Modeling dissolution and spreading of Bi–Sn alloy drops on a Bi substrate

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Abstract

A dissolutive wetting model is employed to study the dynamics of axisymmetric Bi–Sn alloy drops spreading on Bi. The liquid drop surface is assumed to be a spherical cap, while the isothermal model for solute transport with simplified hydrodynamics computes the evolution of the solid–liquid interface. Simulations are performed on a millimeter scale to model experiments. The evolution of the drop radius, the flow and solute concentration profiles near the triple junction, the contact line mobility relationship, the apparent contact angles and the shape of the dissolution boundary during spreading are investigated as functions of initial Sn concentration, model parameters and initial conditions. Good agreement is obtained when compared with the experiments for the cases where diffusion is the dominant transport mode. The shape of the solid–liquid interface is predicted better when the initial experimentally determined dissolution boundary is implemented as the starting point of the subsequent simulation.

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Keywords: Reactive wetting; Contact angle; Dissolution; Numerical simulation

1. Introduction

Reactive wetting refers to a liquid spreading on a solid substrate with reaction or dissolution between the liquid and substrate. A commonly studied configuration is that of a liquid drop wetting and spreading on a solid substrate in sessile drop geometries. Many factors, including the properties of liquid and substrate materials, substrate roughness and temperature, may affect the reactive wetting process [1]. Studying reactive wetting experimentally or theoretically is a difficult task. Experiments are difficult to conduct because it is usually difficult to observe the phase change process in real time. Modeling reactive wetting is challenging due to the evolution of a moving contact line formed by the intersection of two distinct phase boundaries (i.e. the solid–liquid and liquid–vapor interfaces). Accompanying the wetting, spreading and phase transformations are coupled mass, momentum and thermal transport. In addition, due to the involvement of different time and length scales during reactive wetting, it is often convenient to separate the reactive wetting processes into three distinct stages: (i) the initial fast hydrodynamic spreading of the liquid on an inert substrate, where very little dissolution takes place and capillarity is the major driving force; (ii) the solute dissolution-dominated regime, where local equilibrium is established at the solid–liquid interface; and (iii) the solid-state diffusion-controlled regime towards the final macroscopic equilibrium state of the reactive wetting process. This three-regime assumption of the reactive wetting process is well justified by experimental evidence provided in dissolutive wetting of Cu on Si [2] and Sn on Bi [3,4].

Only in the last 10 years or so has progress been made in understanding the complex processes associated with reactive wetting. A number of theoretical studies have attempted to examine the kinetics of reactive wetting by considering relevant driving forces and dissipation mechanisms. Yost et al. [5] used a compact model that explicitly neglects diffusion and convection to investigate the thermodynamic
equilibrium and kinetics of dissolutive wetting of a spherical Bi–Sn drop on a Bi substrate. The wetting kinetics is determined by numerically solving two coupled equations for the wetted area and volume of the liquid drop. Mortensen et al. [6] proposed a simple power law for the drop radius vs. time as $R \sim t^{1/4}$ for the kinetics of diffusive wetting. The model assumes isothermal spreading of a sessile drop driven by the liquid–substrate chemical reaction that is controlled by the diffusion of solute to the triple junction. Similarly, Yost [7] constructed a model for the kinetics of diffusive wetting due to a constituent in the drop reacting with a substrate. Both chemical reaction and diffusion mechanisms are included in the model; a linear $R$–$t$ relation is observed for the wetting kinetics of reaction-controlled spreading. Reaction-controlled wetting kinetics was also studied by Eustathopoulos and co-workers [8–10] for metal/ceramic systems where the diffusion of solute is very fast and the droplet spreading is controlled by the chemical reaction between the liquid drop and the substrate near the triple junction. These simple continuum level models provided power law predictions for the dependence of the radius of the liquid drop, $R$, upon time, $t$, during drop spreading. In addition, atomic scale modeling, such as molecular dynamics simulations [11,12], has provided sufficient resolution to thoroughly explore atomic scale processes of reactive wetting, especially the wetting dynamics and transport behavior near the contact line (e.g. the presence of a precursor foot).

Meanwhile, several experimental studies have been carried out to investigate the dissolution-limited wetting process in metal/metal systems. Sharps et al. [13] investigated the Cu–Ag system and correlated spreading with the activities of the liquid and the solid substrate. Yost and O’Toole [14] tested seven Bi–Sn alloys wetting on Bi substrates and determined the metastable spreading radius and the upper and lower contact angles from postmortem sample cross-sections. Experimental data from several investigators [4,14] also reveal that the surface of the liquid is close to being a spherical section, but that the shape of the solid–liquid interface is distinctly different from spherical. A key question that remains is how the solid–liquid interface evolves in conjunction with the generally rapid spreading of the liquid. The shape of the solid–liquid interface is mainly controlled by reaction, dissolution, and the associated convective and diffusive transport. In terms of the contact line mobility relationship (i.e. contact angle vs. contact line velocity) during reactive wetting, considerable success has been achieved in fitting the experimental mobility data for dissolutive wetting using both the molecular kinetic wetting theory [15] and the hydrodynamic wetting model [4] originated from inert wetting systems. Yin et al. [4,16] have performed comprehensive experimental studies of Bi–Sn and Au–Sn alloys wetting on Bi and Au substrates, respectively. A Bi–Sn alloy spreading on pure Bi is a purely dissolutive system and the absence of intermetallic reactions makes it more conductive to both experimental and theoretical investigations. The work of Yin et al. [4] on Bi–Sn alloy drops spreading on Bi substrates provides a comprehensive set of data to use in the development and validation of theoretical models.

