branch 5 and 6. The same phenomenon could be observed, that is, the remelting started from the tip with coarser necklace until it became part of the primary stalk. Thus, the remelting of the side branches during the initial ripening process would not lead to the detachment.

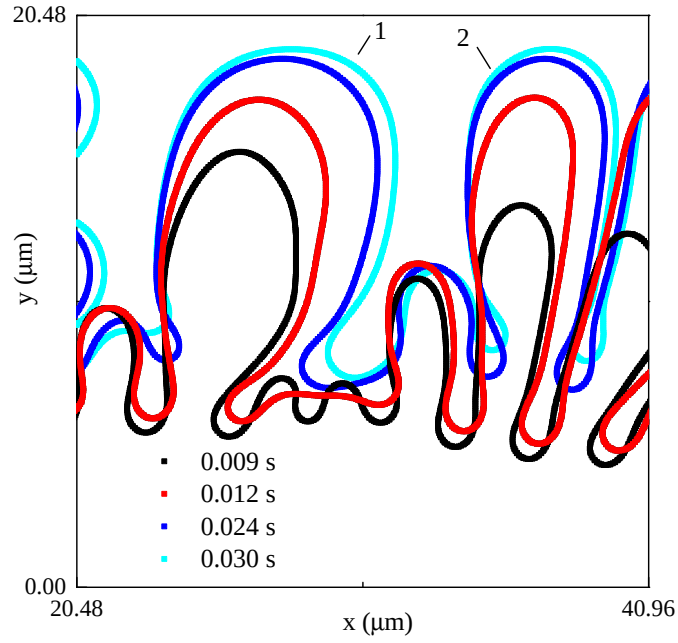


Figure 5.8: Remelting of the side branches between Side-branch 1 and 2 during the initial ripening process under steady-state growth condition.

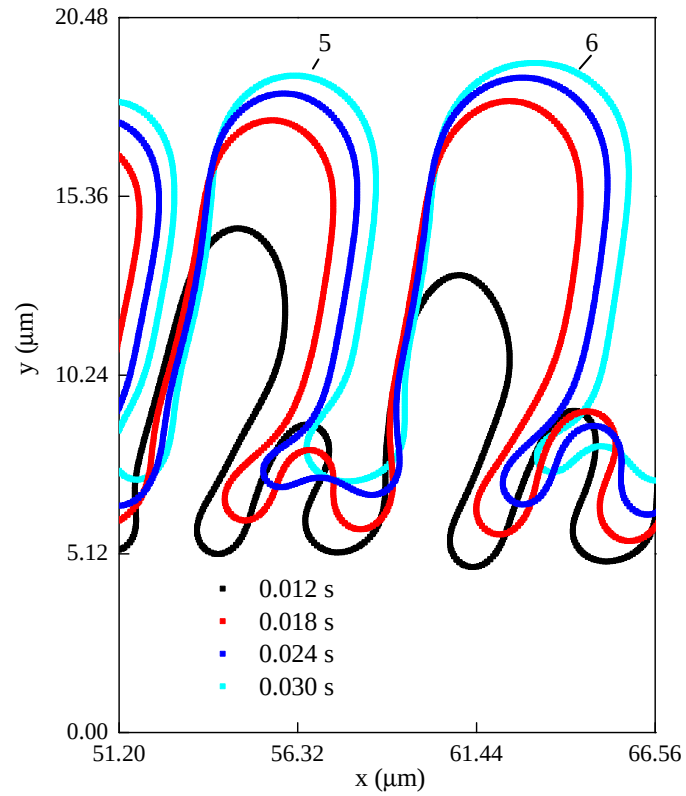


Figure 5.9: Remelting of the side branches between Side-branch 5 and 6 during the initial ripening process under the steady-state growth condition.

Figure 5.10 shows the solute distribution in the liquid surrounding Side-branch 5 and 6 during the remelting of the smaller side branches, i.e. from $t = 0.012$ s to $t = 0.030$ s. Because the solute was rejected from the solid to the liquid during solidification due to the equilibrium partition coefficient is less than one, the solute concentration in the liquid is higher than the alloy composition. For example, at time $t = 0.012$ s, the solute concentration in liquid is between $0.376wt.\%$ and $0.568wt.\%$. Looking at the solute distribution at time $t = 0.012$ s, it can be seen that lower concentration is in the right corner and then gradually increases with distance from the right corner. For the liquid surrounding one side branch, the highest solute concentration was around the necklace, i.e. the root between the side branches.

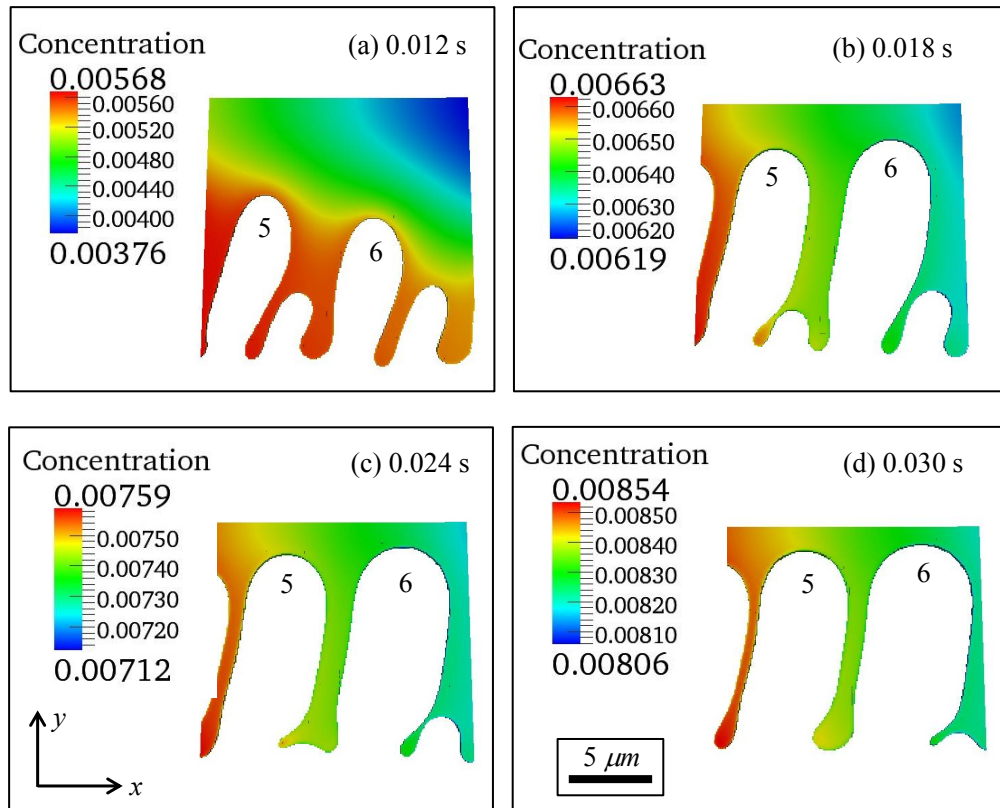


Figure 5.10: Solute distribution during the remelting of the side branches.

As observed, the solute concentration near the tip of the larger side branches (Side-branch 5 and 6) is lower than that near the tip of the smaller ones. As discussed in Chapter 1, the higher solute concentration means higher undercooling is required for solidification. Note that the concerned region is narrow in x axis and thus the temperature can be thought to be isothermal in the concerned region. Therefore, the undercoolings at the tips of the larger side branches are larger than those associated with the tip of the smaller ones. Then the side branches of the larger size grew faster than that of the lower ones and the rejected solute accumulate around the tip of the side branches of small size and the root between side branches, as observed in Figure 5.10. The higher solute concentration resulted in lower melting point and the remelting would happen at the tip of the side branch when the melting point was lower than the local temperature there. At the necklace, although the solute concentration is higher than that at the tip, the minus curvature improved the melting point and thus remelting was not observed at the necklace in Figure 5.10.

During the remelting of the side branches, the surviving side branches became coarser. Although our simulation has not go to further evolution, the following evolution could be predicted according to the Gibbs-Thomson relation. Observing side branches in Figure 5.10d, it can be found that the curvature of Side-branch 5 is larger than that of Side-branch 6, the solute concentration of liquid around the necklace of Side-branch 5 is higher based on the Gibbs-Thomson relation, as shown in Figure 5.10d. Then the solute will diffuse between the neighbouring Side-branch 5 and 6. However, this could expect to be different from the above discussed ripening process because the adjustment of the curvature can decrease the difference in solute concentration, implying that the detachment of side branches will not likely to happen due to the remelting. This implication complies with the experiments that the detachment is not observed under the steady-state growth condition [40, 41, 44–48].

5.6 Conclusions

In this chapter, the dendritic evolution under the steady-state growth was investigated focusing on the evolution of the side branches in terms of the occurrence of the detachment using the PF modelling. A map of the evolution of a dendrite under the steady-state directional solidification is given: the primary stalk evolves in a conserved shape with a constant tip radius and a slightly increasing stalk width during the initial ripening process. The side branches grew out with different growth orientations varying around the preferred orientation leading to different growth velocities and different sizes of side branches. These side branches then experienced the ripening process, during which the side branches with preferred growth orientation survived and the ones of adverse growth orientation remelted.

It was observed that the remelting growth orientation started at the tip of the side branches rather than the necklace. The surviving side branches became coarser during the initial ripening process with both increasing necklace width and the side branch width and the ratio of the side branch width to necklace width increased. These imply that it is difficult for the detachment of side branches happening under the steady state transition whether due to the remelting or the mechanical failure.

CHAPTER SIX

Dendritic Growth under Transient Directional Solidification

In the previous chapter, the variations in morphology and length scale of a dendrite during the initial ripening process under steady-state growth were investigated. In this chapter, the solidification condition was transferred from the steady state to the transient growth condition where pulling velocity was decreased after the dendrite just arrived at the steady state in the initial pulling velocity. Therefore, an emphasis would be put on the difference resulted by the transient growth condition in the primary stalk in this chapter.

6.1 Transient growth condition in the simulations

In the study, transient growth condition was imposed by decelerating the pulling velocity from $V_p = V_0$ to $V_p = V_f$ after the dendritic growth reached the steady state at time $t = t_0$ for the initial directional solidification. A constant thermal gradient G was used through the entire transient growth condition. For the sake of comparison with the dendritic growth under steady state discussed in the previous chapter, the same parameters are used, such as $G = 150$ K/mm, $V_0 = 8$ mm/s, $\Omega = 0.45$, $\lambda_1 = 40.96$ μm . As shown in Figure 5.1, the dendritic growth arrived at steady state at time 0.009 s and therefore the pulling velocity was then changed into V_f at time $t = 0.009$ s. Since then, the dendrite had grown under the transient growth condition until new steady state was achieved for the new directional solidification condition. V_f was varied from 4 mm/s, 2 mm/s to 1 mm/s to obtain different decelerations at

the transient stage.

Figure 6.1 shows the evolution of the tip velocity for various V_f . For each V_f , V_{tip} began to decrease after the pulling velocity was changed. The V_{tip} then arrived at a platform with $V_{tip} < V_p$ and increased to get close to V_f for getting into a new steady state. Our concern is the transient stage and therefore no more calculation is permitted after the arriving at the platform. The average deceleration A_{tip} at time t was calculated using $A_{tip} = \frac{V_{tip}^t - V_{tip}^{t+\Delta t}}{\Delta t}$ with $\Delta t \approx 0.001$ s. The plot of A_{tip} VS. t is displayed in Figure 6.1, showing that the deceleration decreased with time and lower V_f resulted in higher decelerations.

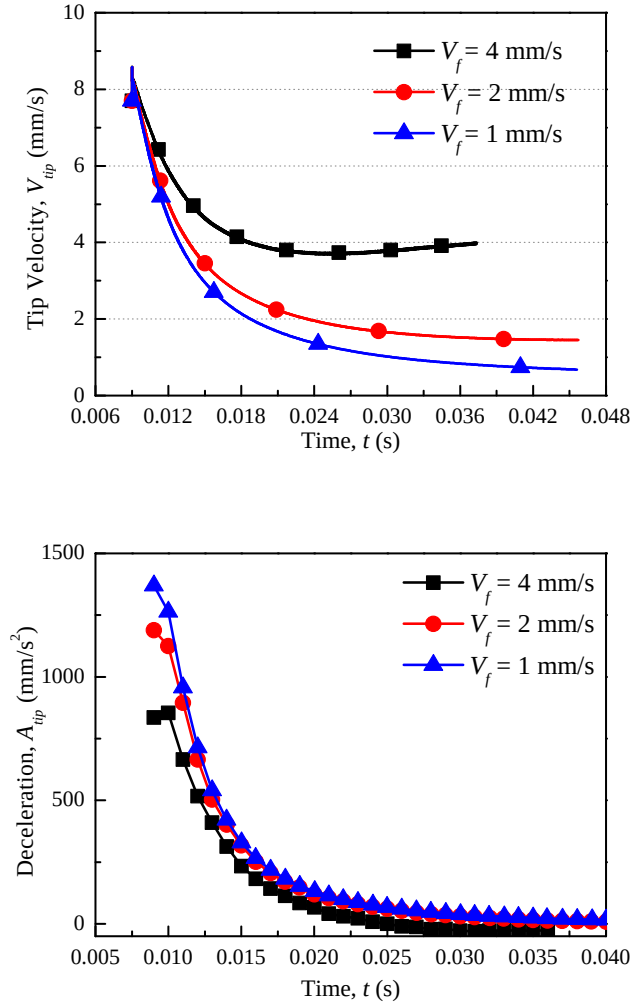


Figure 6.1: Evolution of the tip velocity and the deceleration for various V_f .

6.2 Evolution of the primary stalk under transient growth condition

6.2.1 Tip radius

Figure 6.1 shows the evolution of the tip radius R_{tip} for various V_f . For each V_f , the R_{tip} began to increase after the pulling velocity was changed into V_f , corresponding to the increase in V_p as shown in Figure 6.1. If V_{tip} then increased (line with square symbol in Figure 6.1), R_{tip} was observed to be decreased as shown by the line with squares in Figure 6.2. It qualitatively complies with the trend of the R_{tip} against the V_{tip} predicted by the analytical models [10, 21, 22] discussed in Chapter 1.

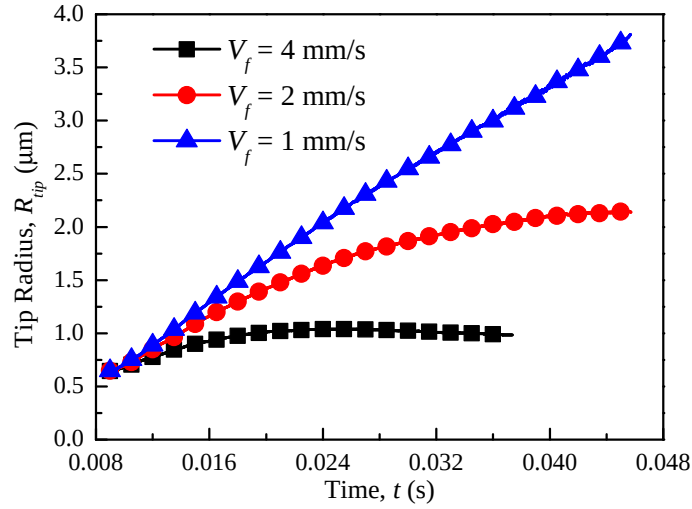


Figure 6.2: Evolution of the tip radius with time.

The R_{tip} of the steady-state dendrite does not change with the primary spacing λ_1 [4, 22, 30, 35] under certain directional solidification. The steady-state R_{tip} vs. V_{tip} was calculated using the evaluated PF model and was plotted in Figure 6.3 as the line with star symbols. R_{tip} VS. V_{tip} under the transient condition for different V_f were also shown in Figure 6.3. It can be seen that when V_{tip} was larger than 2.7 mm/s, the R_{tip} is smaller than its steady-state corresponding which is more clearly seen in the magnified figure (Figure 6.3b), indicating the R_{tip} reacts slower

to the changing tip velocities.

