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Eutectic growth in two-phase multicomponent alloys

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ABSTRACT

A theory of two-phase eutectic growth for a multicomponent alloy is presented. Using the same hypotheses as the Jackson-Hunt theory, we find that the growth law of the microstructure given by Jackson and Hunt for binary alloys can be generalized to systems with N elements. Thermodynamic parameters involved in this theory are linked to the Gibbs free energies of the phases which makes it possible to compute these parameters with CALPHAD tools. A model is derived from this general theory for ternary alloys which does not contain any assumptions on the alloy thermodynamic properties, contrary to previous models. We find that a small addition of a ternary alloying element with a small diffusivity to a binary alloy can significantly alter the spacing of the eutectic.

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1. Introduction

Eutectic alloys possess many advantages compared to single-phase systems. Indeed, they have a low melting point compared to pure components and their composite microstructure gives them superior mechanical properties.

For binary eutectics, Hillert [1] and later Jackson and Hunt [2] analytically determined a scaling law for the microstructure developed by regular eutectics during directional steady state solidification. Moreover, they have established a link between the microstructure developed and the thermodynamic and thermophysical properties of alloys. This scaling parameter has been proved to be very useful in characterizing the eutectic microstructure of many regular binary alloys [3].

However, an analogous theory for alloys with many components and growing as a two-phase eutectic does not exist. Such multicomponent two-phase eutectics are common and have been studied in, Al–Cu–Ag [4], Fe–Si–Mn, Fe–Si–Co [5], Al–Cu–Ni [6] and Ni–Al–Cr–Mo [7]. Moreover, most commercially relevant materials contain still more alloying elements. Unfortunately, a comprehensive model for the growth of these multicomponent

two-phase eutectics does not exist. However, there has been progress towards a general theory. Catalina et al. [8] proposed a model for eutectic growth of two-phase eutectics containing N elements, but restricted the treatment to the case where one of the phases has no solid solubility for the solute elements. Fridberg and Hillert [9] published a model for the growth process of a binary alloy containing a small amount of an additional element. Later, Plapp and Karma [10] analyzed the effect of a small addition of a third element on the morphology of a symmetrical binary eutectic. In ternary alloys, McCartney et al. [11] and DeWilde et al. [12] gave two different models. In the McCartney-Hunt model, simplifying approximations were employed on the alloy phase diagram and the diffusion process. DeWilde et al. employed an approximation for the manner in which the long-range diffusion field decays and for concentration profiles in the liquid phase. While all of these treatments provide important insights into eutectic solidification of multicomponent alloys, they lack the generality needed for many applications.

In this paper, we present a method to compute the mean undercooling of a two-phase eutectic as a function of the eutectic spacing and the velocity for any alloy containing N elements in the spirit of the Jackson Hunt model (Section II). This general method removes the approximations introduced in the models [8,11,12] mentioned above. It is then applied to binary alloys and compared to the Jackson-Hunt theory in section III. The model derived from this general method for ternary alloys is given in

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section IV. This model is then used to analyze the influence of the addition of a low concentration of a third element on the microstructure of a binary alloy. We finally discuss in section VI the use of this model as a way to predict of the eutectic microstructure evolution of an alloy with the addition of a new element. We conclude this paper by a summary of results presented and possible future continuation of this work.

2. Two-phase eutectic growth of alloys with N elements

In this section, we present our general methodology to compute the mean undercooling of any two-phase eutectic alloy with N elements.

We study the directional solidification at steady state of a two-phase eutectic with an initial concentration $(C_2^\infty, \ldots, C_N^\infty)$. In this work, the choice of the element 1, which concentration depends on independent concentrations of elements 2 to N is arbitrary. We assume that this eutectic develops a lamellar morphology such as the one presented in Fig. 1.

By definition, the two-phase eutectic temperature (T_E) is the temperature at which three phases, α, β and liquid are in equilibrium. For systems with more than three elements, this temperature depends on the alloy composition. All quantities referring to the eutectic temperature will be identified with a superscript 'E'. We assume that for any position x at the interface, the solid/liquid interface is at thermodynamic equilibrium at a temperature $T_u(x)$. So for any position x of the interface, the chemical potentials of any specie $i = 1\ldots N$ in the liquid phase and in the solid phase ϕ are equal:

$$\mu_i^\phi\left(C_2^\phi, \ldots, C_N^\phi, T_u, p^\phi\right) = \mu_i^l\left(C_2^l, \ldots, C_N^l, T_u, p^l\right) \quad i = 1, 2\ldots N \quad (1)$$

where C_i is the mole fraction of component i, p is the pressure, and ϕ can be either one of the two solid phases. For a given phase, assuming that $C_2^l \ldots, C_N^l, p^l$ and p^ϕ are known, this gives N equations and N unknowns. Thus once the composition of the liquid at the interface and the pressure in the solid phase are known, and by assuming that p^l does not change from that at the equilibrium state, the composition of the solid phase is known and the undercooling is fixed.