In this paper, a primarily diffusion-based model is used to investigate the dissolution-dominated regime of the dissolutive wetting process of a Bi–Sn alloy sessile drop on a Bi substrate. The effectively one-dimensional transport model developed by Warren et al. [3] is applied both in its original form and with modified initial conditions based on experimental observations. The model assumes averaging of the governing solute transport equation in the drop vertical direction. Convective solute transport is treated in an approximate manner by imposing a flow field that satisfies continuity but not conservation of momentum. The utility of the approximate convective transport is addressed here. Numerical solution of the model equations is obtained based on finite difference approximations using both an explicit and an implicit scheme in time. The present implementation of the model is validated by comparison of results from the two time-marching schemes and with the results of Warren et al. [3]. The present algorithms are then used to simulate several different concentrations of Bi–Sn alloy drops spreading on a Bi substrate. Results are compared with experimental data of Yin [17], who characterized the dynamic behavior of 90Bi10Sn, 85Bi15Sn, 80Bi20Sn, 65Bi35Sn and 57Bi43Sn weight percent alloy sessile drops wetting on a pure Bi substrate at 250 °C. The utility and limitations of the primarily diffusive transport model are discussed.

2. Solute transport model

2.1. Problem description

The model geometry considered here is adopted from Warren et al. [3]. Fig. 1 shows a schematic illustration of the drop geometry employed in this study. The drop is assumed to be axisymmetric and described in terms of a vertical coordinate $z$ and radial coordinate $r$, as illustrated in the figure. The variable $h_b(r, t)$ represents the height of the liquid–vapor interface and $h_d(r, t)$ represents the depth of the solid–liquid interface, measured from the $z = 0$ axis. The angles $\theta_b$, $\theta_L$ and $\theta_L$ are the upper contact angle, lower contact angle and total contact angle, respectively. As assumed in Warren et al. [3], the total contact angle remains fixed in the calculations, which will be discussed further in Section 4.1.
Once validated against the results of Warren et al. [3] for the 80Bi20Sn alloy drop spreading on Bi at 245 °C, the model is used to numerically simulate the drop spreading for five Bi–Sn alloys (listed above) at 250 °C and to compare with data from experiments of Yin [17], where the initial Bi–Sn alloy drop is a sphere with a diameter on the order of 1 mm. The simulation starts after the initial fast spreading process, when the drop shape becomes a spherical cap, as shown in Fig. 1. Because of the scale that is considered in this study, gravity does not play an important role in this model. It is hence assumed in subsequent modeling that the shape of the liquid–vapor interface is not affected by the gravitational force over the time range of computation and, as a result, the liquid–vapor interface can be represented by a spherical cap.

Modeling of drop spreading is difficult owing to hydrodynamic transport in an evolving domain. The need to treat a variety of time and length scales further complicates the development of a complete model of the spreading process. The behavior at the triple junction is paramount, but it still remains unclear how to effectively model the relevant physical mechanisms. Only very recently has a comprehensive hydrodynamic transport model for dissolutive spreading been developed that is based on a diffuse representation of the liquid–vapor and solid–liquid interfaces [18]. The diffuse–interface model offers the potential to examine the nature of the physical mechanisms at the triple junction. However, to date, using parameter values (e.g. viscosity, surface tension and temperature) consistent with real experimental conditions remains a challenge.

2.2. Model equations

The basic model used in this work was first introduced by Warren et al. [3]. The model equations and main assumptions are summarized here. The starting point of the model is the solute conservation equation written in terms of the solute concentration $c$ for a binary alloy (here we define $c$ in terms of the weight fraction of Sn in the Bi–Sn alloy system). The solute conservation equation is written as

$$ \frac{\partial c}{\partial t} + \mathbf{u} \cdot \nabla c = D \nabla^2 c $$

where $\mathbf{u}$ is the velocity vector and $D$ is the solute diffusivity.

