

A diffuse-interface model of reactive wetting with intermetallic formation

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Abstract

A diffuse-interface model of reactive wetting with intermetallic formation is developed that incorporates fluid flow, phase change and solute diffusion. The model is based on the total molar Gibbs energy of a ternary system with four phases. Numerical simulations were performed using a mesh-adaptive finite element method, revealing the complex behavior of the reactive wetting process. The model was verified against equilibrium states derived from the classical phase diagram and from interface energy considerations. Dynamic results show that the intermetallic can either precede or follow the spreading liquid droplet, depending on the time and the choice of interface energy and kinetic coefficients. Despite this difference, the spreading rate was not affected for the cases considered.

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1. Introduction

The joining of solid metals with molten solders or filler metals involves wetting of the solid by the liquid, during which the solid dissolves into the liquid phase, and/or an intermetallic phase or phases form between the spreading liquid and the solid substrate. The strength of the joint depends on many factors, such as wettability, solubility and properties of the formed intermetallic compound.

The mechanisms of reactive wetting in metal/ceramic or metal/metal systems are quite complicated and involve the interplay of fluid flow, heat and mass transport, capillary phenomena and phase transformations (see [1,2] for general discussion). Previous work on reactive wetting can be classified into two cases: first, a partial dissolution of the substrate occurs but no new phase forms between the liquid

and the substrate (see e.g. [3–7]); and second, when such a phase forms between the liquid and the substrate (see [8,9] for recent discussion).

Early work on reactive wetting involved fitting experimental dynamic contact angle $\theta(t)$ or drop base radius $R(t)$ curves by different functions. Ambrose et al. [10] found that the experimental data of Tomsia et al. [11] for Si_3N_4 can be fitted empirically by an exponential form, $(\theta - \theta_\infty) = \text{const} \cdot \exp(-t/\tau)$, where θ_∞ is the stable contact angle assumed after a long time and τ is a characteristic time. For a spherical cap approximation, the empirical model implies that $R(t)$ is also of exponential form. However, in their succeeding work on Ni–P on Fe–Cr [12], they found that their experimental data of $R(t)$ can be described by a power relationship, $R(t) \propto t^{0.1}$, in accord with de Gennes model [13] for nonreactive systems.

In the study of Eustathopoulos [14], it was proposed that reactive systems feature either linear or non-linear $R(t)$ spreading, corresponding to reaction-controlled or diffusion-controlled spreading, respectively. The basis for the proposed linearity stemmed from the argument that the

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rate of reaction is constant in time, hence the velocity of the triple line is also constant. However, the relation between the reaction rate and the contact line velocity is non-trivial and no theoretical proof for the linearity of $R(t)$ has yet been forwarded. Recently, an experimental study by Kim et al. [15] showed that the linear model does not fit their experimental data at any given conditions. Moreover, the model also predicts that the apparent contact angle approaches zero rapidly in time, but this is contrary to what is observed experimentally. In Ref. [16] an equation is derived for $\theta(t)$ which states that the cosine of contact angle decreases exponentially with time between an initial value corresponding to the contact angle of the drop with the fully unreacted substrate and a final value corresponding to a substrate covered by the reaction product. This equation provided a better fit to the experimental data of Kim et al. [15] than the previous linear fit. In the same study [15], however, the model proposed for diffusion-controlled spreading by Mortensen et al. [17] fitted the same experimental data better than the other models that also include a viscous dissipation-limited model and molecular kinetic approach.

In Ref. [14] it is also proposed that the equilibrium contact angle in a reactive system is given by a Young's relation for the angle of the liquid drop with the reaction product (or intermetallic compound). This conclusion was drawn based on long-term spreading, with the observation that the apparent contact angle does not change significantly in time and the reaction product is always ahead of the liquid drop. Young's equation can only be expected to hold when the substrate is constrained to remain flat. Scanning electron microscopy (SEM) images from experiments [18,19] show that the triple line has elevated from its original height and one must therefore apply the full balance-of-tensions argument given by Neumann's construction. Furthermore, it is not at all clear that the intermetallic can form so fast that it always leads the spreading liquid. This may be particularly true in the early stage of wetting. Even at final equilibrium its relative position may also depend on the relative surface and interface energies of the system. Finally, the intermetallic in many situations appears to be composed of discrete grains, a fact that may contribute to its not having a flat interface with the liquid.

A different analysis of the kinetics of reactive wetting has been proposed by Saiz et al. [22]. They argued that the substrate cannot be described as rigid and insoluble, and that, with a sufficient nucleation barrier, a time regime exists in which intermetallic formation lags the liquid front. In this regime, they argue that the contact angles are then dictated by adsorption and the spreading kinetics are controlled by the movement of a ridge formed at the liquid–solid–vapor (L–S–V) triple junction. Although this step can happen only in the early stages of the spreading process, it can play a critical role in the succeeding steps, and they proposed that it should be taken into account when modeling a specific system.

In general, a single empirical formula can hardly describe the behavior of reactive spreading and does not provide much insight into the mechanisms involved in the process. With the complexity and general nonlinear behavior of the spreading kinetics, we propose here a more comprehensive model that can be utilized to study reactive wetting and investigate effects of system parameters on the spreading process. The main drawback of the model is that it requires a more involved numerical calculation of the governing equations than previous models.

In this paper we accordingly develop a diffuse-interface model of reactive wetting with intermetallic formation. The approach is similar to previous work on the modeling of dissolutive wetting [7,23]. The model incorporates fluid flow, phase change and solute diffusion. In Section 2, we present the mathematical model and give a description of a base set of input parameters. Numerical treatment of the model is described in Section 3. In Section 4, the model is verified numerically against multiphase states predicted by the phase diagram and the equilibrium contact angles. Results for the base set of parameters are shown in Section 5, together with a few other cases. In the Appendix we investigate some factors affecting intermetallic phase nucleation on the liquid–solid interface.

2. Mathematical model

We begin by considering the total molar Gibbs energy G of a ternary system consisting of substitutional elements A , B and C with four phases, spreading liquid (denoted by L or sometimes 1 for convenience), solid substrate (S or 2), intermetallic (I or 3) and vapor (V or 4), given by

$$G = \int_{\Omega} \left(\frac{G_m(x_A, x_B, x_C, \phi_L, \phi_S, \phi_I, \phi_V, T)}{V_m} + \sum_{i,j>i}^4 \frac{\epsilon_{ij}^2}{2} |\phi_i \nabla \phi_j - \phi_j \nabla \phi_i|^2 \right) d\Omega \quad (1)$$

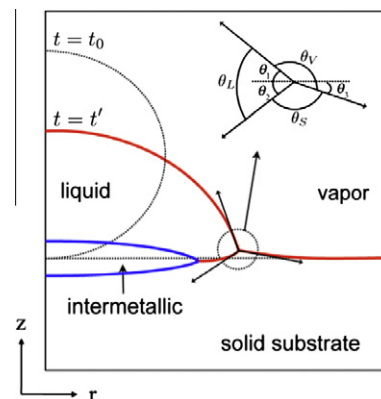


Fig. 1. Schematic diagram of the initial configuration ($t = t_0$) (dashed lines) with three phases, L (spreading liquid), S (solid substrate) and V (vapor), and later time ($t = t'$) reactive spreading (solid lines) with the formation of an intermetallic phase I.

where T is temperature, V_m is the molar volume (assumed constant) and $x_{A,B,C}$ are the mole fractions of A , B , C -atoms, with $x_A + x_B + x_C = 1$; the geometry is shown schematically in Fig. 1. Our approach is similar to that of Villanueva et al. [7], with the main difference being that the gradient energies have an anti-symmetric form. The phase-field variables ϕ_i vary smoothly between 0 and 1 and satisfy $\phi_L + \phi_S + \phi_I + \phi_V = 1$. The molar Gibbs energy is postulated as

$$G_m = \sum_i^4 P(\phi_i) G_m^i + \sum_{i,j>i}^4 W_{ij} \phi_i^2 \phi_j^2 + \sum_{i,j,k>j>i}^4 W_{ijk} \phi_i^2 \phi_j^2 \phi_k^2 + W_{LSIV} \phi_L^2 \phi_S^2 \phi_I^2 \phi_V^2 \quad (2)$$

with the smoothed step function $P(\phi_i) = \phi_i^3(10 - 15\phi_i + 6\phi_i^2)$ [24,25]. The coefficients ϵ_{ij} and the various barrier heights W are related to the interface thicknesses and surface energies.

For simplicity, we assume an ideal solution model for $G_m^{L,S,V}$ and a regular solution model for G_m^I . Thus, the molar Gibbs energies take the form

$$G_m^i = x_A^o G_A^i + x_B^o G_B^i + (1 - x_A - x_B)^o G_C^i + RT(x_A \ln x_A + x_B \ln x_B + (1 - x_A - x_B) \cdot \ln(1 - x_A - x_B)), \quad i = L, S, V \quad (3)$$

and

$$G_m^I = x_A^o G_A^I + x_B^o G_B^I + (1 - x_A - x_B)^o G_C^I + RT(x_A \ln x_A + x_B \ln x_B + (1 - x_A - x_B) \cdot \ln(1 - x_A - x_B)) + \Omega x_A x_B \quad (4)$$

where, for example, $^o G_A^I$ is the molar Gibbs energy of pure A in the liquid phase and R is the gas constant.

Considering an isothermal, viscous and incompressible system, the governing equations, similar to the approach in Refs. [7,23], are the following:

(i) conservative convective concentration equations,

$$\frac{1}{V_m} \left(\frac{\partial x_A}{\partial t} + \mathbf{u} \cdot \nabla x_A \right) = -\nabla \cdot J_A \quad \text{and} \quad (5)$$

$$\frac{1}{V_m} \left(\frac{\partial x_B}{\partial t} + \mathbf{u} \cdot \nabla x_B \right) = -\nabla \cdot J_B \quad (6)$$

where $\mathbf{u}$ is the flow velocity and J_A and J_B are fluxes of A and B measured with respect to the local flow;

(ii) non-conservative convective Allen–Cahn equations for the phase-field variables,

$$\frac{\partial \phi_i}{\partial t} + \mathbf{u} \cdot \nabla \phi_i = -M_{\phi_i} \frac{\delta G}{\delta \phi_i}, \quad i = L, S, I \quad (7)$$

where the M_{ϕ_i} are kinetic mobilities and with natural boundary conditions $n \cdot \nabla \phi_i = 0$;

(iii) a mass continuity equation for incompressible flow,

$$\nabla \cdot \mathbf{u} = 0 \quad (8)$$

(iv) and the Navier–Stokes equations for incompressible flow with added surface tension forces,

$$\rho(\phi) \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = -\nabla \tilde{p} + \nabla \cdot \mu(\phi) (\nabla \mathbf{u} + \nabla \mathbf{u}^T) - \sum_{i=L,S,I} \phi_i \nabla \left(\frac{\delta G}{\delta \phi_i} \right) \quad (9)$$

where $\tilde{p}$ is a nonclassical pressure [23]. The source terms of the Navier–Stokes equations that correspond to the surface tension forces are based on the derivation of Jacqmin Ref. [27].

