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Model Determination and Validation for Reactive Wetting Processes

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Model Determination and Validation for Reactive Wetting Processes

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Abstract

It is shown that dissolutive wetting initially yields a metastable equilibrium. A compact model for the kinetics of approach to this metastable state is described. The technique for constructing these kinetics stems from the early work of Onsager and begins with a relationship for the entropy production. From this, a coupled set of nonlinear, ordinary differential equations can be written directly. The equations are solved numerically for the wetted area and compared with experimental data. The model captures many of the subtle complexities of dissolutive wetting such as multiple metastable states.

Sessile drop experiments involving a variety of Bi-Sn alloys on solid Bi substrates were performed. Substrates prepared from small and large-grained polycrystals and single crystals were used to measure equilibrium and metastable contact angles and estimate the surface tension and equilibrium contact angle of the solid-liquid interface. The substrates were also used to investigate the coupling of the dissolution and wetting processes and to investigate the effect of substrate grain size on wetting. It was determined that the equilibrium wetting geometry is independent of linear scale and that grain size has little influence on wetting or dissolution in the Bi-Sn system.

To investigate the atomic behavior of liquids at interfaces during wetting, we simulated wetting in the Ag-Cu system using molecular dynamics with atomic potentials and observed both atomic dynamics and structural correlations of the liquid-solid interface. We found that spreading is prompted by interactions between the liquid and the substrate surface that cause the liquid layer in contact with the substrate to take on some of the symmetry of the substrate surface and result in the formation of a liquid monolayer that extends beyond the major part of the liquid droplet.

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Summary

Thermodynamic equilibrium conditions were described for a spreading droplet that is simultaneously dissolving a solid substrate. The kinetic equations for wetting were established in the manner of Onsager. These equations were solved numerically and compared with experimental data. It was found that good agreement can be obtained with use of this technique for describing wetting kinetics in the Sn-Bi on Bi system. Time varying quantities, such as atom fraction Bi dissolved in the liquid, were found to converge to the values expected from the metastable equilibrium analysis.

Early in the dissolutive wetting process the system follows a sequence of short-lived metastable states in which the Laplace equation for the liquid-vapor interface is the only equilibrium requirement even close to being met. Under slow wetting conditions the liquid surface is likely to be spherical, but the curvature of this interface will depend on the extent of dissolution. It was shown in this work that long after wetting and spreading stops, the liquid-solid interface has still not reached equilibrium, judging from its nonspherical shape, even though substrate dissolution is sensibly complete. The Laplace requirement for this interface is not met, so the system is metastable and will remain so for a long period of time. This period of time makes measurement of the equilibrium contact angle of this interface untenable and inefficient. It was demonstrated that it may be possible to estimate the true equilibrium contact angle when dissolution is complete and the Laplace condition for the liquid-vapor interface is met. For the Bi-Sn system at 240°C, this angle is approximately 15° and the solid-liquid surface tension is approximately 183 ergs/cm². It was shown that the predicted equilibrium contact angle θ_2 is relatively constant, as was the contact angle θ_1 , over a wide range of alloy compositions. Although the drop diameter increased with increasing Sn content, it did so because more fluid was made available by the dissolution process. The equilibrium wetting configuration should be scale invariant and was experimentally verified.

The solid-vapor interface appeared to be flat in all of the experiments. It was shown that gravitational forces are too small to cause any distortion of this interface near the wetting line. No significant wetting effect due to substrate grain size was found and there did not appear to be any significant preferential dissolution at emerging grain boundaries. The wetting of single crystal substrates appeared to be very similar to wetting of small-grained substrates. This behavior is certainly not to be expected in general, since evidence to the contrary has been reported in the literature for decades.

It should be noted that the classical approach to capillary problems ignores microstructure and defects. It contains the implicit assumption that all phases of the system are homogeneous and structureless which, of course, bears no resemblance to reality except for systems that are totally liquid. Analysis of this wetting problem should consider, for example, grain boundaries in the substrate and reaction product phases in addition to phase interfaces. Such a structure is metastable and will only evolve to equilibrium after a very long period of time, if ever.

We have also shown that, in certain systems, a region of high spatial correlation exists in the liquid near the solid-liquid interface. This correlated region is produced by mutual kinetic and potential interactions of the liquid and solid atoms. Dislocations and other defects were found in this region that may influence wetting kinetics by allowing a mechanism for slip of liquid over the substrate near the wetting line. A relationship for wetting rate and effective viscosity was derived based upon the existence of glissile dislocations. Careful study of the interfacial defects observed here may reveal important information on the nature of slip in wetting systems.