The mass and solute boundary conditions at the liquid–vapor interface are

$$ \mathbf{v} \cdot \mathbf{n} = \mathbf{u} \cdot \mathbf{n} $$

$$ \nabla c \cdot \mathbf{n} = 0 $$

where $\mathbf{n}$ is the unit normal vector and $\mathbf{v}$ is the velocity of the liquid–vapor interface. The mass and solute boundary conditions at the solid–liquid interface are given by

$$ \mathbf{u}_{\text{sol}} \cdot \mathbf{n} = 0 $$

$$ (-D_{\text{liq}} \nabla c_{\text{liq}} + D_{\text{sol}} \nabla c_{\text{sol}}) \cdot \mathbf{n} = v_n (c_{\text{liq}} - c_{\text{sol}}) $$

where the subscripts $\text{liq}$ and $\text{sol}$ denote liquid and solid, respectively, and $v_n$ is the velocity of the interface in the direction of interface normal. Making assumption that the solute is insoluble in the solid phase (i.e. $D_{\text{sol}} = 0$ and $c_{\text{sol}} = 0$), Eq. (5) can be reduced to

$$ -D \nabla c \cdot \mathbf{n} = v_n c_b $$

where $c_b$ is the solute concentration of the liquid at the solid–liquid interface. Based on the assumption that local equilibrium is established at the solid–liquid interface, $c_b$ is given by the following Gibbs–Thompson equation:

$$ c_b = c_e + \Gamma \kappa $$

where $c_e$ is the equilibrium concentration of a flat interface, $\Gamma$ is the normalized solid–liquid surface energy assumed to be constant and $\kappa$ is the curvature of the interface. It is noted that in a cylindrical coordinate system the velocity of the interface $v_n$ is related to the derivative of the drop lower height $h_b$ by

$$ v_n = \frac{\dot{h}_b}{\sqrt{1 + h_b^2}} $$

where the symbol $\dot{}$ denotes a time derivative and $'$ denotes a derivative with respect to the radial coordinate $r$. Combining Eqs. (6) and (8), the evolution of the lower height of the drop is given by

$$ \dot{h}_b = \frac{D}{c_b} \left[ c'_b h_b^b - (1 + h_b^2) \frac{\partial c}{\partial z} \right] $$

In order to solve Eq. (9), the evolution of the solute concentration profile should be determined simultaneously. The concentration profile is governed by Eq. (1). In general, for the axisymmetric domain, the concentration depends on two spatial variables $(r, z)$ and $t$. A reduced model is obtained if the height-averaged concentration is introduced:

$$ \bar{c}(r) = \frac{1}{h} \int_{h_b}^{h} c dz $$

Here, $h = h_t - h_b$ is the total drop height. Integrating Eq. (1) in the vertical direction and introducing Eq. (10) yields

$$ (h_t - h_b) \bar{c} = \bar{c}(h_t)(c_e - \bar{c}) - \bar{c}(h_b)(c_b - \bar{c}) $$

$$ + \left( 1 + h_b^2 \right) \frac{\partial c}{\partial z}_{h_b} + \left( 1 + h_b^2 \right) \frac{\partial c}{\partial z}_{h_b} + 2 h^2 \Gamma $$

$$ - 2 h \Gamma' + 2 h \Gamma' $$

$$ \frac{\partial c}{\partial r} + \frac{1}{D} \int_{h_b}^{h} \mathbf{u} \cdot \nabla c $$

where the operator $\mathcal{D}$ is defined as

$$ \mathcal{D} = \frac{1}{D} \frac{\partial}{\partial r} - \frac{1}{r} \frac{\partial}{\partial r} \frac{\partial}{\partial r} $$

The upper height, $h_t$, can be determined from the assumption that the volume of the drop above the substrate is constant during spreading once the drop radius
or the velocity of triple junction is known. In addition, the Bi–Sn alloy system is assumed to be an ideal system for which the volume of mixing is zero. The velocity \( \mathbf{u} \) in Eq. (11) is calculated by imposing the appropriate boundary conditions and the assumption that the velocity in the \( r \) direction can be approximated in a manner similar to the approach used in the application of lubrication theory for a drop to yield [3]:

\[
u_r = A(r, t) \left( \frac{A^2}{2} \right)
\]

where \( A = (z - h_0)/h(r, t) \) is the dimensionless height above the liquid–solid interface and \( A(r, t) = -3h(t)/h(r, t) \). \( I(r, t) \) is given by

\[
I(r, t) = -\frac{K}{r} \left( \frac{r^2}{2} \frac{da}{dR} - b \frac{db}{dR} \left( b - \sqrt{b^2 - r^2} \right) \right)
\]

where \( a = (R^2 - h_0^2)/2h_0^2 \), \( b = (R^2 + h_0^2)/2h_0^2 \) and \( h_0 \) is the height of the drop in the center. Using continuity, the velocity in the \( z \)-direction can then be written as

\[
u_z = g_0 A + g_1 \frac{A^2}{2} + g_2 \frac{A^3}{3}
\]

where \( g_0 = -3h_0(I, t)/h(r, t) \), \( g_1 = -3(2hI/h - h'I/h - I' - I/r) \) and \( g_2 = 3(3h^2I/2h - I'/2 - I/2r) \). Note that the coefficients \( g_0 \), \( g_1 \) and \( g_2 \) are re-derived here and are different from their original forms in Warren et al. [3].