The density $\rho(\phi)$ and viscosity $\mu(\phi)$ are defined as

$$\rho(\phi) = \rho_L \phi_L + \rho_S \phi_S + \rho_I \phi_I + \rho_V (1 - \phi_L - \phi_S - \phi_I), \quad (10)$$

$$\mu(\phi) = \begin{cases} \mu_i \phi_i, & \text{if } \phi_i \geq 0.9, \text{ for } i = (L, S, I, V) \\ \mu_i + 0.5(\mu_j - \mu_i)[1 + \tanh(2\pi(\phi_j - 0.8)/0.6)], & \text{if } (0.1 < \phi_i < 0.9) \& (0.1 < \phi_j < 0.9) \\ & \& (\phi_i + \phi_j > 0.5) \& (\phi_k < 0.05) \\ & \& (\phi_l < 0.05), \text{ for } (i, j, k, l) = \\ & \{(L, S, I, V), (L, I, S, V), (S, I, L, V)\}, \\ \mu_i + 0.5(\mu_j - \mu_i)[1 + \tanh(2\pi(\phi_j - 0.5)/0.6)], & \text{if } (0.1 < \phi_i < 0.9) \& (0.1 < \phi_j < 0.9) \\ & \& (\phi_i + \phi_j > 0.5) \& (\phi_k < 0.05) \\ & \& (\phi_l < 0.05), \text{ for } (i, j, k, l) = \\ & \{(L, V, I, S), (S, V, L, I), (I, V, L, S)\}, \\ \mu(\phi) = \sum_{i=L,V,S,I} \mu_i \phi_i, & \text{otherwise.} \end{cases} \quad (11)$$

This complicated expression for the dependence of the viscosity on the phase field variable is used to provide more flexibility for the variation of viscosity through the interfacial regions. Because of the large effective bulk viscosity that is assumed for the solid phase, a simpler form for μ that is analogous to that used for the density in Eq. (10) is found to have an excessively large interface viscosity.

To complete the concentration equations (Eqs. (5), (6)), we write the interdiffusion flux of solutes J_A and J_B (with $J_A + J_B + J_C = 0$)

$$J_A = -L_{AA} \nabla \left(\frac{\delta G}{\delta x_A} \right) - L_{AB} \nabla \left(\frac{\delta G}{\delta x_B} \right) \quad \text{and} \quad (12)$$

$$J_B = -L_{AB} \nabla \left(\frac{\delta G}{\delta x_A} \right) - L_{BB} \nabla \left(\frac{\delta G}{\delta x_B} \right) \quad (13)$$

where the variations in G with respect to the compositions x_j are given by

$$\frac{\delta G}{\delta x_j} = \frac{1}{V_m} \frac{\partial G_m}{\partial x_j}, \quad j = A, B \quad (14)$$

and the L_{ij} are [7]

$$L_{AA} = (1 - x_A)^2 x_A M_A(\phi_L, \phi_S, \phi_I, \phi_V) + x_A^2 x_B M_B(\phi_L, \phi_S, \phi_I, \phi_V) + x_A^2 (1 - x_A - x_B) M_C(\phi_L, \phi_S, \phi_I, \phi_V), \quad (15)$$

$$L_{BB} = x_B^2 x_A M_A(\phi_L, \phi_S, \phi_I, \phi_V) + (1 - x_B)^2 x_B M_B(\phi_L, \phi_S, \phi_I, \phi_V) + x_B^2 (1 - x_A - x_B) M_C(\phi_L, \phi_S, \phi_I, \phi_V), \quad \text{and} \quad (16)$$

$$L_{AB} = -(1 - x_A) x_A x_B M_A(\phi_L, \phi_S, \phi_I, \phi_V) - x_A x_B (1 - x_B) M_B(\phi_L, \phi_S, \phi_I, \phi_V) + x_A (1 - x_A - x_B) x_B M_C(\phi_L, \phi_S, \phi_I, \phi_V) \quad (17)$$

The diffusion mobilities of A , B and C can be different in each phase and are given by

$$M_j(\phi_L, \phi_S, \phi_I, \phi_V) = M_j^L \phi_L + M_j^S \phi_S + M_j^I \phi_I + M_j^V (1 - \phi_L - \phi_S - \phi_I), \quad j = A, B, C \quad (18)$$

where $1 - \phi_L - \phi_S - \phi_I$ has been substituted for ϕ_V .

The model allows for a ternary phase diagram such as the one shown as an isothermal section in Fig. 2. The phase diagram is idealized and the parameters are given in Table 1, along with other input parameters.

Given the parameters in Table 1, we can estimate more familiar material parameters such as diffusivities D_i and interface kinetic coefficients k_{coeff} with the following formulas [26]:

$$D_L = M_x^L RT, \quad \text{etc.} \quad (19)$$

$$k_{\text{coeff}} = \frac{V_m}{3RM_\phi \delta} \quad (20)$$

where $M_x^i = M_A^i = M_B^i = M_C^i$, $i = L, S, I, V$, and δ is the interface width. The diffusivities are $D_L = D_V = 10^{-9} \text{ m}^2/\text{s}$ and $D_S = D_I = 10^{-12} \text{ m}^2/\text{s}$, while the kinetic coefficients are $k_{\text{coeff}}^i = 16 \text{ s K/m}$, where $i = L, S, I$.

3. Numerical treatment

The system of partial differential equations (PDEs) are solved using a mesh-adaptive finite element method (see Ref. [28] for details) and implemented in an open-source PDE solver tool called FemLego [29]. All PDEs are discretized in space using piecewise linear functions. Each resulting linear system is solved using Krylov-type iteration methods either by the conjugate gradient method for symmetric and positive-definite systems or the generalized minimal residual method otherwise. The system of Navier–Stokes and continuity equations is solved by an incremental fractional-step algorithm [30] that belongs to a class of

projection methods. A pressure stabilization term is also added in the projection step to improve stability. We have assumed cylindrical symmetry about the z -axis perpendicular to the solid substrate (see Fig. 1).

Adaptive mesh refinement and derefinement allows spatial resolution of the interfaces, as is required when using a phase-field approach. In Fig. 3, regions corresponding to two different times (initial and late stage spreading) are shown illustrating the effective implementation of the mesh refinement and derefinement. An ad hoc error criterion is used to ensure mesh resolution along the vicinity of the interfaces (see [28] for details of the mesh-adaptive finite element scheme). For the typical example shown in Fig. 3, the initial radius of the drop is $R_0 = 20 \text{ nm}$ and the domain size is $60 \text{ nm} \times 90 \text{ nm}$. The minimum mesh size is $h_{\text{min}} = 0.13 \text{ nm}$, with between 9000 and 11,000 nodes and between 19,000 and 22,000 triangular elements.

The capillary time scale $t_c = \mu_L R_0 / (2\gamma_{LV})$ is viewed in this study as being especially important, representing the natural response time of the system in approaching mechanical equilibrium. Parameters such as interface energies, kinetic coefficients and viscosities have been chosen to be as close as is practicable to a reference system, that is, the spreading of Sn on a Cu substrate (see Ref. [23] for details).

A practical limitation of a phase-field calculation is the ratio between the interface thickness, δ , and the characteristic length scale of the system (i.e. drop size) typically being of the order of 0.1–0.01. We are thus forced to choose between a realistic drop size with an extremely thick interface thickness or a realistic interface thickness, say $\delta = 1 \text{ nm}$, but extremely small drop size. In our calculation, we have chosen the latter. An examination of the effect of interface thickness indicates that the L–I–V triple junction speed increases with the interface thickness, which is consistent with previous studies using the phase-field approach [31,32].

Our use of the terms “triple junction,” “interface” and “apparent contact angle” require clarification, since we are employing a diffuse interface model, yet these are sharp interface abstractions. Our approach is again similar to that of Villanueva et al. [23]. Briefly, the L–I–V triple junction is the point where $(\phi_L, \phi_S, \phi_I, \phi_V) \approx (1/3, 0, 1/3, 1/3)$ and the S–I–V triple junction is the point where $(\phi_L, \phi_S, \phi_I, \phi_V) \approx (0, 1/3, 1/3, 1/3)$. Contact angles are obtained from the slopes of $\phi_i = 0.5$ contours at a distance of 2δ from the triple junction point where δ is the interface thickness. We employ terms such as triple junction and interface using these definitions, though with the caveat that they are always diffuse.

There are a number of ways to visualize the spreading process, given the solutions of the phase-field variables and concentration profiles. Concentration profiles provide straightforward information while phase-field profiles can provide ways to define or locate a “sharp interface” from the diffuse-interface profiles. Sharp-interface analogues provide alternative visualization as well as facilitate an

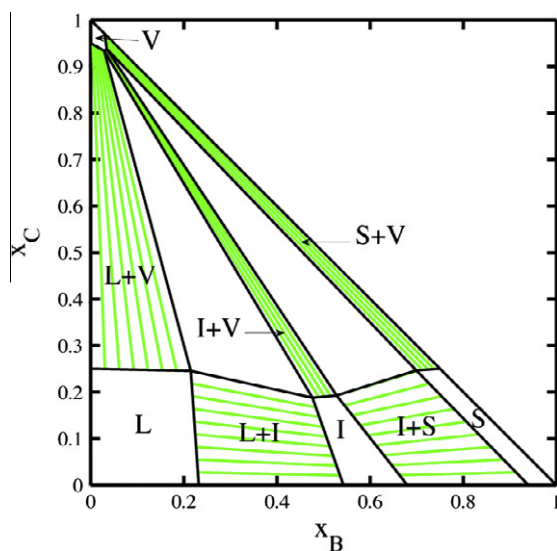


Fig. 2. Idealized phase diagram of a ternary A–B–C system at 450 K.

Table 1

Base set of parameters.