Model Determination and Validation for Reactive Wetting Processes

Introduction

Because of its enormous technological importance, the kinetics of wetting has received considerable recent attention. Much of this work has considered the modeling of a liquid droplet spreading on a smooth, clean substrate. The liquid is assumed to be inert, relative to the substrate and surrounding gaseous ambient, and exhibit negligible evaporation rate. Droplet flow is driven by capillary and gravitational forces and resisted by its own viscosity. A simple treatment of this problem was given by de Gennes [1] and others [2-5] who found that the droplet radius increased as a power law in time. The exponent was 0.1 or 0.125, depending on whether the driving force was capillarity or gravity, respectively. Blake and others [6-9] have presented a different approach that is based upon reaction rate theory. Considerable experimental data [8-12] have corroborated these treatments suggesting that the analytical forms are fundamentally correct for certain wetting systems. However, for wetting systems that involve reaction between liquid and substrate, poor agreement is found between the above wetting theories and experimental results [13,14].

Wetting in technologically important systems involves many other rate controlling effects that must be understood before any agreement between theory and experiment can be expected. These complicating effects include such processes as substrate surface diffusion of droplet constituents, dissolution of substrate material into the wetting liquid, diffusion of liquid constituents into the substrate, and chemical reaction between droplet and substrate. These effects, collectively called reactive or chemical wetting, modify inert spreading results to the extent that theory and experiment can differ by 4 to 5 orders of magnitude [15]. Not only do inert wetting models predict a much faster process than is observed by experiment but the kinetic form of experimental wetting data do not agree with inert wetting models. Consequently, it is important to determine the kinetics of reactive wetting processes so that rate control is understood. In this final report the analyses of both de Gennes and Blake will be briefly reviewed so that their salient parts are understood. This will be followed by a discussion of various reactive wetting mechanisms.

Inert Wetting

de Gennes Approach

Consider a nonvolatile droplet, small enough to be essentially spherical, having a height, z , and radius, r , spreading on a smooth, flat, chemically homogeneous substrate. It is assumed that the substrate does not dissolve or otherwise react with the droplet. The capillary driving force for the uniform advance of the droplet three phase line (TPL) can be written

$$F_d = \gamma_l(\cos \theta_o - \cos \theta) \quad (1)$$

while the viscous force resisting the driving force is taken to be

$$F_v = \eta \frac{r}{z} \frac{dr}{dt} \quad (2)$$

where γ_l is liquid surface energy, θ_o is the equilibrium contact angle, θ is the temporal contact angle, η is bulk liquid viscosity, and t is time. Equating these forces yields the equation of motion for the TPL

$$\frac{dr}{dt} = \frac{\gamma_l z}{\eta r} (\cos \theta_o - \cos \theta). \quad (3)$$

Equation 3 can be solved numerically if it is assumed that the droplet is spherical and liquid volume is conserved. The dimensionless variables, ρ and τ , defined by

$$\rho = \frac{r}{r_o} \text{ and } \tau = \frac{1}{r_o} \frac{\gamma_l}{\eta} t$$

where r_o is the drop radius when the temporal contact angle is 90° (initial condition), were used to obtain the numerical solutions shown in Fig. 1a. Note that wetting is essentially concluded when $\tau=100$ and that for most liquid metal wetting experiments

$$\frac{1}{r_o} \frac{\lambda_l}{\eta} \cong 10^5 \text{ s}^{-1}$$

which means that in real time the wetting process is complete in 10^{-3} s. This stands in stark contrast to the timing of typical wetting experiments which take from 10-100s for completion. If gravity is assumed to be the driving force for wetting, this significant discrepancy between theory and experiment remains.

Blake Approach

Classical reaction rate theory asserts that atomic transport occurs through a sequence of biased jumping events that lead to a net mass displacement away from the source. Blake [8] maintains that advance of the TPL in a wetting process occurs by an atomic jumping process and can be modelled as such with reaction rate theory. Characteristic of reaction rate theory is a thermally activated atomic jump frequency given by

$$K_w = \frac{kT}{h} \exp\left(-\frac{\Delta G_w}{RT}\right) \quad (4)$$

a jump distance, λ , a density, $n \propto \lambda^{-2}$, of sites into which atoms can jump, and a driving force similar in form to that given by eq. 1. The quantities kT , RT , and h have their usual significance while ΔG_w is termed the molar activation free energy of wetting. In this approach, surface and interface energies are dissipated by the atomic jumping events during TPL advance and the rate of wetting is given as

$$\frac{dr}{dt} = 2\lambda K_w \sinh\left\{\frac{\gamma_l}{2nkT} (\cos \theta_o - \cos \theta)\right\}$$