To complete this model, the following condition for the motion of the triple junction is needed:

\[
\dot{R} = -\frac{ID \tan \theta_L K'}{c_8 \tan \theta_b} |_{ij}
\]

Eq. (16) is derived based on the flux boundary condition on the concentration and the assumption that the triple junction does not move in the vertical direction as the drop spreads.

3. Solution procedure and model verification

3.1. Solution procedure

The main objective of this solution procedure is to simultaneously solve for the height-averaged solute concentration \( \bar{c} \), the lower height \( h_0 \) and the drop radius \( R \) as time evolves. A coordinate transformation was employed to refine the mesh near the triple junction as the drop spreads (see Warren et al. [3]).

For completeness, we outline the steps in the solution procedure used here. The model equations given in Section 2.2 are solved in the following manner:

1. Define constant parameters, including the surface energy \( I \), equilibrium concentration \( c_{eq} \), diffusivity of solute in the liquid \( D \), volume of the liquid drop \( V \), total contact angle \( \theta_L \) and coordinate transformation parameter \( \alpha \) (see Eq. (7.1) in Ref. [3]);
2. Initialize the model, including the initial lower height \( h_0 \), initial solute concentration in the drop \( c_0 \) and initial drop radius \( R \);
3. Calculate \( h_0 \) and \( \theta_L \) using the spherical cap assumption;
4. Calculate \( c_0 \) using Eq. (7);
5. Calculate \( c_I \) (Eq. (6.11) in Ref. [3]);
6. Calculate \( R \) using Eq. (16);
7. Calculate \( h_0 \) using Eq. (9);
8. Calculate \( u_r \) and \( u_z \) using Eqs. (13) and (15);
9. Calculate \( \bar{c} \) using Eq. (11);
10. Update \( R, h_0 \) and \( \bar{c} \) for the new time level and repeat the procedure from step (3).

The equations are discretized in space and time by finite differencing. Both an explicit (fixed time step) and an implicit (variable time step) method are employed. For the implicit implementation, the Method of Lines [19] is used to integrate the equations in time with an ordinary differential equation system solver to implement the variable time stepping [20].

3.2. Model validation

The model implementation and numerical procedures used in this study are first verified by comparing the results reported in Warren et al. [3] with the present study using the explicit method for the base set of parameters shown in Table 1. Due to symmetry, only the field equations in the right half of the drop are solved. A total of 300 non-uniform mesh points and a time step of \( 10^{-5} \) s are used in the simulation when an explicit scheme is applied. Fig. 2 shows the evolution of the lower and upper heights, \( h_0 \) and \( h_t \), superimposed with the results of Warren et al. [3]. After 300 s of drop spreading, the drop radius is 0.12% greater than that of Warren et al. [3]. In addition, the implicit scheme is employed to calculate the solution for the same case. Fig. 3 shows the drop radius vs. time for the base set of parameters using both the explicit and implicit schemes. The results from both methods of time differencing are in excellent agreement.

4. Results and discussion

Warren et al. [3] used their model to simulate spreading and dissolution for an 80Bi20Sn alloy case. For the condi-

Table 1

<table>
<thead>
<tr>
<th>Parameter values used in Warren et al. [3].</th>
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<tbody>
<tr>
<td>Capillary length (I), mm</td>
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<tr>
<td>Equilibrium concentration (c_{eq}), mm</td>
</tr>
<tr>
<td>Diffusivity (D), mm^2 s^{-1}</td>
</tr>
<tr>
<td>Initial drop volume (V), mm^3</td>
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<tr>
<td>Total contact angle (\theta_L), degrees</td>
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<tr>
<td>Coordinate transformation parameter (\alpha)</td>
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<tr>
<td>Lower height (h_0), mm</td>
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<tr>
<td>Initial concentration (c_0)</td>
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<tr>
<td>Initial radius of the drop (R_0), mm</td>
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* Material property values at 245 °C.
tions of their experiments, the model predicts an increase in radius of 7% while a 26% increase was observed in their experiment. Here the model is applied to a more extensive set of experimental data obtained in a well-controlled environment and the predictions of the model are compared for a broader set of parameters and initial conditions. Variations in model parameters, including the total contact angle and solute diffusivity, suggested by Warren et al. [3] guide the application of the model to the experiments reported in Yin et al. [4].

