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Off-Eutectic Growth Model for Solidifying Alloy from an Undercooled State

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Abstract: Classical eutectic growth models are based on the use of eutectic composition. These models neglect the effect of primary phase formation, and their direct use in the rapid solidification process of off-eutectic (hypoeutectic and hypereutectic) alloys is absent. Combining the effect of the primary phase in the eutectic transformation and an off-eutectic composition, the solidification growth model is derived in the present work. The effect of the model and material parameters on solidification kinetics is discussed in comparison with experimental data. Computational results on the off-eutectic growth model show that the model agrees well with experimental data on the solidification kinetics of Ni-B and Ti-Si alloys.

Keywords: eutectic growth; model; diffusion; solidification

1. Introduction

Eutectic alloys, especially off-eutectic (hypoeutectic and hypereutectic) alloys, are widely studied in experiments and used in industry [1]. The study of eutectic and off-eutectic alloys is important to compare alloy properties obtained on the ground [2] and under microgravity conditions [3]. Usually, the microstructure of off-eutectic alloys is represented by lamellar colonies. Such lamellas are accompanied by the appearance of dendrites of the growth phase with the coexistence of the two structures over some range of off-eutectic melt compositions [4–7].

Zimmermann et al. [8] reported the results of a series of experiments conducted on an Al–Cu alloy system. They found that an oscillatory lamellar microstructure appears in the off-eutectic region, and destabilization is first caused by the occurrence of an oscillatory morphology that persists over a wide range of compositions and growth rates. Bandaru et al. [9] performed a numerical study on oscillatory and ramped freezing of off-eutectic mixtures in the absence of convection and under the steady state regimes of solidification. Carvalho et al. [10] studied directionally solidified off-eutectic mullite–zirconia fibers. They found that the microstructure of the mullite–zirconia eutectic varies from planar coupled eutectic through mullite columnar growth with coarse zirconia inclusions to faceted mullite eutectic dendrites with increasing pulling rates.

For nucleation, Bluni et al. [11] reported nonreciprocal nucleation characteristics in off-eutectic Al–Zn alloys. As observed, aluminum is a better nucleant of zinc than zinc of aluminum, such that elements with higher solid–liquid interfacial energies are better nucleates than vice versa. Note especially that, in their experiments, Bluni et al. did not measure the thermal gradient which may change the contact angle of nucleation and Gibbs–Thomson characteristics of nucleation. Therefore, the best element for nucleation in the Al–Zn alloys is still under study. Ohsaka et al. [12] formulated the Gibbs free energy change of off-eutectic binary alloys upon solidification. Barclay et al. [13] studied the halo formation theory during the unidirectional solidification of off-eutectic alloys and suggested a model for the halo fraction.
Employing an abrupt increase in growth velocity to produce coupled eutectics in directional solidification of Al–40 wt% Cu off-eutectic alloys, Li et al. [14] found that primary AlCu dendrite growth velocities ranged from 5 to 100 μm/s and coupled eutectic growth velocities were 1 to 100 μm/s. Barcla et al. [15] studied off-eutectic composite solidification and properties in Al–Ni and Al–Co alloys and found that if the solidification rates were high enough, both alloys exhibited coupled zones skewed towards hypereutectic compositions. Zhu et al. [16] simulated the microstructural evolution of both hypoeutectic and hypereutectic spheroidal graphite irons. Their results showed that the growth of a graphite nodule is promoted by the approaching austenite. However, after the nodule is engulfed by the austenite, its growth velocity decreases dramatically, as it is controlled by the solid diffusion of carbon through the austenite shell.

Jackson and Hunt [17,18] established the first detailed analytical model (JH model) for diffusion-limited growth of regular eutectic as the coupled growth of α and β phases. Then, Trivedi et al. [19] extended the JH model to eutectic growth under rapid solidification conditions (TMK model). Taking the interface solute trapping into account, Kurz et al. [20] analyzed the failure of local equilibrium at the solid–liquid interface at high growth velocity within the framework of the JH and TMK models.

Li et al. [21] neglected solute trapping but incorporated kinetic and thermal undercooling into eutectic growth in the analysis of solidification in the bulk undercooled melt (LZ model). Gao [22] studied the growth kinetics of the eutectic dendrite in the presence of an incident flow based on the LZ model. Using the same hypotheses as the JH model, Senninger and Voorhees [23] proposed a model for eutectic growth in two-phase multicomponent alloys. They found that a small addition of a ternary alloying element with a small diffusivity to a binary alloy can significantly alter the spacing of the lamellar eutectic.

Xu and Galenko [24,25] considered the transition to diffusionless growth in eutectic binary alloys. They developed a model to analyze the atomic diffusion ahead of lamellar eutectic couples growing into a supercooled liquid, as well as rod eutectic coupled growth [26,27].