and in dimensionless form

$$\frac{d\rho}{d\tau} = 2 \cdot 10^5 \frac{\lambda}{r_o} \sinh\left\{\frac{\gamma_l}{2nkT} (\cos \theta_o - \cos \theta)\right\}. \quad (5)$$

where dimensionless time is now defined as

$$\tau = 10^{-5} K_w t.$$

Integration of eq. 5 was performed with the volume conservation and spherical shape assumptions used above for the de Gennes approach and with $T=500\text{K}$, $\lambda=1 \text{ nm}$, $r_o = 10^{-3} \text{ m}$, $\gamma_l = 550 \text{ mJ/m}^2$, $n = 1.54 \cdot 10^{17} \text{ m}^{-2}$, while θ_o ranged from 10° to 30° . The general appearance of the solutions, shown in Fig. 1b, are very similar to those shown in Fig. 1a even though the equations are substantially different. Again, the wetting process is essentially complete at $\tau=100$ and if ΔG_w is identified as the activation energy for viscous flow, of for example liquid Sn (1300 cal/mol), then $t \cong 10^{-6} \text{ s}$ which is significantly faster than experimental data indicate. The viscosity of bulk liquid was used in making all of the above calculations. This could be totally inappropriate in that the effective viscosity of a wetting fluid might be significantly larger than that of the bulk. This issue needs to be resolved in future work. If bulk viscosity is appropriate, it is clear that other processes

must control the rate of wetting in more complex systems and that fluid flow can be very rapid. Certain other processes will now be considered as possible rate controlling mechanisms.

Reactive Wetting Processes

The importance of interfacial processes in materials joining has a long history. Certain of these processes have been thought to assist wetting [16-20] by contributing to the total free energy loss due to a virtual wetting increment. Very small additions of a constituent, known to react with the substrate, cause pronounced improvement in wetting and are exploited in braze alloys, especially those used for joining to ceramics [21,22]. Other effects stemming from the use of flux have also been studied. Latin, for example, suggested that chloride flux exerts a "tinning action" through a local electrochemical cell near the TPL that results in improved wetting [23]. Bailey and Watkins [24] even found that spreading of Sn-Pb solder was greater on oxidized Cu than on clean electropolished Cu if zinc/ammonium chloride flux was used. These authors were among the first to attempt a correlation between wetting behavior and alloy thermodynamics. They showed that of 38 binary metal systems examined, 25 wetting couples formed intermetallic compounds (IMC), 7 wetting couples exhibited extensive solubility, while 6 nonwetting or dewetting couples exhibited neither. Other authors have attempted correlations for metal/oxide wetting systems [18,25]. While these correlations are useful in predicting the wetting tendency of a given system, they may also have contributed to the erroneous notion that large free energies of reaction, dissolution, etc. categorically bring about faster wetting than that ordinarily possible by inert wetting described above. A significant amount of work has suggested that processes collateral to wetting can moderate or retard inert wetting rate. Table 1 shows the suggested rate controlling processes, made by the respective authors, of selected wetting studies involving various material combinations [13,22,26-35]. The wide diversity of processes and their possible combinations suggest that various rate laws should be expected for wetting kinetics. Indeed, Nicholas and Poole [30] have observed linear kinetics ($r(t) \approx t$), Bailey and Watkins [24] and others [26,27,34] have seen diffusive kinetics ($r(t) \approx \sqrt{t}$), while the kinetics measured by Kritsalis et al. and Armstrong et al. are exponential in character [22,29]. The following section is an attempt to rationalize these varied kinetic results by providing a method of analyzing the combined rates of two or more wetting processes acting in concert.

Wetting and spreading of molten metal on solid metal substrates often involves dissolution of and subsequent reaction with substrate constituents. When the local concentration of a critical substrate constituent reaches its saturation limit in the liquid, an intermetallic reaction occurs between that constituent and liquid constituents. For example, when Sn wets Cu, the compound Cu_6Sn_5 is formed soon after relatively little Cu is dissolved. The exact timing of these events is not known and attempts to capture details by rapid quenching of macroscopic specimens have failed because the individual process kinetics are themselves faster than typical quench rates. As discussed by Bailey and Watkins [24], some wetting systems only involve dissolution of the substrate.

To construct models of the reactive wetting process it was decided to address the problem of dissolutive wetting. Important cases of dissolutive wetting can be studied with the help of alloys made with Sn and either Pb or Bi. Both of these binary systems form simple eutectics so that a liquid alloy can be made to wet a solid, pure substrate that will dissolve into the liquid to saturation. The alloy system chosen for this LDRD project is the Sn-Bi system because of the very limited solid solubility exhibited by Bi for Sn. This limited solubility allows for simplification of the models that were developed in this project. Equilibrium and dynamic data were measured with use of Sn-Bi alloys, then models and data were compared to evaluate the models.

