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General concept for a stability analysis of a planar interface under rapid solidification conditions in multi-component alloy systems

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Abstract

Stability analysis of a growing planar solid/liquid interface is not only important for predicting the limit of constitutional supercooling, V_C, or the limit of absolute stability, V_{abs}, but also for the formulation of the so-called marginal stability criterion. This criterion is widely used as an approximate theory for dendritic growth. In this paper, a general concept is introduced which allows analysis of the stability of a planar solid/liquid interface in technical, i.e. multi-component alloys. Capillarity and kinetic effects, and off-equilibrium thermodynamics are taken into account by solving an adequate non-linear system of equations. It is shown that dendrite tip radii and dendrite tip temperatures can be estimated as a function of growth rate and temperature gradient for multi-component alloys. For this the solution of a second linear system of equations coming from the general stability analysis is necessary. © 2001 Published by Elsevier Science B.V.

Keywords: Solid/liquid interface; Constitutional supercooling; Absolute stability; Multi-component alloys

1. Introduction

The linear stability of a planar interface was first analysed by Mullins and Sekerka [1] in 1964 for a dilute binary system and low Péclet numbers. In 1986, their theory was extended for large Péclet numbers by Trivedi and Kurz [2]. A year later Coriell et al. [3] proposed a similar concept extended to multi-component alloy systems. Generally, a stability analysis of a growing solidification front covers an initially planar interface moving with a constant velocity V_0 in the Z-direction. The planar front is thought to coincide with the plane $Z = 0$. The stability of the planar interface is then examined by imposing an infinitesimal perturbation in the shape on the interface such that the interface is described by the equation

$$Z = \phi(X, t) = \delta(t) \sin \omega X \tag{1}$$

where δ is the amplitude, ω the wave number ($= 2\pi/\lambda$), and λ the wavelength. X and Z are spatial co-ordinates and t the time. With this formulation, the interface velocity at the perturbed front is given by $V = V_0 + \delta V = V_0 + \dot{\phi}/\phi$ and the curvature by $K = K_0 + \delta K = 0 + \omega^2\phi$.

The planar interface is thought to be stable when $\dot{\phi}/\phi < 0$ for all perturbation wavelengths λ, and unstable when $\dot{\phi}/\phi > 0$ for at least one λ. Thus, the marginal stability condition can be obtained by examining the condition $\dot{\phi}/\phi = 0$.

Assuming a species diffusion ahead of the interface independent on the nature of an n-component alloy a solution of the heat and solute diffusion equations can be obtained [1] such that

$$T = T_0 + \delta T = T_0 + a\phi \tag{2a}$$

$$C_L^i = C_{L,0}^i + \delta C_L^i = C_{L,0}^i + b_L^i \phi, \quad i = 1, \ldots, n \tag{2b}$$

$$C_S^i = C_{S,0}^i + \delta C_S^i = C_{S,0}^i + b_S^i \phi, \quad i = 1, \ldots, n \tag{2c}$$

where T is the temperature at the perturbed interface, T_0 the temperature at the unperturbed flat interface, C_L^i the concentration of the ith species in the liquid at the perturbed interface and $C_{L,0}^i$ the concentration at the unperturbed flat interface. C_S^i and $C_{S,0}^i$ are the corresponding solid quantities. a, $b_L^1, \ldots, b_L^n$ and $b_S^1, \ldots, b_S^n$ are parameters which have to be determined by additional conditions. From the thermal flux balance at the interface, a can be expressed as a function of ω and $\dot{\phi}$ (Appendix A). From the solute flux balances, b_S^i can be expressed as function of b_L^i, ω, and $\dot{\phi}$ (Appendix B). The remaining equations to determine $b_L^1, \ldots, b_L^n$ and $\dot{\phi}$ are taken from thermodynamic considerations. However, due to the lack of alternatives the standard conditions for dilute multi-component systems are commonly used:

$$C_S^i = k^i C_L^i, \quad i = 1, \ldots, n \tag{3}$$

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$$T = T_\mathrm{f} + \sum_i m^i C_\mathrm{L}^i - \Gamma K - \frac{V}{\mu} \tag{4}$$

Here k^i is the distribution coefficient and m^i the liquidus slope of the ith species (which may depend on V), T_f the melting point of the pure solvent, $\Gamma := \gamma v_\mathrm{mol}/\Delta S_\mathrm{f}$ the Gibbs–Thomson coefficient, γ the surface tension, v_mol the molar volume, $\Delta S_\mathrm{f} = \Delta H_\mathrm{f}/T_\mathrm{f}$ the entropy of fusion, $\mu := \Delta H_\mathrm{f} V_\mathrm{max}/R_\mathrm{g} T_\mathrm{f}^2$ the kinetic coefficient, V_max the maximal velocity at infinite driving force and R_g the gas constant. $\Delta T_\mathrm{K} := V/\mu$ is called the kinetic undercooling and $\Delta T_\mathrm{R} := \Gamma K$ the capillary or curvature undercooling [4].

