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Simulation of dendrite growth in ternary alloys

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Abstract

The conventional theory of constrained dendrite growth for binary alloys was extended to multicomponent alloys, taking into account the solute interactions in each phase. These interactions influence not only the phase equilibria between liquid and solid but also the diffusion behaviors. This is not possible for conventional methods that apply constant parameters, typically approximated from the corresponding binary systems. Their influence on the kinetics of dendrite growth was demonstrated quantitatively in Cu–Sn–Zn ternary systems. The great difference from the simulated results without solute interactions demonstrated its necessity of coupling thermodynamic databases in the simulation of solidification process.

Keywords: Dendrite growth; Ternary alloys; Diffusion; Thermodynamics

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1. Introduction

Dendrite structures are the predominant microstructural constituents of solidified alloys. In 1947, Ivantsov had already acquired the analytical solution of the steady state solute field around the dendrite tip by assuming the interface as a paraboloid. [1]. In the following decades, great advances were made in developing the theories of constrained growth of columnar dendrites [2–5]. The theories have primarily been applied to binary alloys, but some approximation to multicomponent alloys was also presented [6]. In multicomponent alloys, however, the composition equilibria at the solid–liquid interface and the diffusion matrix cannot be easily determined from the corresponding binary systems. The conventional solution avoided this difficulty by applying constant parameters, typically approximated from corresponding binary systems. In this case, the solute distributions in each phase and the composition equilibria cannot be reliably predicted in the simulation process.

In this paper, a convenient way to solve this problem is developed by determining the phase equilibria and diffusion matrix with a new method using thermodynamic databases and the diffusion mobility coefficients. The calculation was applied to Cu–Sn–Zn alloys as an example to compare this method with the conventional models.

2. Theoretical model

2.1. Multicomponent thermodynamics

In the case of multicomponent alloys, the equilibrium liquidus and solidus concentrations are defined by the tie-line of phase diagram if the temperature is known. The integral Gibbs energy for each phase depends on its constitutions, temperature and pressure, and is described by the thermodynamic models in the CALPHAD method [7].

There are a large number of thermodynamic models for various substances in different state, such as the Redlich–Kister–Muggianu formalism for fcc, bcc and hcp solid solution phases and the sublattice model for the description of the phase with two or more sublattices. Such work is near fruition, since there are now several available software

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systems capable of estimating the phase equilibrium as a function of pressure, temperature and the chemical composition. The prediction of phase equilibrium between liquid and solid and the phase diagram characteristic (i.e., the liquidus slope and the freezing range) is easily accomplished by calling to Thermo-Calc through the TQ interface [8]. In this software, the tie-line are calculated minimizing the Gibbs free energy of the system with respected to temperature, number and composition of phases and, if relevant, to pressure.

2.2. The solute diffusion in multicomponent alloys

A more general representation of multicomponent diffusion fluxes is given by [9]

$$J_i = -\sum_{j=1}^{n-1} D_{ij}^n \nabla C_j \tag{1}$$

where n is the number of components in the system and the D_{ij}^n are the multicomponent diffusion coefficients. The subscript i and j refer to the solute i and j, respectively. The summation in Eq. (1) is over only $n-1$ components because the concentration of the nth component can always be written in terms of a linear combination of the other $n-1$ components.

For the case that the elements are substitutional, the diffusion coefficient defined in the volume-fixed frame of reference, D_{ij}^V, can be expressed as

$$D_{ij}^V = \sum_{k=1}^{n} (\delta_{ki} - x_i) x_k \Omega_k \frac{\partial \mu_k}{\partial x_j} \tag{2}$$

where x_i is the mole fraction of component i, μ_k is the chemical potential of component k, δ_{ki} is the Kronecker delta, i.e., $\delta_{ki}=1$ when $i=k$ and 0 otherwise. It can be observed that the quantity $\partial\mu_k/\partial x_j$ is a purely thermodynamic parameter and corresponds to the thermodynamic factor [10]. This quantity can thus be evaluated from the thermodynamic description of the system. The parameter Ω_k is the mobility of specie k in a given phase and will be discussed later.

The chemical diffusion coefficients, by eliminating the concentration element n, can be deduced as

$$D_{ij}^n = D_{ij}^V - D_{in}^V \tag{3}$$

where n is the solvent and D_{ij}^V are given in Eq. (2). The diffusivity D_{ij}^n is the most convenient one for practical calculations.

Determination of the diffusion mobility parameter in Eq. (2) requires the use of experimental diffusion data. Tracer or self diffusivities, D_i^*, is generally determined from diffusion studies using isotopes and directly related to the mobility Ω_k by means of the Einstein relation

$$D_i^* = RT\Omega_i. \tag{4}$$

Using the diffusion coefficient expression in Eq. (3), the concentration of element n is eliminated and an $(n-1)\times(n-1)$ chemical diffusion matrix is obtained.

2.3. Dendritic growth in multicomponent alloys

During dendrite growth, solute will be piled up ahead of the dendrite tips and the constitution undercooling may be introduced. Under steady state, the composition field around a dendrite tip is governed by the Ivantsov's equations in binary alloys. This can be extended to multicomponent alloys with a linear combination of $n-1$ terms corresponding to the binary solution [11]:

$$C_i(\eta) - C_i^\infty = \sum_{j=1}^{n-1} F_{ij} \left[\int_{\eta Pe_j}^{\infty} \frac{\exp(-u)}{u} du \Big/ \int_{Pe_j}^{\infty} \frac{\exp(-u)}{u} du \right] \tag{5}$$

where C_i^∞ is the concentration of solute i in the far field. The dendrite tip interface can be described by $\eta=1$. The Peclet number Pe_j is defined separately by each eigenvalue B_j of the diffusion matrix $\mathbf{D}^n$

$$Pe_j = \frac{rV}{2B_j} \tag{6}$$

where r is the dendrite tip radius and V is its growth velocity. The coefficients F_{ij} are the components of the corresponding vectors $\boldsymbol{F}_j$, which are related to the corresponding unit length eigenvectors $\boldsymbol{N}_j$ of matrix $\mathbf{D}^n$ by

$$F_{ij} = \|\boldsymbol{F}_j\| \boldsymbol{N}_{ij} \tag{7}$$

The magnitude of $\boldsymbol{F}_j$, $\|\boldsymbol{F}_j\|$ is still to be determined.

The boundary condition along the solid–liquid interface can be deduced from Eq. (5) as

$$\frac{rV}{2}\left(C_{i,\mathrm{L}}^* - C_{i,\mathrm{S}}^*\right) = \sum_{j=1}^{n-1} D_{ij} \sum_{k=1}^{n-1} F_{jk} \left[\exp(-Pe_k) \Big/ \int_{Pe_k}^{\infty} \frac{\exp(-u)}{u} du \right] \tag{8}$$

where $C_{i,\mathrm{L}}^*$ and $C_{i,\mathrm{S}}^*$ are the concentrations of the liquid and solid at the interface, respectively. Worth noting here is that the phase equilibrium is determined with consideration of all the solute interactions in each phase. This is not possible for conventional methods that apply constant value partition coefficients of solutes, typically approximated from binary phase diagrams.

The interface composition is then given by Eq. (5) with $\eta=1$

$$C_{i,\mathrm{L}}^* = C_i^\infty + \sum_{j=1}^{n-1} F_{ij}. \tag{9}$$

Thus the coefficients F_{ij} can be determined from Eqs. (5)–(9). The concentration of the liquid at the interface C_L^*