Modeling dendrite growth in undercooled concentrated multi-component alloys

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Abstract

Most theoretical work on dendrite growth has focused on dilute binary alloys, while most industrial alloys are concentrated multi-component systems. By incorporating the local non-equilibrium effects both at the interface and in the bulk liquid, the thermodynamic database and diffusional interaction, a model was developed for dendrite growth in undercooled concentrated multi-component alloys. An experimental study of dendrite growth in undercooled Ni–18 at.% Cu–18 at.% Co melts was carried out and the measured interface velocities (V) were well predicted by the present model over the whole undercooling range ($\Delta T = 30$–313 K). During dendrite growth the partition coefficients change non-monotonically due to interaction between the species and changes in the dendrite tip radius. Interaction between the species also leads to a lower interface velocity and larger ΔT and V as the ΔT–V relation plateaus. The previous definition of constitutional undercooling, i.e. the sum of the contributions of each solute, is not applicable to concentrated multi-component alloys. The controlling mechanisms during dendrite growth are discussed with respect to the results of the calculations.

1. Introduction

Dendrite growth has been an important scientific and practical subject for several decades [1–3]. A great deal of theoretical work has been carried out, prompted by the need to predict microstructure formation during solidification [1,4]. Although the approach of combining the transport solution of Ivantsov [5,6] with the marginal stability criterion (i.e. IMS models) [2,7] is not completely fundamentally correct, compared with solvability theory [1], good model predictions can be obtained over a substantial range of undercoolings for a large number of metals and alloys [8,9], even without adjustable parameters [10]. Therefore, the IMS models are still useful for quantitative prediction of dendrite growth velocities [9]. Among them, the model of Boettinger, Coriell and Trivedi (BCT) [11] for local non-equilibrium interface conditions is the most

widely accepted, due to its mathematical simplicity. Despite its remarkable success, the BCT model is limited to an ideal dilute binary alloy system with a linear liquidus/solidus (LLS) and local equilibrium diffusion (LED) in the liquid.

Although adopted extensively by early solidification models the assumption of LLS is applicable to very limited alloy systems. For most alloys with a typically curved liquidus/solidus physically unrealistic model predictions are inevitable [12–16]. Divenuti and Ando (DA) [12] incorporated the effect of a non-linear liquidus/solidus (NLLS) into linear stability analysis [17,18] and proposed an extended dendrite growth model. In contradiction to the results of both experiments [19] and molecular dynamics simulations [20] complete solute trapping occurs at an infinite interface velocity due to the assumption of LED in the liquid.

Departing from extended irreversible thermodynamics (EIT) [21], Sobolev and Galenko [22–25] extended the interface kinetic model to local non-equilibrium diffusion

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(LNED) in a bulk liquid. After that Galenko et al. carried out a linear stability analysis [26] and proposed a modified dendrite growth model [27,28]. A comparison with experimental results for a dilute Ni–Zr alloy [29] showed that the model with LLS deviates from the experimental results in the solute-controlled stage. Wang et al. considered the effects of both LNED in the bulk liquid and NLLS on linear stability analysis [15,16], dendrite growth [13,14], dendrite fragmentation [30] and overall solidification kinetics [31,32]. Their models [13–16,30–32], however, are limited to dilute binary alloys.

The interface kinetic models for concentrated binary alloys were recently revised by integrating the effects of LNED and the thermodynamic database [33–35]. On this basis the linear stability analysis and free dendrite growth model of Wang et al. [13–15] were extended [36,37]. Compared with the BCT model, the latest dendrite growth model [37] incorporating the effects of NLLS, interaction in the concentrated solution and LNED at the interface and in the bulk liquid is more physically realistic in describing dendrite growth in highly undercooled melts.