Taking the total derivation of Eqs. (3) and (4):

$$\delta C_\mathrm{S}^i = k^i \delta C_\mathrm{L}^i, \quad i = 1, \ldots, n \tag{5}$$

$$\delta T = T_\mathrm{f} + \sum_i m^i \delta C_\mathrm{L}^i - \Gamma \delta K - \frac{\delta V}{\mu} \tag{6}$$

and inserting Eqs. (2a)–(2c) and the relations for a and b_S^i from Appendices A and B, a linear system of equations for the unknown $b_\mathrm{L}^1, \ldots, b_\mathrm{L}^n$ and $\dot{\phi}$ arises. Since, apart from the last column and the last row, the off-diagonal elements of the governing matrix are all zero (because the species are not related to each other), the linear system of equations can easily be solved analytically. The solution is found to be [2]

$$-\Gamma\omega^2 - G_\mathrm{eff} + \sum_i m^i G_{\mathrm{C},0}^i \xi_\mathrm{C}^i = \frac{\dot{\phi}}{\phi} f(\omega) \tag{7}$$

where G_eff is defined in Appendix A. $G_{\mathrm{C},0}^i$ is the concentration gradient of the ith species in the liquid ahead of the unperturbed interface. For the definition of the stability functions ξ_L, ξ_S and ξ_C^i at that of $f(\omega)$ see [2,5]. Since it can be shown that $f(\omega)$ is always positive, the marginal stability condition is obtained by setting the right-hand side of Eq. (7) equal to zero.

The decisive importance of Eq. (7) is based on the fact that dendritic growth theory utilises the marginal stable wavelength as the operating point for the dendritic tip ($R = \lambda_i$ with tip radius R) [6–8]. The question then arises how Eq. (7) would look for non-dilute arbitrary n-component alloy systems. The derivation of a general expression for the marginal stability criterion is the major object of this paper.

2. Theory

2.1. Stability analysis for arbitrary n-component systems

Generally for an n-component alloy system it must be assumed that the solute incorporated into the growing solid $(C_\mathrm{S}^1, \ldots, C_\mathrm{S}^n)$ and the interface temperature T is related to the growth velocity V, the curvature at the interface K and the solute in the liquid ahead of the front $(C_\mathrm{L}^1, \ldots, C_\mathrm{L}^n)$:

$$C_\mathrm{S}^i = g_\mathrm{C}^i(C_\mathrm{L}^1, \ldots, C_\mathrm{L}^n, K, V), \quad i = 1, \ldots, n \tag{8}$$

$$T = g_\mathrm{T}(C_L^1, \ldots, C_L^n, K, V) \tag{9}$$

These relations reflect the off-equilibrium "thermodynamic" conditions at the interface, which are especially important for strong curvatures and/or rapid solidification. We will discuss the specific form of these relations in Chapter 2.2.

The main idea behind the general concept of the stability analysis of a planar interface in arbitrary n-component alloy systems is to replace the thermodynamic conditions for dilute n-component systems (Eqs. (5) and (6)) by their generalised counterparts (Eqs. (8) and (9)).

Thus, we consider the total derivation of Eqs. (8) and (9)

$$\delta C_\mathrm{S}^i = \sum_{j=1}^n \frac{\partial g_\mathrm{C}^i}{\partial C_\mathrm{L}^j} \delta C_\mathrm{L}^j + \frac{\partial g_\mathrm{C}^i}{\partial K} \delta K + \frac{\partial g_\mathrm{C}^i}{\partial V} \delta V \tag{10}$$

$$\delta T = \sum_{j=1}^n \frac{\partial g_\mathrm{T}}{\partial C_\mathrm{L}^j} \delta C_\mathrm{L}^j + \frac{\partial g_\mathrm{T}}{\partial K} \delta K + \frac{\partial g_\mathrm{T}}{\partial V} \delta V \tag{11}$$

and inserting again Eqs. (2a)–(2c) and the relations for a and b_S^i from Appendices A and B. Eq. (10) is with $i = 1, \ldots, n$. This procedure produces to a linear system of equations for the unknown $b_\mathrm{L}^1, \ldots, b_\mathrm{L}^n$ and $\dot{\phi}$ where now the off-diagonal elements of the governing matrix are no longer zero! On account of the long calculation we will only give the final version of the generalised system of equation:

$$\sum_{j=1}^n \left(\frac{\partial g_\mathrm{C}^i}{\partial C_\mathrm{L}^j} + \delta_{ij}\tau^i \right) b_\mathrm{L}^j + \left(\frac{\partial g_\mathrm{C}^i}{\partial V} - \frac{C_{\mathrm{L},0}^i - C_{\mathrm{S},0}^i}{V_0} \right) \frac{\dot{\phi}}{\phi} = G_{\mathrm{C},0}^i \tau^i - \frac{\partial g_\mathrm{C}^i}{\partial K} \omega^2, \quad i = 1, \ldots, n \tag{12}$$

$$\sum_{j=1}^n \left(\frac{\partial g_\mathrm{T}}{\partial C_\mathrm{L}^j} \right) b_\mathrm{L}^j + \left(\frac{\partial g_\mathrm{T}}{\partial V} - \frac{\Delta H_\mathrm{f}}{(k_\mathrm{S}\omega_\mathrm{S} + k_\mathrm{L}\omega_\mathrm{L})} \right) \frac{\dot{\phi}}{\phi} = G_\mathrm{eff} - \frac{\partial g_\mathrm{T}}{\partial K} \omega^2 \tag{13}$$

Eq. (12) is with $i = 1, \ldots, n$. δ_{ij} is the Dirác delta function. Note that $\tau^i/(\tau^i - k^i) = \xi_\mathrm{C}^i$. The question, when non-zero off-diagonal elements affect the predictions of the stability analysis significantly, can not be answered in this paper. It will be tackled in a further paper of the authors [5].