${}^o G_A^L = -5.0 \times 10^3 \text{ J/mol}$ ${}^o G_B^L = {}^o G_C^L = {}^o G_A^S = {}^o G_C^S = {}^o G_C^I$ $= -1/2 \cdot {}^o G_A^L$ ${}^o G_B^S = {}^o G_A^I = 1/4 \cdot {}^o G_A^L$ ${}^o G_B^I = -1/8 \cdot {}^o G_A^L$ ${}^o G_A^V = -{}^o G_A^L$ ${}^o G_B^V = -2 \cdot {}^o G_A^L$ ${}^o G_C^V = 1/2 \cdot {}^o G_A^L$ $\Omega_{AB} = 5/4 \cdot {}^o G_A^L$ $M_A^L = M_B^L = M_C^L = M_A^V = M_B^V = M_C^V = 2.67 \times 10^{-13} \text{ mol m}^2/\text{J s}$ $M_A^S = M_B^S = M_C^S = M_A^I = M_B^I = M_C^I = 10^{-3} \cdot M_A^L$ $M_{\phi_L} = M_{\phi_S} = M_{\phi_I} = 25 \text{ m}^3/\text{m J s}$ $\mu_L = 4.0 \times 10^{-3} \text{ Pa s}$ $\mu_S = \mu_I = 10^6 \cdot \mu_L$ $\mu_V = 10^{-2} \cdot \mu_L$ $V_M = 1.0 \times 10^{-5} \text{ m}^3/\text{mol}$	$T = 450 \text{ K}$ $W_{LS} = 2.21 \times 10^5 \text{ J/mol}$ $W_{LI} = 1.91 \times 10^4 \text{ J/mol}$ $W_{LV} = 1.43 \times 10^5 \text{ J/mol}$ $W_{SI} = 2.54 \times 10^4 \text{ J/mol}$ $W_{SV} = 2.49 \times 10^5 \text{ J/mol}$ $W_{IV} = 2.33 \times 10^5 \text{ J/mol}$ $W_{ijk} = W_{LSIV} = 8.75 \times 10^6 \text{ J/mol}$ $\epsilon_{LS}^2 = 6.32 \times 10^{-9} \text{ J/m}$ $\epsilon_{LI}^2 = 6.71 \times 10^{-10} \text{ J/m}$ $\epsilon_{SI}^2 = 7.40 \times 10^{-10} \text{ J/m}$ $\epsilon_{LV}^2 = 5.99 \times 10^{-9} \text{ J/m}$ $\epsilon_{SV}^2 = 8.24 \times 10^{-9} \text{ J/m}$ $\epsilon_{IV}^2 = 7.94 \times 10^{-9} \text{ J/m}$ $\rho_L = 10^3 \text{ kg/m}^3$ $\rho_S = \rho_I = 1.05 \cdot \rho_L$ $\rho_V = 10^{-3} \cdot \rho_L$ $R = 8.31 \text{ J/mol K}$
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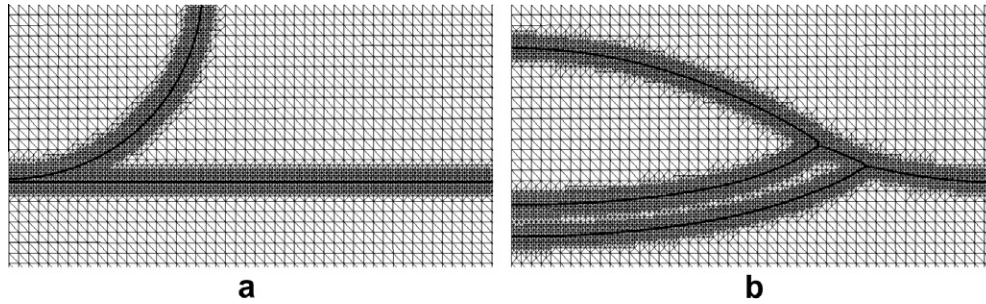


Fig. 3. Adaptive mesh refinement and derefinement of cut-off regions corresponding to two different times with superimposed 0.5 contours of the phase-field variables ϕ_L , ϕ_S and ϕ_I .

Table 2

Comparison between analytical and numerical simulation (evaluated at $t/t_c = 2000$) for the S–I–V coexistence.

	x_A^V	x_B^V	x_A^I	x_B^I	x_A^S	x_B^S	f^V	f^I
Analytical	0.0278	0.0346	0.2794	0.5281	0.0543	0.6993	0.1798	0.3664
Simulation	0.0275	0.0347	0.2775	0.5298	0.0530	0.7013	0.1780	0.3760

effective measurement of contact angles (see [23] for more details). In some figures (i.e. Fig. 9), we use a “dominant-phase” plot where at every discrete point in the domain we find the phase-field variable that has a maximum and then designate a corresponding color.

4. Model verification: equilibrium states

In this section, we describe calculations that were performed to verify the proposed mathematical model. These include verifying equilibrium concentrations and phase fractions, comparing equilibrium contact angles with contact angles extracted from long time simulations and confirming the existence of a critical size for growth of an intermetallic seed. We should note that the calculations in this section were done by setting higher diffusion coefficients and lower viscosity in the solid phase. The changes

result in faster dynamics, but do not affect the equilibrium values.

4.1. Equilibrium concentrations and phase fractions

Tables 2 and 3 show a comparison of phase compositions and phase fractions for the three-phase S–I–V and L–I–V coexistence obtained by two methods. The first method is a classical analytical solution based on the phase diagram and solute balance (lever law), and the second method is obtained from a numerical simulation using the governing equations given in Section 2. The classical analytical calculation involves solving a system of equations that include the solute balance (lever rule), equating chemical potentials, differences in molar Gibbs energies and sum of phase fractions (being equal to 1). For the S–I–V coexistence, the phase-field simulation starts with a

Table 3
Comparison between analytical and numerical simulation (evaluated at $t/t_c = 4000$) for the L–I–V coexistence.

	x_A^V	x_B^V	x_A^I	x_B^I	x_A^L	x_B^L	f^V	f^I
Analytical	0.0373	0.0290	0.3359	0.4763	0.5396	0.2151	0.0973	0.3053
Simulation	0.0366	0.0292	0.3339	0.4796	0.5363	0.2185	0.0940	0.3250

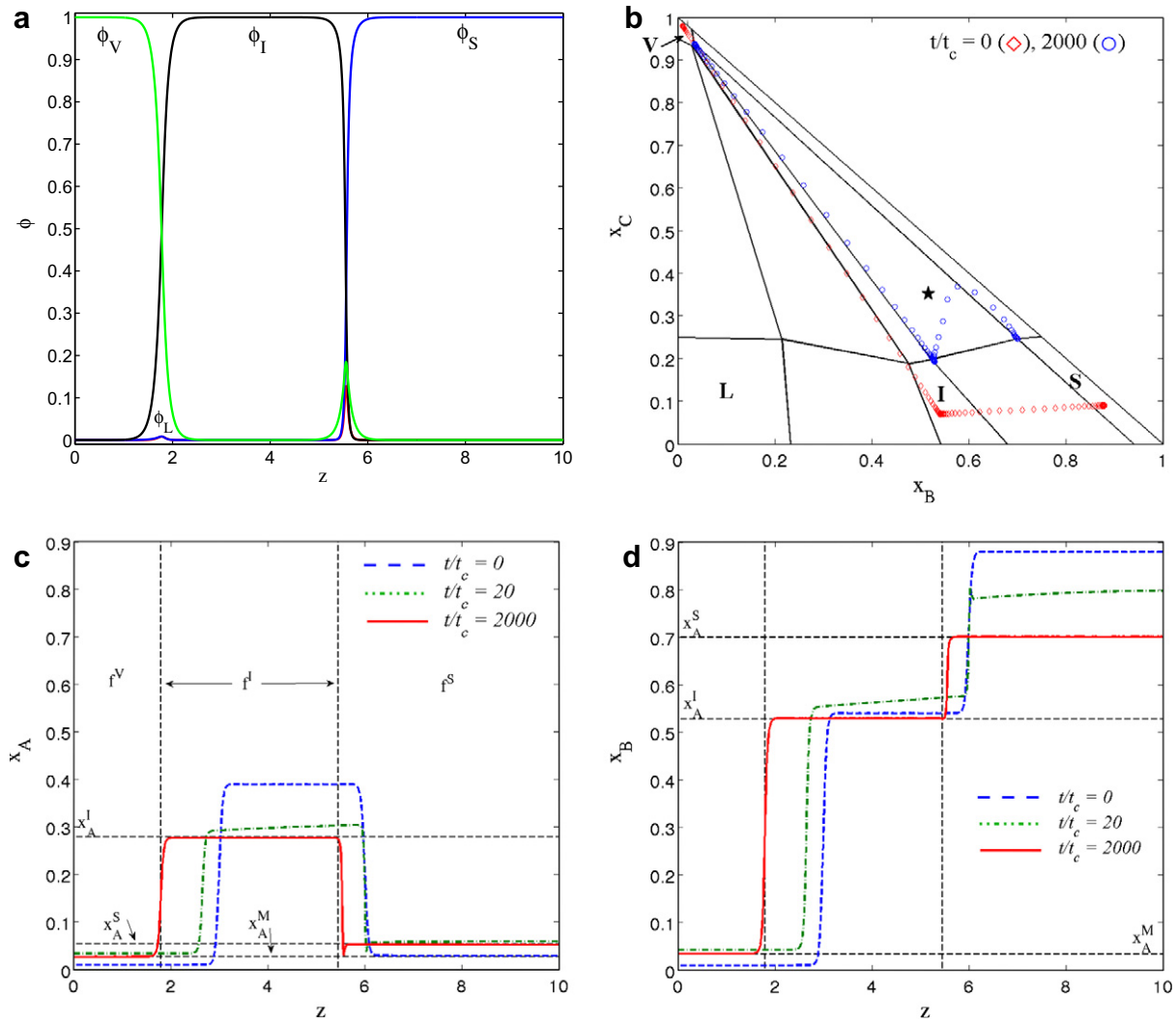


Fig. 4. Numerical simulation of a slab divided into three phases (S, I and V) that are not in equilibrium both in concentration and phase fractions. The late-stage phase-field profiles at $t/t_c = 2000$ are shown in (a). The average concentration is shown as a star symbol in the phase diagram (b). Hence, the three phases S, I and V must coexist at equilibrium. Analytical results for the concentrations in each phase and phase fractions are also superimposed in (c) and (d).

slab divided perpendicularly into three phases (S, I and V) that are not in equilibrium, either in concentration or phase fractions. Fig. 4b–d shows the initial concentrations and phase fractions. The average concentration is shown as a star symbol in the phase diagram (see Fig. 4b). Hence, the three phases S, I and V must coexist at equilibrium. The evolution of the concentration fields at times $t/t_c = 0, 20, 2000$ are shown in Fig. 4c and d, while the phase-field profiles at $t/t_c = 2000$ are shown in Fig. 4a. Excellent agreement between the numerical simulation (evaluated at $t/t_c = 2000$) and the analytical calculation has been obtained

for the concentrations in each phase and phase fractions, as shown in Fig. 4c and d and summarized in Table 2. Similarly, Fig. 5c and d and Table 3 show excellent agreement between numerical simulation and analytical calculation for the L–I–V coexistence.