The preceding sections of this report serve as a starting point for the work performed during this two year LDRD project. The work actually performed is attached as four separate reports that have been submitted or will be submitted for publication in technical journals. The first report entitled "Energetics and Kinetics of Dissolutive Wetting Processes" (SAND97-0591J) has been accepted for publication in *Acta Materialia*. The second report entitled "Metastable and Equilibrium Wetting States in the Bi-Sn System" (SAND97-2485J) has been submitted for publication in the same journal. The third report entitled "The Triple Line in Reactive Wetting" (SAND97-2522J) has been submitted for publication to *Scripta Materialia*. The fourth report entitled "Molecular Dynamic Studies of Wetting in Ag-(111) Cu EAM Systems" has also been submitted for publication to *Scripta Materialia*.

Conclusions

Each of the following four reports contains a Conclusions section, so the technical conclusions of the LDRD report will not be discussed here. These conclusions will pertain to the overall goal of the project itself. It was originally hoped that with the fundamental understanding generated during this project we could construct a valid model for any type of reactive wetting process. In this, we were quite wrong. We chose to model a wetting phenomenon that has just one subsidiary process; dissolution. Yet a number of difficulties arose, some of them subtle, that caused some perplexity. It would have been much more difficult to model a wetting process with more subsidiary processes, such as occurs in soldering or brazing. Much more work must be done on reactive wetting processes, in general, before it can be said that they are adequately understood. However, the progress that was made on dissolutive wetting is valuable and will prove useful to those who might continue research on the problem of wetting in technologically important systems.

References

1. P. G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985).
2. L. H. Tanner, *J. Phys. D* **12**, 1473 (1979).
3. P. Neogi and C. A. Miller, *J. Colloid Interface Sci.*, **86**, 525 (1982).
4. P. J. Haley and M. J. Miksis, *J. Fluid Mech.*, **223**, 57 (1991).
5. P. Ehrhard and S. H. Davis, *J. Fluid Mech.*, **229**, 365 (1991).
6. T. D. Blake and J. M. Haynes, *J. Colloid Interface Sci.*, **30**, 421 (1969).
7. B. W. Cherry and C. M. Holmes, *J. Colloid Interface Sci.*, **29**, 174 (1969).
8. T. D. Blake, in *Wettability*, edited by J. C. Berg, Marcel Dekker, Inc., New York, NY (1993).
9. R. L. Hoffman, *J. Colloid Interface Sci.*, **94**, 470 (1983).
10. L. M. Hocking, *J. Fluid Mech.*, **239**, 671 (1992).
11. A. Cazabat, *Contemp. Phys.*, **28**, 347 (1987).
12. M. D. Lelah and A. Marmur, *J. Colloid and Interface Sci.*, **82**, 518 (1981).
13. J. C. Ambrose, M. G. Nicholas, and A. M. Stoneham, *Acta metall. mater.*, **40**, 2483 (1992).
14. J. C. Ambrose, M. G. Nicholas, and A. M. Stoneham, *Acta metall. mater.*, **41**, 2395 (1993).
15. F. G. Yost, F. M. Hosking, and D. R. Frear, in *The Mechanics of Solder Alloy Wetting and Spreading*, edited by F. G. Yost, F. M. Hosking, and D. R. Frear, Van Nostrand Reinhold, New York, NY (1993).
16. J. Schatz, *Schweissen u. Schneiden*, **9**, 522 (1957).
17. I. A. Aksay, C. E. Hoge, and J. A. Pask, *J. Phys. Chem.*, **78**, 1178 (1974).
18. J. V. Naidich, *Prog. Surface and Membrane Sci.*, **14**, 353 (1981).