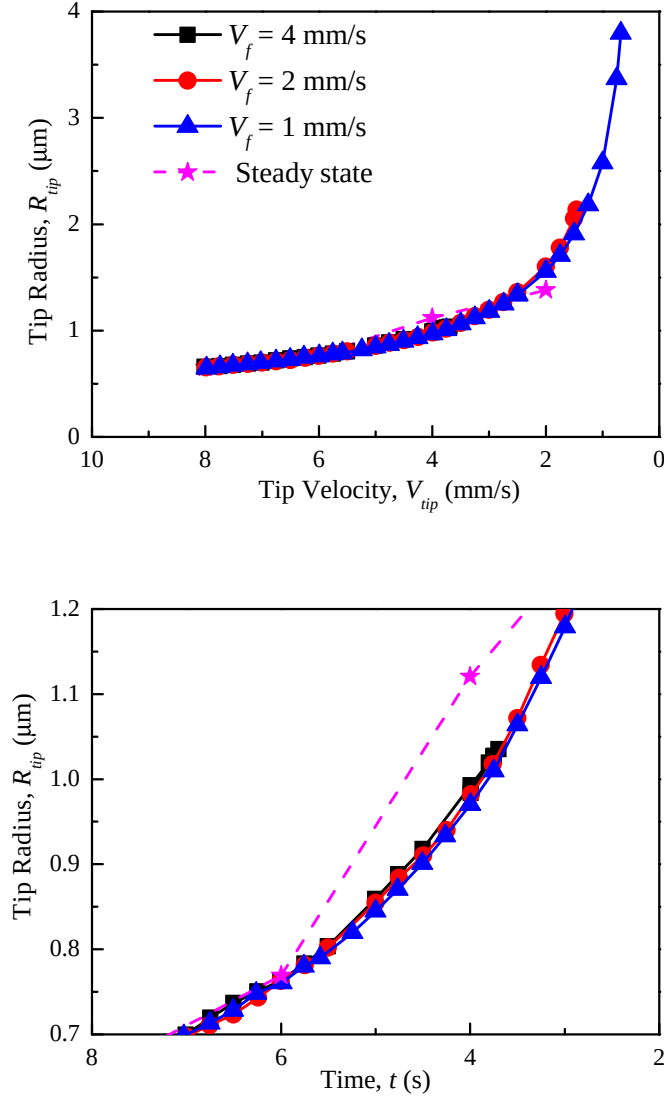


Figure 6.3: (a) Reaction of the tip radius to the tip velocity under the transient condition for various V_f , and (b) the magnification of the figure (a).

It can also be seen that the plots of R_{tip} VS. V_{tip} at the end stage for $V_f = 2$ mm and $V_f = 1$ mm is almost vertical to the x-axis, indicating sharp increase in tip radius during that period. This leads to the R_{tip} under transient condition is larger than its corresponding. This is probably due to the selection of the primary spacing in the simulations. The lower limit of the primary spacing λ_{lower} is increased with the velocity [4,30,31]. If the assumed λ_1 is smaller than the lower limit, i.e. $\lambda_1 < \lambda_{lower}$,

then there is not room for the solute near the tip to be rejected to the boundary and the accumulation of solute near the tip would lead to the sharp increase in radius. In the simulation, the assumed λ_1 was maintained the same although the decrease in V_{tip} and may become lower when V_{tip} was decreased to a point. From the Figure 6.3, the assumed primary spacing was not proper when $V_{tip} < 2.7$ mm/s. If proper R_{tip} was assumed, the R_{tip} under transient condition should be larger than its steady-state corresponding because of the slower reaction which was also found in the experimental observation in Ref. [37].

6.2.2 Primary stalk width

Figure 6.4 shows the morphologies when the growth velocities arrived at the platforms for various V_f shown as black lines. The morphology at the transient point $t = 0.009$ s was also drawn, shown as the red line at each sub-figure for comparison. Looking at any of the morphologies, it can be seen that the primary stalk width (Z_r) slightly increased compared to its starting point during the transient stage. For the newly formed primary stalk, the Z_r gradually increased along the growth direction as a reaction to the decrease in growth velocity. Because the assumed primary spacing kept constant, the increase in primary stalk width would be so large that there was insufficient room for the outgrowth of side branches. As shown in the morphology for $V_f = 2$ mm/s and $V_f = 1$ mm/s, the outgrowth of the side branches were suppressed at the coarse primary stalk.

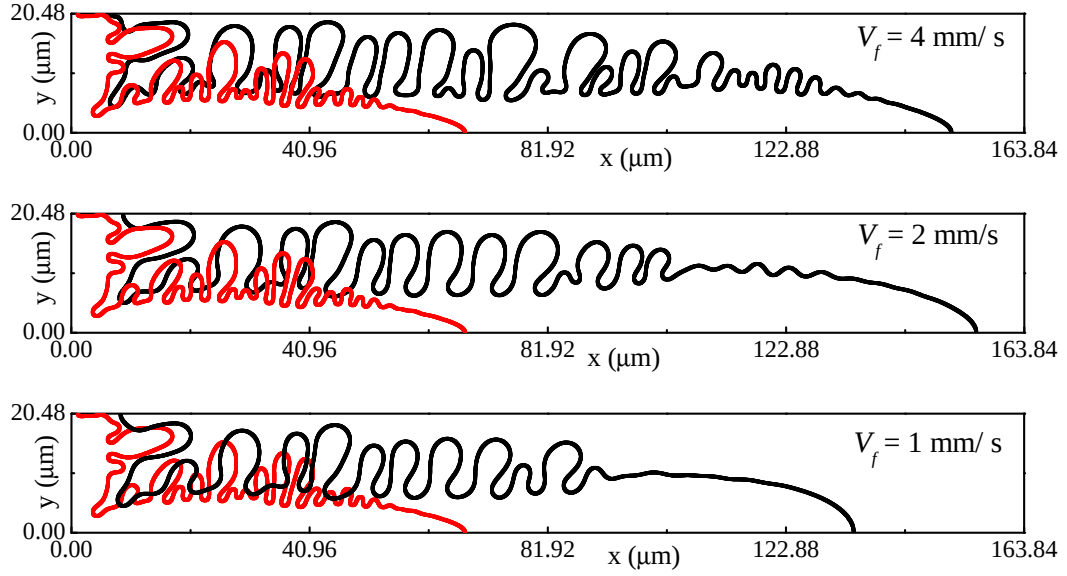


Figure 6.4: Morphologies at the time when the growth velocity arrived at the platform for various V_f comparing with the morphology at the transient point (red line in each figure).

The variation in stalk width Z_r of the formed primary stalk before the transient growth was examined. The measured results of Z_r are shown in Figure 6.5. It was found that the stalk width is the least at the smallest V_f , which is surprisingly opposite to the common sense that the primary stalk width increases with the growth velocity decreasing as indicated by the newly formed stalk in Figure 6.4. This opposition demonstrates that the primary stalk width is highly historical and its length scale is determined by that formed before the transient growth condition.

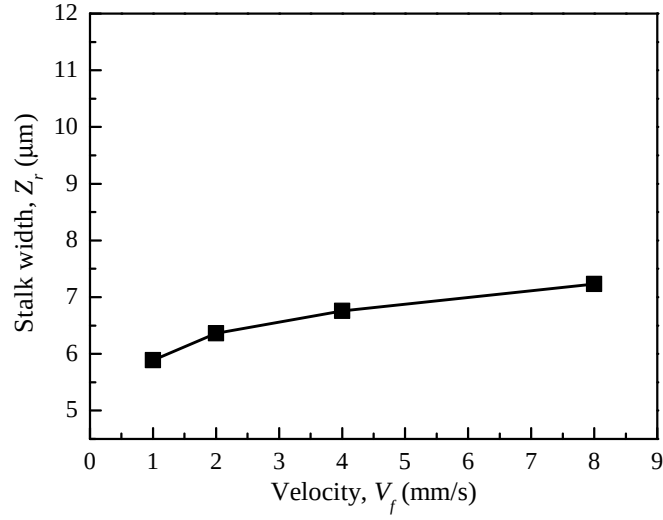


Figure 6.5: Stalk width Z_r of the formed primary stalk after the transient stage.

6.3 Evolution of side branches under transient growth condition

6.3.1 Morphology

Figure 6.6 shows the morphologies after the initial ripening process for various V_f . The morphology of the side branches under steady state, i.e. $V_f = 8$ mm/s, were also shown for comparison. It can be seen that the surviving side branches, marked as numbers, have the same growth orientation, indicating that the similar remelting process happened under the transient growth condition.

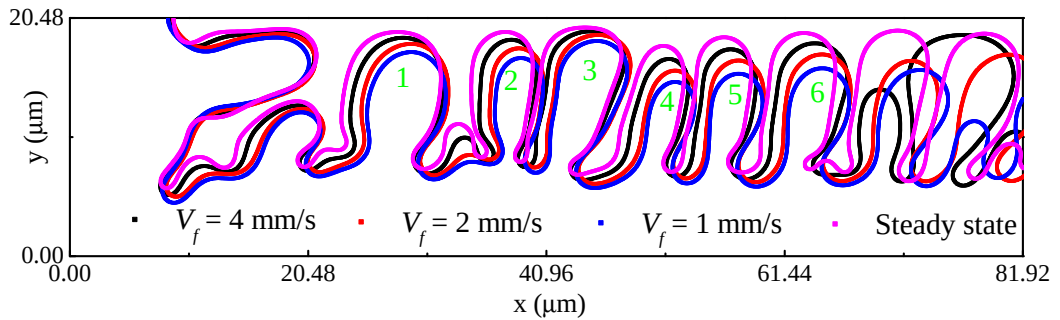


Figure 6.6: Side branches after the initial ripening process for various V_f .

The remelting of the side branches between Side-branch 1 and 2 were tracked when $V_f = 1$ mm/s as shown in Figure 6.7. As observed, the side branches of small sizes between the Side-branch 1 and 2 were remelted, and meanwhile the Side-branches 1 and 2 became coarser whether in the height, half width W_{hf} or the necklace width W_{nc} . Again, the remelting of the side branches starts from the tip while the necklace width increased.

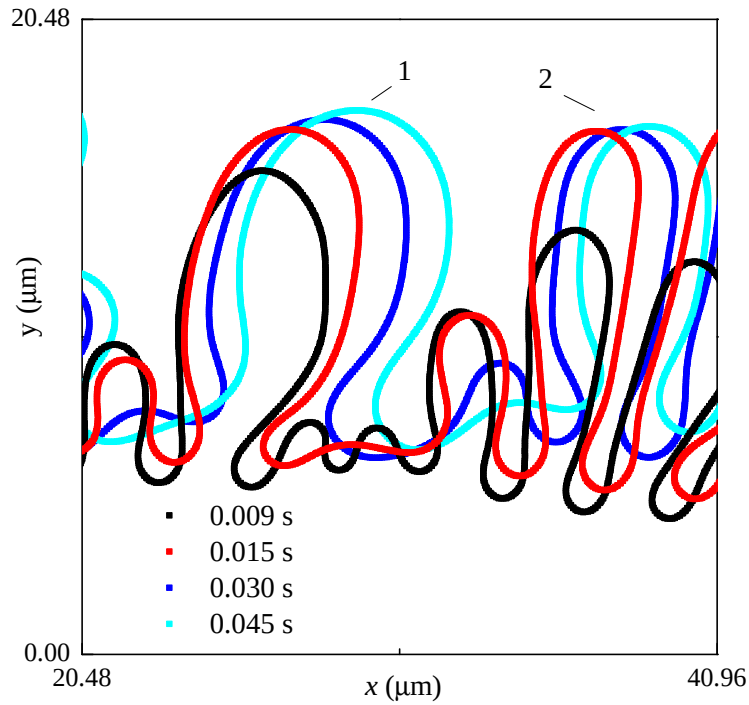


Figure 6.7: Remelting of side branches between Side-branch 1 and 2 under transient growth condition when $V_f = 1$ mm/s.

An interesting phenomenon different from the steady-state evolution lies in the shape of the surviving side branches. The surviving side branches have the trend to be a sphere connected by a fine necklace under the transient growth condition. However, the shape of the side branches through steady state evolution is more like a cylinder where there is a part with almost the same width and the curvature of that part is almost zero. The same spheroidization of the side branches could be found when the evolution of the Side-branch 5 and 6 were tracked, as shown in Figure 6.8.

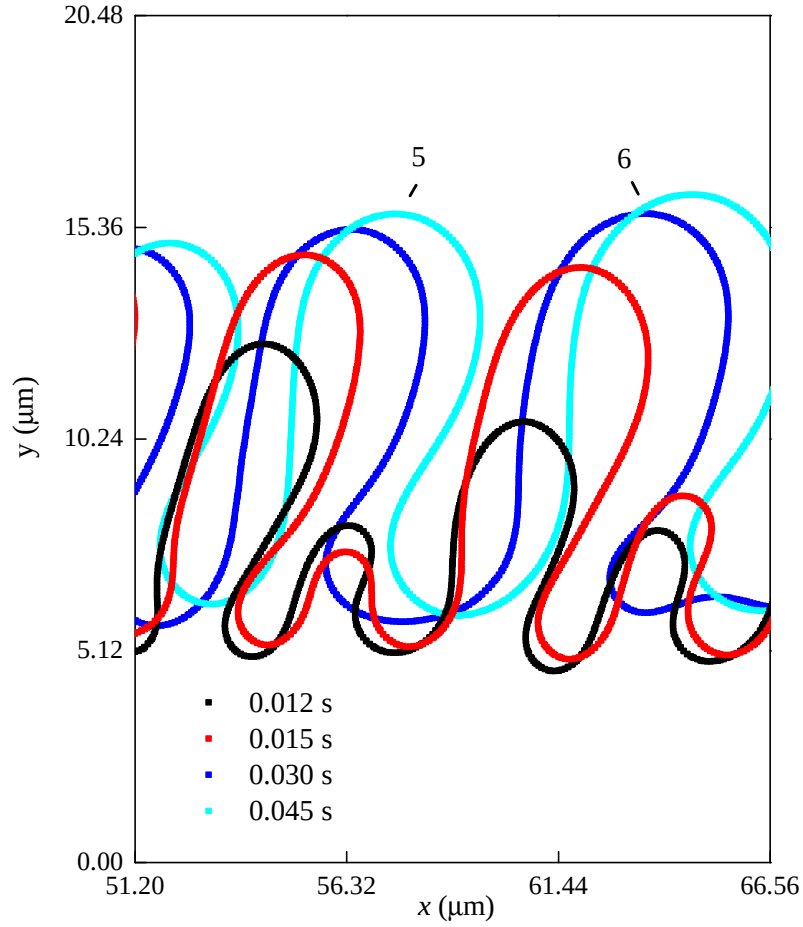


Figure 6.8: Remelting of side branches between Side-branch 5 and 6 under transient growth condition when $V_f = 1$ mm/s.

6.3.2 Solute distribution

Figure 6.9 shows the solute distribution in the liquid surrounding Side-branch 1 and 2 during the remelting of the smaller side branches, i.e. from $t = 0.012$ s to $t = 0.045$ s. In this case, $V_f = 1$ mm/s. Likewise, the solute concentration was higher due to the growth of the Side-branch 1 and 2 during the ripening process. However, it can be noted that the increase in solute concentration became milder under the transient growth condition, indicating that less solute was rejected during the coarsening of the side branches. In such a short time iteration and short offset along x-axis, it could be supposed that the environmental temperature is the same under any

condition. According to the Gibbs-Thomson relation, to keep local equilibrium at the S/L interface, the S/L interface at the side branch side needed to be more curved compared to that under the steady state, as observed in Figure 6.6 that the side branches were more like a sphere.