4.2. Equilibrium contact angles

To evaluate the equilibrium contact angles, we first calculate the interface energies of each pair of phases (LS, LI, LV, SI, SV and IV) with the following expression,

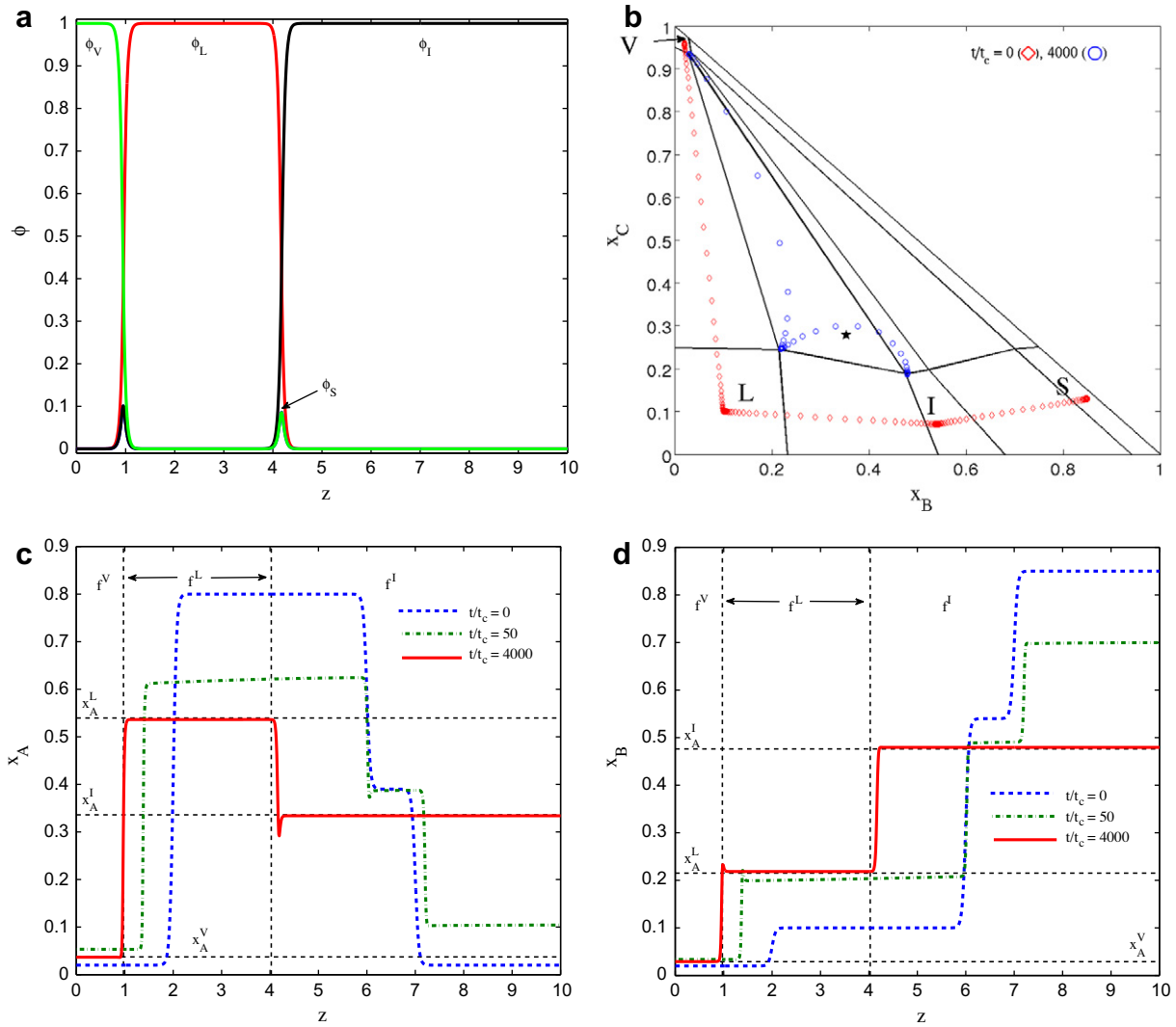


Fig. 5. Numerical simulation of a slab divided into four phases (L, S, I and V) that are not in equilibrium both in concentration and phase fractions. The average concentration is shown as a star symbol in the phase diagram (b). Hence, the three phases L, I and V must coexist at equilibrium. Analytical results for the concentrations in each phase and phase fractions are also superimposed in (c) and (d).

$$\gamma = \int_{-\infty}^{\infty} \left[\frac{1}{V_m} ((G_m(x_i(z), \phi_i(z); T) - G_m(x_i(\pm\infty), \phi_i(\pm\infty); T)) - \sum_{i=1}^2 \frac{\partial G_m(x_i, \phi_i; T)}{\partial x_i} \Big|_{z=\pm\infty} \cdot (x_i(z) - x_i(\pm\infty))) + \sum_{i,j>i}^4 \frac{\epsilon_{ij}^2}{2} \left| \phi_i \frac{d\phi_j}{dz} - \phi_j \frac{d\phi_i}{dz} \right|^2 \right] dz \quad (21)$$

Corresponding concentration and phase-field profiles are obtained from one-dimensional (1-D) simulations of each pair of phases. The interface energies are summarized in Table 4. Using the Neumann construction (balance of tensions), the calculated equilibrium contact angles for the four possible triple junctions (LSV, LSI, LIV and SIV) are given in Table 5. Values in parentheses are obtained from phase-field simulations at late times for LIV and SIV triple junctions. As an example, Fig. 6a shows a 2-D axisymmetric liquid drop on a solid substrate. The average composition of the initial L–S–V configuration is in the

Table 4

Calculated interface energies γ_{ij} s using parameters of Table 1.

$\gamma_{LS} = 2.55 \text{ J/m}^2$	$\gamma_{LV} = 1.91 \text{ J/m}^2$
$\gamma_{SV} = 2.17 \text{ J/m}^2$	$\gamma_{LI} = 0.29 \text{ J/m}^2$
$\gamma_{SI} = 0.35 \text{ J/m}^2$	$\gamma_{IV} = 1.99 \text{ J/m}^2$

^a Since the liquid–solid interface is unstable with the given base set of parameters, the liquid–solid interface energy is calculated by suppressing the formation of the intermetallic phase.

S–I–V three-phase triangle of the phase diagram. Thus, as expected, the intermetallic forms and grows while the liquid dissolves (see the successive images in Fig. 6b and c). The measured contact angles in Fig. 6c for SIV are $\theta_S = 129.9^\circ$, $\theta_I = 56.5^\circ$ and $\theta_V = 173.6^\circ$, while the calculated equilibrium contact angles given by the Neumann construction are $\theta_S^e = 125.0^\circ$, $\theta_I^e = 63.3^\circ$ and $\theta_V^e = 171.7^\circ$.

Table 5
Calculated equilibrium angles for the four possible triple junctions.

LSV	LSI ^a	LIV	SIV
$\theta_L^e = 124.0^\circ$	$\theta_L^e = 180^\circ$	$\theta_L^e = 78.1^\circ (67.3^\circ)$	$\theta_S^e = 125.0^\circ (129.9^\circ)$
$\theta_S^e = 133.1^\circ$	$\theta_S^e = 180^\circ$	$\theta_V^e = 171.8^\circ (173.6^\circ)$	$\theta_I^e = 63.3^\circ (56.5^\circ)$
$\theta_V^e = 102.9^\circ$	$\theta_I^e = 0^\circ$	$\theta_I^e = 110.1^\circ (119.1^\circ)$	$\theta_V^e = 171.7^\circ (173.6^\circ)$

Values obtained from phase field simulations in Fig. 6b and c for LIV and SIV triple junctions are given in parentheses.

^a The intermetallic wets the LS interface.

It is also interesting to note that the measured contact angles for SIV in Fig. 6c agree with the corresponding measured contact angles in Fig. 6b. Also, in Fig. 6b, the measured LIV triple junction angles agree with angles taken from a separate simulation (not shown) with an average composition in the L–I–V three phase triangle. Discrepancies are due to the inherent imprecision in measuring contact angles in diffuse interface simulations [23].

4.3. Critical nucleus size

The base set of parameters in Table 1 yield spontaneous nucleation and growth of an intermetallic phase on an L–S interface, as shown in Fig. 6. In order to illustrate the existence of a critical nucleus size for growth or decay, we altered the W_{ij} and ϵ_{ij} in such a way that we can calculate a critical size (see Appendix for details). Fig. 7 shows the dissolution of seed intermetallic phase at snapshot times $t/t_c = 0, 10^3$ and 2×10^3 . The initial base radius is 4 nm, which is smaller than the computed critical base radius of 4.33 nm (given the angles $\theta^+ = 30^\circ$ and $\theta^- = 40^\circ$). With a larger seed of intermetallic phase, and keeping all other parameters the same, the growth of the seed is observed as shown in Fig. 8 at snapshot times of $t/t_c = 0, 10^3$ and 10^4 . Full droplet spreading calculations with these parameters involved excessive computing time and were not pursued further.

5. Reactive wetting with intermetallic formation

Given the base set of parameters in Table 1, Fig. 9 shows the spreading of a molten metal drop on a solid substrate with the nucleation and growth of an intermetallic phase between the drop and the substrate. The initial configuration is a drop that barely touches the substrate and initially

has an apparent contact angle close to 180° . In the early stage of spreading, viscous or inertial forces dominate, resulting in relatively rapid spreading. This is followed by slower, progressive spreading as diffusion becomes the dominant process. In the case of dissolutive wetting (no intermetallic formation), phase change was found to affect the spreading process in both stages [23]. An early time $t/t_c = 1$ is shown in Fig. 9b, where the drop has rapidly spread on the substrate with a base radius that has increased to $R/R_0 = 1.07$ and the apparent contact angle has decreased to about 132.3° . The growth of the intermetallic phase is also rapid and has grown ahead of the spreading liquid which forms LIV and SIV triple junctions (see the magnified view of Fig. 9b). Note that the drop profile including the structure of the contact line region is qualitatively similar to SEM images of an Sn–0.7Cu solder on a Cu substrate performed experimentally by Nogita et al. [19] (see Fig. 10). At a later time $t/t_c = 200$ the drop continues to spread further to a base radius $R/R_0 = 2.14$, while the intermetallic phase thickens and remains ahead of the spreading liquid. In the magnified view of the contact line region, one can observe that the substrate is not planar, nor is the intermetallic phase, which is consistent with SEM images of contact line regions reported in the literature [18,19].

A detailed hydrodynamic analysis is beyond the scope of this paper. Briefly, however, the results on the wetting speed indicate that the liquid drop, for the base set of parameters, spreads slower than the predictions of Cox's hydrodynamic model [20] for nonreactive systems. Fig. 11 shows examples of the flow pattern and concentration field in the vicinity of the substrate and moving contact line region for early $t/t_c = 1$ and later $t/t_c = 200$ times. The 0.5 contour level of the phase-field variables ϕ_L , ϕ_S and ϕ_I are also superimposed. At $t/t_c = 1$ (see Fig. 11a), the flow pattern consists of a vortex with center outside of the drop and near the liquid–vapor interface, and a flow downward from the top of the drop then redirected to the contact line region. There is negligible flow in the solid substrate and the intermetallic phase due to the chosen high viscosity for these phases. At a later time $t/t_c = 200$ (see Fig. 11b), the flow pattern is generally the same compared to the previous time $t/t_c = 1$ except that the vortex moves further away from the solid substrate and the L–I–V triple junction speed decreases by two orders of magnitude.