2.2. Response functions

For an n-component alloy system, the solid/liquid interface reacts to a deviation from thermodynamic equilibrium by a displacement of the interface position accompanied by a redistribution of solute across the interface. With liquid concentrations $(C_\mathrm{L}^1, \ldots, C_\mathrm{L}^n)$ and solid concentrations $(C_\mathrm{S}^1, \ldots, C_\mathrm{S}^n)$ this reaction can be expressed by $(n+1)$ response functions, which correspond to the general form [9]

$$C_\mathrm{S}^i = f_1^i(T, V, C_\mathrm{L}^1, \ldots, C_\mathrm{L}^n, C_\mathrm{S}^1, \ldots, C_\mathrm{S}^n), \quad i = 1, \ldots, n \tag{14}$$

$$V = f_2(T, C_L^1, \ldots, C_L^n, C_S^1, \ldots, C_S^n, K) \quad (15)$$

The relations in Eq. (14) are named first response functions and Eq. (15) second response function. Only $(n-1)$ first response functions are independent as the constraints $C_L^1 + \cdots + C_L^n = 1$ and $C_S^1 + \cdots + C_S^n = 1$ yield.

Recently, Ludwig [9] has derived the following expressions for the first response functions:

$$(C_L^j - C_S^j)\frac{V}{V_D} = \sum_{i=1}^{n}(C_L^i C_S^j - \chi^{i,j} C_S^i C_L^j) \quad (16)$$

with

$$\chi^{i,j} := \exp\left(-\frac{\Delta\tilde{\mu}^j - \Delta\tilde{\mu}^i}{R_g T}\right), \quad j, i = 1, \ldots, n \quad (17)$$

V_D is commonly approximated by $V_D = D/\delta$ (δ is the interface width) [3,10]. In [9], it is assumed that V_D is equal for the different species, so that this quantity needs no species index. The redistribution potential of the ith component, $\tilde{\mu}^i$, is given as the difference between the chemical potential and the contribution from the ideal mixing entropy [11]

$$\tilde{\mu}^i(T, C^1, \ldots, C^n) := \mu^i(T, C^1, \ldots, C^n) - RT\ln C^i \quad (18)$$

and thus

$$\Delta\tilde{\mu}^i := \tilde{\mu}_S^i - \tilde{\mu}_L^i = \Delta\mu^i - RT\ln\left(\frac{C_S^i}{C_L^i}\right) \quad (19)$$

For a dilute binary alloy with $V \ll V_D$, Eqs. (16) and (17) can be simplified to give Eq. (3) [9].

For the second response function, the following expression is proposed [9]:

$$V = V_0\left[1 - \exp\frac{(\Delta G_{DF}|_{K=0} + \Delta G_K)}{R_g T}\right] \quad (20)$$

with

$$\Delta G_{DF}|_{K=0} = \sum_{i=1}^{n} C_S^i \Delta\mu^i, \qquad \Delta G_K = \gamma v_{mol} K \quad (21)$$

In the expression for the free energy change due to the existence of a curvature it is assumed that the anisotropy of surface tension γ is small and that the shape of the interface at the considered position can adequately be described by a single mean curvature K. For a dilute binary alloy with $\Delta G \ll R_g T$, Eqs. (20) and (21) can be simplified to give Eq. (4) [9].

The $n+1$ response functions in their general form (Eqs. (14) and (15)), or in the form proposed in [9] (Eqs. (16), (17), (20) and (21)), establish a non-linear system of equations which relates $(C_S^1, \ldots, C_S^n, T)$ with $(C_L^1, \ldots, C_L^n, K, V)$ [9]. Thus, no simple analytical relation can be specified for $g_C^1, \ldots, g_C^n$ and g_T, but rather a non-linear system of equations defines the functional relation mentioned in Eqs. (8) and (9).

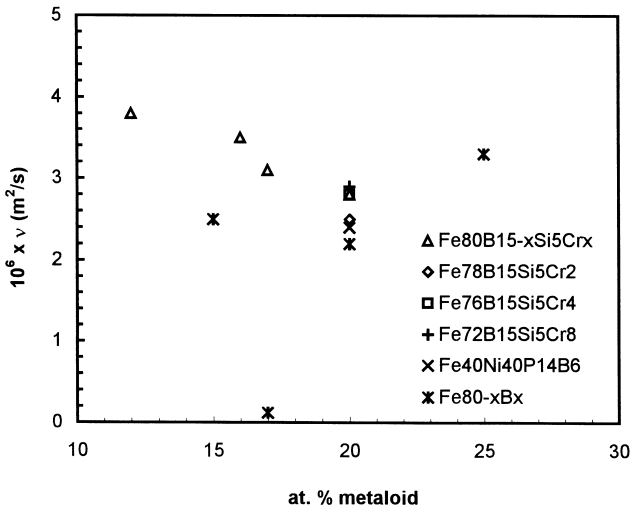

Fig. 1. Unstable region in the λ–V diagram for $C_L^{Cu} = 8$ mol% and $C_L^{Si} = 7$ mol%. A limit of constitutional undercooling which is proportional to G_{eff} and an absolute stability limit independent of G_{eff} is predicted.