As a general note, one must note that the classical eutectic growth models [17,18] are based on eutectic composition alloys and a single transition in solidification. This hypothesis might be applicable for directional solidification but not true for undercooled rapid solidification since there are often several separate transitions for off-eutectic alloys. Although the classical eutectic theories considered the composition change, it was discovered that the composition effect was mainly on the expression of each eutectic fraction, and they never considered the separate primary phase as the first forming phase [17,18]. For example, the primary α-Ni dendrite phase (Figure 1a) forms before the eutectic transition in the hypoeutectic Ni–Ni3B alloy, while the primary Ni-B phase (Figure 1b) forms before the eutectic transition in the hypereutectic Ni–Ni3B alloy. The composition has little effect on the ratio of the two eutectic phases, but it has a significant effect on the fraction of the primary phase, as well as the eutectic transition kinetics. Therefore, the straightforward use of classical eutectic models describing off-eutectic alloys is questionable.

**Figure 1.** Primary phase and eutectic phase in the Ni–Ni3B alloy: (a) hypoeutectic alloy and (b) hypereutectic alloy. 1—primary phase α-Ni, 2—eutectic phase Ni/Ni3B, 3—primary phase NiB.
In the present study, we consider the influence of the existence of primary phases, combining the theory of diffusion-controlled and diffusionless transformation [28] with using similar hypotheses as the classical theory [17–22]. Thus, considering the effect of the primary phase, a model for off-eutectic growth is derived and solved in comparison with the accessible experimental data.

2. Model Equations

2.1. The Model Statement

Many studies have shown that the diffusion coefficient for both liquid and solid phases changes with concentration. For instance, in Al–Cu hypoeutectic alloys, the diffusion coefficient of liquid was found to decrease with increasing solution content [29]. In contrast, the diffusion coefficient of the solid phase was found to increase with the solution content [30]. As a result, it is difficult to determine whether the composition increased or decreased the transformation rate.

The concentration change in the off-eutectic can directly lead to the primary phase fraction change. With the primary phase existence, the eutectic reaction only occurs in the interdendritic region (Figure 2); therefore, the characteristic length scale for eutectic pattern formation is longer than that without the primary phase. On the other hand, with the presence of the primary phase, the residual liquid decreases, and the solidification area decreases. Therefore, it is difficult to determine whether the concentration change increases or reduces the growth velocity. In what follows, the concentration effect on the off-eutectic alloy is measured by taking the diffusion coefficient change into account.

![Scheme of the eutectic phase diagram (a) and the growing lamellar eutectic structure in the presence of the primary (dendritic) phase (b).](image)

Figure 2. Scheme of the eutectic phase diagram (a) and the growing lamellar eutectic structure in the presence of the primary (dendritic) phase (b).

As an additional assumption, we have to especially note that the characteristic length scale of the temperature field (minimum) is one thousand times larger than the characteristic solute diffusion length scale. Therefore, we do not consider this multi-scale problem of thermal and chemical diffusion.

Assume that for the eutectic composition alloy, there is no primary phase, and the diffusion coefficient is \( D \). Then, one can accept that far from the eutectic composition, almost the whole liquid phase becomes the primary phase before the eutectic transition, and the diffusion coefficient is \( D_p \). According to the Darken law, the diffusion for any concentration can be given as

\[
D = f_p D_p + f_e D.
\] (1)

Where \( D_r = k_o D \) and \( k_o \) is constant, representing the difference ratio of the diffusion coefficient in the eutectic composition and far from the eutectic composition, where the microstructure is mainly the primary phase. \( f_p \) and \( f_e \) are the phase fractions of the primary phase and eutectic phase, respectively, such that \( f_p + f_e = 1 \). Neglecting the effect of eutectic
undercooling on the primary phase, the primary phase fraction is determined according to the level law:

\[ f_p = \frac{(C_t - C_e)}{(C_t - C_i)} \]  

(2a)

\[ f_x = \frac{(C_x - C_e)}{(C_t - C_i)} \]  

(2b)

where \( C_t \) is the eutectic composition, \( C_i \) is the alloy concentration, and \( C_x \) is one of the eutectic phase compositions. Equation (2a) indicates that the primary phase fraction \( f_p \) is a function of the concentration determined by the initial composition \( C_e \). From Equations (1) and (2), one obtains

\[ D_c = (f_p k_D + f_x) D \]  

(3)

If \( k_D > 1 \), the overall diffusion coefficient (3) in the eutectic composition has the minimum value. In contrast, if \( k_D < 1 \), the overall diffusion coefficient (3) in the eutectic composition reaches the maximum value. When the primary phase does not exist \( (f_p = 0) \), or it has no effect on the diffusion coefficient, i.e., \( k_D = 1 \), the diffusion coefficient \( D_c = D \).