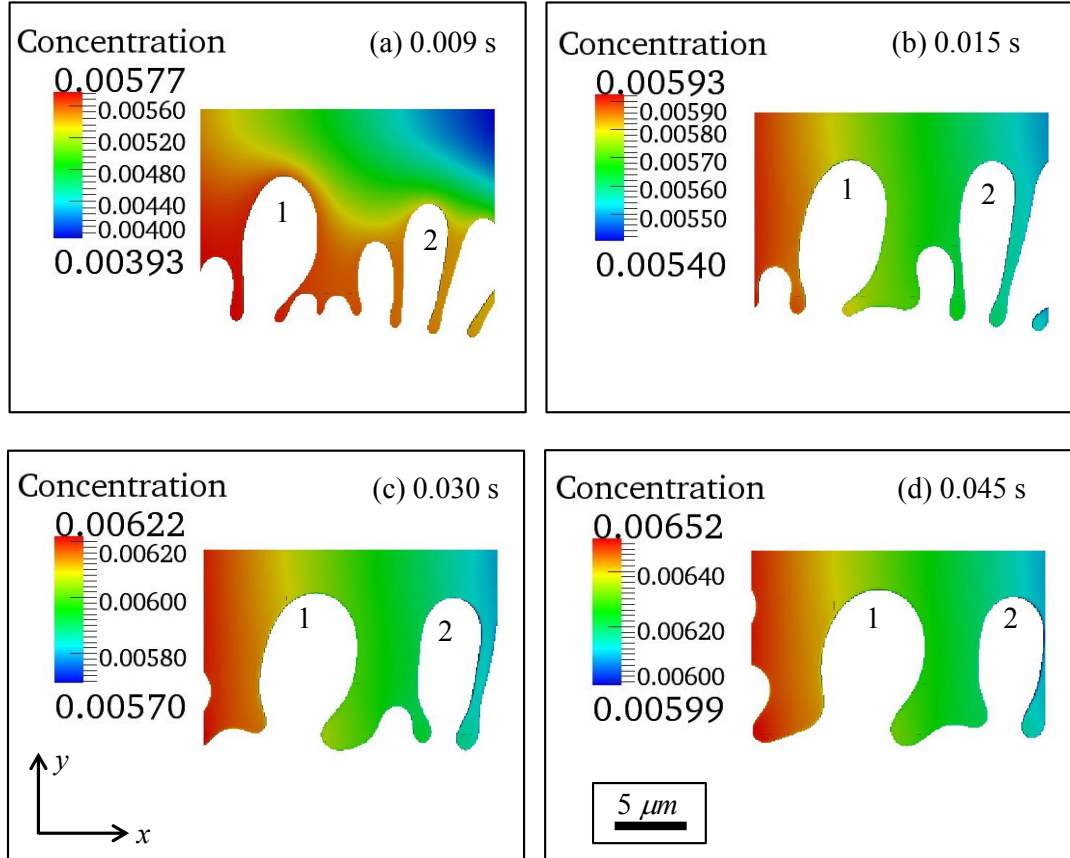


Figure 6.9: Solute distribution surrounding Side-branch 1 and 2 during the initial ripening process when $V_f = 1 \text{ mm/s}$.

Figure 6.10 gave a comparison of the solute distribution after the smaller side branches between Side-branch 1 and 2 were remelted under different conditions. It can be seen that the more change in the solidification condition, i.e. the growth velocity in this study, the less solute concentration around the side branches.

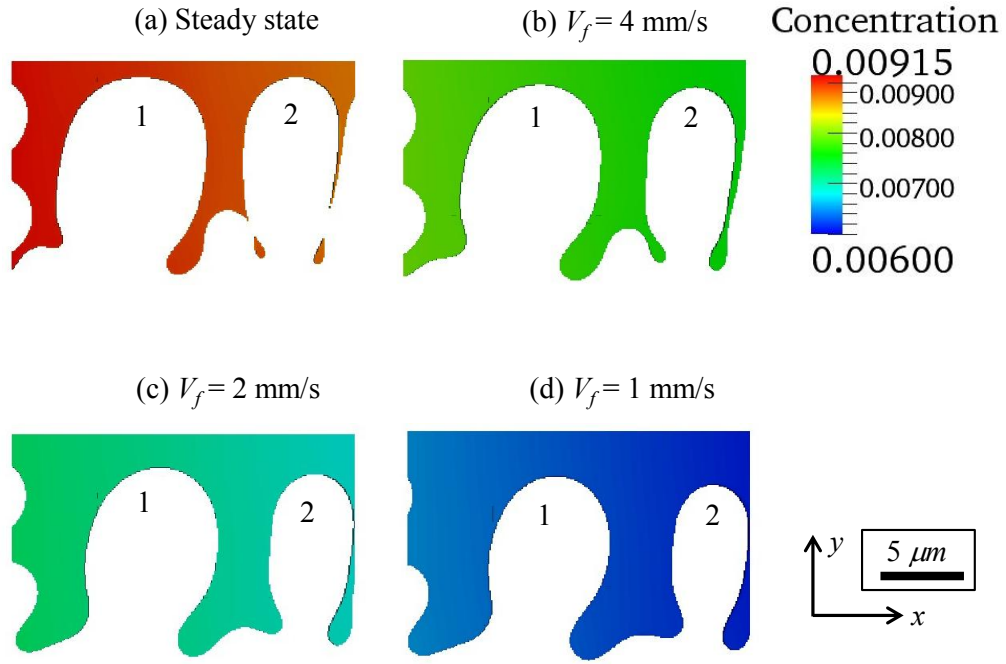


Figure 6.10: Solute distribution surrounding Side-branch 1 and 2 during the initial ripening process for various V_f .

6.3.3 Necklace width

The necklace width (W_{nc}) and the side branch width (W_{hf}) were measured, and the results are shown in Figure 6.11. It can be seen that W_{nc} and W_{hf} under the transient growth condition are smaller than those of their counterparts under steady state. Furthermore, with the decrease in V_f , W_{nc} and W_{hf} decreased. The ratio of W_{hf} to W_{nc} was calculated as shown in Figure 6.11c. Although both the W_{nc} and W_{hf} decreased, however, the ratio of W_{hf} to W_{nc} is increased which means the necklace of the side branches become more finer under the transient growth condition. The detachment of the side branches would be more likely to happen under the same stress.

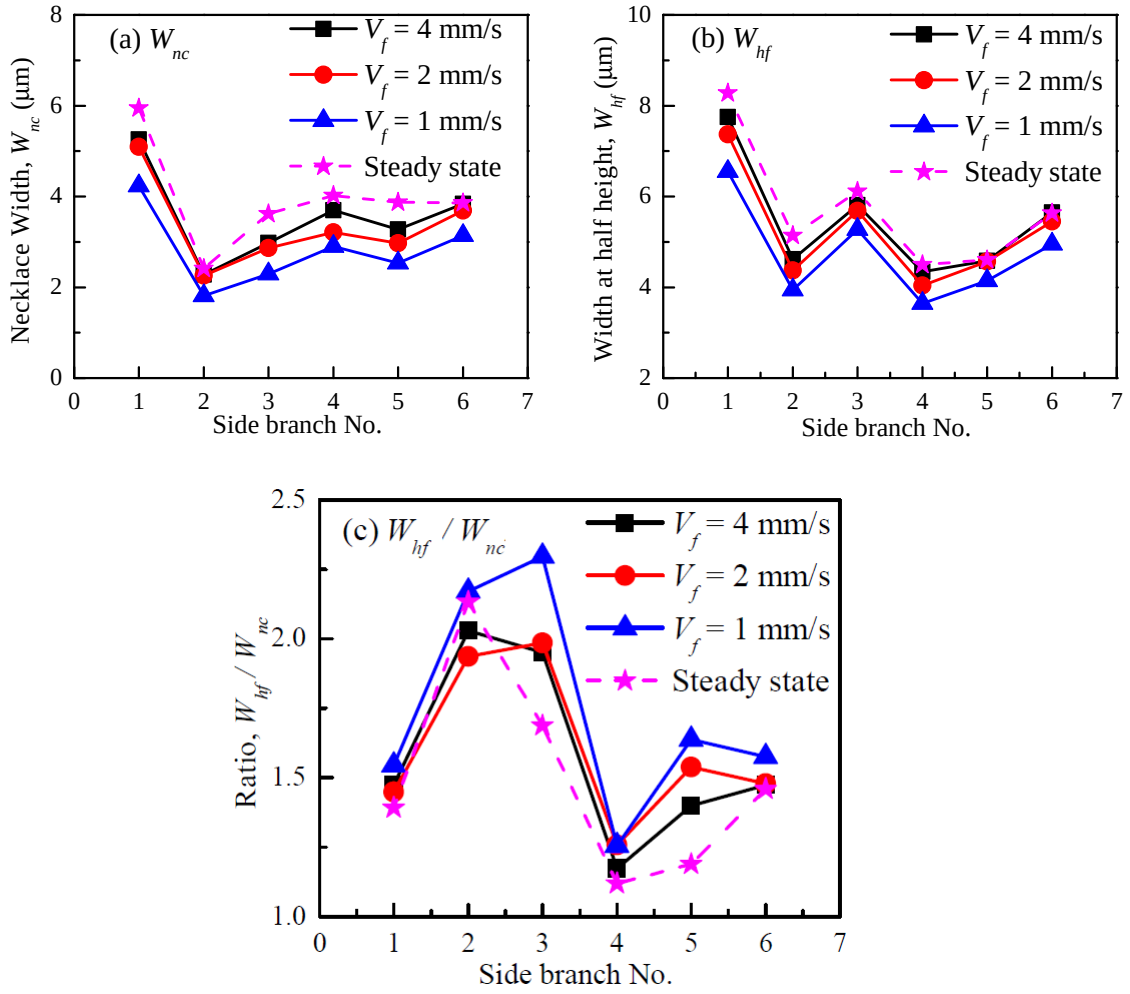


Figure 6.11: The necklace width (W_{nc}), the side branch width (W_{hf}) and the ratio of W_{hf} to W_{nc} after the initial ripening process under the transient growth condition.

6.4 A proposal: The reflection of the side branches to the stalk tip

As the above results shown, the side branches growing out under the transient growth conditions are finer with a finer necklace connected to the primary stalk, implying that it is more likely for the detachment happening. Lu *et al* [37] reported that detachments happened under the transient directional solidification condition by decelerating the pulling velocity after the dendritic growth arrived steady state. They supposed a mechanism for it; in this supposed mechanism, they thought the

primary stalk width kept constant reacting to the variation in condition and therefore the solute concentration was thought to become higher, leading to the remelting at the necklace. However, they did not measure the primary stalk width and checked the solute concentration in their study. In our results, we confirmed that the primary stalk width slightly changed during the evolution similar as their guess. Difference is that the solute concentration was found to be lower than that under the steady state. The necklace width is determined by the curvatures of the parts of the side branches, which should follow the Gibbs-Thomson relation and thus is determined by the solute distribution at the root between the neighbouring side branches. Therefore, we only carefully attributed the variation in side branches in such an aspect: the imposing transient condition on a growing dendrite change the solute distribution around the side branch root and then change the shape and size of the side branches. The variation in the solute distribution around the side branch root is through as a reflection to the stalk tip during the transient growth, we suggest. The schematic of this mechanism is shown in Figure 6.12.

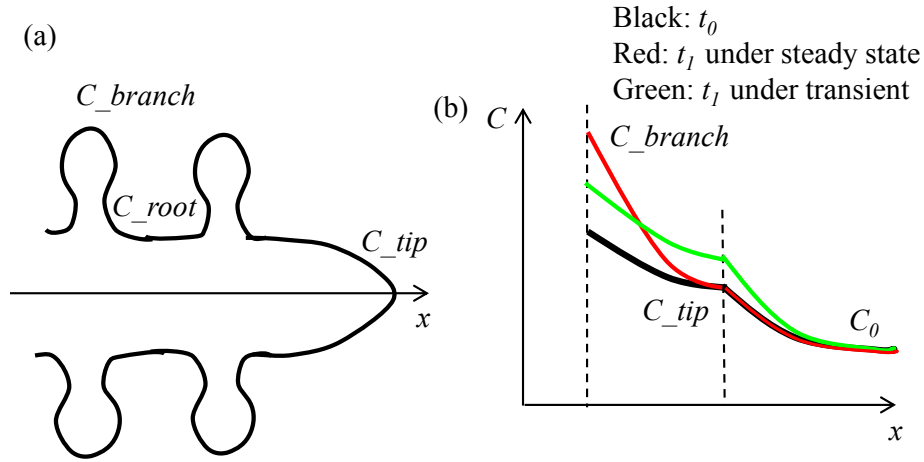


Figure 6.12: Schematic of solute diffusion crossing from the tip to the side branches under steady-state and transient growth conditions, showing the reflection of the side branches to the stalk tip during the transient growth in terms of solute distribution.

As shown in Figure 6.12a, a simple model of a dendrite is considered, which consists of a primary stalk and two side branches providing a root region between the side branches. Then, the solute concentration involve: the solute concentration around the side branch tip C_branch , the solute concentration at the root C_root , and the solute concentration around the stalk tip C_tip . Supposing at an initial directional solidification condition with initial velocity $V_p = V_0$, for example in this study $V_0 = 8\text{mm/s}$, the steady state just arrives at time $t = t_0$. Figure 6.12b shows a schematic of the solute concentrations at time $t = t_0$ (black line) and $C_branch > C_tip$ was plotted based on the observation in the figures showing the solute distribution in Chapter 5 and this chapter, such as Figure 5.10. Then solute diffuses from the side branches to the tip, driving the growth of the side branches. Then, the rejected solute will accumulate at the root, leading to the increase in C_root .

Under the steady-state growth, as shown in Chapter 5, the tip regions are of

the same morphology with a constant tip radius, indicating that the concentration around the tip is constant upon the steady-state evolution, as shown in 6.12b. The constant solute concentration around the tip region is confirmed and calculated by Hunt *et al* [4,27,29–32]. The C_{branch} increases due to the solute rejection because of the growth of the side branches. However, if the tip velocity decreased under the transient growth, as shown in Figure 6.4, the primary stalk and tip radius increased, leading to the increase in C_{tip} . Then the solute gradient between the side branches and the tip decreases, which results in the slower growth of the side branches. As observed in Figure 6.6, the heights of the side branches under the transient growth condition are lower than those under the steady state growth condition. The slower growth of the side branches would lead to less solute rejected and further decreased the diffusion between the side branches and the dendrite tip. Less solute rejected means less solutes would accumulate at the roots, i.e. smaller C_{root} , as shown in Figure 6.10. This variation in C_{root} shall have an effect on the shape and size of the side branches. As observed, the shape of the side branches is more like sphere and the necklace width is finer.

As the proposed mechanism, the stalk tip of a dendrite reacts to the variation in solidification condition, such as the variation in growth velocity in this study, and then the thermal gradient between the tip and side branches varies leading to a reflection of the side branches in the solute distribution at the root and thus the shape and size.

6.5 Conclusions

The evolution of the dendrite under the transient condition was investigated and compared with that under the steady state. It was found that

- (1) The primary stalk reacts slowly to the tip velocity; the tip radius is smaller than that of the steady state under the same velocity. Meanwhile, the stalk

width only has a slight variation.

- (2) The side branches has the trend to be a sphere under the transient growth condition compared to a cylinder under the steady state during the ripening process. Solute concentration is much lower at the side branch roots under the transient growth condition.
- (3) The necklaces of the side branches are finer compared to those under the steady state and the ratio of the necklace to the width of the side branches decreases. It implies that it is more likely for the occurrence of the detachment due to the mechanical failure.
- (4) It is proposed that the variation in the side branches is attributed to their reflection to the variation in dendrite tip with the growth velocity changing during the dendritic growth.

CHAPTER SEVEN

Extending Karma's PF Model to Ternary Alloys Including the Solid Diffusivity

A ternary model is needed for simulating the dendritic growth in Fe-C-Mn alloys. In this chapter, a quantitative thin-interface PF model for ternary alloy solidification is developed based on the binary alloy thin-interface PF model proposed by Karma *et al* [66]. In the proposed ternary model, the schemes of the thin-interface limit analysis and the anti-trapping current in Karma's PF model were adopted, promising the calculation accuracy and efficiency simultaneously. Furthermore, OM scheme to include the solid diffusivity was used to include the solid diffusivity of each solute. The validation in this chapter shows that this model can lead to creditable results and have good convergence behaviour.