Unlike most theoretical work, industrial alloys usually contain more than two components and thus the application of solidification theories in practice is limited by our ability to model the solidification of multi-component alloys [9]. Assuming LED and LLS, diffusional interaction was introduced into the diffusion matrix by Hunziker [38] and dendrite growth was found to be significantly influenced by the non-monotonic concentration profile at the dendrite front. Theoretical and experimental studies in Fe–Ni–Cr [39,40] and dilute Ni–Zr–Al ternary alloys [41] were carried out in which solute trapping models for binary alloys [33,42] were adopted and the constitutional undercooling (ΔT_C) was obtained by summing the contributions of each solute. The models are, however, not applicable to concentrated multi-component alloys [43,44]. Based on EIT and the thermodynamic extremal principle Wang et al. [45] recently derived a self-consistent sharp interface kinetic model for concentrated multi-component alloys. It was found that the partition coefficient changed non-monotonically at a significantly lower interface temperature as a result of interaction between different species.

The present work aims to model the free dendrite growth during rapid solidification of concentrated multi-component alloys. In terms of our sharp interface kinetic model [45], an extended stability analysis is carried out and an extended free dendrite growth model is proposed (Section 2). To test the present model dendrite growth in undercooled Ni–18 at.% Cu–18 at.% Co melts is studied. The experimental procedures are given in Section 3, and the results are presented and compared with the present model predictions in Section 4. To show the characteristics of the present model interactions in concentrated solution, the definition for ΔT_C and the controlling mechanisms during dendrite growth are discussed with respect to the results of the calculations (Section 5). Finally, our main conclusions are summarized in Section 6.

2. Model derivation

2.1. Governing equations and boundary conditions

The steady-state rapid solidification of an n component concentrated substitutional alloy system is considered. Due to the constraint $\sum_{j=1}^{n} x_j = 1$ with x_j as the molar fraction (i.e. the concentration) of component j, the concentrations of the solute species with $j = 2, 3, \ldots, n$ are chosen as the independent variables. The solid/liquid (S/L) interface moves toward the melt (in the Z direction) with a constant velocity V. Attaching the moving reference coordinate to the interface, the diffusion equation of component j is usually given as [13,28],

$$-V\frac{\partial x_j}{\partial Z} = D_j \psi_j \frac{\partial^2 x_j}{\partial Z^2} + D_j \frac{\partial^2 x_j}{\partial X^2} \tag{1}$$

where D_j is the diffusion coefficient, $\psi_j (= 1 - V^2/(V_j^L)^2)$ is the non-equilibrium diffusion factor and V_j^L is the diffusion speed in the liquid [22,23]. In this case the diffusion of component j is independent of other species. For the present concentrated alloy system the diffusional interaction among different species needs to be considered [38], and Eq. (1) is modified as:

$$-V\frac{\partial x_j}{\partial Z} = \sum_{k=1}^{n}\left(D_{jk}\psi_k \frac{\partial^2 x_k}{\partial Z^2} + D_{jk}\frac{\partial^2 x_k}{\partial X^2}\right) \tag{2}$$

where D is the diffusion matrix with its element D_{jk} representing the interaction between the components j and k. For a planar interface there is no lateral diffusion (i.e. diffusion in the X direction) and the solution of Eq. (2) is [38],

$$x_j^L - x_j^{il} = \sum_{i=1}^{n} L_{ji}\left[1 - \exp\left(-\frac{VZ}{B_i}\right)\right] \tag{3}$$

Then substituting Eq. (3) into Eq. (2) yields,

$$B_i L_{ji} = \sum_{k=1}^{n}(D_{jk}\psi_k L_{ki}) \tag{4}$$

where x_j^{il} and x_j^L are the concentrations of component j at the liquid side of the interface and in the bulk liquid, respectively, B_i is the eigenvalue of the effective diffusion matrix ($D\psi$) and L_i is the corresponding eigenvector with L_{ji} as its jth element. The matrix for non-equilibrium diffusion factors ψ is defined as,

$$\psi = \begin{pmatrix} \psi_1 & 0 & \cdots & 0 \\ 0 & \psi_2 & \cdots & 0 \\ \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & \cdots & \psi_n \end{pmatrix} \tag{5}$$

The derivative of Eq. (3) with respect to Z yields the concentration gradient at the liquid side of the interface G_j^{il},

$$G_j^{il} \equiv \left.\frac{\partial x_j^L}{\partial Z}\right|_{Z=0} = \sum_{i=1}^{n} L_{ji}\frac{V}{B_i} \tag{6}$$