Defining the composition factor \( k_c \) as

\[ k_c = f_p k_D + f_x \]  

(4)

the diffusion coefficient (3) for the primary phase becomes [28]

\[ D_c = \begin{cases} 
D \left( 1 - V^2 / V_D^2 \right) k_c, & V < V_D \\
0, & V \geq V_D
\end{cases} \]  

(5)

2.2. Diffusion Equation for Eutectic Growth

Consider the solidification of a binary system consisting of atoms A and B and having a eutectic point with equilibrium temperature \( T_e \) and concentration \( C_e \), as shown in Figure 2a. \( \Delta C_\alpha \) and \( \Delta C_\beta \) are the concentration differences between phases \( \alpha \) and \( \beta \) and eutectic point \( C_e \), respectively.

Assume that undercooling \( \Delta T \) in the liquid provides a motion of the interface with velocity \( V \) comparable to the solute diffusion speed \( V_D \) in the bulk liquid [31]. The diffusion in the \( \alpha \) and \( \beta \) phases, which have the form of the lamellar eutectic microstructure, is neglected. Then, for the concentration \( C(x,y) \) of B atoms in the liquid A solidifying in a steady-state regime, the two-dimensional diffusion equation is given by [32]

\[ \frac{\partial^2 C}{\partial x^2} + k_c \left( 1 - \frac{V^2}{V_D^2} \right) \frac{\partial^2 C}{\partial y^2} + \frac{V}{D} \frac{\partial C}{\partial y} = 0 \]  

(6)

This equation is valid for concentration \( C(x,y) \) in the spatial reference frame \( (x, y) \) moving at a constant velocity \( V \) at the interface \( z = 0 \). For eutectic transformation, the boundary conditions are as follows:

- periodicity: in the \( x \) direction, \( C(x+\lambda) = C(x) \), here \( \lambda = 2(S_\alpha + S_\beta) \)
- symmetry: \( \partial C / \partial x = 0 \) for \( x = 0 \) and \( x = \lambda / 2 = S_\alpha + S_\beta \)
- far-field: \( C = C_e \) for \( z \rightarrow \infty \)

where \( S_\alpha \) and \( S_\beta \) represent half of the interlamellar spacing for each phase such that \( \lambda = 2(S_\alpha + S_\beta) \) is the lamellar spacing (see Figure 2b).

Equations (6) and (7) have an analytical solution to the problem of lamellar eutectic patterns under local nonequilibrium conditions in the solute diffusion field [28]. This general solution for the growth of periodic lamellas is described by

\[ C = C_e + B_0 \exp(-V \frac{z}{D_c}) + \sum_{n=1}^{\infty} B_n \cos(b_n x) \exp(-\omega_n z) \]  

(8a)

for \( V < V_D \).
\[ C = C_w \quad V \geq V_b \]  
\[ \omega_n = \frac{V}{2D_C} + \left[ \frac{V}{2D_C} \right]^2 + b_n^2 \]  
\[ b_n = n\pi/(S_a + S_\beta) \]

where \( B_0 \) and \( B_n \) are the Fourier coefficients and \( n \) belongs to a set of integer values.

To calculate Fourier coefficients, the boundary conditions from mass conservations are needed:

- solute balance at the interface for the \( \alpha \) phase \((0 \leq x < S_\alpha)\)

\[ -D_C \left( \frac{\partial C}{\partial z} \right)_{z=0} = V (C_{x_a} - C_{x_a}) = VC(x, 0) \left( 1 - k_\alpha \right) \]  

- solute balance at the interface for the \( \beta \) phase \((S_\alpha \leq x < S_\alpha + S_\beta)\)

\[ -D_C \left( \frac{\partial C}{\partial z} \right)_{z=0} = -V (C_{y_\beta} - C_{x_\beta}) = -V(1 - C(x, 0)) \left( 1 - k_\beta \right) \]  

Here, \( k_\alpha \) and \( k_\beta \) are the velocity-dependent solute partitioning functions for the \( \alpha \) phase and \( \beta \) phase, respectively, at the interface; \( C_{x_a} \) and \( C_{x_\beta} \) are the concentrations of the \( \alpha \) phase and \( \beta \) phase in the liquid, respectively. \( C_{y_\alpha} \) and \( C_{y_\beta} \) are the concentrations of the \( \alpha \) phase and \( \beta \) phase in the solid (see Figure 2b).

From Equation (8), it follows that if \( V \geq V_b \), the lamellar eutectic structure does not form. Therefore, the case of \( V < V_b \) is considered first. A discussion of the high-rate regime \( V \geq V_b \) will be provided second.