7.1 Introduction

Basically there are two types of thin-interface PF models according to the interface constructions. The above mentioned Karma's thin-interface PF models [61–66] belong to one type. The schematic of the S/L interface construction is shown as Figure 7.1a. In these models, the interface is treated as a field with a composition C (Eq. (i)) and thus the Gibbs free energy of the entire solidification domain depends on the only composition variable C (Eq.(ii)), which can be directly obtained by solving the solute diffusion equation.

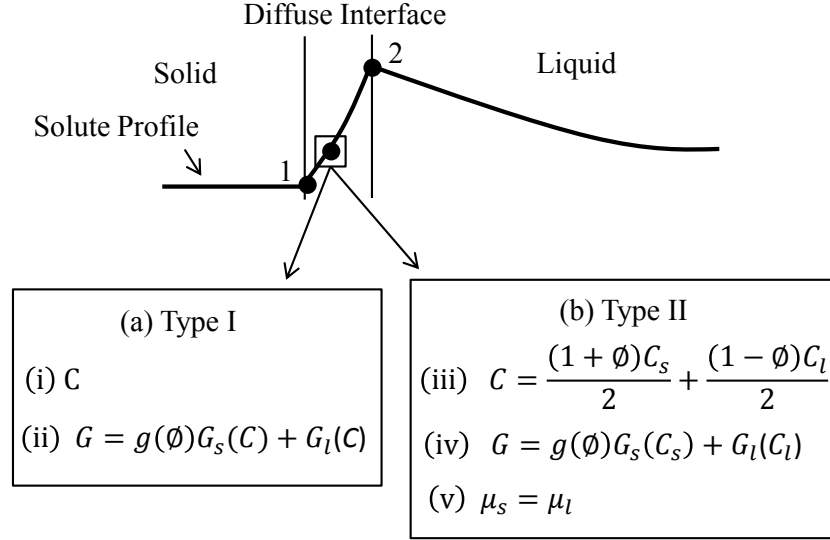


Figure 7.1: Schematic of the two types of the available thin-interface PF models

Another type is used in Steinbach's [67,68] and Kim's [70–73] PF models with the schematic shown in Figure 7.1b. By contrast, the interface in these models is constructed as a mixture of the co-existent solid and liquid phases, with the compositions C_s and C_l respectively. The overall composition (C) at the interface field is interpolated between C_s and C_l , as shown in Eq. (i). Thus the Gibbs free energy at the entire solidification domain, interpolated between the Gibbs free energy in solid (G_s) and liquid (G_l), is dependent on two composition variables C_s and C_l , as shown in Eq. (iv). The concern is that C_s and C_l could not be directly obtained by solving the solute diffusion equation, which is different from the Type I. To obtain C_s and C_l , the chemical potentials are assumed equal in the mixing solid and liquid at any point of the interface (Eq. (v)). It should be noted that this assumption is different from the thermodynamic equilibrium condition. Under the thermodynamic equilibrium, equal chemical potentials are achieved between the solid side (point1) and the liquid side (point 2) of the S/L interface. For this reason, the assumption (Eq. (ii)) in Steinbach's scheme is termed as quasiequilibrium condition. By combining Eq. (iii) and Eq. (v) in Figure 7.1, C_s and C_l can be obtained after solving the solute diffusion equation.

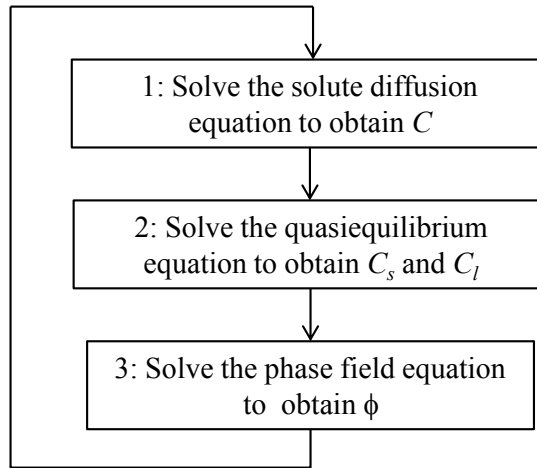


Figure 7.2: Flow chart for the models of Type II

Figure 7.2 gives the flow chart for PF models of Type II. At each time step, the step of solving the quasiequilibrium equations is necessary before solving the phase field equation. The models of this type have been available for ternary, multi-component or even for multi-phase systems. However, the step 2 shall increase the calculation cost, particularly for ternary or multi-component alloys, because the number of quasiequilibrium equations increases with the number of the components in the alloy system.

The models of Type I, e.g. Karma's model, can skip this step, and however these models are only limited to pure and binary alloy systems. Extension of these models is needed and in our work we successfully extend it to multi-component alloys which will be presented in this chapter.

The structure of this chapter is as follows. The sharp-interface model for multi-component alloys was firstly derived in Section 7.2. The governing equations of the extended ternary model was derived in Section 7.3, followed by the thin-interface limit analysis to define the phase field parameters and the anti-trapping current in Section 7.4. To be simplified, zero solid diffusivity, i.e. $D_s = 0$, was assumed in the thin-interface limit analysis, and thus next in Section 7.5 the inclusion of the solid diffusivity was realized by adopting the Ohno and Matsuura's scheme [92] which

has been evaluated in Chapter 3. The proposed ternary model was validated in Section 7.6 followed by the conclusions of the chapter.

7.2 Sharp-interface model for multi-component alloys

Gibbs-Thomson relation and the mass conservation equation govern the S/L evolution during solid growth. In Chapter 1, the Gibbs-Thomson relation for binary alloys was presented and here we will derive the Gibbs-Thomson relation for multi-component alloys. The interface temperature T_l^0 is expressed as

$$T_l^0 = T_m + \sum_{i=1}^n m_i C_{il}^* - \Gamma_{sl} \kappa - \frac{1}{\mu_k} V_n \quad (7.1)$$

where C_{il}^* is the composition at the interface in the liquid side, m_i the liquidus slope of solute i , Γ_{sl} the Gibbs-Thomson coefficient, κ the curvature, μ_k the kinetic coefficient and V_n the growth velocity of the S/L interface. Eq. (7.1) is a comprehensive consideration of constitutional undercooling (second term of the right hand side (RHS)), curvature undercooling (the third term of RHS) and kinetic undercooling (the last term of RHS). Eq. (7.2) is also established according to the equilibrium phase diagram

$$T_l^0 = T_m + \sum_{i=1}^n m_i C_{il}^0 \quad (7.2)$$

where C_{il}^0 is the equilibrium composition at the temperature T_l^0 .

Therefore, combining Eq. (7.1) with Eq. (7.2) gives

$$\sum_{i=1}^n |m_i| (C_{il}^* - C_{il}^0) = -\Gamma_{sl} \kappa - \frac{1}{\mu_k} V_n \quad (7.3)$$

Define solutal capillary length as $d_i = \frac{\Gamma_{sl}}{|m_i| C_{il}^0 (1 - k_i^e)}$ and then $\frac{d_i}{d_1} = \frac{|m_1| C_{1l}^0 (1 - k_1^e)}{|m_i| C_{il}^0 (1 - k_i^e)}$.

Divide both sides of Eq. (7.3) by $|m_1| C_{1l}^0 (1 - k_1^e)$ and Eq. (7.3) becomes

$$\sum_{i=1}^n \frac{C_{il}^* - C_{il}^0}{C_{il}^0 (1 - k_i^e)} \frac{d_1}{d_i} = - \frac{\Gamma_{sl}}{|m_1| C_{1l}^0 (1 - k_1^e)} \kappa - \frac{\frac{1}{\mu_k}}{|m_1| C_{1l}^0 (1 - k_1^e)} V_n \quad (7.4)$$

The supersaturation are next defined as $U_i = \frac{C_{il} - C_{il}^0}{C_{il}^0 (1 - k_i^e)}$; at the liquid side of the interface $U_i|^{+} = \frac{C_{il}^* - C_{il}^0}{C_{il}^0 (1 - k_i^e)}$. Then the Eq. (7.4) can be written as

$$\sum_{i=1}^n U_i|^{+} \frac{d_1}{d_i} = -d_1 \kappa - \beta V_n \quad (7.5)$$

with $\beta = \frac{\frac{1}{\mu_k}}{|m_1| C_{1l}^0 (1 - k_1^e)}$. Eq. (7.5) is the Gibbs-Thomson relation for multi-component alloys. For ternary alloys, it is

$$U_1|^{+} + \frac{d_1}{d_2} U_2|^{+} = -d_1 \kappa - \beta V_n \quad (7.6)$$

The mass conservation equation excluding the solute diffusion in the solid is

$$[1 + (1 - k_i^e) U_i|^{+}] V_n = -D_{il} \partial_n U_i|^{+} \quad (7.7)$$

where D_{il} is the liquid diffusivity of solute i . It can be noted in Eq. (7.7) that only self-diffusivity is considered and the interactive diffusion is not included.

7.3 Our extension to ternary with D_s

The extension includes two aspects: (1) governing equation derivation and (2) thin-interface analysis. Equation derivation will be described in this section while thin-interface analysis will be presented in Section 7.4. In the multi-component alloy system, it contains $(n+1)$ elements and the $(n+1)$ th component is the solvent; $n=1$ for binary alloys, and $n=2$ for ternary alloys.

7.3.1 Phenomenological free energy of the system

ϕ is the phase field variable; $\phi = +1$ in solid, $\phi = -1$ in liquid, and changes from +1 to -1 across S/L interface. The evolution equation of phase field with time t is

$$\frac{\partial \phi}{\partial t} = -K_\phi \frac{\delta F}{\delta \phi} \quad (7.8)$$

where K_ϕ is a temperature-dependent kinetic constant and $F(C_i, \phi, T)$ is the phenomenological free energy of the system. To obtain the evolution equation of the phase field according Eq. (7.8), the expression of $F(C_i, \phi, T)$ is firstly derived in this part.

$F(C_i, \phi, T)$ is contributed by three parts: (1) the interface gradient energy $\frac{\sigma}{2} |\nabla \phi|^2$, (2) the double-well potential $H(-\phi^2/2 + \phi^4/4)$, and (3) the Gibbs free energies of the liquid and solid phases $f(C_i, \phi, T)$. $F(C_i, \phi, T)$ is given by

$$F = \int_{dV} \left[\frac{\sigma}{2} |\nabla \phi|^2 + H(-\phi^2/2 + \phi^4/4) + f(C_i, \phi, T) \right] \quad (7.9)$$

For dilute multi-component alloys, $f_v(C_{iv}, T)$ of a single phase ($i = l$ for liquid and $i = s$ for solid) is

$$f_v(C_{iv}, T) = f_v^A(T_m) - s_v(T - T_m) + \frac{RT}{v_0} \sum_{i=1}^n (C_{iv} \ln C_{iv} - C_{iv}) + \sum_{i=1}^n \varepsilon_{iv} C_{iv} \quad (7.10)$$

where $f_v^A(T_m)$ is the Gibbs free energy of pure A at melting temperature T_m ; $s_v = -\partial f_v^A / \partial T$ is the entropy density of the S/L at T_m in the state of phase v , $\varepsilon_{iv} C_{iv}$ is the change of internal energy density because of the addition of the solute i with ε_{iv} the enthalpy. According to the thermodynamics, the Gibbs free energy of pure A in the solid is equal to that in the liquid at the equilibrium melting point, i.e. $f_s^A(T_m) = f_l^A(T_m) = f^A(T_m)$.

At the equilibrium, it has

$$\frac{\partial f_l(C_{il}, T)}{\partial C_{il}}|_{C_{il}^e} = \frac{\partial f_s(C_{is}, T)}{\partial C_{is}}|_{C_{is}^e} = \mu_i^e(T) \quad (7.11)$$

where C_{is}^e and C_{il}^e are the equilibrium compositions in solid and liquid at certain temperature T . μ_i^e is the equilibrium chemical potential. In a multi-component system, C_{is}^e , C_{il}^e and μ_i^e are not only dependent on the temperature but also depend on the system composition C_{i0} , which is different from that in binary system,. However, note that under certain system with composition C_{i0} , those three variables are determined by the operating temperature. For dilute alloy system, the equilibrium coefficient is constant, given by

$$k_i^e = \exp\left(-\frac{v_0 \Delta \varepsilon_i}{RT_m}\right) \quad (7.12)$$

where $\Delta \varepsilon_i = \varepsilon_{is} - \varepsilon_{il}$. Furthermore, the liquidus slope m_i can be calculated based on the equation expressed as

$$\frac{L}{T_m}(T - T_m) \frac{v_0}{RT_m} = -\sum_{i=1}^n (1 - k_i^e) C_{il}^e \quad (7.13)$$

where $L = T_m(s_l - s_s)$ is the latent heat during the solidification.

The Gibbs free energy ($f(C_i, \phi, T)$) through the entire solidification domain in Eq. (7.9) is

$$f(C_i, \phi, T) = f^A(T_m) - s(\phi)(T - T_m) + \frac{RT}{v_0} \sum_{i=1}^n (C_i \ln C_i - C_i) + \sum_{i=1}^n \varepsilon_i(\phi) C_i \quad (7.14)$$

where $s(\phi)$ and $\varepsilon_i(\phi)$ are the functions interpolated between the corresponding functions of the bulk phases, given by

$$s(\phi) = \frac{s_s + s_l}{2} + \frac{s_s - s_l}{2} \tilde{g}(\phi); \quad \varepsilon_i(\phi) = \frac{\varepsilon_s + \varepsilon_l}{2} + \frac{\varepsilon_{is} - \varepsilon_{il}}{2} \bar{g}_i(\phi) \quad (7.15)$$

with $\tilde{g}(\phi)$ and $\bar{g}_i(\phi)$ the interpolation functions. To ensure that Gibbs free energy $f_c(C_i, \phi, T)$ is equal to $f_l(C_i, T)$ in liquid ($\phi = -1$) and $f_s(C_i, T)$ in solid ($\phi = +1$), it requires that that $\tilde{g}(\pm 1) = \pm 1$ and $\bar{g}_i(\pm 1) = \pm 1$.

7.3.2 Solution of the stationary equilibrium

Supposing that the phase field and the solute field in one dimension are $\phi_0(x)$ and $C_{i0}(x)$ at the stationary equilibrium,, they should satisfy

$$\frac{\partial F}{\partial C_i} = \mu_i^e(T) \quad (7.16)$$

$$\frac{\delta F}{\delta \phi} = 0 \quad (7.17)$$

Combining Eq. (7.11) with Eq. (7.16) gives

$$\frac{C_{i0}}{C_{il}^e} = \exp \left[(\ln k_i^e) \frac{1 + \bar{g}_i(\phi_0)}{2} \right] = (k_i^e)^{\frac{1 + \bar{g}_i(\phi_0)}{2}} \quad (7.18)$$

Substituting the expression of phenomenological free energy given in the previous part into Eq. (7.17), Eq. (7.17) becomes

$$\sigma \frac{d^2 \phi_0}{dx^2} + H(\phi_0 - \phi_0^3) = -\frac{RT_m}{2v_0} \sum_{i=1}^n C_{il}^e \left[\tilde{g}'(\phi_0) (1 - k_i^e) + (k_i^e)^{\frac{1 + \bar{g}_i(\phi_0)}{2}} (\ln k_i^e) \bar{g}_i'(\phi_0) \right] \quad (7.19)$$

To simplify the above equation, we force its right hand side to be zero by valuing

$$\tilde{g}'(\phi_0) (1 - k_i^e) + (k_i^e)^{\frac{1 + \bar{g}_i(\phi_0)}{2}} (\ln k_i^e) \bar{g}_i'(\phi_0) = 0 \quad (7.20)$$

which means the two interpolations introduced to describe the Gibbs free energy for the entire solidification domain is not independent. Eq. (7.20) gives

$$\bar{g}_i(\phi) = \frac{2}{\ln k_i^e} \ln \left(\frac{1 + k_i^e - (1 - k_i^e) \tilde{g}(\phi)}{2} \right) - 1 \quad (7.21)$$

When Eq. (7.21) is satisfied, according to Eq. (7.16) and Eq. (7.17), it is drawn out

$$C_{i0} = \frac{C_{il}^e + C_{is}^e}{2} + \frac{\tilde{g}(\phi_0)(C_{is}^e - C_{il}^e)}{2} \quad (7.22)$$

$$\phi_0 = -\tanh\left[x/\sqrt{2}w\right] \quad (7.23)$$

with the interface width $w = (\sigma/H)^{1/2}$. Eq. (7.22) clearly shows that the equilibrium concentration across the entire system is interpolated between those in solid and liquid phases. The interfacial energy is $\gamma_{sl} = IwH$ with I further defined as below.