3. Results and discussion

For a Al–Si–Cu alloy with $C_L^{Cu} = 8$ mol% and $C_L^{Si} = 7$ mol%, the linear system of equation (Eqs. (12) and (13)) was solved to determine the value of $\dot{\phi}/\phi$ as a function λ and V. To do so, we used the functional relations (Eqs. (8) and (9)) resulting from the solution of the non-linear system of equation given by the $n+1$ response functions (Eqs. (16), (17), (20) and (21)). The thermodynamic programme ChemApp™ was used to evaluate the necessary thermodynamic information ($\mu^i(T, C^1, \ldots, C^n)$ for the liquid and solid).

Fig. 1 shows the calculated unstable region in the λ–V diagram and how a positive and constant temperature gradient G_{eff} affects this region. The stabilising effect of an increasing G_{eff}, well known for the dilute alloy case, is obvious. Absolute stability independent of G_{eff} is predicted. The bottom edge of the unstable "island" represents the marginal stable wavelength and thus the dendrite tip radius.

Fig. 2 shows C_S^{Cu}, C_S^{Si} and T as a function of V for $G_{eff} = 0$ m/s and the marginal stable wavelength. Notice that in the two figures the "input" concentration, C_L^{Cu} and C_L^{Si}, represents the liquidus concentration right at the interface rather than the concentration in the bulk of the melt. For small V, C_S^{Cu}, C_S^{Si} and T are defined by their equilibrium values. For $V > 10^{-2}$ m/s, solute trapping occurs and thus T decreases, and C_S^{Cu} and C_S^{Si} increases.

Very recently, Coriell et al. (unpublished research) worked out a similar concept to the one presented here, whereby they used the relations resulting from on-line thermodynamic calculations for the response functions rather than Eqs. (16), (17), (20) and (21). Thus, they can only predict stability in multi-component systems without considering solute trapping effects. In addition, they considered curvature only with a curvature undercooling term.

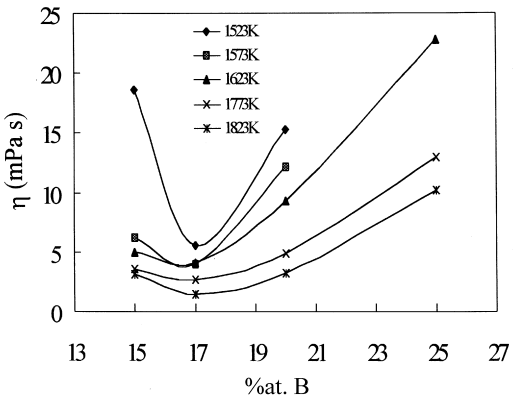

Fig. 2. C_S^{Cu}, C_S^{Si} and T as a function of V for $G_{eff} = 0\,m/s$ and the marginal stable wavelength for $C_L^{Cu} = 8\,mol\%$ and $C_L^{Si} = 7\,mol\%$. Solute trapping decreases T and increases C_S^{Cu} and C_S^{Si} for large V.

4. Summary

A general concept for a stability analysis of a planar interface in arbitrary n-component alloy systems is presented. This concept is based on (i) the principle of linear stability analysis for n-component alloy systems, (ii) the assumption that the diffusion of each species in the melt is independent of each other, (iii) a non-linear system of equations presented in [9] instead of the widely used thermodynamic relations for dilute n-component alloy systems and (iv) on-line thermodynamic calculations.

For a Al–Si–Cu alloy with $C_L^{Cu} = 8\,mol\%$ and $C_L^{Si} = 7\,mol\%$, the resulting linear system of equations is solved for obtaining the value of $\dot{\phi}/\phi$ as a function λ and V. Thus, it is shown how the marginal stable wavelength, and with that the dendrite tip radius, can be estimated for a non-dilute multi-component alloy system.

Appendix A. Thermal flux balance

The production rate of latent heat of fusion released at the solid–liquid interface must be balanced with the thermal fluxes away from the interface. This condition can be expressed as

$$V\,\Delta H_f = k_S G_S - k_L G_L \tag{A.1}$$

where k_L and k_S are the thermal conductivity of the liquid and solid, and ΔH_f the enthalpy of fusion.

In their classical paper, Mullins and Sekerka [1] gave the solution of the governing differential equation which satisfies Eq. (2a). From the solutions of the thermal diffusion fields around the perturbed interface, the gradients can be estimated as

$$G_L = G_{L,0} + \phi\left\{G_{L,0}\left(\omega_L - \frac{V_0}{a_L}\right) - \omega_L a\right\} \tag{A.2}$$

$$G_S = G_{S,0} + \phi\left\{G_{S,0}\left(-\omega_S - \frac{V_0}{a_S}\right) + \omega_S a\right\} \tag{A.3}$$

where $G_{L,0}$ and $G_{S,0}$ are the temperature gradient in the liquid and solid at the unperturbed flat interface. For the definition of ω_L and ω_S, see [2]. Inserting Eqs. (A.2) and (A.3) into the thermal flux balance and using the terms which arise from the perturbation gives, after rearrangement

$$\begin{aligned} a &= [\bar{k}_S G_{S,0}\xi_S + \bar{k}_L G_{L,0}\xi_L] + \frac{\dot{\phi}}{\phi}\frac{\Delta H_f}{(k_S\omega_S + k_L\omega_L)} \\ &=: G_{eff} + \frac{\dot{\phi}}{\phi}\frac{\Delta H_f}{(k_S\omega_S + k_L\omega_L)} \end{aligned} \tag{A.4}$$

with $\bar{k}_S := k_S/(k_S + k_L)$ and $\bar{k}_L := k_L/(k_S + k_L)$.