**2.3. Fourier Coefficients**

To obtain the solution for \( B_0 \) and \( B_n \), the treatments of TMK [19] are used with the two special types of phase diagrams. The solution for the concentration gradient ahead of the eutectic interface is found by differentiating Equation (8a) with respect to \( z \).

\[ \frac{\partial C}{\partial z} \bigg|_{z=0} = -\frac{V}{D_C} B_0 - \sum_{n=1}^{\infty} B_n \frac{n\pi (S_a + S_\beta)}{S_a + S_\beta} \cos \left( \frac{n\pi S_a}{S_a + S_\beta} \right) \]  

Substituting Equation (10) into Equation (9) and integrating it, one can obtain the Fourier coefficients for the two-case phase diagram:

Case I: cigar-shaped phase diagram[19]

For this type of phase diagram, the solidus and the liquidus lines are parallel below the eutectic temperature. In this case, for any undercooling, one obtains \( C_{x_\alpha} = C_{x_\alpha} = \Delta C_\alpha = const \) and \( C_{y_\beta} = C_{y_\beta} = \Delta C_\beta = const \) [19], leading to the following expressions for the Fourier coefficients:

\[ B_0 = \frac{\Delta C_\alpha S_a - \Delta C_\beta S_\beta}{S_a + S_\beta} \]  
\[ B_n = \frac{2}{(n\pi)^2} \omega_n \frac{V}{D_C} \Delta C_0 \sin \left( n\pi f \right) \]

where \( \Delta C_\gamma = \Delta C_\alpha + \Delta C_\beta \).
Case II: equal distribution coefficients for the two phases [21]
For this case, $k$ is an arbitrary constant, but $k_a = k_\beta = k$, leading to the following expression: $\Delta C_\alpha + \Delta C_\beta = \Delta C = 1 - k$. Additionally, for this type of phase diagram, the solid concentration $C_{sa}$ of the $\alpha$ phase increases with $C_E$, and the solid concentration $C_{s\beta}$ of the $\beta$ phase increases with $(1 - C_E)$. Generally, if the solid solubility of the two eutectic phases is small, the equations of case II can be used. Then, expressions for the Fourier coefficients are

$$B_0 = \frac{(1 - k) C_{sa} S_\alpha - (1 - C_{sa}) S_\beta}{S_a + S_\beta} \quad (12a)$$

$$B_n = \frac{2(S_a + S_\beta) V}{(n\pi)^2} \frac{p_n (1 - k) \sin(n\pi f)}{D \left[1 + \left(p_n (1 - V^2/V_D^2) k_c\right)^2\right]} - 1 + 2k \quad (12b)$$

where $p_n = 2n\pi/Pe$ with the eutectic Peclet number $Pe = VA/(2D)$.

2.4. Interfacial Chemical Composition

For the undercooling calculation, the interfacial average composition in liquid is obtained from the TMK model [19]. Using Equation (8a), the results are as follows:

- in front of the $\alpha$ phase

$$\bar{C}_\alpha = C_\alpha + B_0 + \frac{2(S_a + S_\beta) V}{S_a D (1 - k) P} \quad (13a)$$

- in front of the $\beta$ phase

$$\bar{C}_\beta = C_\beta + B_0 - \frac{2(S_a + S_\beta) V}{S_\beta D (1 - k) P} \quad (13b)$$

The function $P$ in Equation (13) is obtained according to the above two cases of the phase diagram as follows:

Case I: cigar-shaped phase diagram

$$P = \sum_{n=1}^{\infty} \sin^2\left(\frac{n\pi f}{n\pi}\right) \frac{p_n}{(n\pi)^3} \frac{p_n k_c (1 - V^2/V_D^2)}{1 + \left[p_n k_c (1 - V^2/V_D^2)\right]^2} + 1 \quad (14a)$$

$$P + \lambda \frac{\partial P}{\partial \lambda} = \sum_{n=1}^{\infty} \sin^2\left(\frac{n\pi f}{n\pi}\right) \frac{p_n k_c (1 - V^2/V_D^2)}{1 + \left[p_n k_c (1 - V^2/V_D^2)\right]^2} + 1 \left[p_n k_c (1 - V^2/V_D^2)\right] \quad (14b)$$

Case II: diagram with equal distribution coefficients

$$P = \sum_{n=1}^{\infty} \sin^2\left(\frac{n\pi f}{n\pi}\right) \frac{p_n}{(n\pi)^3} \frac{p_n}{1 + \left[p_n k_c (1 - V^2/V_D^2)\right]^2} - 1 + 2k \quad (15a)$$

$$P + \lambda \frac{\partial P}{\partial \lambda} = \sum_{n=1}^{\infty} \sin^2\left(\frac{n\pi f}{n\pi}\right) \frac{p_n k_c (1 - V^2/V_D^2)}{1 + \left[p_n k_c (1 - V^2/V_D^2)\right]^2} + 1 \left[p_n k_c (1 - V^2/V_D^2)\right] \quad (15b)$$
As a result, expressions (13)–(15) completely define the concentration at the interface. Note that if \( k \to 1 \), case II transforms to case I.

### 2.5. Interfacial Undercooling \( (V < V_D) \)

The undercooling at the interface “liquid—eutectic pattern” consists of four terms: constitutional undercooling \( (\Delta T_c) \), curvature undercooling \( (\Delta T_r) \), kinetic undercooling \( (\Delta T_k) \), and thermal undercooling \( (\Delta T_t) \). The sum of the first three terms comprises the so-called interfacial undercooling.