7.3.3 Dimensionless variable u_i defined for concentration C_i

The driving force for solidification is undercooling or the chemical potential deviation from the equilibrium one $\mu_i^e(T, C_{i0})$. To measure the departure of chemical potential (μ_i) of solute i from the equilibrium one $\mu_i^e(T_l^0, C_{i0})$ at the reference temperature T_l^0 , dimensionless variable μ_i is introduced, defined as

$$u_i = \frac{v_0}{RT_m} (\mu_i - \mu_i^e(T_l^0)) \quad (7.24)$$

Combining with Eq. (7.10) and Eq. (7.14), Eq. (7.24) becomes

$$u_i = \ln \frac{2C_i}{C_{il}^0 [1 + k_i^e - (1 - k_i^e) \tilde{g}(\phi)]} \quad (7.25)$$

Using the nonvariational scheme, Eq. (7.25) is modified into

$$u_i = \ln \frac{2C_i}{C_{il}^0 [1 + k_i^e - (1 - k_i^e) h(\phi)]} \quad (7.26)$$

Combining Eq. (7.14), Eq. (7.21) with Eq. (7.24), the formula of $\frac{\partial f}{\partial \phi}$ is then expressed as

$$\frac{\partial f}{\partial \phi} = \frac{RT_m}{2Hv_0} \tilde{g}'(\phi) \sum_{i=1}^n (1 - k_i^e) C_{il}^0 \left(e^{u_i} - 1 - \frac{C_{il}^e - C_{il}^0}{C_{il}^0} \right) \quad (7.27)$$

7.3.4 Phase field equation

The governing equations consist of phase field equation and the solute diffusion equation of each solute. Having Eq. (7.9) and Eq. (7.27), the phase field equation Eq. (7.8) becomes

$$\tau \frac{\partial \phi}{\partial t} = w^2 \nabla^2 \phi + \phi - \phi^3 - \sum_{i=1}^n \tilde{\lambda}_i \frac{\tilde{g}'(\phi)}{1 - k_i^e} \left(e^{u_i} - 1 - \frac{C_{il}^e - C_{il}^0}{C_{il}^0} \right) \quad (7.28)$$

where $w = \left(\frac{\sigma}{H}\right)^{1/2}$, $\tau = \frac{1}{K_\phi H}$, and $\tilde{\lambda}_i = \frac{RT_m(1-k_i^e)^2 C_{il}^0}{2v_0 H}$. Defining $\lambda_i = \frac{15}{8} \tilde{\lambda}_i$ and $g(\phi) = \frac{8}{15} \tilde{g}(\phi) = \phi - \frac{2}{3} \phi^3 + \frac{1}{5} \phi^5$, the Eq. (7.28) becomes

$$\tau \frac{\partial \phi}{\partial t} = w^2 \nabla^2 \phi + \phi - \phi^3 - \sum_{i=1}^n \lambda_i \frac{g'(\phi)}{1 - k_i^e} \left(e^{u_i} - 1 - \frac{C_{il}^e - C_{il}^0}{C_{il}^0} \right) \quad (7.29)$$

Eq. (7.29) is the phase field equation for multi-component alloys. Comparing with the phase-field model for dilute binary alloys presented in Chapter 2, the difference lies in the last term of the right-hand side which indicates the driving force of the solid growth, i.e. the undercooling during solidification. For the multi-component system, this term is an integrated effect of all the solutes, as shown in Eq. (7.29), which reflects that the undercooling is contributed by the addition of all the solutes. It also can be seen that this equation can be reduced to the binary one [66] when $i = 1$.

7.3.5 Solute diffusion equations

The solute diffusion equation is

$$\frac{\partial C_i}{\partial t} = \nabla \cdot (D_{ii} \tilde{q}(\phi) \nabla C) - j_{at} \quad (7.30)$$

Note the interaction of the diffusion between solutes is not considered and thus Eq. (7.30) has the same expression of the diffusion equation of solute in binary

alloys. An anti-trapping current j_{at} is introduced to the diffusion equation to reduce the artificial solute trapping as that in the binary model proposal by Karma, and it is given by

$$j_{at} = a(\phi) w(1 - k_i^e) C_{il}^0 e^{u_i} \frac{\partial \phi}{\partial t} \frac{\nabla \phi}{|\nabla \phi|} \quad (7.31)$$

As derived above, sets of Eq. (7.29) and Eq. (7.30) are the governing equations for the multi-component alloy solidification and for ternary alloy $i = 2$. In the governing equations, phase-field parameters (e.g. w) and functions (e.g. $a(\phi)$) need to be defined to complete this ternary PF model, which is presented in the following section.

7.4 Thin-interface limit analysis

In this section the thin-interface limit analysis will be presented as follows: (1) Dimensionless PF and sharp-interface models in curvilinear coordinate system; (2) Matching conditions in curvilinear coordinate system; and (3) Solving the phase field equation and the solute diffusion equation in the inner region during which the phase-field parameters and the interpolated functions will be defined.

7.4.1 Dimensionless PF and sharp-interface models in curvilinear coordinate

Defining $U_i = \frac{e^{u_i} - 1}{1 - k_i^e}$ and $q(\phi) = \tilde{q}(\phi) \frac{1 + k_i^e - (1 - k_i^e)h(\phi)}{2}$ and measuring length in the unit of d_1 and the time in d_1^2/D_{1l} , the non-dimensionalisation of PF model for ternary alloy is

$$\alpha \varepsilon^2 \partial_t \phi = \varepsilon^2 \nabla^2 \phi + \phi - \phi^2 - g'(\phi) \alpha_1 \varepsilon \left(U_1 + \frac{d_1}{d_2} U_2 \right) \quad (7.32)$$

$$\begin{aligned} \left[\frac{1 + k_i^e}{2} - \frac{1 - k_i^e}{2} h(\phi) \right] \partial_t U_i &= \nabla \cdot \left\{ \frac{D_{il}}{D_{1l}} q(\phi) \nabla U_i + \varepsilon a(\phi) [1 + (1 - k_i^e) U_i] \partial_t \phi \frac{\nabla \phi}{|\nabla \phi|} \right\} \\ &+ [1 + (1 - k_i^e) U_i] \frac{1}{2} \partial_t h(\phi) \end{aligned} \quad (7.33)$$

where $\varepsilon = w/d_1$, $\alpha = \tau \frac{D_{1l}}{w^2}$ and $\alpha_1 = \text{frac} \lambda_1 \varepsilon$.

Likewise, the dimensionless form of the sharp-interface model (Eq. (7.6) and Eq. (7.7)) reads,

$$[1 + (1 - k_i^e) U_i]^+ \nu_n = - \frac{D_{il}}{D_{1l}} \partial_n U_i \Big|_+^+ \quad (7.34)$$

$$U_1|^+ + U_2|^+ \frac{d_1}{d_2} = -\tilde{\kappa} - \tilde{\beta} \nu_n \quad (7.35)$$

where $\nu_n = \frac{V_n d_1}{D_{1l}}$, $\tilde{\kappa} = \kappa d_1$ and $\tilde{\beta} = \frac{\beta D_{1l}}{d_1}$.

To solve the phase-field model in the inner region, the curvilinear coordinate (r, s) anchored onto the S/L interface is used. In this system, r measures the length along the normal direction to the interface and s measures the arc length along the interface. r is rescaled by $\eta = \frac{r}{\varepsilon}$ and the PF model in curvilinear coordinate is

$$\begin{aligned} & \partial_{\eta\eta}^2 \phi - f'(\phi) + \varepsilon \left[(\alpha v_n + \tilde{\kappa}) \partial_\eta \phi - \alpha_1 g'(\phi) \left(U_1 + \frac{d_1}{d_2} U_2 \right) \right] \\ & + \varepsilon^2 [\partial_{ss}^2 \phi - \tilde{\kappa}^2 \eta \partial_\eta \phi] = O(\varepsilon^3) \end{aligned} \quad (7.36)$$

$$\begin{aligned} & \varepsilon^{-2} \partial_\eta \left(\frac{D_{il}}{D_{1l}} q(\phi) \partial_\eta U_i \right) + \varepsilon^{-1} \left\{ \left[v_n \left(\frac{1+k_i^e}{2} - \frac{1-k_i^e}{2} h(\phi) \right) + \tilde{\kappa} \frac{D_{il}}{D_{1l}} q(\phi) \right] \partial_\eta U_i \right. \\ & + v_n \partial_\eta (a(\phi) [1 + (1 - k_i^e) U_i]) \partial_\eta \phi - \frac{v_n}{2} [1 + (1 - k_i^e) U_i] \partial_\eta h(\phi) \Big\} \\ & + \varepsilon^0 \left\{ \partial_s \left(\frac{D_{il}}{D_{1l}} q(\phi) \partial_s U_i \right) - \tilde{\kappa}^2 \eta \frac{D_{il}}{D_{1l}} q(\phi) \partial_\eta U_i + \alpha v_n \tilde{\kappa} [1 + (1 - k_i^e) U_i] \partial_\eta \phi \right\} = O(\varepsilon) \end{aligned} \quad (7.37)$$

with $f'(\phi) = \phi - \phi^2$. As can be seen in the above equations, ε is treated as a small expanded parameter.

7.4.2 Matching conditions in curvilinear coordinate system

The interface corresponds to $r \rightarrow \pm 0$ in terms of the outer region and $\eta \rightarrow \pm \infty$ in terms of the inner region where $+$ means the interface boundary at the liquid side

and $-$ at the solid side. The matching conditions could be expressed as

$$\phi(\eta \rightarrow \pm\infty) = \mp 1 \quad (7.38)$$

$$U_i(\eta \rightarrow \pm\infty) = \tilde{U}_i \Big|^\pm \quad (7.39)$$

A perturbation analysis in power of ε is made in the inner and outer regions, $U_i = U_{i0} + \varepsilon U_{i1} + \varepsilon^2 U_{i2} + O(\varepsilon^2)$ for example. The matching condition in different powers read,

$$\varepsilon^0 : U_{i0}(\eta \rightarrow \pm\infty) = \tilde{U}_{i0} \Big|^\pm \quad (7.40)$$

$$\varepsilon : U_{i1}(\eta \rightarrow \pm\infty) = \eta \partial_\eta \tilde{U}_{i0} \Big|^\pm + \tilde{U}_{i1} \Big|^\pm \quad (7.41)$$

$$\varepsilon^2 : U_{i2}(\eta \rightarrow \pm\infty) = \tilde{U}_{i2} \Big|^\pm + \eta \partial_{\eta\eta} \tilde{U}_{i1} \Big|^\pm + \frac{1}{2} \eta^2 \partial_{\eta\eta} \tilde{U}_{i0} \Big|^\pm \quad (7.42)$$

7.4.3 Solutions to the PF equations in the inner region

7.4.3.1 Zeroth-order in ε solution

In this order, for the phase field equation, it is $\partial_{\eta\eta}^2 \phi_0 - f'(\phi_0) = 0$ and it gives

$$\phi_0(\eta) = -\tanh\left(\frac{\eta}{\sqrt{2}}\right) \quad (7.43)$$

For the solute equation, $\partial_\eta \left(\frac{D_{il}}{D_{1l}} q(\phi_0) \partial_\eta U_{i0} \right) = 0$, leading to

$$\frac{D_{il}}{D_{1l}} q(\phi_0) \partial_\eta U_{i0} = A_{i0} \quad (7.44)$$

where A_{i0} is the integration constant. According to the matching condition shown as Eq. (7.40), it has $A_{i0} = 0$, and therefore

$$U_{i0} = \bar{U}_{i0}(s) \quad (7.45)$$

which means that U_{i0} is a constant, equating $\bar{U}_{i0}(s)$, along the direction normal to the S/L interface.

7.4.3.2 First-order in ε solution

The phase field equation in this order is

$$\partial_{\eta\eta}^2 \phi_1 - f''(\phi_0) \phi_1 - \alpha_1 g'(\phi_0) \left(U_{10} + \frac{d_1}{d_2} U_{20} \right) + (\alpha v_n + \tilde{\kappa}) \partial_\eta \phi_0 = 0 \quad (7.46)$$

A linear differential operator $L = \partial_{\eta\eta}^2 - f''(\phi_0)$ is defined and then Eq. (7.36) becomes

$$\int_{-\infty}^{+\infty} L \phi_1 \partial_\eta \phi_0 d\eta = \int_{-\infty}^{+\infty} \left[\alpha_1 g'(\phi_0) \left(U_{10} + \frac{d_1}{d_2} U_{20} \right) - (\alpha v_n + \tilde{\kappa}) \partial_\eta \phi_0 \right] \partial_\eta \phi_0 d\eta \quad (7.47)$$

Considering Eq. (7.43), $\partial_{\eta\eta}^2 \phi_0 - f'(\phi_0) = 0$, and Eq. (7.47) becomes

$$\int_{-\infty}^{+\infty} \left[\alpha_1 g'(\phi_0) \left(U_{10} + \frac{d_1}{d_2} U_{20} \right) - (\alpha v_n + \tilde{\kappa}) \partial_\eta \phi_0 \right] \partial_\eta \phi_0 d\eta = 0 \quad (7.48)$$

Substituting Eq. (7.45) into Eq. (7.48), it becomes

$$\alpha_1 \left(\bar{U}_{10} + \frac{d_1}{d_2} \bar{U}_{20} \right) J = -(\alpha v_n + \tilde{\kappa}) I \quad (7.49)$$

with $I = \int_{-\infty}^{+\infty} \partial_{\eta\eta}^2 \phi_0 d\eta$, and $J = -\int_{-\infty}^{+\infty} g'(\phi_0) \partial_\eta \phi_0 = g(+1) - g(-1)$. Considering that $\alpha_1 = I/J$ [66], and Eq. (7.49) leads to

$$\bar{U}_{10} + \frac{d_1}{d_2} \bar{U}_{20} = -(\alpha v_n + \tilde{\kappa}) \quad (7.50)$$

It should be noticed that it is the Gibbs-Thomson form in the zeroth power if $\tilde{\beta} = \tilde{\beta}_0 = \alpha$

For the solute equation, it is

$$\begin{aligned} \partial_\eta \left(\frac{D_{il}}{D_{1l}} q(\phi_0) \partial_\eta U_{i1} \right) + v_n \partial_\eta \{ a(\phi_0) [1 + (1 - k_i^e) U_{i0}] \partial_\eta \phi_0 \} \\ - \frac{v_n}{2} [1 + (1 - k_1^e) U_{i0}] \partial_\eta h(\phi_0) = 0 \end{aligned} \quad (7.51)$$

Integrate it once with respect to η yields

$$\begin{aligned} \left(\frac{D_{il}}{D_{1l}} q(\phi_0) \partial_\eta U_{i1} \right) = -v_n \{ a(\phi_0) [1 + (1 - k_i^e) U_{i0}] \partial_\eta \phi_0 \} \\ + \frac{v_n}{2} h(\phi_0) [1 + (1 - k_i^e) U_{i0}] + A_{i1}(s) \end{aligned} \quad (7.52)$$

where $A_{i1}(s)$ is the integration constant which can be obtained considering the limit $\eta \rightarrow -\infty$ in the solid. For simplification, here still suppose that there is no solute diffusion in the solid and then the left-hand side in the solid is equal to zero. Because the anti-trapping term only exists at the interface, the first term in the right-hand side is also equal to zero, and therefore Eq. (7.52) becomes

$$A_{i1}(s) = -\frac{v_n}{2} [1 + (1 - k_i^e) \bar{U}_{i0}] \quad (7.53)$$

Substituting Eq. (7.53) into Eq. (7.52) and integrating it once more between 0 and η , Eq. (7.53) becomes

$$U_{i1} = \bar{U}_{i1} + \frac{D_{1l} v_n}{D_{il} 2} [1 + (1 - k_i^e) \bar{U}_{i0}] \int_0^\eta \frac{h(\phi_0) - 1 - 2a(\phi_0) \partial_\eta \phi_0}{q(\phi_0)} d\eta \quad (7.54)$$

where $\bar{U}_{i1}$ is the value of $\bar{U}_i$ at the interface ($\phi = 0$).

