Available online at www.sciencedirect.com
ScienceDirect
Acta Materialia 57 (2009) 3110–3122
Acta MATERIALIA
www.elsevier.com/locate/actamat

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

Shun Su, Liang Yin, Ying Sun *, Bruce T. Murray, Timothy J. Singler

*Department of Mechanical Engineering, State University of New York at Binghamton, Binghamton, NY 13902, USA*

Received 26 December 2008; received in revised form 8 March 2009; accepted 8 March 2009
Available online 6 April 2009

## 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.

*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

---

* Corresponding author. Tel.: +1 607 777 3881; fax: +1 607 777 4620.
*E-mail address:* ysun@binghamton.edu (Y. Sun).

1359-6454/$36.00 © 2009 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.
doi:10.1016/j.actamat.2009.03.015

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 reactivities 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 $h_t(r, t)$ represents the height of the liquid–vapor interface and $h_b(r, t)$ represents the depth of the solid–liquid interface, measured from the $z = 0$ axis. The angles $\theta_t$, $\theta_b$ 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.

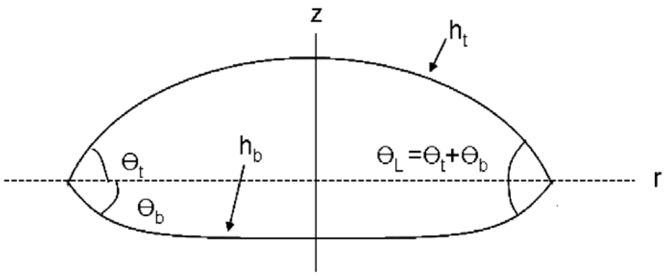

Fig. 1. Schematic illustration of the wetting geometry.