4.1. Parameters and initial conditions

In the experiments, drops for five Bi–Sn alloy compositions (90Bi10Sn, 85Bi15Sn, 80Bi20Sn, 65Bi35Sn and 57Bi43Sn) spreading on pure Bi substrates at 250 °C were investigated. Both the spreading radius and contact angle (θt) vs. time were determined for each experiment. From cross-section images of solidified alloy drops, the total apparent contact angle between the liquid surface and solid–liquid interface can be determined. Fig. 4 shows the total contact angle of the drop final wetting state as a function of Bi composition. Here, the notion of “final wetting state” is used when the motion of the contact line has stopped, dissolution has nominally ceased and the upper and lower contact angles appear to be static. A constant total contact angle close to 90° was observed in previous experiments for most of the Bi–Sn alloys studied [4,14]. It is also suggested by Warren et al. [3] that the solid–liquid interface “wants” to meet the liquid–vapor interface at a right angle (90°) because the solid–liquid interface is nearly an iso-concentration while the liquid–vapor interface permits no-flux of solute. Therefore, for all the simulations, the total contact angle is assumed to remain constant throughout the spreading calculation. A total contact angle of either 82° or 88° was used for the 85Bi15Sn, 80Bi20Sn, 65Bi35Sn and 57Bi43Sn alloy cases, covering the range of the angles obtained experimentally. For these cases, both angles yielded equivalent spreading behavior. For the 90Bi10Sn alloy case, two total angle values were considered (65° and 55°), as will be discussed in more detail later. The use of a different angle for high Bi contents was also based on the experimental observations from Yin et al. [4] and Yost and O’Toole [14]. In these cases, the concentration gradients in the triple junction regions are much reduced, so that the dissolution in the region is rather limited, and cannot proceed in such a way that the solid–liquid interface meets the liquid–vapor interface at right angles. If the initial Bi content is at equilibrium (saturated), the system becomes an inert system. No dissolution is permitted and the total angle varies with time during spreading. It is assumed in the present model that the liquid surface of the drop remains a spherical cap. No solute dissolution is assumed to occur during the initial hydrodynamic stage of the spreading (not treated in the model) because the dissolution time scale is much longer than the characteristic time of the initial fast spreading of the drop [21]. Hence, the initial dissolution depth is assumed to be zero and the initial lower contact angle (θb) is small. Based on the initial volume of the drop and the upper contact angle, the initial drop radius can be determined as listed in Table 2. Because the viscosity values for the Bi–Sn alloys at 250 °C are not available, the viscosity of 1.63 mPa·s for the pure liquid

Fig. 2. Evolution of hb and ht for the parameters given in Table 1. Solid lines denote the present study; dashed lines are results from Warren et al. [3].

Fig. 3. Drop radius vs. time for the parameters given in Table 1 comparing the explicit and implicit time schemes.

Fig. 4. Total contact angle vs. Bi concentration determined at the final wetting state.
Bi at 271°C was used in all the simulations. The surface tension of the liquid–vapor interface, $\sigma_{LV}$, as a function of the Sn concentration at 250°C is given by Moser [22]:

$$\sigma_{LV} = 729.17 \cdot X_{Sn}^3 - 991.07 \cdot X_{Sn}^2 + 497.62 \cdot X_{Sn} + 334$$

(17)

where $X_{Sn}$ is the molar fraction of Sn. All the other properties required in the calculations are listed in Table 2.

### 4.2. Drop spreading kinetics

The first set of simulation results are shown in Fig. 5, where the drop radius vs. time is shown by the solid lines for the 90Bi10Sn alloy case for two total contact angles: (a) $\theta_L = 65^\circ$ and (b) $\theta_L = 55^\circ$. The experimental data points for this alloy composition are plotted as well. When the experimentally determined total contact angle of 65° is used in the model, the simulation predictions fall below the experimental data. There are a number of factors regarding the experiments for this alloy case that should be mentioned due to the alloy’s proximity to the equilibrium concentration (93 wt.% Bi) at 250°C:

(i) The liquidus temperature for this alloy is 245°C, so that the time needed to form a liquid spherical cap in the experiment is significantly longer than other alloys studied, i.e. ~2 s vs. hundreds of ms typically. The initial liquid shape when spreading starts may not be a fully spherical cap and may not be well represented by the initial shape assumed in the model. Note that the experiments were carried out by placing a solid alloy sphere on a heated Bi substrate and allowing the solid sphere to melt on the substrate.

(ii) The experimental data indicates that the extent of spreading is limited for this case, owing to the lower driving force. Not only was the spreading rather limited, but the drop was also not perfectly axisymmetric, as shown by the experimental images in Fig. 6 (top view of the drop at two different times in the experiment). It is possible that for this case, due to the slower melting and the lower driving force, the drop spreading may be sensitive to substrate surface inhomogeneities, such as roughness and grain boundaries.

(iii) The deviation from axisymmetric spreading led to significant variation in the measured value of the upper contact angle which results from distortion in the side view image used to determine the contact angle. Similar variations in the lower contact angle were also observed in sample cross-sections. Consequently, the experimentally determined total angle of ~65° has a much larger uncertainty associated with it, compared with those of other alloys.

Because of the lower driving force and slower liquid drop formation, it may be reasonable to assume a smaller dissolution depth and therefore a smaller total angle. In the model, if a 55° total contact angle is used to simulate the 90Bi10Sn case, much better agreement with the experimental data is obtained, as shown in Fig. 5b. The model

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**Table 2**

<table>
<thead>
<tr>
<th>Parameter values used in the present study.</th>
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<tr>
<td><strong>Capillary length ($l$), mm</strong></td>
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<tr>
<td><strong>Equilibrium concentration ($c_e$)</strong></td>
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<tr>
<td><strong>Viscosity ($\mu$), mPa s</strong></td>
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<td><strong>Total contact angle ($\theta_L$)</strong></td>
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<tr>
<td><strong>Coordinate transformation parameter ($a$)</strong></td>
</tr>
<tr>
<td><strong>Lower height ($h_0^L$), mm</strong></td>
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<tr>
<td><strong>Initial concentration ($c_0$)</strong></td>
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<td><strong>Initial radius of the drop ($R_0$), mm</strong></td>
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$a$ Material property values at 250°C.