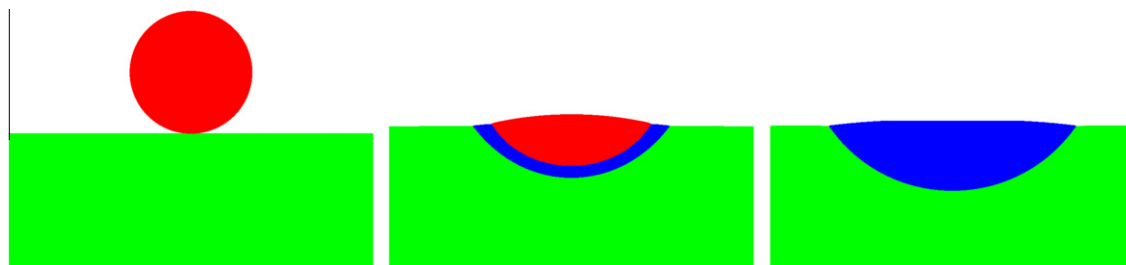


Fig. 6. Full dissolution of the liquid drop on the solid substrate and formation of the intermetallic at times $t/t_c = 0, 100, 500$.

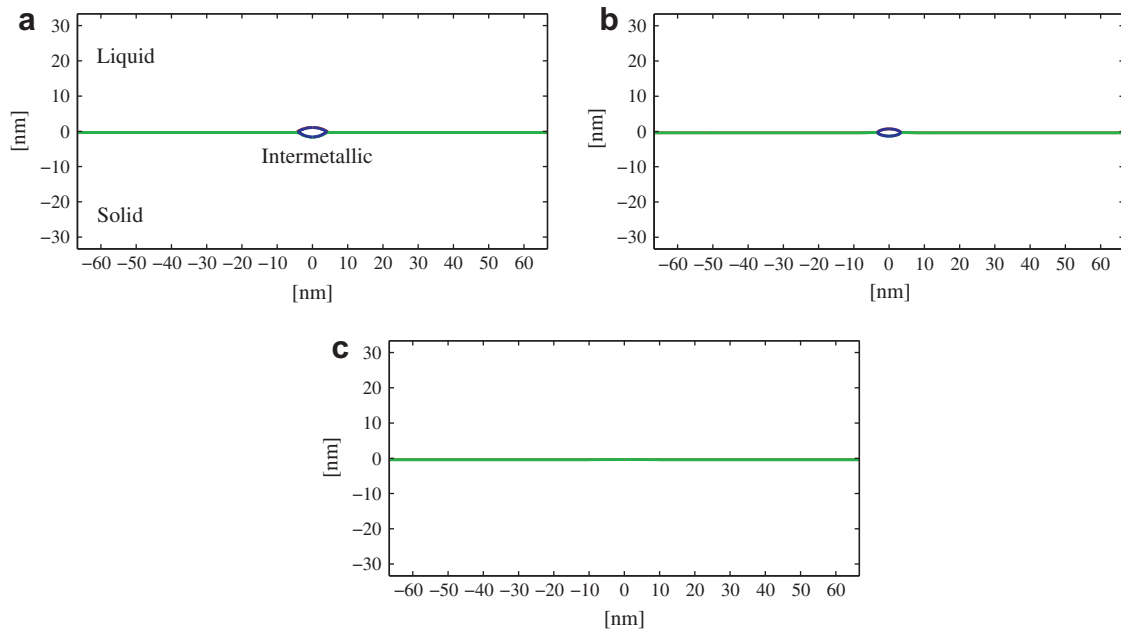


Fig. 7. Dissolution of a seed of intermetallic phase on a solid–liquid interface at times $t/t_c = 0, 200, 700$.

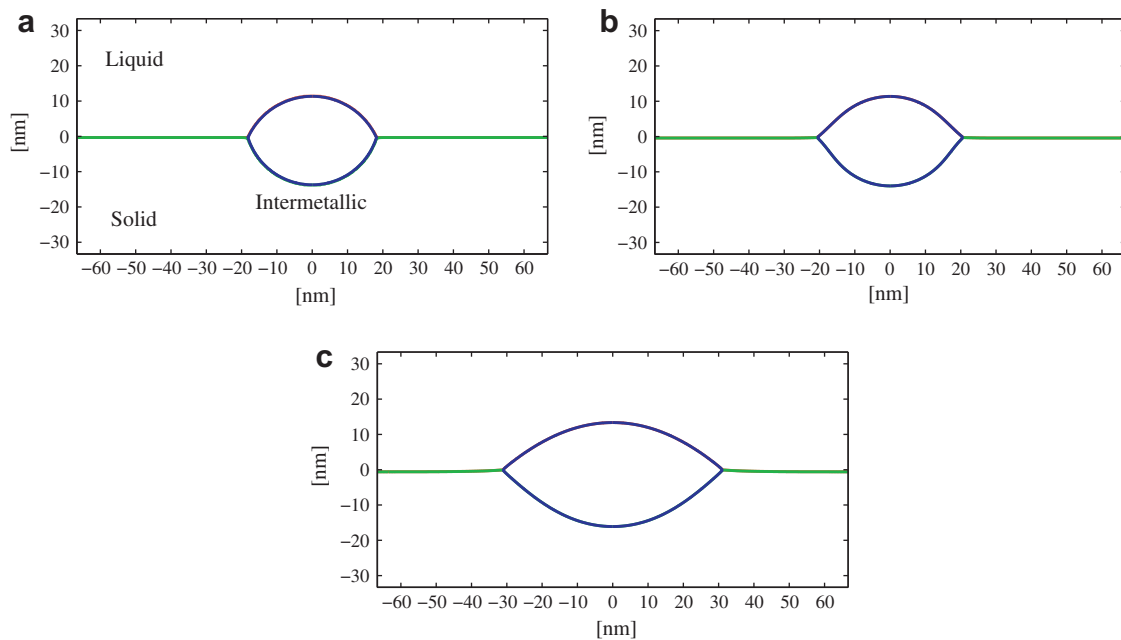


Fig. 8. Growth of a seed of intermetallic phase on a solid–liquid interface at times $t/t_c = 0, 10^3, 10^4$.

Concentration profiles of B are shown in Fig. 11 at times $t/t_c = 1, 200$. At equilibrium, the liquid phase is rich in A while the substrate is rich in B. Initially, we start with the substrate having equilibrium values of $x_A^S = 0.05$ and $x_B^S = 0.70$ while the liquid has a lower concentration of B, $x_B^L \approx 0.05$, than the equilibrium value of $x_B^L = 0.22$ but a higher concentration of A, $x_A \sim 0.85$, than the equilibrium value of $x_A^L = 0.54$. Solute diffusion is much slower than fluid flow. So, as expected, the concentration of B in the

liquid does not change considerably from its initial value to time $t/t_c = 1$ (which can be seen as the relatively homogeneous dark blue color in Fig. 11a), while its dynamic contact angle has decreased by more than 40° . At a later time, $t/t_c = 200$, the concentration of B in the liquid (the lighter blue color in Fig. 11b) has started to increase with the transport of B components from the B-rich substrate. The transport of B from the substrate to the liquid also aids in the growth of the intermetallic layer. More discussion is

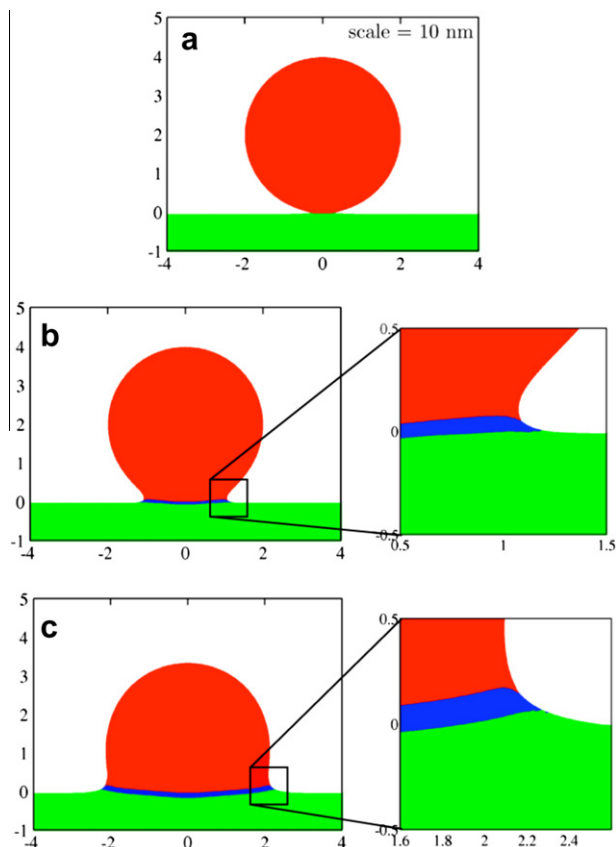


Fig. 9. Maximum phase-field plot at $t/t_c = 0, 1, 200$ with the base set of parameters (Table 1).

given in Ref. [21], where it is concluded that solute trapping is likely occurring in the rapidly forming intermetallic.

Fig. 12 shows the change with time of the dynamic contact angle θ_1 . The early stage shows a rapid decrease in which viscous effects dominate, followed by a slow decrease as diffusion becomes the dominant process. Phase change can also affect the spreading kinetics in both stages, as was found in Ref. [23] for dissolutive wetting. The change in time of the scaled base radius $R/(\frac{1}{2}R_0)$, where R is equal to the radial coordinate of the triple junction L–I–V, is also shown in Fig. 12. The behavior follows a similar but opposite trend to the dynamic contact angle. The base radius rapidly increases up to about the drop's initial radius at $t/t_c = 30$, followed by a slow increase of not more than a tenth of the initial drop radius at $t/t_c = 200$, while the decrease in contact angle from time $t/t_c = 30$ to 200 is only 4.9° . We should note here that the liquid drop eventually dissolves and only the solid, intermetallic and vapor remain in an equilibrium which is determined by the initial conditions, the size of the domain and the phase diagram.

5.1. Retarding intermetallic growth

Many factors can affect the nucleation and growth of the intermetallic phase, such as interface energies and kinetic coefficients between the intermetallic and other phases. In this section we present two cases to show that the growth

of the intermetallic phase may be retarded for some materials parameters. First, we examine kinetic retardation by decreasing the mobility M_{ϕ_i} of the phase field for the intermetallic phase. Unfortunately the present phase field model does not cleanly separate the equivalent interface kinetic coefficients for the motion of LI and SI interfaces. Using the approximate formula in Eq. (20), M_{ϕ_i} is lowered by a factor of 12 from the base state, while leaving the rest of the parameters the same. The second approach to retard intermetallic formation is to increase the liquid–intermetallic interface energy γ_{LI} from 0.29 J/m^2 to 1.54 J/m^2 , which is done by modifying the corresponding W_{LI} and ϵ_{LI} . In principle, these quantities can contribute to other interface energies. In this case, however, a 1-D recalculation of the interface energies with the changes $W_{LI} = 1.47 \times 10^5 \text{ J/mol}$ and $\epsilon_{LI} = 3.87 \times 10^{-9} \text{ J/m}$ from the base set (while leaving the rest of the parameters the same) yielded only a slight change in other interface energies (see Table 6).