Appendix B. Solutal flux balances

Similar to the thermal flux, the solute at the interface is also balanced. If the diffusion of the different species ahead of the interface is assumed to be independent of each other (with diffusion coefficient D^i), then for each species the solute flux balance can be expressed as

$$V(C_L^i - C_S^i) = -D^i G_C^i, \quad i = 1, \ldots, n \tag{B.1}$$

In [1], the solution of the governing differential equation satisfying Eqs. (2b) and (2c) is given. For the solute gradient ahead of the perturbed interface, the following expression has been derived in [1]:

$$G_C^i = G_{C,0}^i + \phi\left\{G_{C,0}^i\left(\omega_C^i - \frac{V_0}{D^i}\right) - \omega_C^i b_L^i\right\} \tag{B.2}$$

where $G_{C,0}^i$ is the concentration gradient of the ith species at the unperturbed flat interface. Inserting Eq. (B.2) into the solute flux balances and using the terms which arise from the perturbation gives, after rearrangement

$$\begin{aligned} b_S^i &= (G_{C,0}^i - b_L^i)\tau^i + \frac{\dot{\phi}}{\phi}\left(\frac{C_{L,0}^i - C_{S,0}^i}{V_0}\right), \\ &\text{with} \quad \tau^i := \frac{\omega_C^i - V_0/D^i}{V_0/D^i},\ i = 1, \ldots, n \end{aligned} \tag{B.3}$$

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Update

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Abstract

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1. Introduction

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$$Z = \phi(X,t) = \delta(t)\sin \omega X \tag{1}$$

where δ is the amplitude, ω the wave number ($=2\pi/\lambda$), and λ the wavelength. X and Z are spatial co-ordinates and t the time. With this formulation, the interface velocity at the perturbed front is given by $V = V_0 + \delta V = V_0 + \dot{\phi}/\phi$ and the curvature by $K = K_0 + \delta K = 0 + \omega^2\phi$.

The planar interface is thought to be stable when $\dot{\phi}/\phi < 0$ for all perturbation wavelengths λ, and unstable when $\dot{\phi}/\phi > 0$ for at least one λ. Thus, the marginal stability condition can be obtained by examining the condition $\dot{\phi}/\phi = 0$.

Assuming a species diffusion ahead of the interface independent on the nature of an n-component alloy a solution of the heat and solute diffusion equations can be obtained [1] such that

$$T = T_0 + \delta T = T_0 + a\phi \tag{2a}$$

$$C_L^i = C_{L,0}^i + \delta C_L^i = C_{L,0}^i + b_L^i\phi, \quad i = 1,\ldots,n \tag{2b}$$

$$C_S^i = C_{S,0}^i + \delta C_S^i = C_{S,0}^i + b_S^i\phi, \quad i = 1,\ldots,n \tag{2c}$$

where T is the temperature at the perturbed interface, T_0 the temperature at the unperturbed flat interface, C_L^i the concentration of the ith species in the liquid at the perturbed interface and $C_{L,0}^i$ the concentration at the unperturbed flat interface. C_S^i and $C_{S,0}^i$ are the corresponding solid quantities. $a, b_L^1,\ldots,b_L^n$ and $b_S^1,\ldots,b_S^n$ are parameters which have to be determined by additional conditions. From the thermal flux balance at the interface, a can be expressed as a function of ω and $\dot{\phi}$ (Appendix A). From the solute flux balances, b_S^i can be expressed as function of b_L^i,ω, and $\dot{\phi}$ (Appendix B). The remaining equations to determine $b_L^1,\ldots,b_L^n$ and $\dot{\phi}$ are taken from thermodynamic considerations. However, due to the lack of alternatives the standard conditions for dilute multi-component systems are commonly used:

$$C_S^i = k^i C_L^i, \quad i = 1,\ldots,n \tag{3}$$

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$$T = T_f + \sum_i m^i C_L^i - \Gamma K - \frac{V}{\mu} \quad (4)$$

Here k^i is the distribution coefficient and m^i the liquidus slope of the ith species (which may depend on V), T_f the melting point of the pure solvent, $\Gamma := \gamma v_{mol}/\Delta S_f$ the Gibbs–Thomson coefficient, γ the surface tension, v_{mol} the molar volume, $\Delta S_f = \Delta H_f/T_f$ the entropy of fusion, $\mu := \Delta H_f V_{max}/R_g T_f^2$ the kinetic coefficient, V_{max} the maximal velocity at infinite driving force and R_g the gas constant. $\Delta T_K := V/\mu$ is called the kinetic undercooling and $\Delta T_R := \Gamma K$ the capillary or curvature undercooling [4].