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![Fig. 5. Drop radius vs. time for the 90Bi10Sn alloy case for two different total contact angles.](image-url)
is found to capture the rate of spreading over the range of data fairly well, indicating that dissolution is the main mechanism driving the spreading.

Fig. 7 shows the drop radius vs. time data for the Bi–Sn alloy compositions of 85Bi15Sn, 80Bi20Sn, 65Bi35Sn and 57Bi43Sn spreading on a pure Bi substrate. The simulation results are given by the solid lines and the measured values by the individual data points. The results for the 85Bi15Sn and 80Bi20Sn cases (Fig. 7a and b) show very good agreement with the experimental data. Driven by the difference in local and equilibrium concentrations, the Bi–Sn drop spreads very fast in the first 10 s and slows down after 20 s of spreading, when the concentration profile inside the drop becomes more uniform and closer to the equilibrium concentration. For the 65Bi35Sn and 57Bi43Sn alloy cases shown in Fig. 7c and d, the larger driving force (higher Sn content) leads to more significant early spreading, which is not captured by the model. The discrepancy
between the simulated and measured spreading radii for the pure Sn case is even larger (not shown). For the larger Sn content alloys, more dissolution of the substrate occurs. It is reasonable to expect that the effect of convective transport, especially in the contact line region, may be more significant. The present model includes only an approximate treatment of the fluid dynamics which may not be sufficient to capture the spreading physics for the cases with a high Sn content. However, the model works remarkably well for the lower Sn content alloy cases, where diffusive transport is more important.

It is useful to contrast the agreement between the model and the experiments here to the results reported in Warren et al. [3] for the 80Bi20Sn case. The experiments reported in Warren et al. [3] were conducted for 80Bi20Sn at 245 °C. The equilibrium concentration at that temperature is 90 wt.% Bi, so that the study was done for a 10 wt.% concentration difference. As stated before, the calculated increase in drop spreading radius of 7% was less than the experimentally measured increase of 26%. The difference was attributed to the uncertainties of experimental details, e.g. the atmospheric environment and experimental temperature. In the study by Yin et al. [4], sessile drop wetting experiments were conducted in a well-controlled environmental chamber with a gaseous flux atmosphere, eliminating the use of liquid flux and the related flux–solid and flux–liquid interfaces. The resulting data for spreading kinetics, dynamic contact angle and contact line mobility, with considerably improved temporal and spatial resolutions, provide reliable data sets for the present modeling study. For the present 85Bi15Sn and 80Bi20Sn cases, where the associated concentration differences are 8% and 13%, respectively, the calculated increases in drop spreading radius are 41.8%, and 53.7%, compared to the 44.4% and 52.8% observed experimentally.

4.3. Liquid flow and solute concentration profiles near the triple junction

The contact line region of a sessile drop is believed to be the most active region of fluid flow and mass transport during reactive wetting. Fig. 8 shows the computed liquid velocity vector map and Sn concentration profile within 20 μm adjacent to the triple junction after 13 s of wetting for the 80Bi20Sn alloy case. As shown in Fig. 8a, the liquid flows outward and slightly upward in this region. The no-slip condition is imposed on the solid–liquid interface and the maximum velocity occurs at the triple junction (magnitude displayed by the external arrow). The liquid flow from the drop center brings the solute-rich liquid into the triple junction region, thereby enhancing solute dissolution and drop spreading. The iso-concentrations shown in Fig. 8b are almost parallel to the solid–liquid interface. This is because of the combination of an imposed total contact angle of 88° and the no-flux boundary condition at the liquid surface (i.e. iso-concentrations are perpendicular to the liquid surface). The solute concentration at the solid–liquid is very close to the equilibrium value of 7 wt.% only after 13 s of spreading. The iso-concentrations are equally spaced and the solute concentration increases monotonically from the solid–liquid interface to the liquid surface. This implies that after 13 s the Bi substrate is not in equilibrium with the bulk liquid drop and that the dissolution process at the solid–liquid interface is much faster than the diffusion of Sn from the bulk liquid to the liquid side of the interface.
4.4. Contact line mobility relationship