Snapshots of the first case (slow intermetallic kinetics that corresponds to 192 s K/m) are shown in Fig. 13 side-by-side with the base case (fast intermetallic kinetics that corresponds to 16 s K/m). Fig. 13a, c, e and g correspond to the fast kinetics case with a time sequence, $t/t_c = 1, 1.3, 3, 20$, respectively, while Fig. 13b, d, f and h correspond to the slow kinetics case with the same time sequence, respectively. The intermetallic phase has rapidly grown ahead of the liquid drop with the fast kinetics case (Fig. 13a), whereas no intermetallic phase has yet grown with the slow kinetics case (Fig. 13b). However, the base radii of the liquid drop for both cases are essentially identical. In the succeeding time sequence for the fast kinetics case (Fig. 13c, e and g), the intermetallic phase moves in tandem with, but always ahead of, the liquid drop. In addition, the thickness of the intermetallic phase is also increasing while it slowly penetrates the substrate. The intermetallic phase is non-planar, and so is the substrate. Retarded formation of the intermetallic phase is observed for the slow intermetallic kinetics case (Fig. 13d, f and h), although the dynamics of the spreading liquid is similar to the fast kinetics case. This implies that the early stage of spreading is not significantly affected by the kinetics of the intermetallic phase.

To see the nucleation and growth more clearly, a separate set of higher magnification snapshots at times $t/t_c = 1.3, 3, 12, 20$ is given in Fig. 14. The intermetallic phase nucleates unevenly on the liquid–substrate interface and initially forms island-like structures (Fig. 14a). These structures eventually merge to become a single layer of thin intermetallic phase (Fig. 14b). The intermetallic phase then spreads to briefly form a quadrijunction with the other phases at $t = 12$ (Fig. 14c), passing quickly through this geometry to grow ahead of the liquid drop at time $t/t_c = 20$ (Fig. 14d).

Fig. 15b, d and f shows the second case of hampering the intermetallic phase by increasing the liquid intermetallic interface energy in comparison with the base set (Fig. 15a, c and e) for the time sequence $t/t_c = 0.1, 0.3,$

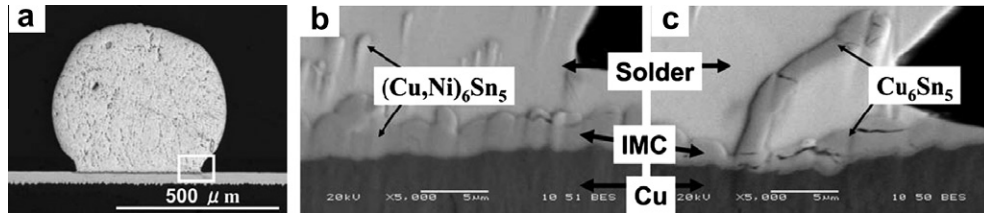


Fig. 10. (a) A typical cross-sectioned ball grid array on Cu substrate, (b) Sn-0.7Cu-0.05Ni solder and (c) Sn-0.7Cu solder. Reprinted with permission from Nogita et al. [19]. ©2009, Springer.

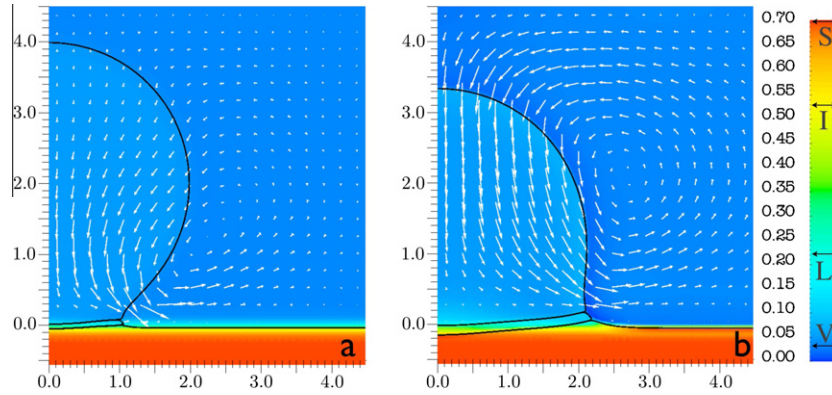


Fig. 11. Concentration profiles of B with the base set of parameters at (a) the early fast-spreading stage $t/t_c = 1$ and (b) the late slow-spreading stage $t/t_c = 100$, with normalized velocity profiles and 0.5 contours of the phase-field variables ϕ_L , ϕ_S and ϕ_I superimposed. The L–I–V triple junction speeds are (a) $U_{TJ}\mu_L/\sigma_{LV} = 0.235$ and (b) $U_{TJ}\mu_L/\sigma_{LV} = 0.001$, where $U_{TJ} \equiv dR/dt$ and R is the base radius of the liquid drop equal to the radial coordinate of the triple junction.

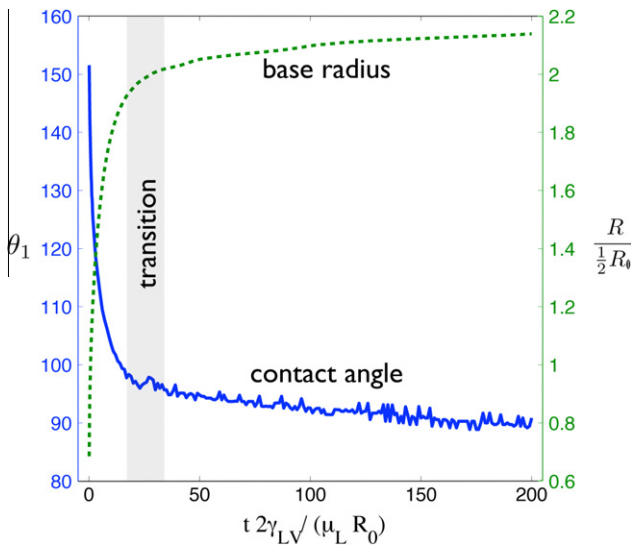


Fig. 12. The dynamic contact angle θ_1 and the scaled base radius $R/(\frac{1}{2}R_0)$ are both plotted against time, which is scaled with $\mu_L R_0/(2\gamma_{LV})$. The angle $\theta_1(t)$ is defined as the angle that the liquid makes with respect to the horizontal plane regardless whether the intermetallic phase is behind or ahead of the contact line. A region of transition from an initial rapid spreading to a slow and progressive spreading is also shown.

1.0, respectively. Again, the dynamics of the spreading liquid is similar to the base set, implying an independent dynamics of the spreading liquid with respect to the nucleation and growth of the intermetallic phase in the early

Table 6

Recalculated interface energies γ_{ijS} with $W_{LI} = 1.47 \times 10^5$ J/mol and $\epsilon_{LI}^2 = 3.87 \times 10^{-9}$ J/m while keeping the rest of the parameters as in Table 1.

$\gamma_{LS} = 2.55$ J/m ²	$\gamma_{LV} = 1.93$ J/m ²
$\gamma_{SV} = 2.17$ J/m ²	$\gamma_{LI} = 1.54$ J/m ²
$\gamma_{SI} = 0.34$ J/m ²	$\gamma_{IV} = 2.03$ J/m ²

^a Since the liquid–solid interface is unstable with the given base set of parameters, the liquid–solid interface energy is calculated by suppressing the formation of the intermetallic phase.

stage of the reactive wetting. The current analysis, however, does not take into account that the intermetallic layer in typical solder joints is composed of many small grains requiring multiple nucleation events; the treatment of this effect is beyond the scope of our investigation.

In an attempt to investigate the nature of the quadri-junction further, an additional set of interface energies was generated that should prevent intermetallic contact with the vapor and so help promote the tendency to form a dynamic quadri-junction. We ran this case with a seed of intermetallic phase for a dimensionless time up to $t/t_c = 10^4$. The intermetallic phase was observed to slowly approach the vicinity of the LSV triple junction, but stopped short of forming a quadri-junction. The spreading dynamics in this case is quite slow and the current

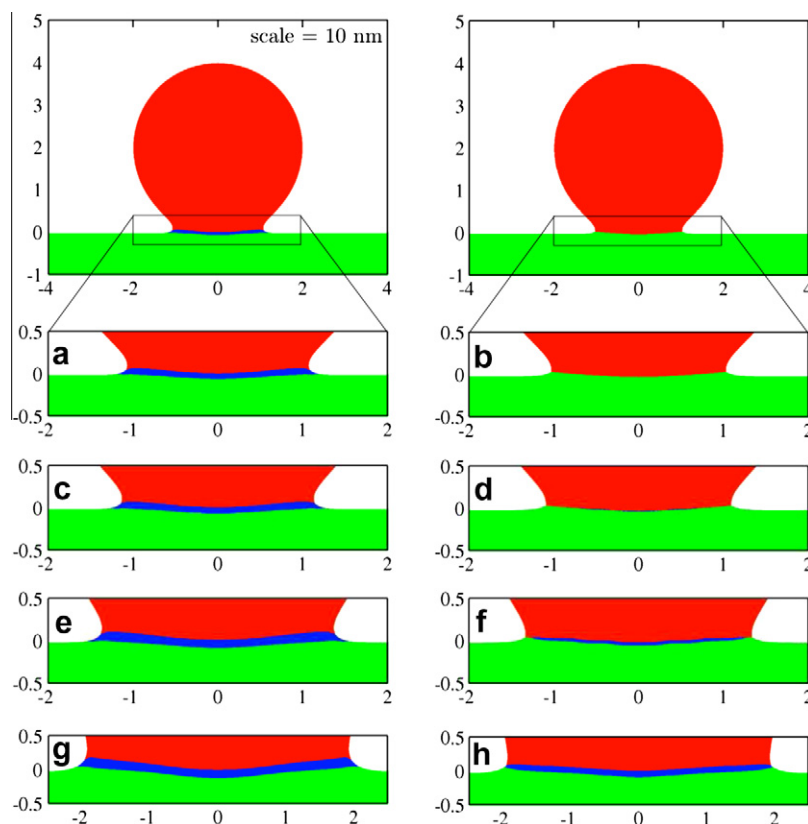


Fig. 13. Comparison of the growth of intermetallic phase between a fast intermetallic kinetics (a, c, e and g) corresponding to times $t/t_c = 1, 1.3, 3, 20$, respectively, and a slow intermetallic kinetics (b, d, f and g) with the same corresponding times, respectively. In both cases the intermetallic phase eventually grows ahead of the spreading liquid drop.