For each phase, it is given by

\[
\Delta T_I = T_k - T_I = \Delta T_c + \Delta T_r + \Delta T_k = m_i (C_k - C) + \Gamma_i \frac{\sin \theta_i}{S_i} + \frac{V}{\mu_i}
\]  

(16)

where \( T_k \) is the equilibrium eutectic temperature, \( m_i \) is the velocity-dependent liquidus line slope, \( \Gamma_i \) is the Gibbs–Thomson coefficient (ratio of the surface energy to melting entropy per unit volume), \( \theta_i \) is the contact angle at the triple point junction (see Figure 2b in which “\( i = \alpha \) or \( \beta \)”), \( S_i \) is half the width of the lamellar structure, and \( \mu_i \) is the effective kinetic coefficient for the growth of each eutectic phase. Following the procedure described by the TMK model [19], the average undercooling at the interface for the lamellar eutectic pattern is obtained by inserting average values for the concentrations \( (\bar{C}_\alpha \) and \( \bar{C}_\beta \) and curvatures \( \sin \theta_\alpha / S_\alpha \) and \( \sin \theta_\beta / S_\beta \) of the \( \alpha \) phase and \( \beta \) phase, respectively.

From Equation (16), the undercoolings at the front of the \( \alpha \)-phase and \( \beta \)-phase are described by [19]

\[
\Delta T_\alpha = m_\alpha (\bar{C}_\alpha - C_E) + \Gamma_\alpha \frac{\sin \theta_\alpha}{S_\alpha} + \frac{V}{\mu_\alpha}
\]  

(17a)

\[
\Delta T_\beta = m_\beta (C_E - \bar{C}_\beta) + \Gamma_\beta \frac{\sin \theta_\beta}{S_\beta} + \frac{V}{\mu_\beta}
\]  

(17b)

The solid–liquid interfaces of regular lamellar eutectics are usually assumed to be isothermal. Therefore, one can accept the equality \( \Delta T_\alpha = \Delta T_\beta = \Delta T_I \). To eliminate the terms involving \( \bar{C}_\alpha \) we combine Equation (13) with Equation (17) and find the interfacial undercooling as [19]

\[
\Delta T_I = m^v \left[ (Q_0^v \lambda + \frac{1}{\mu}) V + a^v \frac{1}{\lambda} \right]
\]  

(18)

where

\[
Q_0^v = \frac{1 - k}{f_\alpha f_\beta} \frac{P}{D}
\]  

(19)

\[
a^v = 2 \left( \frac{\Gamma_\alpha \sin \theta_\alpha + \Gamma_\beta \sin \theta_\beta}{m_\alpha f_\alpha + m_\beta f_\beta} \right)
\]  

(20)

\[
m^v = \frac{m_\alpha m_\beta}{m_\alpha^v + m_\beta^v}
\]  

(21)
Now, consider the macrointerface as the dendritic surface with the dendrite tip radius \( R \), which is much larger than the interlamellar spacing, \( \lambda \ll R \) (Figure 3). Considering the transition from a eutectic pattern to a eutectic dendrite at high undercooling, the thermal undercooling can be described as

\[
\Delta T_i = \frac{\Delta H}{C_p} \text{Iv}(P_i)
\]  

(23)

where \( \Delta H = f_\alpha \Delta H_\alpha + f_\beta \Delta H_\beta \) is the weighted heat of fusion of two eutectic phases and \( C_p \) is the specific heat of the liquid. \( \text{Iv}(P_i) \) is the Ivantsov function.

Combining Equations (18)–(23), one obtains the melt undercooling \( \Delta T \) as the sum of \( \Delta T_i \) and \( \Delta T_t \):

\[
\Delta T = \Delta T_i + \Delta T_r + \Delta T_k + \Delta T_t = m_r \left[ \left( \frac{Q_0 \lambda + 1}{\mu} \right) V + \frac{a^l}{\lambda} \right] + \frac{\Delta H}{C_p} \text{Iv}(P_i)
\]  

(24)

To analyze the behaviour of the interlamellar spacing \( \lambda \), we apply the minimum undercooling principle [21] given by the natural condition \( \partial \Delta T / \partial \lambda = 0 \). Using Equation (24) leads to the following relationship for the lamellar spacing as a function of velocity:

\[
\lambda^2 \frac{V}{a^l} = \frac{Q^l}{Q^l}
\]  

(25)

\[
Q^l = \frac{1}{f_\alpha f_\beta} \frac{1 - k}{D} \left( P + \lambda \frac{\partial P}{\partial \lambda} \right)
\]  

(26)

From Equation (25) and Equation (26), the relationship of undercooling and interlamellar spacing is obtained as

\[
\Delta T = m_r \frac{a^l}{\lambda} \left[ 1 + \frac{P}{P + \lambda \frac{\partial P}{\partial \lambda}} + \frac{1}{\mu Q^l \lambda} \right] + \frac{\Delta H}{C_p} \text{Iv}(P_i)
\]  

(27)
As a result of Solutions (24)–(27), the growth velocity \((V)\) and lamellar spacing \((\lambda)\) are determined as a function of the melt undercooling \((\Delta T)\). Under local equilibrium conditions in the diffusion field, \(V_0 \to \infty\) and \(k_c \to 1\), and the system of Equations (24)–(27) transforms to the expression \(\Delta T-V-\lambda\) previously obtained in the LZ model (with thermal and kinetic contributions to undercooling) or T Mk model (without thermal and kinetic contributions to undercooling).