7.4.3.3 Second-order in ε solution

The phase field equation in this order is

$$\begin{aligned} & \partial_{\eta\eta}^2 \phi_2 - f''(\phi_0) \phi_2 - \frac{1}{2} f'''(\phi_0) \phi_1^2 + (\alpha v_n + \tilde{\kappa}) \partial_\eta \phi_1 - \alpha_1 g'(\phi_0) \left(U_{11} + \frac{d_1}{d_2} U_{21} \right) \\ & - \alpha_1 g''(\phi_0) \phi_1 \left(U_{10} + \frac{d_1}{d_2} U_{20} \right) + \partial_{ss} \phi_0 - \tilde{\kappa}^2 \eta \partial_\eta \phi_0 = 0 \end{aligned} \quad (7.55)$$

Recalling $L = \partial_{\eta\eta}^2 - f''(\phi_0)$, Eq. (7.55) becomes

$$\begin{aligned} L\phi_2 &= \frac{1}{2} f'''(\phi_0) \phi_1^2 - (\alpha v_n + \tilde{\kappa}) \partial_\eta \phi_1 + \alpha_1 g'(\phi_0) \left(U_{11} + \frac{d_1}{d_2} U_{21} \right) \\ &+ \alpha_1 g''(\phi_0) \phi_1 \left(U_{10} + \frac{d_1}{d_2} U_{20} \right) + \tilde{\kappa}^2 \eta \partial_\eta \phi_0 \end{aligned} \quad (7.56)$$

Eq. (7.56) can lead to

$$\begin{aligned} & \frac{1}{2} \int_{-\infty}^{+\infty} f'''(\phi_0) \phi_1^2 \partial_\eta \phi_0 d\eta - \int_{-\infty}^{+\infty} (\alpha v_n + \tilde{\kappa}) \partial_\eta \phi_1 \partial_\eta \phi_0 d\eta \\ & + \alpha_1 \int_{-\infty}^{+\infty} g'(\phi_0) \left(U_{11} + \frac{d_1}{d_2} U_{21} \right) \partial_\eta \phi_0 d\eta \\ & + \alpha_1 \left(\bar{U}_{10} + \frac{d_1}{d_2} \bar{U}_{20} \right) \int_{-\infty}^{+\infty} g''(\phi_0) \phi_1 \partial_\eta \phi_0 d\eta + \tilde{\kappa}^2 \int_{-\infty}^{+\infty} \eta \partial_\eta \phi_0 \partial_\eta \phi_0 d\eta = 0 \end{aligned} \quad (7.57)$$

Substituting the expression of U_{i1} of Eq. (7.54) into the above equation and deleting the zero items of the odd functions [66], it obtains

$$\begin{aligned} & \left(\bar{U}_{11} + \frac{d_1}{d_2} \bar{U}_{21} \right) \int_{-\infty}^{+\infty} g'(\phi_0) \partial_\eta \phi_0 d\eta \\ & + \frac{v_n}{2} \left\{ [1 + (1 - k_1^e) \bar{U}_{10}] + \frac{D_{1l}}{D_{2l}} \frac{d_1}{d_2} [1 + (1 - k_2^e) \bar{U}_{20}] \right\} \times \\ & \int_{-\infty}^{+\infty} \int_0^\eta \frac{h(\phi_0) - 1 - 2a(\phi_0) \partial_\eta \phi_0}{q(\phi_0)} d\eta g'(\phi_0) \partial_\eta \phi_0 d\eta \end{aligned} \quad (7.58)$$

Set $K = \int_{-\infty}^{+\infty} \int_0^\eta \frac{h(\phi_0) - 1 - 2a(\phi_0) \partial_\eta \phi_0}{q(\phi_0)} d\eta g'(\phi_0) \partial_\eta \phi_0 d\eta$, and then it follows

$$\bar{U}_{11} + \frac{d_1}{d_2} \bar{U}_{21} = \frac{K}{2J} v_n \left\{ [1 + (1 - k_1^e) \bar{U}_{10}] + \frac{D_{1l}}{D_{2l}} \frac{d_1}{d_2} [1 + (1 - k_2^e) \bar{U}_{20}] \right\} \quad (7.59)$$

According to the above matching conditions in Eq. (7.41), it has

$$\begin{aligned}
 & \left(\tilde{U}_1 + \frac{d_1}{d_2} \tilde{U}_2 \right) \Big|^\pm \\
 &= \left(\tilde{U}_{10} \Big|^\pm + \frac{d_1}{d_2} \tilde{U}_{20} \Big|^\pm \right) + \varepsilon \left(\tilde{U}_{11} \Big|^\pm + \frac{d_1}{d_2} \tilde{U}_{21} \Big|^\pm \right) \\
 &= \left(\bar{U}_{10} + \frac{d_1}{d_2} \bar{U}_{20} \right) + \varepsilon \left[(U_{11} - \eta \bar{U}_{10}) + \frac{d_1}{d_2} (U_{21} - \eta \bar{U}_{20}) \right], \eta \rightarrow \infty \quad (7.60)
 \end{aligned}$$

Substitute the inner solutions derived above into Eq. (7.60), Eq. (7.60) becomes

$$\begin{aligned}
 & \left(\tilde{U}_1 + \frac{d_1}{d_2} \tilde{U}_2 \right) \Big|^\pm \\
 &= - \left[a - \varepsilon \frac{K + JF^\pm}{2J} \left\{ [1 + (1 - k_1^e) \bar{U}_{10}] + \frac{d_1}{d_2} \frac{D_{1l}}{D_{2l}} [1 + (1 - k_1^e) \bar{U}_{10}] \right\} \right] v_n - \tilde{\kappa} \quad (7.61)
 \end{aligned}$$

where $F^\pm = \int_0^{\pm\infty} \frac{h(\phi_0) - 1 - 2a(\phi_0)\partial_\eta\phi_0}{q(\phi_0)} d\eta$.

Eq. (7.61) is the Gibbs-Thomson relation at the thin interface and it can be seen that it contains the phase field parameters, such as $\varepsilon = w/d_1$. Comparing with the Gibbs-Thomson relation (Eq. (7.6)), according to $\tilde{\beta} = \frac{\beta D_{1l}}{d_1}$, $\varepsilon = w/d_1$ and $\alpha = \tau \frac{D_{1l}}{w^2}$, it requires

$$\beta = \alpha_1 \frac{\tau}{\lambda_1 w} \left\{ 1 - \alpha_2 \frac{w^2}{\tau} \left\{ \frac{\lambda_1}{D_{1l}} [1 + (1 - k_1^e) U_{10}] + \frac{\lambda_2}{D_{2l}} [1 + (1 - k_2^e) U_{20}] \right\} \right\} \quad (7.62)$$

to satisfy the Gibbs-Thomson relation at the thin interface in PF model. Eq. (7.62) could be extended to the multi-component as

$$\beta = \alpha_1 \frac{\tau}{\lambda_1 w} \left\{ 1 - \frac{\alpha_2 w^2}{\tau} \sum_{i=1}^n \frac{\lambda_i}{D_{il}} [1 + (1 - k_i^e)] \bar{U}_{i0} \right\} \quad (7.63)$$

To establish the interpolation functions, $h(\phi)$, $a(\phi)$ and $\tilde{q}(\phi)$, we should check the solute equation in the second-order. However, it is obviously observed that the solute equation is the same as that of the phase-field model for binary alloys.

Therefore, the conclusions drawn in the binary model can be used here. That is to reduce the artificial solute trapping, $h(\phi)$, $a(\phi)$ and $\tilde{q}(\phi)$ satisfy the following equation,

$$a(\phi) = \frac{[h(\phi) - 1][1 - q(\phi)]}{\sqrt{2}(\phi^2 - 1)} \quad (7.64)$$

where $q(\phi) = \tilde{q}(\phi) \frac{1+k_i^e - (1-k_i^e)h(\phi)}{2}$.

7.5 Extending to include the solid diffusivity

We use the same choice in Ref. [66] for the functions, that is $\tilde{q}(\phi) = \frac{1-\phi}{1+k_i^e - (1-k_i^e)\phi}$, $q(\phi) = \frac{1-\phi}{2}$, $h(\phi) = \phi$ and $a(\phi) = \frac{1}{2\sqrt{2}}$. With this choice, $\alpha_1=0.8839$ and $\alpha_2=0.6267$.

The scheme to include D_s for binary alloys is directly adopted here for this proposed ternary model to include the D_{is} for each solute. Then, to include D_{is} , $\tilde{q}(\phi)$ and $a(\phi)$ are modified into

$$\tilde{q}(\phi) = \frac{1 - \phi + k_i^e \frac{D_{is}}{D_{il}}(1 + \phi)}{1 + k_i^e - (1 - k_i^e)\phi} \quad (7.65)$$

$$a(\phi) = \frac{1}{2\sqrt{2}} \left(1 - k_i^e \frac{D_{is}}{D_{il}} \right) \quad (7.66)$$

Based on the above derivations, the present model that can include the solid diffusivity is summarized as follows

$$\tau \frac{\partial \phi}{\partial t} = w^2 \nabla^2 \phi + \phi - \phi^3 - \sum_{i=1}^2 \frac{\lambda_i}{1 - k_i^e} g'(\phi) \left(e^{u_i} - 1 - \frac{\Delta T_i}{m_i C_{il}^0} \right) \quad (7.67)$$

$$\begin{aligned} \frac{\partial C_i}{\partial t} = & \nabla \cdot \left(D_{il} \tilde{q}(\phi) \frac{e_i^u C_{il}^0 [1 + k_i^e - (1 - k_i^e)h(\phi)]}{2} \nabla u_i \right) \\ & + \nabla \cdot a(\phi) w (1 - k_i^e) C_{il}^0 e^{u_i} \frac{\partial \phi}{\partial t} \frac{\nabla \phi}{|\nabla \phi|} \end{aligned} \quad (7.68)$$

$$u_i = \ln \frac{2C_i}{C_{il}^0 [1 + k_i^e - (1 - k_i^e)h(\phi)]} \quad (7.69)$$

with the limitation

$$\lambda_i = \alpha_1 \frac{w}{d_i} \quad (7.70)$$

$$\beta = \alpha_1 \frac{\tau}{\lambda_1 w} \left\{ 1 - \alpha_2 \frac{w^2}{\tau} \left\{ \frac{\lambda_1}{D_{1l}} [1 + (1 - k_1^e) \bar{U}_{10}] + \frac{\lambda_2}{D_{2l}} [1 + (1 - k_2^e) \bar{U}_{20}] \right\} \right\} \quad (7.71)$$

where $\alpha_1=0.8839$ and $\alpha_2= 0.6267$ and the interpolation functions

$$g(\phi) = \phi - \frac{2}{3}\phi^3 + \frac{1}{5}\phi^5 \quad (7.72)$$

$$h(\phi) = \phi \quad (7.73)$$

$$\tilde{q}(\phi) = \frac{1 - \phi + k_i^e \frac{D_{is}}{D_{il}} (1 + \phi)}{1 + k_i^e - (1 - k_i^e) \phi} \quad (7.74)$$

$$a(\phi) = \frac{1}{2\sqrt{2}} \left(1 - k_i^e \frac{D_{is}}{D_{il}} \right) \quad (7.75)$$

7.6 Validation

The proposed thin-interface PF model for the ternary alloy solidification has been validated in two perspectives, including (1) A comparison of the predictions from the proposed ternary model with that from binary model; (2) A comparison of the predictions from the proposed ternary model with that from the thermodynamic calculations. The results showed that the proposed model can accurately predict the dendrite growth for the ternary alloy solidification and the results will be presented in the following.

7.6.1 Comparison with the binary model

A binary alloy with composition C was solidified at the temperate T_l^0 where the equilibrium liquid composition is C_l^0 , and $C = 0.5325C_l^0$. The properties of the alloy are: equilibrium partition coefficient $k_e = 0.15$ and the anisotropy coefficient $\varepsilon_4 = 0.02$. The dendrite growth of this binary alloy solidification system can be

simulated by the binary PF model proposed by Karma *et al*. In simulation, the interface width is $w = 5d_0$ where d_0 is the capillary length, and the calculation domain is set as $(L_x, L_y, L_z) = (204.8, 204.8, 6.4)w$. The calculated evolution of the tip radius (R_{tip}) with time is shown as black line in Figure 7.3.

This solidification system can also be simulated by the proposed ternary PF model if we treated this binary alloy as a ternary alloy system where the two constituent solutes have the same thermodynamic properties. For example, they have the equal equilibrium partition coefficients and the equal liquidus slope, i.e. $k_1^e = k_2^e$ and $m_{1l}^e = m_{2l}^e$. Furthermore, the sum of the solute compositions is equal to the composition of the binary alloy, i.e. $C_1 + C_2 = C$. Specially, we suppose $C_1 = C_2$. The plot of the red line in Figure 7.3 is the calculated tip radius by the proposed ternary model. It exactly overlaps that obtained by the binary model, indicating that the proposed model can accurately simulate the dendrite growth for the ternary alloys.

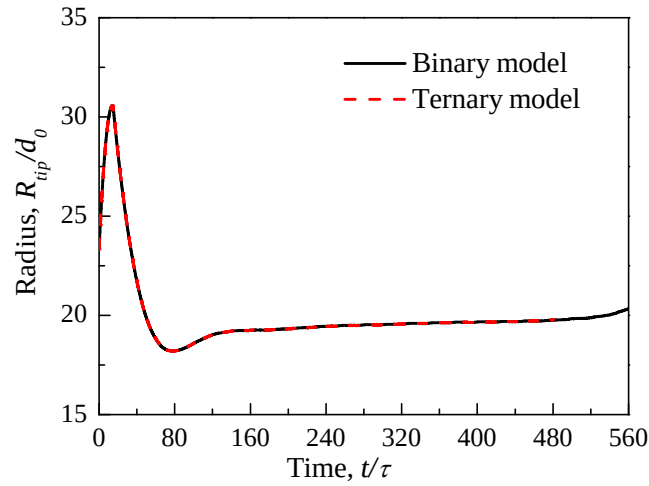


Figure 7.3: Evolution of tip radius with time calculated using the binary PF model (black line) and ternary PF model (red line).

7.6.2 Comparison with the thermodynamic calculations

Simulating the dendritic growth for Fe-C-Mn alloys motivates the proposal of this new ternary PF model, however because the material properties were difficult to be found in the literatures, especially the interfacial energy and the anisotropy, Al-Si-Mg system of which the material properties can be found easier was selected for the validation instead. The material properties of Al-Si-Mg alloy are shown in Table 7.1.

Table 7.1: Material properties used in the simulations of Al-Mg-Si system.