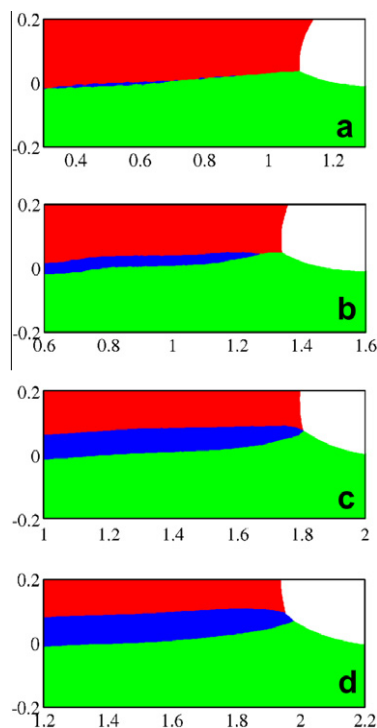


Fig. 14. Nucleation and growth of intermetallic phase at times $t/t_c = 1.3, 3, 12, 20$ with slow intermetallic kinetics.

numerical methodology cannot handle much longer transients efficiently. In order to investigate further the dynamics of quadrijunctions, a more efficient methodology such as implicit schemes for the system of PDEs should be employed or an approximate model with reduced complexity can be implemented. We note that the phase diagram does not admit four-phase equilibria, so the formation of quadrijunctions is necessarily a transient phenomena.

6. Conclusion

We have developed and presented a diffuse-interface model of reactive wetting with intermetallic formation based on a ternary system with four phases. The model incorporates fluid flow, phase change and solute diffusion. Numerical simulations were performed that successfully revealed the complex behavior of the reactive wetting process, including the nucleation and growth of an intermetallic phase. We have shown that the formation of the intermetallic phase can be controlled by the kinetic coefficient of the intermetallic phase and/or the interface energy associated with it. We have examined only a small part of the materials parameter space for this complex problem. Nevertheless, we have exposed two cases, one where the intermetallic forms before any appreciable spreading and one that occurs somewhat later. Thus, in the former case,

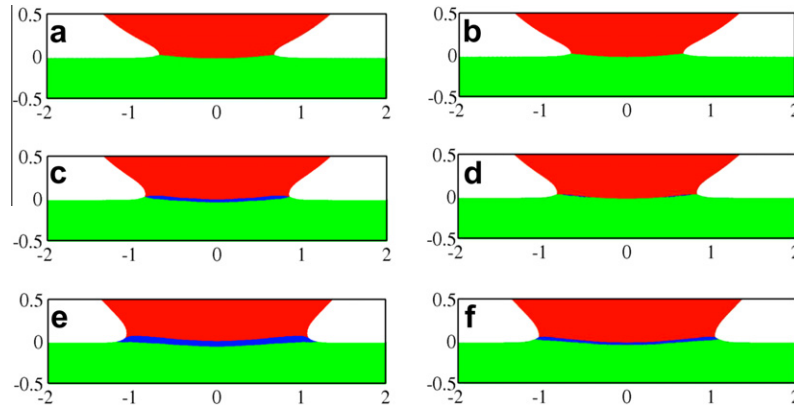


Fig. 15. Comparison of the growth of intermetallic phase with different liquid–intermetallic interface energies: (a, c and e) $\gamma_{LI} = 0.29 \text{ J/m}^2$ at times $t/t_c = 0.1, 0.3, 1.0$, respectively, and (b, d and f) $\gamma_{LI} = 1.54 \text{ J/m}^2$ at times $t/t_c = 0.1, 0.3, 1.0$, respectively.

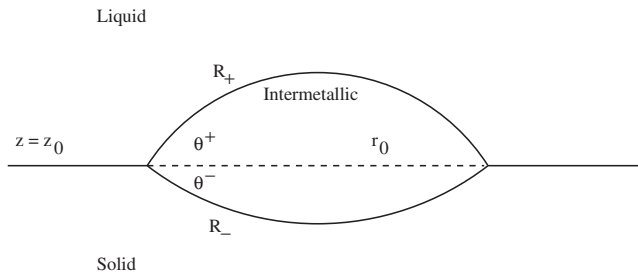


Fig. 16. Schematic diagram showing the geometry of a critical nucleus of intermetallic phase located on the interface between liquid and solid phases.

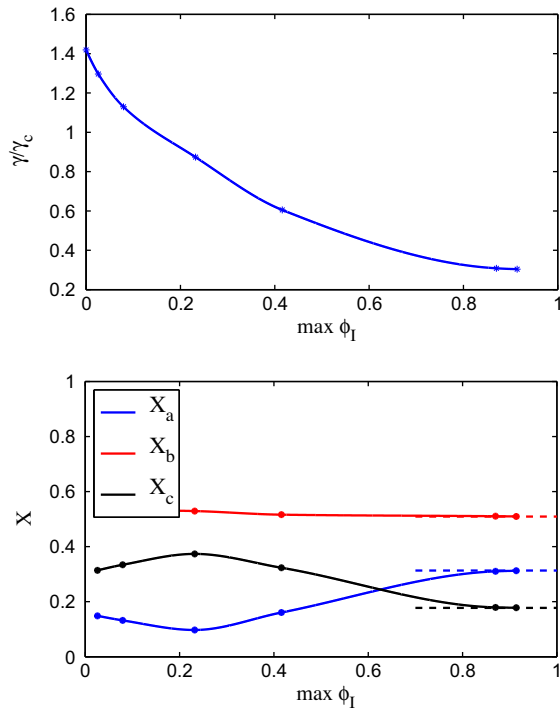


Fig. 17. Constrained equilibrium of a solid–liquid interface. Top: surface energy (normalized by $\gamma_c = 1.7944 \text{ J m}^{-2}$) vs. the maximum value of ϕ_I that occurs under the constraint conditions. Bottom: values of the mole fractions in the interfacial region (where ϕ_I reaches its maximum) vs. ϕ_I .

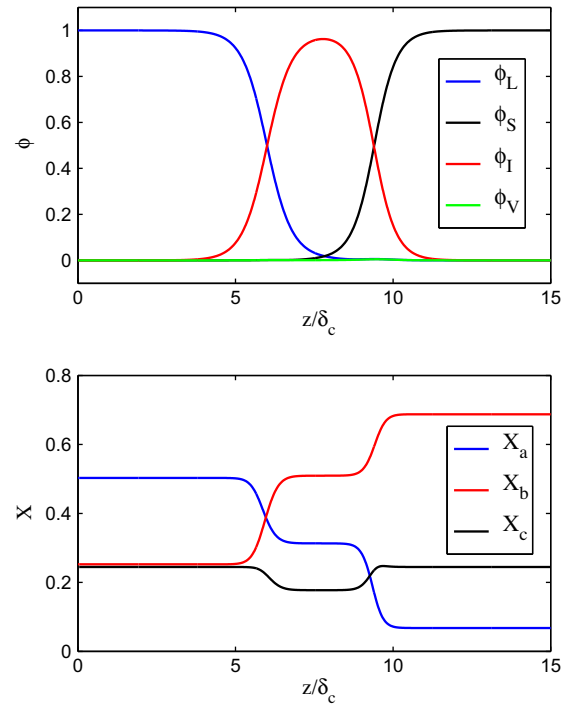


Fig. 18. Constrained equilibrium profiles of the phase fields and mole fractions when the solid–liquid interface is strongly ‘wetted’ by the intermetallic phase.

the liquid actually spreads on a layer of intermetallic rather than on the base solid. In the latter case, the liquid spreads on the base solid for a transient period of time. Thus, the angles at the triple junction differ in the two cases. In the present simulations, this small period of time occurs during the inertial period of spreading, so little difference is seen in the rate of spreading. In the process, we observe the interesting case of a transient quadrjunction LIVS during spreading. The triple junction pair LSV and LSI are replaced by the triple junction pair LIV and SIV as the intermetallic phase nucleates and grows along the L–S interface to form an interface with the vapor. Whether this process plays a significant role in the spreading dynamics

will require the examination of a larger materials parameter space, which must await an improved numerical scheme and/or a more approximate model.

Appendix A

Here we consider the effects of surface energy on the bulk nucleation of a given phase at an interface separating two other phases, and also consider the related question of how interfacial “wetting” by such a nucleating phase can affect the surface energy and adsorption of the interface. To illustrate, we consider the specific case of the nucleation of intermetallic phase at a liquid–solid interface.

A.1. Nucleation

We first summarize the conditions for nucleation of an intermetallic phase at a planar liquid–solid interface in terms of the mole fractions of each phase and the geometry of the critical nucleus.

For thermodynamic equilibrium at a given temperature and pressure the mole fractions X_A^L , X_B^L and X_C^L of the liquid phase and X_A^S , X_B^S and X_C^S of the solid phase satisfy $\mu_j^L(X_A^L, X_B^L, X_C^L) = \mu_j^S(X_A^S, X_B^S, X_C^S)$ for each species j , $j = A, B$ and C . Converting small numbers of moles ΔN_j^L and ΔN_j^S of the liquid and solid phases into the equivalent number of moles $\Delta N_j^I = \Delta N_j^L + \Delta N_j^S$ of the intermetallic phase produces a change in free energy $\Delta G = [\Delta N_A^I + \Delta N_B^I + \Delta N_C^I] \Delta G_M$ proportional to the number of moles that are converted into the intermetallic phase. The change in molar free energy, ΔG_M , can be written in terms of X_B^I and X_C^I :

$$\Delta G_M = G_M^I(X_B^I, X_C^I) - [1 - X_B^I - X_C^I] \mu_A^I - X_B^I \mu_B^I - X_C^I \mu_C^I \quad (22)$$

where we have eliminated $X_A^I = 1 - X_B^I - X_C^I$, used the solid–liquid equilibrium conditions $\mu_j^L = \mu_j^S$ and written the molar free energy of intermetallic as $G_M^I(X_B^I, X_C^I)$. The appropriate mole fractions X_B^I and X_C^I for (metastable) equilibrium of the nucleated intermetallic phase are then obtained by setting $\partial \Delta G_M / \partial X_B^I = \partial \Delta G_M / \partial X_C^I = 0$, which produces the parallel tangent conditions

$$\mu_B^I - \mu_A^I = \mu_B^L - \mu_A^L, \quad \mu_C^I - \mu_A^I = \mu_C^L - \mu_A^L \quad (23)$$

where we have used $\partial G_M^I(X_B^I, X_C^I) / \partial X_B^I = \mu_B^I - \mu_A^I$, etc. Thus, for example, given a value of X_B^L on the liquid–solid tie-line (coexistence curve), the remaining liquid–solid mole fractions X_C^L , X_B^S , and X_C^S follow from the three (common tangent) conditions $\mu_j^L = \mu_j^S$, and the intermetallic mole fractions X_B^I and X_C^I follow from the two (parallel tangent) conditions in Eq. (23).