2.6. Solute Distribution Coefficient and Liquidus Line Slope

To obtain the model predictions, the solute distribution coefficient is needed first. Using generalized Fick’s law that accounts for the finite relaxation time of the diffusion flux into its steady state, one can find the solute segregation coefficient (see overview [28] and references therein):

\[
k(V, V_D) = \frac{(1-V^2/V_D^2)[k_c + (1-k_c)C_o]}{1-V^2/V_D^2 + V/V_D} \quad \text{for} \quad V < V_D \tag{28a}
\]

\[
k(V, V_D) = 1 \quad \text{for} \quad V \geq V_D \tag{28b}
\]

Where \(V_D\) is the speed of diffusion at the interface and \(C_o\) is the initial composition in atomic fraction for the primary (dendritic) phase.

For a eutectic alloy, the initial composition for two different phases becomes different, such that the solid concentration is \(C_o = C_{\alpha}\) for the \(\alpha\)-phase and \(C_o = 1 - C_{\beta}\) for the \(\beta\) phase in the steady-state regime of solidification. Then, taking the concentration effect into account, Equation (28) becomes

\[
k(V, V_D, k_c) = \frac{k_c(1-V^2/V_D^2)[k_c + (1-k_c)C_o]}{k_c(1-V^2/V_D^2) + V/V_D} \quad \text{for} \quad V < V_D \tag{29a}
\]

\[
k(V, V_D, k_c) = 1 \quad \text{for} \quad V \geq V_D \tag{29b}
\]

Second, the liquidus line slope \(m=(T_m-T_e)/C_e\) means the change in liquidus temperature with a composition that allows us to predict the melting points for the \(\alpha\) phase and \(\beta\) phase. Hence, a general case of kinetic liquidus can be described (see overview [28] and references therein):

\[
m_i = m_i \frac{1-k + \ln(k / k_c) + [(1-k)(V/V_D)]^2}{1-k_c} \tag{30}
\]

where \(m_i\) is the liquidus line slope of the \(\alpha\) phase or \(\beta\) phase in the equilibrium phase diagram of the phase state in the coordinates “temperature-concentration”.

3. Results

In this section, different effects of material parameters on the kinetics of solidification are demonstrated. In particular, the effects of bulk interdiffusion, atomic redistribution at the interface, and peculiarity of the phase diagram (through different values of the liquidus line slope) are discussed.

3.1. Comparison with Other Models

Compared to the LZ model [21], the present model adds the parameters \(V_D\) and \(k_0\), but the calculation process remains as simple as that of the LZ model. Figure 4 shows the \(\Delta T-V\) curves calculated from different models with the same parameters: \(C_e=50\ \text{at.\%}, k = k_s = k_p = 0.04, T_e = 1400\ \text{K}, C_{\alpha} = C_{\beta} = 0.02\ \text{at.\%},\) and \(m_\alpha = m_\beta = 500\ \text{K/\text{at.\%}}\). The \(\Delta T-V\) curve calculated from the JH model with the constant diffusion coefficient \(D\) shows an \(n\)-power re-
The relationship. The $\Delta T-V$ curve of the TMK model exhibits saturation (Figure 4), appearing mainly due to the temperature dependence of the diffusion coefficient. The kinetic curve for the LZ model lies lower than that of the TMK model and JH model because the kinetic undercooling maintains the coupled eutectic growth to higher undercooling. If $\mu$ is large enough, the kinetic curve for the LZ model may quantitatively converge with the prediction of the TMK model (Figure 4).

The kinetic curve given by the present model may lie lower or higher than the other models that depend on the value of solute diffusion speed ($V_0$) (Figure 4). If $V_0$ is large enough and the solute distribution coefficient is the same as that of the LZ model, then the kinetic curve of the present model becomes the same as that of the LZ model. In the range of small undercooling, the kinetic curves of all models become quantitatively and qualitatively similar due to the smallest growth velocity in comparison with the intensity of the interface and bulk diffusion processes.

![Figure 4](image)

**Figure 4.** The calculated curves of different models with the same material parameters: $C_i=50$ at.%, $k=\bar{k}=0.04$, $T_e=1400$ K, $C_{Si}=C_{Si}=0.02$ at.%, $m_{\alpha}=m_{\beta}=500$ K/at.%, and $V_0=0.4$ m/s.