Mobility relationships (i.e. contact angle vs. contact line velocity) for dissolutive wetting have been studied by Yin et al. [4] and Saiz and Tomsia [15]. Yin et al. [4] determined experimentally the mobility relationship for various Bi–Sn alloy drops wetting on a pure Bi substrate at 250 °C. In the experiments, the “apparent” contact angle is measured, since the contact angle can only be determined at a finite distance away from the contact line. Also, only the evolution of the apparent contact angle between the original substrate surface and liquid surface, the upper contact angle, can be readily measured. In Fig. 9, the experimental data for the 80Bi20Sn alloy drop case is fitted using the following hyperbolic tangent function employed for inert wetting [23]:

\[
\frac{\cos \theta_i - \cos \theta_D}{\cos \theta_i + 1} = a \tanh(bC_a)
\]  

where \( \theta_i \) is the static contact angle, \( \theta_D \) is the dynamic contact angle, and \( a, b \) and \( c \) are fitting parameters. Here, the capillary number \( C_a \) is defined by \( C_a = \mu U_{cl}/\sigma \), where \( U_{cl} \) is the contact line velocity. The figure illustrates that a very good fit of the data can be obtained using Eq. (18), where \( a, b \) and \( c \) are 0.27, 8 \( \times 10^7 \) and 1.17, respectively.

It is worthwhile comparing the measured mobility data with the predictions from the model. In the simulation, because of the spherical cap assumption, the relationship between the dynamic contact angle and the contact line velocity is readily obtained. Also, the apparent upper contact angle is equivalent to the actual upper angle at the contact line. The simulated contact line mobility relationships for the Bi–Sn alloy compositions of 90Bi10Sn, 85Bi15Sn, 80Bi20Sn, 65Bi35Sn and 57Bi43Sn spreading on Bi are shown in Fig. 10, together with experimental results obtained by processing a sequence of images during drop spreading. Note that, because the drop spreading speed at the initial wetting stage (corresponding to a larger upper contact angle) is faster than that of the later stage in wetting, Fig. 10 should be viewed from right to left. For the lower Sn content cases (e.g. 90Bi10Sn), the simulated mobility curves can approximately capture the behavior exhibited by the experimental data. However, the experimental results show a more rapid decrease in the contact angle for the higher Sn content cases (e.g. 65Bi35Sn and 57Bi43Sn), indicating a more hydrodynamic type of spreading behavior that is not fully accounted for in the simulation. For all the alloys considered, the simulated contact angles change more gradually with the capillary number. In other words, the model overestimates the time needed for a spreading drop to reach its equilibrium contact angle. The equilibrium contact angles at the final wetting state for the 90Bi10Sn, 85Bi15Sn and 80Bi20Sn alloys are within 10% of experiments. However, the disparities between the experiment and simulation increase for the 65Bi35Sn and 57Bi43Sn alloys cases due to relatively stronger effects of convective flow.

4.5. Apparent contact angle

Fig. 11 shows the evolution of apparent contact angles (total, upper and lower) during 600 s of drop spreading for the 80Bi20Sn case. The apparent contact angles are calculated 20 µm away from the triple junction, identical to the distance used in the experiments of Yin et al. [4] to minimize the effect of optical distortion. As shown in Fig. 11a, the apparent total contact angle reaches its maximum value of 88° soon after the initial fast spreading (<2 s) and then slowly decreases. In contrast, the upper and lower contact angles vary monotonically with time. After 200 s, all the apparent contact angles, including the total, lower and upper contact angles, remain roughly constant, which implies that the system reaches a quasi-steady state. The close-up view of the early stage of spreading using a logarithm scale in time is shown in Fig. 11b. At the initial fast spreading regime, the lower contact angle is very close to 0. After 0.003 s, the dissolution starts to occur and the total and lower contact angles grow quickly as the upper contact angle decreases. At around \( t = 0.7 \) s, the total contact angle reaches its maximum value and then decreases as spreading continues. Meanwhile, the lower contact angle continues to increase at a lower rate after 0.7 s compared to that during 0.003–0.7 s of drop spreading.

The comparison of the apparent upper and lower contact angles vs. time between simulations and experiments for the 90Bi10Sn and 80Bi20Sn alloy cases are shown in Fig. 12. For both cases, simulations match reasonably well with experiments. The apparent upper and lower contact angles change dramatically with time in the first 2 s and follow with more gradual variations in time until the system reaches a quasi-steady state at which the upper and lower contact angles appear to be static. It is noticed that the upper contact angle reaches its equilibrium value more quickly in the experiment. In contrast, the experimentally determined lower contact angle increases more slowly as time evolves compared to that of the simulation for both alloy cases.
4.6. Evolution of solid–liquid interface

Fig. 13 shows both the experimental and simulation results for the evolution of the solid–liquid interface for the 80Bi20Sn alloy case. The experimental data is presented in Fig. 13a at four time values ($t = 2, 4, 12$ and $41$ s). The predicted shapes of the solid–liquid interface are shown in Fig. 13b at these same four time levels plus one additional time level of $t = 300$ s. The following initial conditions were used in the simulation: the drop radius is 0.65 mm, the dissolution depth $h_b$ is zero and the height-averaged concentration $c_0$ is 0.2. Reasonable agreement is reached for the depth of the dissolved region for the intermediate time values (e.g. $t = 41$ s). At early times, there is more pronounced dissolution close to the contact line as a result of the larger fixed total contact angle specified in the model in conjunction with the initial flat shape of the solid–liquid interface, i.e. a small depression is formed at the contact line. As a consequence, the small depression leads to a deeper dissolution well near the contact line, while the calculated loca-