Given the mole fractions of the liquid, solid and intermetallic phases, we assume the geometry of the critical nucleus is given by a lens-shaped inclusion of intermetallic that subtends a planar liquid–solid interface located at $z = z_0$, with liquid phase ($z > z_0$) lying above the solid phase ($z < z_0$) (see Fig. 16). The liquid–intermetallic

interface forms a hemispherical cap of radius R_+ , and the solid–intermetallic interface forms a hemispherical cap of radius R_- . The two caps intersect at the liquid–solid interface, where the edge of the intermetallic lens-shaped region is a disc of radius r_0 lying in the plane $z = z_0$. The angles θ^+ and θ^- that determine the geometry of the liquid–solid–intermetallic trijunction are determined by the surface energies γ_{LS} , γ_{SI} and γ_{LI} ,

$$\begin{aligned} \gamma_{LI}^2 &= \gamma_{SI}^2 + \gamma_{LS}^2 - 2\gamma_{SI}\gamma_{LS} \cos \theta^-, \\ \gamma_{SI}^2 &= \gamma_{LI}^2 + \gamma_{LS}^2 - 2\gamma_{LI}\gamma_{LS} \cos \theta^+ \end{aligned} \quad (24)$$

and the remaining unknown is the overall length scale, given by, say, $r_0 = r_c$, which determines the other length scales $R_{\pm} = r_0 / \sin \theta^{\pm}$. The critical length scale is determined by requiring the difference in the total free energy of the system with and without the critical nucleus to be stationary to changes in r_c . This, in turn, represents a balance between the change in the bulk free energy, varying with r_0^3 , and the change in the total surface energy, varying with r_0^2 , upon introduction of a critical seed. The difference in total energy ΔG_T between a planar liquid–solid interface with and without a lenticular inclusion of intermetallic phase is given by

$$\begin{aligned} \Delta G_T &= \frac{1}{V_M} [G_M^I - G_M^L] V^+ + \frac{1}{V_M} [G_M^I - G_M^S] V^- \\ &\quad + \gamma_{LI} A^+ + \gamma_{SI} A^- - \pi r_0^2 \gamma_{LS} \end{aligned} \quad (25)$$

Here V_M is the (constant) molar volume, and $V^{\pm}$ and $A^{\pm}$ are the volumes and areas of the portions of the seed above (+) and below (−) the plane $z = z_0$, specifically $V^{\pm} = \pi r_0^3 v(\theta^{\pm}) / 3$ and $A^{\pm} = 2\pi r_0^2 \alpha(\theta^{\pm})$, where $v(\theta) = [\cos^3 \theta - 3\cos \theta + 2] / \sin^3 \theta$ and $\alpha(\theta) = [1 - \cos \theta] / \sin^2 \theta$. Setting $d\Delta G_T / dr_0 = 0$ for $r_0 = r_c$ then gives

$$r_c = \frac{2V_M[2\gamma_{LI}\alpha(\theta^+) + 2\gamma_{SI}\alpha(\theta^-) - \gamma_{LS}]}{[G_M^L - G_M^I]v(\theta^+) + [G_M^S - G_M^I]v(\theta^-)} \quad (26)$$

As an example, we consider a liquid–solid interface for the conditions of Table 1, but with the surface energies $\gamma_{LS} = 0.323 \text{ J m}^{-2}$, $\gamma_{LI} = 0.220 \text{ J m}^{-2}$ and $\gamma_{SI} = 0.172 \text{ J m}^{-2}$. The molar free energies corresponding to the parallel tangent construction are $G_L = -5154.1 \text{ J mol}^{-1}$, $G_S = -3013.2 \text{ J mol}^{-1}$ and $G_I = -4420.9 \text{ J mol}^{-1}$. The above expression then gives a critical radius of $r_c = 4.33 \text{ nm}$, with $\theta^+ = 30^\circ$, $\theta^- = 40^\circ$, $R_+ = 8.66 \text{ nm}$ and $R_- = 6.74 \text{ nm}$.

A.2. Interface wetting

The computation of the surface energies of inter-phase boundaries is complicated by the tendency of the interface to become “wet” by an additional phase, which can result in a lower value of the surface energy compared to a “dry” interface in which the additional phase is artificially constrained to be absent. For example, the surface energy γ_{LS} of a “dry” planar liquid–solid interface can be computed by first setting $\phi_I = \phi_V = 0$ in the free energy functional

and then solving the steady-state ordinary differential equations that result from minimizing the energy. The resulting value of γ_{LS} is then generally higher than that for an unconstrained solution, since allowing additional degrees of freedom can only result in a lower minimum energy. Note that the wetting of a liquid–solid phase boundary by a localized region (layer) of intermetallic phase can occur even if a planar liquid–intermetallic interface or a solid–intermetallic interface is not possible under the conditions of bulk equilibrium, i.e. no common tangent exists between the intermetallic free energy (at any concentration) and the liquid or solid free energies (at their equilibrium concentrations). Nevertheless, the tendency for wetting to occur is particularly strong if, for example, γ_{LS} is not much smaller than the sums $\gamma_{LI} + \gamma_{SI}$ for “nearby” configurations of equilibrium between intermetallic and liquid or solid phases. An example is the case given in Table 4, where the surface energy $\gamma_{SL} = 2.55 \text{ J m}^{-2}$ (under conditions of liquid–solid–vapor equilibrium coexistence) is much higher than the sum of the energies $\gamma_{LI} = 0.29 \text{ J m}^{-2}$ (under conditions of three-phase liquid–vapor–intermetallic coexistence) and $\gamma_{SI} = 0.35 \text{ J m}^{-2}$ (under conditions of three-phase solid–vapor–intermetallic coexistence; note here that γ_{SL} was computed with the constraints $\phi_I = 0$).

To study the wetting behavior quantitatively, we have examined the constrained equilibrium in more detail by adding an integral constraint

$$\int_{-\infty}^{\infty} [\phi_I(z)]^2 dz = \text{given} \quad (27)$$

to the surface energy functional in Eq. (21) with an associated Lagrange multiplier. The resulting modified equations produce a “dry” interface (with respect to intermetallic formation) when the constraint is strongly enforced (large Lagrange multiplier), leading to $\phi_I \rightarrow 0$, whereas a “wet” interface is obtained when the constraint is inactive (small Lagrange multiplier), leading to $\phi_I \rightarrow 1$ in the interfacial region. An example is shown in Fig. 17a, where the decrease in surface energy is shown as a function of the maximum value of ϕ_I that occurs in the interfacial region. The decrease is associated with the appearance of a layer of intermetallic phase with distinct mole fractions X_j^I that are depicted in Fig. 17b; the resulting profiles of phase and solute are shown in Fig. 18 in a case with strong wetting (maximum $\phi_I \approx 0.9$). The mole fractions that are obtained for this case tend to the values given by the same parallel tangent condition given in Eq. (23). This case can therefore be interpreted as wetting by a “surface” phase of intermetallic.

A.3. Interface adsorption

The formalism of Cahn [33] allows a derivation of a Gibbs adsorption equation that is independent of the dividing surface conventions. In our case, this provides an expression for the rate of change of the surface energy along a tie line, reflecting the single degree of freedom available to the system while maintaining a two-phase equilibrium at

constant temperature and pressure; we also continue to assume a constant molar volume. For a one-dimensional system with equilibrium profiles of mole fraction $[X_A(z), X_B(z), X_C(z)]$, the chemical potential of each species, $\mu_j(X_A(z), X_B(z), X_C(z))$, is uniform. In particular, the bulk equilibrium values $[X_A^-, X_B^-, X_C^-]$ far to the left of the interface and the bulk equilibrium values $[X_A^+, X_B^+, X_C^+]$ far to the right of the interface have equal chemical potentials $\mu_j^-(X_A^-, X_B^-, X_C^-) = \mu_j^+(X_A^+, X_B^+, X_C^+) = \mu_j$. A key role in Cahn’s approach is played by the Gibbs–Duhem relation, which relates incremental changes in chemical potential along a tie line. Evaluating this expression far to the left and right of the interface gives the two relations

$$\begin{aligned} 0 &= X_A^+ \delta\mu_A + X_B^+ \delta\mu_B + X_C^+ \delta\mu_C \\ 0 &= X_A^- \delta\mu_A + X_B^- \delta\mu_B + X_C^- \delta\mu_C \end{aligned} \quad (28)$$

These equations can be solved to give the relation between the changes in two of the chemical potentials in terms of the third, giving, for example,

$$\begin{aligned} \delta\mu_B &= \frac{-[X_A^+ X_C^- - X_A^- X_C^+]}{[X_B^+ X_C^- - X_B^- X_C^+]} \delta\mu_A \\ \delta\mu_C &= \frac{-[X_A^+ X_B^- - X_A^- X_B^+]}{[X_C^+ X_B^- - X_C^- X_B^+]} \delta\mu_A \end{aligned} \quad (29)$$

The corresponding change in the surface energy $\delta\gamma$ that results in an incremental shift along the tie line is then found to be proportional to $\delta\mu_A$, and can be written as $\delta\gamma = -\Gamma_A \delta\mu_A$, where the adsorption Γ_A depends on the equilibrium profiles of the mole fractions,

$$\begin{aligned} \Gamma_A &= \frac{1}{V_m} \int_{-\infty}^{\infty} \left\{ X_A(z) - \frac{[X_A^+ X_A^- - X_C^- X_A^+]}{[X_C^+ X_B^- - X_C^- X_B^+]} X_B(z) \right. \\ &\quad \left. - \frac{[X_A^+ X_B^- - X_A^- X_B^+]}{[X_C^+ X_B^- - X_C^- X_B^+]} X_C(z) \right\} dz \end{aligned} \quad (30)$$

We note that the coefficients of the mole fractions $X_j(z)$ are such that the integrand tends to zero as $z \rightarrow \pm\infty$, so that the integral is well defined and is independent of a dividing surface convention.

As an example, consider the case of the liquid–solid interface given in Table 4 with the computed surface energy $\gamma_{LS} = 2.55319 \text{ J m}^{-2}$. This state corresponds to the conditions of three-phase equilibrium between the liquid, solid and vapor phases. The chemical potential of species A at this point is $\mu_A = -7571.7 \text{ J mol}^{-1}$ ($= \mu_A^L = \mu_A^S = \mu_A^V$), and the adsorption for this interface is computed to be $\Gamma_A = -1.77297 \times 10^{-5} \text{ mol m}^{-2}$. For a nearby point on the liquid–solid tie line with $\mu_A' = -7563.6 \text{ J mol}^{-1}$ ($= \mu_A^L = \mu_A^S$), the interfacial energy is computed to be $\gamma'_{LS} = 2.55333 \text{ J m}^{-2}$ and the adsorption is $\Gamma'_A = -1.76641 \times 10^{-5} \text{ mol m}^{-2}$. The adsorption equation in the approximate form $\Delta\gamma_{LS} = -\bar{\Gamma}_A \Delta\mu_A$ is then satisfied with a relative error of $|\Delta\gamma_{LS} + \bar{\Gamma}_A \Delta\mu_A|/|\Delta\gamma_{LS}| = 4.3 \times 10^{-4}$. Here $\Delta\gamma_{LS} = [\gamma_{LS} - \gamma'_{LS}]$, $\Delta\mu_A = [\mu_A - \mu'_A]$, and $\bar{\Gamma}_A = [\Gamma_A + \Gamma'_A]/2$.

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