Taking the total derivation of Eqs. (3) and (4):

$$\delta C_S^i = k^i \delta C_L^i, \quad i = 1,\ldots,n \quad (5)$$

$$\delta T = T_f + \sum_i m^i \delta C_L^i - \Gamma \delta K - \frac{\delta V}{\mu} \quad (6)$$

and inserting Eqs. (2a)–(2c) and the relations for a and b_S^i from Appendices A and B, a linear system of equations for the unknown $b_L^1,\ldots,b_L^n$ and $\dot{\phi}$ arises. Since, apart from the last column and the last row, the off-diagonal elements of the governing matrix are all zero (because the species are not related to each other), the linear system of equations can easily be solved analytically. The solution is found to be [2]

$$-\Gamma\omega^2 - G_{eff} + \sum_i m^i G_{C,0}^i \xi_C^i = \frac{\dot{\phi}}{\phi} f(\omega) \quad (7)$$

where G_{eff} is defined in Appendix A. $G_{C,0}^i$ is the concentration gradient of the ith species in the liquid ahead of the unperturbed interface. For the definition of the stability functions ξ_L, ξ_S and ξ_C^i at that of $f(\omega)$ see [2,5]. Since it can be shown that $f(\omega)$ is always positive, the marginal stability condition is obtained by setting the right-hand side of Eq. (7) equal to zero.

The decisive importance of Eq. (7) is based on the fact that dendritic growth theory utilises the marginal stable wavelength as the operating point for the dendritic tip ($R = \lambda_i$ with tip radius R) [6–8]. The question then arises how Eq. (7) would look for non-dilute arbitrary n-component alloy systems. The derivation of a general expression for the marginal stability criterion is the major object of this paper.

2. Theory

2.1. Stability analysis for arbitrary n-component systems

Generally for an n-component alloy system it must be assumed that the solute incorporated into the growing solid ($C_S^1,\ldots,C_S^n$) and the interface temperature T is related to the growth velocity V, the curvature at the interface K and the solute in the liquid ahead of the front ($C_L^1,\ldots,C_L^n$):

$$C_S^i = g_C^i(C_L^1,\ldots,C_L^n,K,V), \quad i = 1,\ldots,n \quad (8)$$

$$T = g_T(C_L^1,\ldots,C_L^n,K,V) \quad (9)$$

These relations reflect the off-equilibrium "thermodynamic" conditions at the interface, which are especially important for strong curvatures and/or rapid solidification. We will discuss the specific form of these relations in Chapter 2.2.

The main idea behind the general concept of the stability analysis of a planar interface in arbitrary n-component alloy systems is to replace the thermodynamic conditions for dilute n-component systems (Eqs. (5) and (6)) by their generalised counterparts (Eqs. (8) and (9)).

Thus, we consider the total derivation of Eqs. (8) and (9)

$$\delta C_S^i = \sum_{j=1}^n \frac{\partial g_C^i}{\partial C_L^j}\delta C_L^j + \frac{\partial g_C^i}{\partial K}\delta K + \frac{\partial g_C^i}{\partial V}\delta V \quad (10)$$

$$\delta T = \sum_{j=1}^n \frac{\partial g_T}{\partial C_L^j}\delta C_L^j + \frac{\partial g_T}{\partial K}\delta K + \frac{\partial g_T}{\partial V}\delta V \quad (11)$$

and inserting again Eqs. (2a)–(2c) and the relations for a and b_S^i from Appendices A and B. Eq. (10) is with $i = 1,\ldots,n$. This procedure produces to a linear system of equations for the unknown $b_L^1,\ldots,b_L^n$ and $\dot{\phi}$ where now the off-diagonal elements of the governing matrix are no longer zero! On account of the long calculation we will only give the final version of the generalised system of equation:

$$\sum_{j=1}^n \left(\frac{\partial g_C^i}{\partial C_L^j} + \delta_{ij}\tau^i\right) b_L^j + \left(\frac{\partial g_C^i}{\partial V} - \frac{C_{L,0}^i - C_{S,0}^i}{V_0}\right)\frac{\dot{\phi}}{\phi} = G_{C,0}^i \tau^i - \frac{\partial g_C^i}{\partial K}\omega^2, \quad i = 1,\ldots,n \quad (12)$$

$$\sum_{j=1}^n \left(\frac{\partial g_T}{\partial C_L^j}\right) b_L^j + \left(\frac{\partial g_T}{\partial V} - \frac{\Delta H_f}{(k_S\omega_S + k_L\omega_L)}\right)\frac{\dot{\phi}}{\phi} = G_{eff} - \frac{\partial g_T}{\partial K}\omega^2 \quad (13)$$

Eq. (12) is with $i = 1,\ldots,n$. δ_{ij} is the Dirác delta function. Note that $\tau^i/(\tau^i - k^i) = \xi_C^i$. The question, when non-zero off-diagonal elements affect the predictions of the stability analysis significantly, can not be answered in this paper. It will be tackled in a further paper of the authors [5].

2.2. Response functions

For an n-component alloy system, the solid/liquid interface reacts to a deviation from thermodynamic equilibrium by a displacement of the interface position accompanied by a redistribution of solute across the interface. With liquid concentrations ($C_L^1,\ldots,C_L^n$) and solid concentrations ($C_S^1,\ldots,C_S^n$) this reaction can be expressed by $(n+1)$ response functions, which correspond to the general form [9]

$$C_S^i = f_1^i(T,V,C_L^1,\ldots,C_L^n,C_S^1,\ldots,C_S^n), \quad i = 1,\ldots,n \quad (14)$$

$$V = f_2(T, C_L^1, \ldots, C_L^n, C_S^1, \ldots, C_S^n, K) \quad (15)$$

The relations in Eq. (14) are named first response functions and Eq. (15) second response function. Only $(n-1)$ first response functions are independent as the constraints $C_L^1 + \cdots + C_L^n = 1$ and $C_S^1 + \cdots + C_S^n = 1$ yield.