Material Properties			
Liquidus slope for Si	m_{Si}	-6.0	$K (at.\%)^{-1}$
Liquidus slope for Mg	m_{Mg}	-4.9	$K (at.\%)^{-1}$
Equilibrium partition coefficient for Si	k_{Si}^e	0.13	
Equilibrium partition coefficient for Mg	k_{Mg}^e	0.30	
Liquid diffusivity for Si	D_{Si}^l	0.33×10^{-4}	$cm^{-2}s^{-1}$
Liquid diffusivity for Mg	D_{Mg}^l	0.33×10^{-4}	$cm^{-2}s^{-1}$
Gibbs-Thomson coefficient	Γ_{sl}	0.90×10^{-5}	cmK

Simulations were carried out to predict the equilibrium properties, including the equilibrium compositions in liquid and solid, and the solid and liquid fractions, for Al-1at.%Si-1at.%Mg alloy at certain undercoolings (temperatures) using the proposed ternary model. The scanned undercoolings (ΔT) are $2.5K$, $5K$ and $10K$. The interface widths w were selected as $5d_0$ for ΔT and $1.6d_0$ for ΔT . Calculation domain was set as $(Lx, Ly, Lz)=(512, 1, 1)w$ for each case and it could be seen that it was quasi-onedimensional simulation because $Lx \gg Ly$ and $Lx \gg Lz$. Time step Δt was 0.01τ . As a start, a part of length $10w$ was set as solid with the compositions $C_{is} = k_i^e C_{i0}$ where C_{i0} is the nominal composition of solute i with $i = 1$ for Si and $i = 2$ for Mg. The composition of liquid part is the alloy compo-

sition. To simulate the equilibrium solidification, the solid diffusivity was assumed equal to the liquid diffusivity and therefore the solute concentration would become uniform gradually during solidification.

Figure 7.4 and Figure 7.5 show the solute profiles of Si and Mg respectively at different times, including $t = 50\tau$, $t = 1000\tau$, $t = 2000\tau$, $t = 3000\tau$, $t = 4000\tau$, $t = 5000\tau$, $t = 6000\tau$, when solidified at the undercooling $\Delta T = 5K$. With the time increasing, the solid fraction would increase and thus we did not mark the time for each plot in the figures. Looking at Figure 7.4(a), the solute concentration in the liquid gradually increased and gradually became uniform. A magnified figure was drawn to clearly display the solute profile evolution in the solid part, shown as Figure 7.4(b). In the beginning, the solid concentration increased and then gradually decreased. Because we assume non-zero solid diffusivity in simulations, the solute distribution also became uniform which fitted the equilibrium solidification. The Mg solute has the similar evolution, as shown in Figure 7.5.

It could be observed that the increased solid fraction became less during the same solidification time, meaning the solid growth velocity decreased with time. It could be expected that the growth velocity would become zero when it arrived at the equilibrium state. When it arrived the equilibrium state, we could obtain the compositions of liquid and solid, and the solid fraction through the solute profile. Tabel 7.2 lists the equilibrium concentrations in the liquid and solid and the equilibrium solid fractions at different temperatures (undercoolings) for the alloy Al-1at.% Si-1at.% Mg. The corresponding values obtained from thermodynamics calculations were also listed in Tabel 7.2 for comparison. The well agreements show that the accuracy of the proposed ternary PF model.

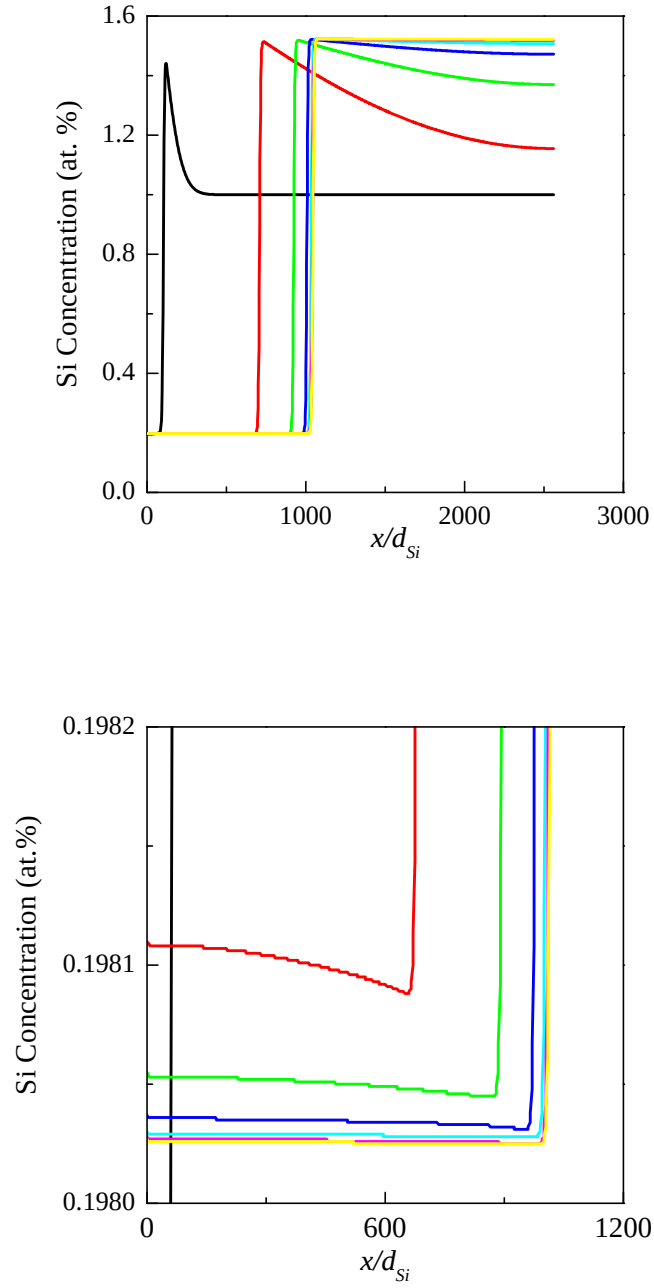


Figure 7.4: (a) Evolution of the solute profile of Si along x-axis, and (b) magnified figure of (a) to clearly show the solute profile in the solid; undercooling is $5K$.

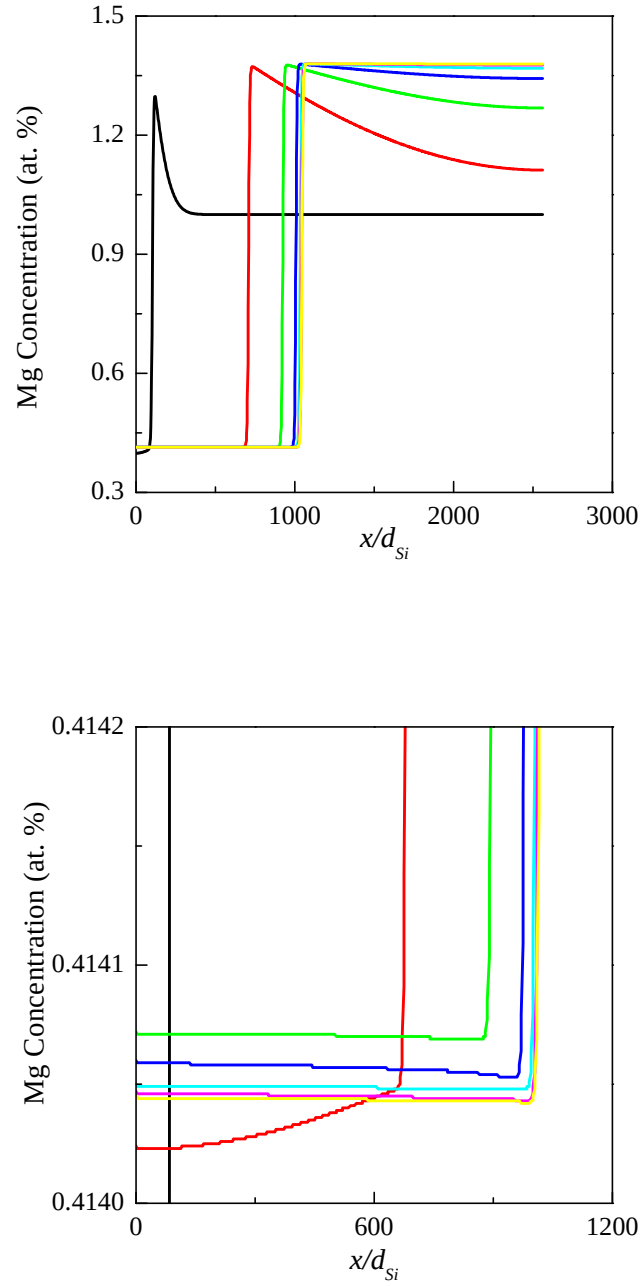


Figure 7.5: (a) Evolution of the solute profile of Mg along x-axis, and (b) magnified figure of (a) to clearly show the solute profile in the solid; undercooling is $5K$.

Table 7.2: Comparison of the equilibrium concentrations in the liquid and solid and the equilibrium solid fractions at different temperatures (undercoolings) for the alloy Al-1at.% Si-1at.% Mg, predicted by thermodynamics and the proposed tertiary PF model; in the symbols, 1 means solute Si and 2 means solute Mg.

	Undercooling $\Delta T = 2.5K$		Undercooling $\Delta T = 5K$		Undercooling $\Delta T = 10K$	
	Thermodynamics	PF	Thermodynamics	PF	Thermodynamics	PF
C_{1l}^e	1.256	1.25	1.52	1.52	2.081	2.08
C_{1s}^e	0.163	0.163	0.198	0.198	0.271	0.271
C_{2l}^e	1.196	1.19	1.38	1.38	1.718	1.71
C_{2s}^e	0.359	0.359	0.414	0.414	0.5154	0.515
f_s	0.234	0.25	0.393	0.408	0.597	0.607

7.6.3 Convergence behaviour

Two-dimensional simulations were carried out to investigate the effect of anti-trapping term added to the Fick's diffusion equation, shown as Eq. (7.30). The solidification starts with a sphere seed with radius $r_0 = 10d_{Si}$ and it would be solidified under the isothermal condition of undercooling ΔT . The calculation domain is $(L_x, L_y, L_z) = (3200, 800, 25)d_{Si}$ where the L_x was long enough for the dendrite to grow freely into the steady state, L_y was shorter than L_x to save the calculation time and L_z was thin enough to assure that there was no solute diffusion in z-direction and thus the two dimensional simulations. A variety of interface width w spanning from $6.4d_{Si}$ to $12.8d_{Si}$ was used for analysing the convergence behaviour of this proposed ternary model.

Figure 7.6 shows the typical steady-state morphology visualized by the Si concentration and Mg concentration. It could be seen that the solutes are rich in the liquid close to the S/L interface with minus curvature. In this case, the interface width w is $8.4d_{Si}$. The growth velocity of the dendrite depends on the diffusion

of the solutes from the S/L interface to the boundary because less concentration means less undercooling is needed for solidification and also as shown by Eq. (1.3). As listed in Table 7.1, the diffusivity of Si and Mg are the same, and however it can be seen in Figure 7.6 that more Si solute was accumulated ahead of the S/L interface than Mg solute does, which can be attributed to the less equilibrium partition coefficient of Si. Therefore, the diffusion of the Si solute will predominantly control the dendritic growth of Mg-Al-Si system.

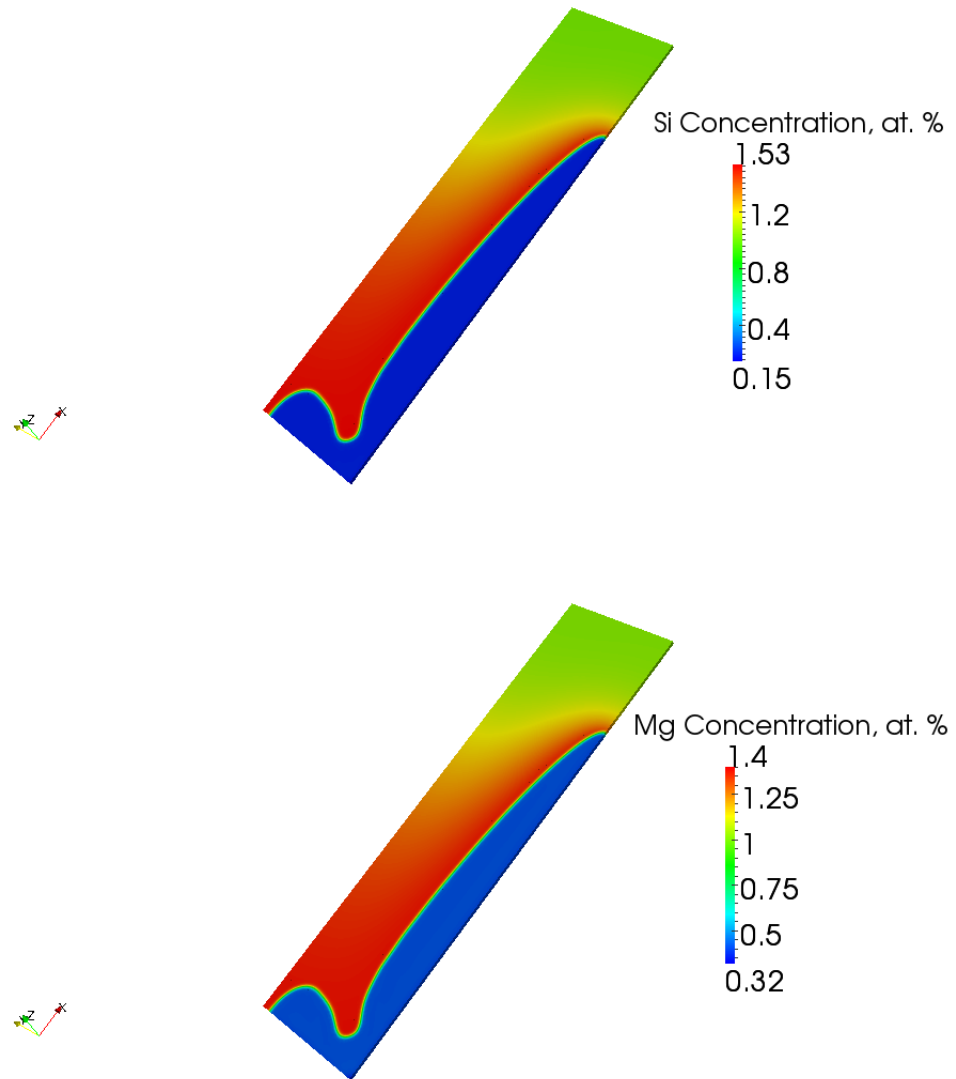


Figure 7.6: Typical steady-state morphologies visualized by Si concentration and Mg concentration; the interface width is $8.4d_0$.

The evolutions of the tip radius R_{tip} and tip velocity V_{tip} of the same example were shown in Figure 7.7. The Tip radius increased with time while the tip velocity decreased with time until the steady state was achieved. Thus, steady-state tip radius and tip velocity can be obtained through the plots, which would be used to examine the convergence behavior of the proposed model, as shown below.

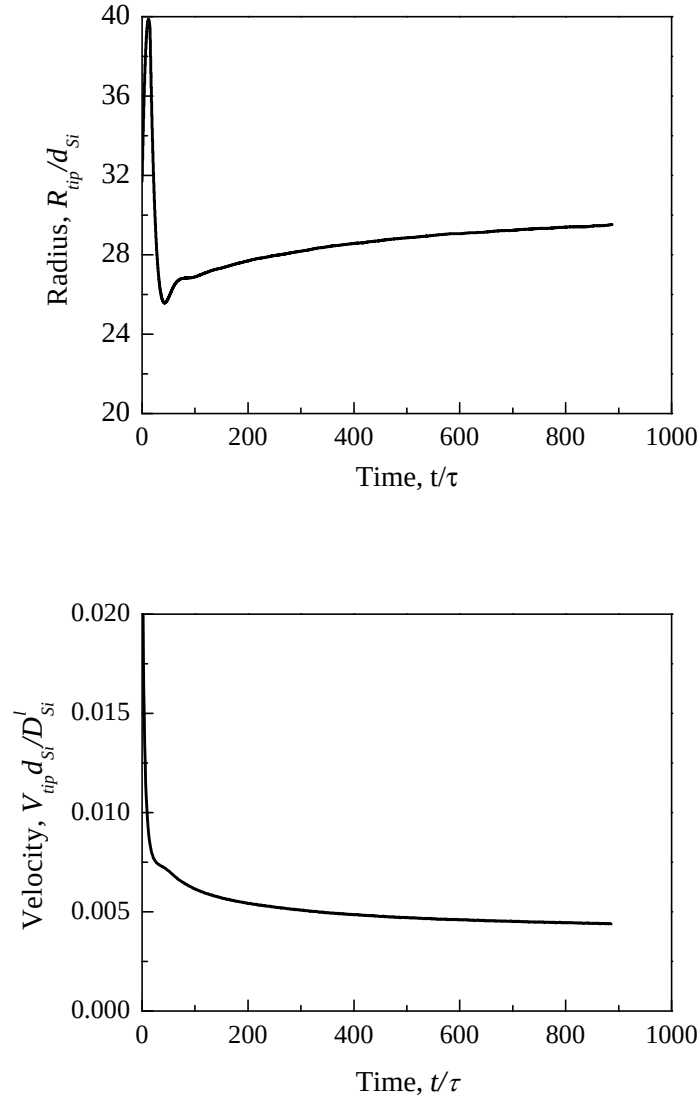


Figure 7.7: Evolution of (a) tip radius and (b) tip velocity with time; the interface width is $8.4d_0$.

