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Morphological instability of a solid sphere of dilute ternary alloy growing by diffusion from its melt

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ABSTRACT

The diffusion-limited growth of an initially spherical particle of dilute ternary alloy in contact with its melt has been studied from a theoretical point of view and the effects of interface kinetics and multi-component diffusion have been characterized on the development of a shape perturbation of the sphere. When both concentrations of the diffusing species are imposed in the far-field, the different radii related to the absolute and relative stability of the particle with respect to the development of spherical harmonics have been determined when a linear kinetics law is considered for the solid/liquid interface. The development of the shape fluctuations of the sphere has been also characterized when the flux of both species are set in the far-field.

1. Introduction

The control of the shape evolution of solid spheres of alloy growing by diffusion or heat flow from their melt is of paramount importance in materials science and metallurgy. In particular, the morphological instability of the alloy particles has been the topic of intensive research from both experimental and theoretical point of view. Mullins and Sekerka have determined the critical radius, in the linear regime of evolution by diffusion and/or heat flow, beyond which the development of shape perturbations is favourable in the case of a sphere [1]. These authors also investigated the case of a planar solid of binary alloy in contact with a melt [2]. The effect of interface kinetics on the stability of the sphere growing in a supercooled melt has been then characterized in the cases where linear and square kinetic laws are considered, when the temperature field [3] is imposed in the far-field. When the flux is imposed, the morphological change of the crystal has been also studied in the linear and non-linear regimes of evolution [4–6]. In the case of a planar solid–liquid interface, the linear stability analysis has been performed for large thermal Peclet numbers [8] and when the segregation coefficient and interface temperature depend on the pulling speed [9,10]. Likewise, the destabilizing effect of stress resulting from the concentration dependence of the lattice parameters of binary alloy has been characterized [7]. The stability of the solid–liquid interface has been studied during the solidification of dilute ternary alloys. Assuming that local equilibrium condition is satisfied at the interface, it has been shown that the Mullins–Sekerka stability criterion can be extended [11]. Likewise, the Ostwald ripening in ternary [12] and multi-component alloys [13] has been investigated and the temporal exponents for the average particle radius have been found to be identical to the ones in the binary limit. Recently, the planar and dendritic growth in multicomponent systems has been considered and the effect of diffusive interactions between species has been characterized [14]. The equiaxed globular solidification has been also investigated and the interdiffusion phenomena have been analysed [15]. In this paper, the conjugated effects of interface kinetics and diffusion of the two species have been studied on the morphological evolution of a ternary alloy growing by diffusion in its melt. The case of dilute alloy is also discussed.

2. Modelling and discussion

The diffusion-limited growth at constant temperature T is considered for a solid sphere in contact with its melt in the case of a dilute ternary alloy of solute concentrations c_i^L in the liquid phase and c_i^S in the solid one, with $i=1,2$ for the two solute species. The following approximations have been used. There is no convection in the melt and no diffusion in the solid phase. In the dilute approximation, the off-diagonal terms of the diffusion

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coefficients are neglected in the liquid phase, i.e. $D_{12}=D_{21}=0$. The diffusion coefficients are independent of the concentration fields of the solute species and are set positive [14,16], i.e. $D_{11}\geq 0, D_{22}\geq 0$. The solute concentrations in the liquid phase are assumed to satisfy, in the spherical coordinate system (r,θ,φ), the Laplace equation [1]:

$$\Delta c_i^L(r,\theta,\varphi)=0, \tag{1}$$

where Δ is the Laplacian operator. At the solid–liquid interface, the generalized Gibbs–Thomson equation has been written in the case where the liquidus slope is assumed to be constant and a linear interface kinetic law is considered [3,14]. It yields:

$$m_1\left(c_1^L(\mathbf{r_I})-c_1^{L,0}\right)+m_2\left(c_2^L(\mathbf{r_I})-c_2^{L,0}\right)=\Gamma\kappa+\frac{v_n}{\mu}, \tag{2}$$

with m_i being the liquidus slope of solute i, $\mathbf{r}_I$ the position vector of the solid–liquid interface, $c_i^{L,0}$ the solute concentration at equilibrium near a planar interface for the species i in the liquid, μ the constant interface kinetic coefficient, v_n the normal velocity of the interface, κ the interface curvature taken positive for convex profile and $\Gamma=\gamma/L$, where γ is the interfacial free-energy and L the latent heat of the solvent per unit volume. At this point, it can be underlined that the study of the effect of interface velocity on the segregation coefficient and liquidus slopes is beyond the scope of the present analysis. The mass balance at the interface, assuming that the molar volume of both phases are the same, leads to:

$$\left[c_i^S(\mathbf{r_I})-c_i^L(\mathbf{r_I})\right]v_n=D_{ii}\left.\frac{\partial c_i^L}{\partial r}\right|_{\mathbf{r_I}}, \tag{3}$$

with $i=1,2$ (no summation over repeated indices).