### 3.2. Effect of $V_0$ on $\Delta T$ and $\lambda$-$\Delta T$

The solute diffusion speed ($V_0$) limits the critical growth velocity for the eutectic reaction from diffusion-limited growth to a diffusionless transition [32]. Figure 5a shows the $\Delta T-V$ curves changing with different $V_0$. It can be found that a smaller $V_0$ leads to a lower $\Delta T-V$ curve. Figure 5b shows $\lambda$-$\Delta T$ curves in which the value of $V_0$ mainly affects the maximal undercooling but has a small effect on the value of $\lambda$. This is due to the smaller diffusion coefficient $D$, and if $V\to V_0$, the lamellar eutectic growth is gradually suppressed in such a case.

![Figure 5](image)

**Figure 5.** Effect of $V_0$ on the growth velocity and interlamellar spacing: (a) $\Delta T-V$; (b) $\lambda$-$\Delta T$. 
3.3. Effect of $k_0$ on $\Delta T$-$V$ and $\lambda$-$\Delta T$ Curves

Figure 6 shows the effect of the composition factor $k_0$ on the $\Delta T$-$V$ and $\lambda$-$\Delta T$ curves with a eutectic composition (CE = 50 at%) and hypoeutectic composition (CE = 40 at%). For the eutectic composition, $k_0$ has no effect on the relation of $\Delta T$-$V$-$\lambda$ because $k_0$ from Equation (4) is always equal to 1. For off-eutectic hypoeutectic alloys, the results depend on the value of $k_0$ relative to 1.

If $k_0>1$, the growth velocity is higher than that of the eutectic composition. The increase in $k_0$ leads to an increase in the distance between the eutectic curve and the off-eutectic curve. The farther the composition was from the eutectic point, the larger the gap between the growth rate and eutectic composition was (see left panel in Figure 6).

If $0<k_0<1$, the growth velocity of the off-eutectic alloy is lower than that of the eutectic composition (see the left panel in Figure 6). The farther away the composition was from the eutectic point, the larger the gap between the growth rate and eutectic components was.

Finally, $k_0$ has a very small effect on lamellar spacing (right panel in Figure 6).

![Figure 6. Effect of $k_0$ on the model calculation: (a) $\Delta T$-$V$; (b) $\lambda$-$\Delta T$.](image)

4. Comparisons with Experiments

In a comparison of the present model predictions with experiments, Figure 7a shows the experimental results of $\Delta T$-$V$ for different compositions of Ni–B hypoeutectic alloy. The experimental method has been described elsewhere [33]. In the hypoeutectic alloy (boron content < 16.5 at% B), the average growth velocity is larger than that of the eutectic alloy (boron content = 16.5 at% B) in the measured undercooling range. Using the present model Equations (24)–(27), it can be found that the calculated results from eutectic to hypoeutectic composition are consistent with the experimental results if $k_0=5$ (Figure 7a). Figure 7b shows the experimental data for the $\Delta T$-$V$ relationship obtained in the hypereutectic Ni–B alloy (boron content > 16.5 at% B). Due to the method used [33], the experimental data have a large scatter in a rather wide range of undercoolings. The overall trend of theoretical predictions, however, still shows the trend of experimentally measured data $\Delta T$-$V$ correctly. The average growth velocity of the hypereutectic alloy is also larger than that of the eutectic alloy (boron content = 16.5 at% B). Using the present model Equations (24)–(27), the theoretical predictions are consistent with the experimental data if $k_0=5$ (Figure 7b).
Figure 7. Experimental results and model predictions of off-eutectic Ni–B alloy growth velocity: (a) hypoeutectic alloy and (b) hypereutectic alloy. Material parameters for calculations are taken from Table 1.

Table 1. The parameters for the model calculation of Ni/Ni3B eutectic growth [33].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_\alpha$ (Jmol$^{-1}$)</td>
<td>$2.24 \times 10^4$</td>
<td>$C_{sat}$</td>
<td>0.0029</td>
</tr>
<tr>
<td>$\Delta H_\beta$ (Jmol$^{-1}$)</td>
<td>$1.38 \times 10^4$</td>
<td>$C_{sat}$</td>
<td>0.25</td>
</tr>
<tr>
<td>$m_\alpha$ (Kat$^{-1}$)</td>
<td>2168</td>
<td>$T_e$ (K)</td>
<td>1360.6</td>
</tr>
<tr>
<td>$m_\beta$ (Kat$^{-1}$)</td>
<td>787.5</td>
<td>$T_e$ (K)</td>
<td>0.17</td>
</tr>
<tr>
<td>$\Gamma_\alpha$ (K m)</td>
<td>$1.33 \times 10^{-7}$</td>
<td>$\alpha$ (m$^2$s$^{-1}$)</td>
<td>$1.5 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\Gamma_\beta$ (K m)</td>
<td>$1.89 \times 10^{-7}$</td>
<td>$k_\alpha$, $k_\beta$</td>
<td>0.001</td>
</tr>
<tr>
<td>$V_0$ (m s$^{-1}$)</td>
<td>0.45</td>
<td>$D_0$ (m$^2$s$^{-1}$)</td>
<td>$1.7 \times 10^{-9}$</td>
</tr>
<tr>
<td>$V_{II}$ (m s$^{-1}$)</td>
<td>0.055</td>
<td>$C_r$ (J mol$^{-1}$K$^{-1}$)</td>
<td>50</td>
</tr>
</tbody>
</table>