The variations in the rejection of solutes in front of solid phases, α and β, induce changes in the concentrations in the liquid phase at

the interface compared with the equilibrium state, $(C_2^{lE}, \ldots, C_N^{lE})$. In addition, the interface curvature due to the surface energies equilibrium at the trijunctions (points where the two solid phases are in contact with the liquid phase) induces a variation of the internal pressure in solid phases. Since local equilibrium is assumed to hold, these variations in the liquid composition induce changes in concentrations in solid phases from their equilibrium values, and a change in the interface temperature from Ref. T_E. The compositions of the solid, liquid and the temperature are related by N chemical potential equations for each solid phase. Unfortunately, these equations are nonlinear, and thus we assume small deviations from the equilibrium temperature, and phase compositions to relate the solid phase compositions and undercooling temperature to the liquid composition. The development of these N equalities (Eq. (1)) for each phase is given in the appendix A. This development leads to a matrix expressing the change in the concentration in solid phases from equilibrium, $\Delta C_i^\phi = C_i^{\phi E} - C_i^\phi (i = 2\ldots N)$ and the undercooling $\Delta T = T_E - T_u$ as a function of the concentration in the liquid phase $\Delta C_i^l = C_i^{lE} - C_i^l$ and of pressure in the solid phase Δp^ϕ.

At a given point x along the interface, the undercooling ΔT is thus expressed as a sum of a solutal (ΔT_C) and a curvature (ΔT_R) undercooling (see appendix A):

$$\Delta T(x) = \Delta T_C(x) + \Delta T_R(x) \quad (2)$$

where

$$\Delta T_C(x) = \sum_{i=2}^{N} m_i^\phi\left(C_i^{lE} - C_i^l(x)\right) \quad (3)$$

$$\Delta T_R(x) = -\frac{V_m^\phi}{\Delta S_{\phi l}}\Delta p^\phi(x) \quad (4)$$

where m_i^ϕ is a slope of a liquidus surface, V_m^ϕ is a molar volume, and $\Delta S_{\phi l}$ are defined in appendix A as functions of derivatives of molar Gibbs free energies of the solid and liquid phases. As $\Delta p^\phi = -\sigma_{\phi l}\kappa(x)$ where $\sigma_{\phi l}$ is the ϕ/l surface energy and $\kappa(x)$ is the interface curvature at x, Eq. (4) can be re-written:

$$\Delta T_R(x) = \Gamma_{\phi/l}\kappa(x) \quad (5)$$

where $\Gamma_{\phi/l} = \frac{V_m^\phi}{\Delta S_{\phi l}}\sigma_{\phi l}$ is the ϕ/l Gibbs Thomson coefficient.

As stated by Jackson and Hunt [2], the mean undercooling at the interface can be computed on half of a eutectic period:

$$\overline{\Delta T} = \frac{2}{\lambda}\int_0^{\lambda/2} \Delta T(x)dx \quad (6)$$

From Eq. (2), this mean eutectic undercooling can be separated as a mean solutal undercooling $\overline{\Delta T}_C$ and a mean curvature undercooling $\overline{\Delta T}_R$. Hillert [1], and Jackson and Hunt [2] have shown that for microstructures similar to Fig. 1, the mean curvature undercooling has the expression:

$$\overline{\Delta T}_R = \frac{K_R}{\lambda} \quad (7)$$

with

$$K_R = 2\left(\Gamma_{\alpha/l}\sin(|\theta_\alpha|) + \Gamma_{\beta/l}\sin\left(|\theta_\beta|\right)\right) \quad (8)$$
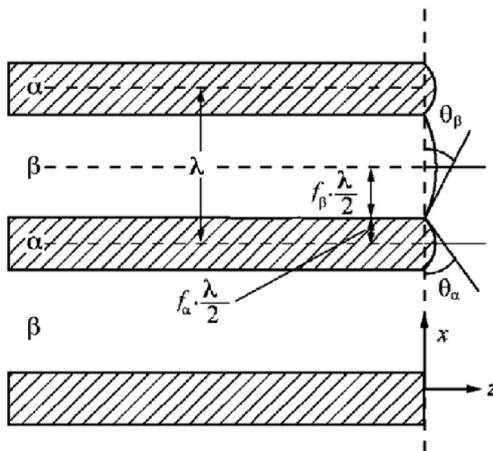
Fig. 1. Schematic representation of steady state directional growth with a lamellar morphology. Quantities reported on the figure are: eutectic spacing λ, solid fraction of α phase (f_α) and β phase (f_β), angles of curvature of α phase (θ_α) and β phase (θ_β) at the tri-junction (After Ludwig et al. [30]).