Fig. 10. Mobility relationships for the five alloy composition cases.
tion of the solid–liquid interface near the center of the drop is not as deep. However, the difference in the dissolution depth decreases as time progresses. Also, in the experiment the dissolution begins near the drop center before the drop forms a spherical cap, the starting point of the simulation. In other words, this implies that the time scales for dissolution and initial fast spreading cannot be clearly separated for the experimental conditions considered here. In order to further explore the behavior of the model regarding the evolution of the solid–liquid interface, the drop shape from the experiment at $t = 2$ s is employed as the initial shape of interface for the simulation and the
initial concentration is calculated from the conservation of solute. With this modification, the initial fast spreading regime of the drop is skipped and the starting point of the simulation is from a state where the drop upper contact angle is around 40°. In the experiments, dissolution starts at the point of contact of the melting sphere rather than over a more uniform area, as in the original model initial configuration. The simulation results based on the modified initial dissolution profile are shown in Fig. 14a. There is only a slight increase in the dissolution depth of the solid–liquid interface near the center of the drop. It appears that the solute transport predicted by the model, at least for the base set of parameters, is not sufficient to adequately predict the evolution of the solid–liquid interface. Given the uncertainty in the value of the liquid diffusivity, Fig. 14b shows the corresponding simulation results using a 50% larger value of the solute diffusivity ($D = 1.5 \times 10^{-3}$ mm$^2$/s). Note that, based on Eq. (16), increasing the diffusivity $D$ results in an increase in the drop spreading rate $\dot{R}$, i.e. the spreading kinetics. Warren et al. explored the effect of the magnitude of the diffusivity on the $R$ vs. $t$ behavior. They found that increasing the diffusivity by a factor of 16 resulted in only about a 5% increase in the spreading radius. In addition to the kinetics of the contact line, the diffusivity impacts the solute conservation boundary condition at the solid–liquid interface, and the balance of terms in the solute transport equation. As shown in Fig. 14b, the dissolution depth increases with the increase in $D$. Interestingly, the extent of spreading is not affected significantly since the initial fast spreading is bypassed by using the experimental profile as the initial condition. However, the evolution of the solid–liquid interface depth is better captured with the enhanced diffusivity compared with the results in Fig. 14a. The depth of the simulated solid–liquid interface near the center of the drop at 13 and 41 s is in much better agreement with the experimental data shown in Fig. 13a. Also, it is important to note here that the final dissolution volume evaluated at 300 s from the simulation is 0.67 mm$^3$, matching well with the theoretical value of 0.64 mm$^3$ calculated following the method of Yost and O’Toole [14]. Essentially, the greater dissolution depth results from the enhanced transport, either in the bulk or near the interface, due to the larger diffusivity value.

5. Conclusion

The diffusion-dominated dissolutive wetting model of Warren et al. [3] was used to study Bi–Sn alloy drops wetting on a Bi substrate. Two separate numerical schemes were implemented to solve the model equations with ample verification. The predictions from the model were compared extensively with the experimental data of Yin et al. [4] for 90Bi10Sn, 85Bi15Sn, 80Bi20Sn, 65Bi35Sn and 57Bi43Sn alloy drops. Good agreement for the spreading distance is obtained for low Sn content alloys (less than 13 wt.% concentration difference from the equilibrium value). Moreover, good agreement between the model prediction and experiment is obtained for the equilibrium apparent contact angles for the 90Bi10Sn, 85Bi15Sn and 80Bi20Sn cases. Similar to the experiment, the calculated apparent total contact angle of the 80Bi20Sn drop remains roughly constant soon after the initial fast spreading (~2 s). The evolution of the solid–liquid interface was then studied using different initial conditions. When the initial drop shape is a spherical cap with the solid–liquid interface corresponding to the original flat substrate, the evolution of the drop profile does not match well with the experiment. However, if the experimentally measured solid–liquid interface shape at $t = 2$ s is implemented as the initial condition, the subsequent evolution of the solid–liquid interface shape agrees reasonably well with the experimental observation. A 50% higher solute diffusivity value, which enhances both the spreading and the dissolution rate, provides very good agreement between the simulations and the experimental data.

Besides the simplified treatment of the convective transport, which is based on an approximate flow field, the model also assumes separation in the time scales for the

![Fig. 14. Simulated solid–liquid interface with initial $h_0 = -0.05$ mm, $\varepsilon_0 = 0.16$ and $R_0 = 0.8$ mm based on the experimental measurements at $t = 2$ s.](image)
initial fast hydrodynamic spreading and dissolution controlled spreading. This may not be appropriate for the cases where the gradient is large between the initial concentration of the liquid drop and the equilibrium concentration of the alloy system at the experimental temperature. In addition, the assumption of a fixed total contact angle during drop spreading should be explored in a future model that couples hydrodynamic and solute transport for dissiputive spreading.

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References