Figure 7.8 shows the solute profiles of Si and Mg along x-axis in the solid part, calculated by the models with and without anti-trapping models. Two interface

widths were used, i.e. $w = 6.4d_0$ and $w = 8.4d_0$. Looking at the solute profiles of Si solute in Figure 7.8a, the calculated solute profiles converge well respect to the interface width by the model with anti-trapping term, and in contrast the calculated solute concentration obviously increases with the interface increasing. It could be found that the solute concentrations calculated by the model without the anti-trapping term are larger than those obtained by the model without the anti-trapping term. This is attributed to the artificial solute trapping because of the use of the thin interface width. Similar phenomenon can be observed in the solute profiles of Mg, as shown in Figure 7.8b. Thus, Figure 7.8 demonstrates that the anti-trapping term in the proposed model can large reduce the artificial solute trapping and lead to higher calculation accuracy. Figure 7.9 shows the calculated steady-state tip radius and tip velocities using different interface widths. It could be seen that the results converges well until interface width is increased to $12.8d_{Si}$, which demonstrates that this model is convergent in a relatively broad interface width range.

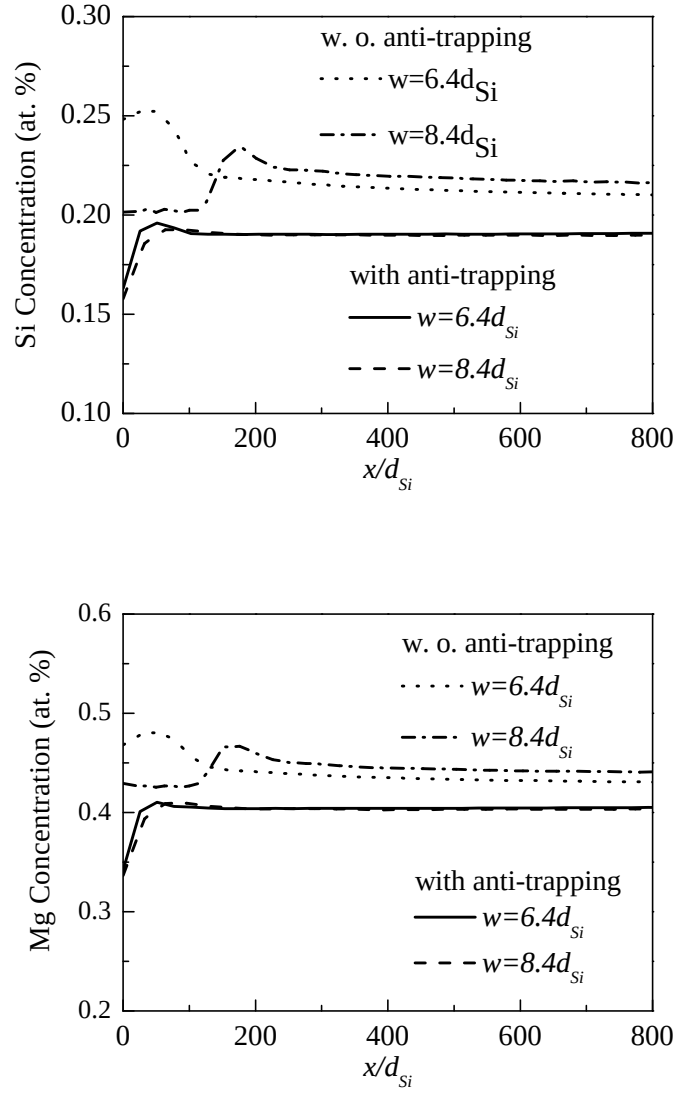


Figure 7.8: Calculated solute profiles in the solid by the models with and without anti-trapping term; the interface widths are $w = 6.4d_{Si}$ and $8.4d_{Si}$.

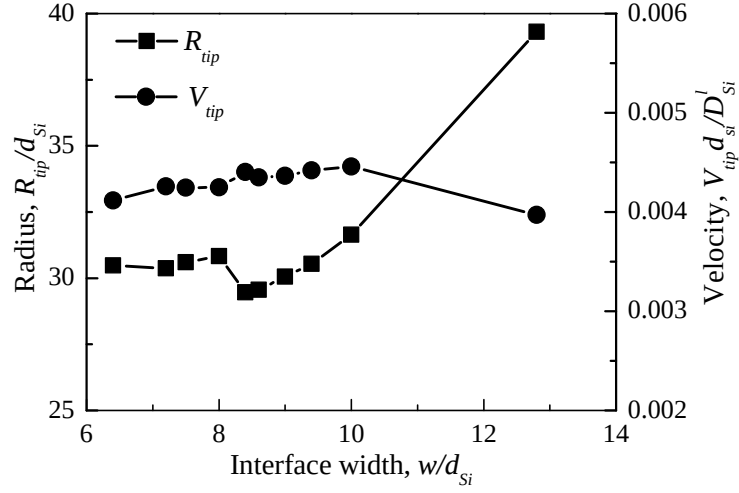


Figure 7.9: Calculated tip radius and tip velocities using different interface widths, showing the good convergence behaviour of the proposed model.

7.7 Conclusions

A quantitative thin-interface PF model for ternary alloy solidification is developed based on the binary alloy thin-interface PF model proposed by Karma *et al* [66]. Thin-interface limit analysis used in the proposal model to define the phase field parameters (e.g. the interface width) shall recover the Gibbs-Thomson relation at the thin interface. Meanwhile, an anti-trapping current introduced to the diffusion equation for each solute shall reduce the artificial solute trapping. Overcoming Karma's model assuming zero solute flux in the solid, the solute diffusion in the solid can be included in this model by adopting the scheme proposed by Ohno and Matsuura's for binary alloys [92].

Numerical predictions from the proposed model were compared to those from the binary phase-field model and thermodynamic calculations. Well agreements were found, meaning the proposal model can give accurate simulation results. Convergence behaviour of this model shows it converged well in an interface range.

It may be noted that the model begins with the expression of the Gibbs free

energy of the dilute alloy, which means constant equilibrium partition coefficients and the liquidus slopes during the solidification and thus simplifies the derivation process. Therefore, if constant material properties are used in the simulations, this model is only applicable to the alloys in which the concentrations in the liquid vary in a narrow range during the solidification process. If this model is used to simulated for the concentrated alloys or the solidification in which the partition coefficients and the liquidus slopes vary with the concentrations varying in the liquid, the material properties need to be updated during the solidification, which can be realised by linking the PF modelling to the thermodynamic calculations.

CHAPTER EIGHT

Conclusions and Future Work

8.1 Extending the thin-interface phase-field models to include solid diffusivity

Ohno and Matsuura (OM) [92] extended Karma's thin-interface PF models [65, 66] with anti-trapping term to alloy solidification involving solute diffusion in the solid. The issue of this model is that the solute flux term in solid $\chi(s)$ needs to be input as a parameter for PF simulation and however it is an output of a simulation. Possibility of using $\chi(s) = 0$ was mathematically and numerically validated in this study.

It can be used mathematically because $\chi(s)$ contributes a correction that vanishes as the interface width tends to zero. In numerical tests, the predicted results using the PF model and those from Gibbs-Thomson relation for alloys with non-zero solid diffusivity were compared. Good agreement demonstrates that the developed model with the anti-trapping term can improve the simulation accuracy with much reduced artificial solute trapping. The results converge well in a finite range of interface width w through convergence behavior analysis. Furthermore, the inclusion of the finite D_s has little influence on the convergence zone because the upper limit of the interface Peclet number at the maximum interface width are almost the same.

8.2 Effect of finite solid diffusivity on free-growth dendrite

The effect of D_s on the steady-state dendrite under free growth was investigated using the evaluated PF model that can include the solid diffusivity. The microsegregation, the steady-state tip radius R_{tip} and the steady-state tip velocity V_{tip} were calculated at various D_s and k_e . The results show that the inclusion of D_s decreases the degree of microsegregation in solid. The R_{tip} increases while V_{tip} decreases with the increase in D_s . Furthermore, the effect of D_s on a freely growing dendrite was found to be influenced by the value of k_e . A map was given based on the error resulted by the exclusion of the finite D_s for various D_s and k_e . The D_s can be negligible in simulations when (1) $D_s < 0.0001$ or (2) $k_e > 0.8$ and $0.0001 < D_s < 0.01$. The C diffusion in the solid for Fe-C alloys should be included.

8.3 Dendritic growth under directional solidification

The dendritic evolution under the steady-state directional solidification was investigated in terms of the primary stalk and the side branches using the evaluated PF model including the C diffusion in the solid. A map of the evolution of a dendrite under the steady-state directional solidification can be given: the primary stalk evolves in a conserved shape with a constant tip radius and a slightly increasing stalk width due to the remelting of the side branches during the initial ripening process. The irregular side branches grew out with different growth orientations varying around the preferred orientation, different growth velocities and different side-branch sizes. These irregular side branches then experienced the ripening process, during which the side branches with preferred growth orientation survived and the ones of adverse growth orientation remelted.

The remelting process of the side branches was tracked. It was found that the remelting started at the side branch tip rather than the necklace, implying that the remelting during the initial ripening process would not lead to the detachment of

side branches. The survival side branches became coarser with increasing necklace width and side branch width. However, the ratio of the necklace width to the width of the side branches increases. The evolution of the side branches during the initial ripening process implies that it is difficult for the occurrence of detachment of side branches under the steady state transition whether due to the remelting or the mechanical failure.

8.4 Dendritic growth under transient directional solidification

The evolution of the dendrite under the transient condition was investigated and compared with that under the steady state. It was found that

- (1) The primary stalk reacted slow to the tip velocity: the tip radius is smaller than that of the steady state under the same velocity, and the stalk width only has a slight variation;
- (2) The side branches has the trend to be a sphere compared to a cylinder under the steady state during the ripening process. Solute concentration is much lower at the side branch roots under the transient growth condition.
- (3) The necklaces of the side branches are finer compared to those under the steady state and the ratio of the necklace to the width of the side branches decreases. It implies that it is easier for the detachment of the side branches due to the mechanical failure.
- (4) It is proposed that the variation in the side branches is attributed to their feedback to the variation in dendrite tip with the growth velocity changing during the dendritic growth;

8.5 Extending Karma's thin-interface phase-field model to ternary alloys including solid diffusivity

A quantitative thin-interface PF model for ternary alloy solidification is developed based on the binary alloy thin-interface PF model proposed by Karma *et al* [66]. Thin-interface limit analysis used in the proposal model to define the phase field parameters (e.g. the interface width) shall recover the Gibbs-Thomson relation at the thin interface. Meanwhile, an anti-trapping current introduced to the diffusion equation for each solute shall reduce the artificial solute trapping. Overcoming Karma's model assuming zero solute flux in the solid, the solute diffusion in the solid can be included in this model by adopting the scheme proposed by Ohno and Matsura's for binary alloys [92]. Numerical predictions from the proposed model were compared to those from the binary phase-field model and thermodynamic calculations. Well agreements were found, meaning the proposal model can give accurate simulation results. Convergence behaviour of this model shows it converged well in an interface range.

8.6 Future work

As a continues of the work presented in the thesis, future work will focus on two aspects:

- (1) Directional solidification of Fe-C-Mn alloys; As concluded above, a tertiary phase-field model is proposed and validated under the isothermal solidification using the Al-Si-Mg alloys. To fit the purpose of the MintWeld project, simulating the dendritic growth for Fe-C-Mn alloys is required and furthermore a model for the directional solidification is needed. When the solidification of Fe-C-Mn alloys is simulated, the solid diffusivity of the solute C will be considered. Unlike the Al-Si-Mg alloys we used for validating the proposed ternary

model where the diffusivity of Si is the same as that of Mg in the liquid, the diffusivity of C is much faster than Mn either in the liquid or in the solid meaning that the diffusion of C is much faster than that of Mn. However, the solid process and the length scale of the dendrite are also influenced by the partition coefficient as indicated in Chapter 4 and the liquidus slope. Therefore, it would be interesting to investigate the addition of Mn on the dendritic growth.

- (2) Coupling the transient solidification conditions obtained by the front-tracking modelling with the phase-field model; As concluded on the dendritic growth under the transient growth, the variation of the condition during the dendritic growth will have an obvious effect on the morphology (shape and size) of the side branches and the solute surrounding the side branches as well. However, as we referred, this transient condition in our simulation is created by changing the velocity in the midway, which is a simpler compared to the real variation in the welding condition. Therefore, to exactly simulate the transient condition in a weld pool, a data flow of the transient solidification condition is required to be fed into the phase-field simulations with time.

Another issue which has been discussed in Chapter 5 and Chapter 6 is the calculation efficiency in phase-field simulation. Although we have improve the calculation efficiency using a thin-interface scheme with anti-trapping term, and the adaptive algorithm, the solidification time is up to 0.1 s. To fulfil the second aspect of the future work, it is necessary to parallelising the code.

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Appendices

Appendix A: Publications and Conferences

Yu Xie, Hongbiao Dong, Jonathan Dantzig, Using the interface Peclet number to select the maximum simulation interface width in phase-field solidification modelling, *Computational Materials Science*, 2013(70)71

Yu Xie, Hongbiao Dong, Jun Liu, et al, A multi-scale approach to simulate solidification structure evolution and solute segregation in a weld pool, *Journal of Algorithms & Computational Technology* (Accepted)

Yu Xie, Hongbiao Dong, Jonathan Dantzig, An extension of a thin-interface binary phase-field model involving solid diffusivity to ternary systems, Under preparation for Physical Review E.

Mingming Tong, Jun Liu, **Yu Xie**, et al, An integrated framework for multi-scale multi-physics numerical modelling of interface evolution in welding, *IOP Conference Series: Materials Science and Engineering*, 2012(33)012029

Mingming Tong, Gregory Duggan, Jun Liu, **Yu Xie**, et al, Multi-scale multi-physics numerical modelling of fusion welding with experimental characterisation and validation, *JOM*, 2013(65)99

Christopher E. Goodyer, Peter K. Jimack, Andrew M. Mullis, Hongbiao Dong, **Yu Xie**, On the fully implicit solution of a phase-field model for binary alloy solidification in three dimensions, *Advances in Applied Mathematics and Mechanics*, 2012(4)665-684

Yu Xie, Hongbiao Dong, Jun Liu, et al, A multi-scale approach to simulate solidification structure evolution and solute segregation in a weld pool, EGH1012 Workshop on Applied and Numerical Mathematics, June 2012, Greenwich, UK (Oral Presentation)

Yu Xie, Hongbiao Dong, Jonathan Dantzig, Solute trapping in phase-field modelling of alloy solidification with asymmetric solute diffusivity, EuroMat 2011, September 2011, Montpellier, France (Oral Presentation)

Yu Xie, Hongbiao Dong, Jonathan Dantzig, Simulation of rapid solidification in Fe-C alloys, 1st UK-China Steel Research Forum, July 2010, Leicester, UK (Oral Presentation)

Yu Xie, Hongbiao Dong, Jonathan Dantzig, Progress of phase-field modelling for welding, Consortium Meeting of MintWeld Project, held every six months since Sep, 2009 (Oral Presentation)