2.1. Applied far-field condition for the concentrations

The case where both concentrations of the diffusing species are set at constant values in the far-field is first considered. Taking thus,

$$c_i^L(r\to\infty,\theta,\varphi)=c_i^{L,\infty}, \tag{4}$$

a classical linear stability analysis of the sphere evolution has been conducted following the approaches developed in [1,3,11]. Following [1,12,13], it is also assumed that $c_i^S(\mathbf{r_I})-c_i^L(\mathbf{r_I})\sim c_i^{S,0}-c_i^{L,0}=\Delta C_i^0$ in Eq. (3) such that it reduces to:

$$v_n=\frac{D_{ii}}{\Delta C_i^0}\left.\frac{\partial c_i^L}{\partial r}\right|_{\mathbf{r_I}}, \tag{5}$$

with $c_i^{S,0}$ being the equilibrium concentrations in the solid near a planar interface and $i=1$ or 2. The radius of the sphere r_I, the interface velocity v_n and interface curvature κ are developed as:

$$r_I=R+\delta Y_l^m(\theta,\varphi), \tag{6}$$

$$v_n=\frac{dR}{dt}+\frac{d\delta}{dt}Y_l^m(\theta,\varphi), \tag{7}$$

$$\kappa=\frac{2}{R}+(l-1)(l+2)\frac{\delta}{R^2}Y_l^m(\theta,\varphi), \tag{8}$$

with R being the radius of the unperturbed sphere, δ the infinitesimal perturbation amplitude ($\delta\ll R$), $Y_l{}^m$ a spherical harmonics and t the time variable. The general form of the concentration field satisfying Eq. (1) is given by:

$$c_i^L(\mathbf{r})=A_i^0+\frac{B_i^0}{r}+\frac{B_i^1}{r^{l+1}}\delta Y_l^m(\theta,\varphi), \tag{9}$$

with A_i^0, B_i^0 and $B_i{}^1$ being three constants that can be determined to the first order in δ from Eqs. (2), (4), (5), (6), (7), (8) and (9). Introducing $\Delta^\infty=\Delta_1^\infty m_1+\Delta_2^\infty m_2$, the constant related to the supersaturations Δ_i^∞ and liquidus slopes m_i of the two species, with $\Delta_i^\infty=c_i^{L,\infty}-c_i^{L,0}$ being the concentration gradient of the diffusion species i in the liquid phase, the problem of the radial growth has been solved as follow. Re-writing Eqs. (2) and (5) to the zeroth order in δ as,

$$m_1\Delta C_{1,0}^L+m_2\Delta C_{2,0}^L=2\frac{\Gamma}{R}+\frac{v_{n,0}}{\mu}, \tag{10}$$

$$\frac{D_{11}}{\Delta C_1^0}\frac{\Delta C_{1,0}^L-\Delta_1^\infty}{R}=\frac{D_{22}}{\Delta C_2^0}\frac{\Delta C_{2,0}^L-\Delta_2^\infty}{R}=-v_{n,0}, \tag{11}$$

with $v_{n,0}$ and $\Delta C_{i,0}^L$ being the development of the interface velocity v_n and concentration variation $c_i^L(R)-c_i^{L,0}$ to the order zero in δ, respectively, the unknown concentrations $\Delta C_{i,0}^L$ have been determined and the radial growth of the particle has been found to be:

$$v_{n,0}=\frac{dR}{dt}=\frac{\Delta D}{R}\frac{\Delta^\infty-\frac{2\Gamma}{R}}{K+\frac{\Delta D}{\mu R}}, \tag{12}$$

with

$$\Delta D=D_{11}D_{22}, \tag{13}$$

$$K=D_{11}\Delta C_2^0 m_2+D_{22}\Delta C_1^0 m_1. \tag{14}$$

Since D_{11}, D_{22}, ΔD and $\Delta C_i^0 m_i$ are assumed to be positive, it is deduced that the constant K defined in Eq. (14) is also positive [11,14]. The growth or decay of the sphere is thus governed by the sign of the numerator in Eq. (12). The critical nucleation radius R_* beyond which the particle growth takes place is given by:

$$R_*=\frac{2\Gamma}{\Delta^\infty}. \tag{15}$$

It can be observed from Eq. (15) that when $\Delta_1^\infty m_1>0$ and $\Delta_2^\infty m_2>0$, both solute species contribute positively to the growth of the sphere in a sense that the minimum radius required for the growth of the sphere decreases as each $\Delta_i^\infty m_i$ product increases. It can also be stated that the basic condition for the particle growth for the ternary alloy is $\Delta^\infty>0$. Introducing the dimensionless coefficient α,

$$\alpha=\frac{\Delta D}{\mu K R_*}=\frac{D_{11}D_{22}L}{2\gamma\mu}\frac{\Delta_1^\infty m_1+\Delta_2^\infty m_2}{D_{11}\Delta c_2^0 m_2+D_{22}\Delta c_1^0 m_1}, \tag{16}$$

Eq. (12) of the particule radial growth has been written as:

$$\frac{dR}{dt}=\frac{\Delta D}{R}\Delta^\infty\frac{1-\frac{R_*}{R}}{1+\alpha\frac{R_*}{R}}, \tag{17}$$

and the growth rate of the perturbation has been determined using a procedure equivalent to the one already detailed in Eqs. (10) and (11) to determine $v_{n,0}$. It yields:

$$\frac{1}{\delta}\frac{d\delta}{dt}=\frac{l-1}{R^2}\frac{\Delta D}{K}\Delta^\infty\frac{1-\frac{R_*}{2R}\left(4+l(l+3)+\alpha\frac{R_*}{R}(l+1)(l+2)\right)}{\left(1+\alpha\frac{R_*}{R}\right)\left(1+\alpha\frac{R_*}{R}(l+1)\right)}. \tag{18}$$

The early stages of the shape fluctuation development can be thus characterized in the linear regime from Eq. (18). Indeed, when $1/\delta(d\delta/dt)\geq 0$, it is stated that the development of the $Y_m{}^l$ harmonics becomes favourable on the surface of the sphere. This condition allows thus for determining a radius of the sphere R_a beyond which the particle is morphologically unstable, this radius being related to the absolute stability criterion [1]. Assuming that the denominator in Eq. (18) is always positive, the critical radius R_a beyond which an harmonics $Y_l{}^m$ will develop and satisfying [1],