To further show the applicability of the present model, the relationship between the growth velocity and the undercooling of Ti–Si eutectic alloy measured experimentally by Luo et al. [34] was used. As shown in Figure 8, the experimental data can be described well in an undercooling range of 50 K to 243 K. When the undercooling is smaller than 50 K, our model disagrees with the experimental data. The reason why we obtained such deviation of the theory from experimental measurements is that the robust accuracy of measurements lies in the undercooling range higher than 40–50 K for electrostatic and electromagnetic levitation methods. Additionally, if the undercooling is higher than 243 K, the growth mode can be drastically changed. Instead of coupled growth of eutectic lamellas, one can obtain strongly irregular eutectics, which obviously cannot be described by the present model.

Figure 8. Eutectic growth velocity in solidifying Ti$_{86.33}$Si$_{13.67}$ alloy. The present model calculations (the solid curve) are shown in comparison with experimental results [34]. Material parameters for calculations are taken from Table 2.
Table 2. The parameters for the model calculation of eutectic growth for Ti6.3Si3.87 alloy [35].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta H_t) (J·mol(^{-1}))</td>
<td>1.545 \times 10^4</td>
<td>(C_{ss}) (at.%)</td>
<td>0.04</td>
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<tr>
<td>(\Delta H_{fus}) (J·mol(^{-1}))</td>
<td>7.412 \times 10^4</td>
<td>(C_{pf}) (at.%)</td>
<td>0.345</td>
</tr>
<tr>
<td>(n_a) (K·at(^{-1}))</td>
<td>45</td>
<td>(T_e) (K)</td>
<td>1618</td>
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<tr>
<td>(n_p) (K·at(^{-1}))</td>
<td>90</td>
<td>(C_{ss}) (at.%)</td>
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</tr>
<tr>
<td>(V_0) (m·s(^{-1}))</td>
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<td>(\alpha) (m(^2)·s(^{-1}))</td>
<td>1.5 \times 10^{-6}</td>
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<tr>
<td>(V_{\beta}) (m·s(^{-1}))</td>
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<td>(k_s, k_\beta) (-)</td>
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<tr>
<td>(C_p) (J·mol(^{-1})·K(^{-1}))</td>
<td>50</td>
<td>(D_h) (m(^2)·s(^{-1}))</td>
<td>3.8 \times 10^{-12}</td>
</tr>
</tbody>
</table>

5. Discussion

The experimental results show that the growth velocity for off-eutectic alloys is always larger than that for eutectic alloys due to the composition effect. The change in composition leads to the diffusion coefficient change that provides the following effects:

1. The primary phase prevents the eutectic phase from growing fastest [36].
2. The diffusion coefficient of the solid phase increases with increasing composition; however, the liquid phase decreases with increasing alloy composition [29,30], and the mixture of liquid diffusion and solid diffusion leads to a possible increase or decrease in the growth velocity of the off-eutectic alloy.
3. For hypoeutectic alloys, the composition is far from the eutectic point, and the liquid phase fraction is relatively small during solidification after the primary transition, such that the solidification rate should be faster. For hypereutectic alloys and before eutectic transformation, the presence of the primary phase increases the nucleation rate of eutectic patterns.

All these results lead to the growth velocity of the eutectic transition for the off-eutectic composition being larger than that for the eutectic composition for a given undercooling.

Finally, one should mark that we only analyzed the growth of phases, i.e., their ability to grow for the formed undercooling in the bulk phases and at the solid–liquid interface. However, we also know that the microstructure formation in eutectic mixtures is always a process that is usually dictated by the competition between the growth and nucleation of phases. Therefore, the analysis of rapid (off) eutectic solidification with a coupled process which includes the growth of phases and their nucleation is seen by us as a future advancement of the present work.

6. Conclusions

The eutectic growth model considering the composition effect on crystallization kinetics is proposed based on the theory for the transformations in off-eutectic alloys.

The effects of solute diffusion speed \((V_\beta)\) and composition factor \((k_\beta)\) on the theoretical predictions are discussed. If \(V_{\beta_{\infty}}\) and \(k_\beta=1\), the present model predictions converge with the results of the LZ model [21], but with novel advancements, such as the composition effect on the solidification kinetics.

A comparison of the present model predictions with the growth velocity for off-eutectic Ni–B and Fe–Ni–B alloys found experimentally shows the model's consistency in describing the solidification kinetics at small and large values of undercooling.

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References


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