Recently, Ludwig [9] has derived the following expressions for the first response functions:

$$(C_L^j - C_S^j)\frac{V}{V_D} = \sum_{i=1}^{n} (C_L^i C_S^j - \chi^{i,j} C_S^i C_L^j) \quad (16)$$

with

$$\chi^{i,j} := \exp\left(-\frac{\Delta\tilde{\mu}^j - \Delta\tilde{\mu}^i}{R_g T} \right), \quad j,i = 1,\ldots,n \quad (17)$$

V_D is commonly approximated by $V_D = D/\delta$ (δ is the interface width) [3,10]. In [9], it is assumed that V_D is equal for the different species, so that this quantity needs no species index. The redistribution potential of the ith component, $\tilde{\mu}^i$, is given as the difference between the chemical potential and the contribution from the ideal mixing entropy [11]

$$\tilde{\mu}^i(T, C^1, \ldots, C^n) := \mu^i(T, C^1, \ldots, C^n) - RT \ln C^i \quad (18)$$

and thus

$$\Delta\tilde{\mu}^i := \tilde{\mu}_S^i - \tilde{\mu}_L^i = \Delta\mu^i - RT \ln\left(\frac{C_S^i}{C_L^i}\right) \quad (19)$$

For a dilute binary alloy with $V \ll V_D$, Eqs. (16) and (17) can be simplified to give Eq. (3) [9].

For the second response function, the following expression is proposed [9]:

$$V = V_0 \left[1 - \exp\frac{(\Delta G_{DF}|_{K=0} + \Delta G_K)}{R_g T} \right] \quad (20)$$

with

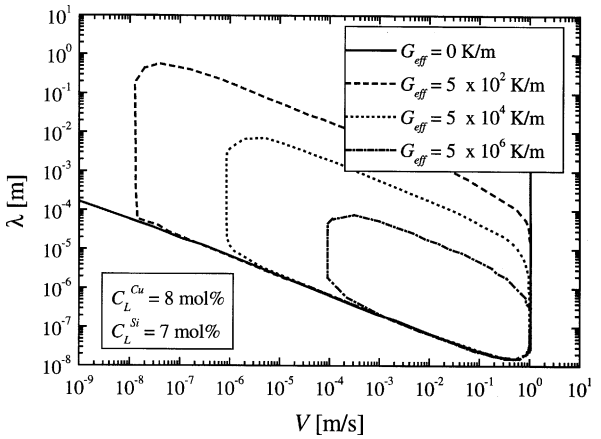

Fig. 1. Unstable region in the λ–V diagram for $C_L^{Cu} = 8$ mol% and $C_L^{Si} = 7$ mol%. A limit of constitutional undercooling which is proportional to G_{eff} and an absolute stability limit independent of G_{eff} is predicted.

$$\Delta G_{DF}|_{K=0} = \sum_{i=1}^{n} C_S^i \, \Delta\mu^i, \qquad \Delta G_K = \gamma v_{mol} K \quad (21)$$

In the expression for the free energy change due to the existence of a curvature it is assumed that the anisotropy of surface tension γ is small and that the shape of the interface at the considered position can adequately be described by a single mean curvature K. For a dilute binary alloy with $\Delta G \ll R_g T$, Eqs. (20) and (21) can be simplified to give Eq. (4) [9].

The $n+1$ response functions in their general form (Eqs. (14) and (15)), or in the form proposed in [9] (Eqs. (16), (17), (20) and (21)), establish a non-linear system of equations which relates $(C_S^1, \ldots, C_S^n, T)$ with $(C_L^1, \ldots, C_L^n, K, V)$ [9]. Thus, no simple analytical relation can be specified for $g_C^1, \ldots, g_C^n$ and g_T, but rather a non-linear system of equations defines the functional relation mentioned in Eqs. (8) and (9).

3. Results and discussion

For a Al–Si–Cu alloy with $C_L^{Cu} = 8$ mol% and $C_L^{Si} = 7$ mol%, the linear system of equation (Eqs. (12) and (13)) was solved to determine the value of $\dot{\phi}/\phi$ as a function λ and V. To do so, we used the functional relations (Eqs. (8) and (9)) resulting from the solution of the non-linear system of equation given by the $n+1$ response functions (Eqs. (16), (17), (20) and (21)). The thermodynamic programme ChemApp™ was used to evaluate the necessary thermodynamic information ($\mu^i(T, C^1, \ldots, C^n)$ for the liquid and solid).

Fig. 1 shows the calculated unstable region in the λ–V diagram and how a positive and constant temperature gradient G_{eff} affects this region. The stabilising effect of an increasing G_{eff}, well known for the dilute alloy case, is obvious. Absolute stability independent of G_{eff} is predicted. The bottom edge of the unstable "island" represents the marginal stable wavelength and thus the dendrite tip radius.

Fig. 2 shows C_S^{Cu}, C_S^{Si} and T as a function of V for $G_{eff} = 0$ m/s and the marginal stable wavelength. Notice that in the two figures the "input" concentration, C_L^{Cu} and C_L^{Si}, represents the liquidus concentration right at the interface rather than the concentration in the bulk of the melt. For small V, C_S^{Cu}, C_S^{Si} and T are defined by their equilibrium values. For $V > 10^{-2}$ m/s, solute trapping occurs and thus T decreases, and C_S^{Cu} and C_S^{Si} increases.

Very recently, Coriell et al. (unpublished research) worked out a similar concept to the one presented here, whereby they used the relations resulting from on-line thermodynamic calculations for the response functions rather than Eqs. (16), (17), (20) and (21). Thus, they can only predict stability in multi-component systems without considering solute trapping effects. In addition, they considered curvature only with a curvature undercooling term.

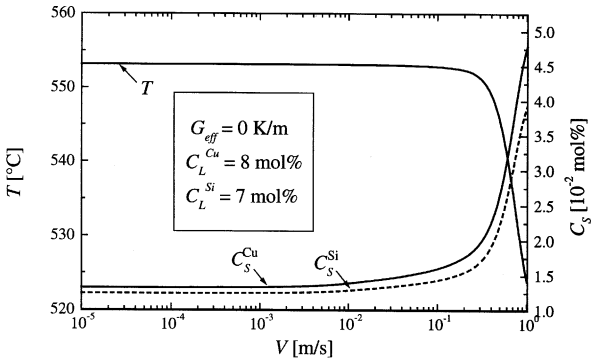

Fig. 2. C_S^{Cu},C_S^{Si} and T as a function of V for $G_{eff} = 0$ m/s and the marginal stable wavelength for $C_L^{Cu} = 8$ mol% and $C_L^{Si} = 7$ mol%. Solute trapping decreases T and increases C_S^{Cu} and C_S^{Si} for large V.

4. Summary

A general concept for a stability analysis of a planar interface in arbitrary n-component alloy systems is presented. This concept is based on (i) the principle of linear stability analysis for n-component alloy systems, (ii) the assumption that the diffusion of each species in the melt is independent of each other, (iii) a non-linear system of equations presented in [9] instead of the widely used thermodynamic relations for dilute n-component alloy systems and (iv) on-line thermodynamic calculations.

For a Al–Si–Cu alloy with $C_L^{Cu} = 8$ mol% and $C_L^{Si} = 7$ mol%, the resulting linear system of equations is solved for obtaining the value of $\dot{\phi}/\phi$ as a function λ and V. Thus, it is shown how the marginal stable wavelength, and with that the dendrite tip radius, can be estimated for a non-dilute multi-component alloy system.

Appendix A. Thermal flux balance

The production rate of latent heat of fusion released at the solid–liquid interface must be balanced with the thermal fluxes away from the interface. This condition can be expressed as

$$V\,\Delta H_f = k_S G_S - k_L G_L \tag{A.1}$$

where k_L and k_S are the thermal conductivity of the liquid and solid, and ΔH_f the enthalpy of fusion.

In their classical paper, Mullins and Sekerka [1] gave the solution of the governing differential equation which satisfies Eq. (2a). From the solutions of the thermal diffusion fields around the perturbed interface, the gradients can be estimated as

$$G_L = G_{L,0} + \phi\left\{G_{L,0}\left(\omega_L - \frac{V_0}{a_L}\right) - \omega_L a\right\} \tag{A.2}$$

$$G_S = G_{S,0} + \phi\left\{G_{S,0}\left(-\omega_S - \frac{V_0}{a_S}\right) + \omega_S a\right\} \tag{A.3}$$

where $G_{L,0}$ and $G_{S,0}$ are the temperature gradient in the liquid and solid at the unperturbed flat interface. For the definition of ω_L and ω_S, see [2]. Inserting Eqs. (A.2) and (A.3) into the thermal flux balance and using the terms which arise from the perturbation gives, after rearrangement

$$a = [\bar{k}_S G_{S,0}\xi_S + \bar{k}_L G_{L,0}\xi_L] + \frac{\dot{\phi}}{\phi}\frac{\Delta H_f}{(k_S\omega_S + k_L\omega_L)}$$
$$=: G_{eff} + \frac{\dot{\phi}}{\phi}\frac{\Delta H_f}{(k_S\omega_S + k_L\omega_L)} \tag{A.4}$$

with $\bar{k}_S := k_S/(k_S + k_L)$ and $\bar{k}_L := k_L/(k_S + k_L)$.

Appendix B. Solutal flux balances

Similar to the thermal flux, the solute at the interface is also balanced. If the diffusion of the different species ahead of the interface is assumed to be independent of each other (with diffusion coefficient D^i), then for each species the solute flux balance can be expressed as

$$V(C_L^i - C_S^i) = -D^i G_C^i, \quad i = 1,\ldots,n \tag{B.1}$$

In [1], the solution of the governing differential equation satisfying Eqs. (2b) and (2c) is given. For the solute gradient ahead of the perturbed interface, the following expression has been derived in [1]:

$$G_C^i = G_{C,0}^i + \phi\left\{G_{C,0}^i\left(\omega_C^i - \frac{V_0}{D^i}\right) - \omega_C^i b_L^i\right\} \tag{B.2}$$

where $G_{C,0}^i$ is the concentration gradient of the ith species at the unperturbed flat interface. Inserting Eq. (B.2) into the solute flux balances and using the terms which arise from the perturbation gives, after rearrangement

$$b_S^i = (G_{C,0}^i - b_L^i)\tau^i + \frac{\dot{\phi}}{\phi}\left(\frac{C_{L,0}^i - C_{S,0}^i}{V_0}\right), \quad \text{with} \quad \tau^i:$$
$$= \frac{\omega_C^i - V_0/D^i}{V_0/D^i}, \; i = 1,\ldots,n \tag{B.3}$$

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