19. F. G. Yost and A. D. Romig, Jr.: in *Electronic Packaging in Materials Science III*, vol. 108, edited by R. Jaccodine, K. A. Jackson, and R. C. Sundahl, Materials Research Society, Pittsburgh, PA (1987).
20. J. A. Pask and A. P. Tomsia, in *Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems*, edited by J. A. Pask and A. P. Tomsia, Plenum Press, New York, NY, (1981).
21. M. Humenik, Jr. and W. D. Kingery, *J. Amer. Ceramic Soc.*, **37**, 18 (1954).
22. P. Kritsalis, L. Coudurier, and N. Eustathopoulos, *J. Mater. Sci.*, **26**, 3400 (1991).
23. A. Latin, *J. Inst. Metals*, **72**, 265 (1946).
24. G. L. J. Bailey and H. C. Watkins, *J. Inst. Metals*, **80**, 57 (1951).
25. N. Eustathopoulos and B. Drevet, in *Joining and Adhesion of Advanced Inorganic Materials*, edited by A. H. Carim, D. S. Schwartz, and R. S. Silbergliitt, Materials Research Society, Pittsburgh, PA (1993).
26. F. W. Spiers, *Phil. Mag.* **7**, 1048 (1933).
27. T. Alty and A. R. Clark, *Trans. Faraday Soc.*, **31**, 648 (1935).
28. C. C. Addison, W. E. Addison, D. H. Kerridge, and J. Lewis, *J. Chem. Soc. (London)*, **1**, 1454 (1956).
29. W. M. Armstrong, A. C. D. Chaklader, and D. J. Rose, *Trans. Met. Soc. AIME*, **227**, 1109 (1963).
30. M. Nicholas and D. M. Poole, *Trans. Met. Soc. AIME*, **236**, 1535 (1966).
31. K. Nogi and K. Ogino, *Trans. Japan Inst. Metals*, **29**, 742 (1988).
32. F. Hezlot, A. M. Cazabat, and N. Fraysse, *J. Phys.: Condens. Matter*, **1**, 5793 (1989).
33. X. M. Xue, J. T. Wang, and M. X. Quan, *J. Mater. Sci.* **26**, 6391 (1991).
34. X. Chen, A. F. Sprecher, and H. Conrad, in *Materials Developments in Microelectronics Packaging: Performance and Reliability*, edited by P. J. Singh, ASM International, Materials Park, OH (1991).
35. J. G. Li, *J. Mater. Sci. Letters*, **11**, 1551 (1992).

TABLE 1: Suggested Rate Controlling Processes for Reactive Wetting
Involving a Variety of Liquid and Substrate Materials

Liquid	Substrate	Suggested Rate Controlling Process	Reference
Cu-Ti	Alumina	Ti Adsorption Rate	22
Hg	Sn	Diffusion of Hg on and into Sn	26
Hg	Sn	Surface Diffusion of Hg on Sn	27
Na	Zn	Diffusion of Zn through ZnO	28
Fe	MgO	Reaction and Slag Accumulation	29
Various	Various	Diffusion into Substrate at TPL	30
Various	SiC	Displacement Reaction	31
Polymer	Silica	Surface Diffusion	32
Al	BN	Reaction and Diffusion	33
Pb-Sn	Ag-Pt	Surface Diffusion	34
Cu-Ti	Alumina	Adsorption of Ti followed by Reaction	35
Braze	Fe-Cr	Viscous Damping Near S-L Interface	14

Figure 1a. Dimensionless radius versus dimensionless time as predicted by the de Gennes wetting model. Equilibrium contact angles of 10° , 20° , and 30° were used as parameters.

Figure 1b. Dimensionless radius versus dimensionless time as predicted by the Blake wetting model. An equilibrium contact angle of 30° and mobilities of 0.01, 0.10, and 1.00 were used as parameters.

ENERGETICS AND KINETICS OF DISSOLUTIVE WETTING PROCESSES

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Abstract

Dissolutive wetting occurs when a liquid wets and spreads over a solid surface with simultaneous dissolution of the solid into the liquid. It is shown that this process initially yields a metastable equilibrium and a compact model for the kinetics of approach to this metastable state is described. The technique for constructing these kinetics stems from the early work of Onsager and begins with a relationship for the entropy production. From this, a coupled set of nonlinear, ordinary differential rate equations can be written directly. The equations are solved numerically for the wetted area and compared with experimental data. The model captures many of the subtle complexities of dissolutive wetting such as metastable equilibria. The main weaknesses of the model are the assumptions of fully-stirred liquid and a spherical solid/liquid interface which were made to keep the analysis simple.

Introduction

Because of its enormous technological importance, the kinetics of wetting has received considerable recent attention. Much of this work has considered the modeling of a liquid droplet spreading on a smooth, clean substrate. The liquid is assumed to be inert relative to both the substrate and to surrounding gaseous ambient, and to exhibit negligible evaporation rate. Droplet flow is driven by capillary and gravitational forces and resisted by its own viscosity. A simple treatment of inert wetting was given by de Gennes [1] and others [2-5]. Blake has presented a different approach to wetting kinetics based upon reaction rate theory [6-9]. Considerable experimental data [8-12] have corroborated these treatments suggesting that the analytical forms are fundamentally correct for certain wetting systems. However, for wetting systems that involve reaction between liquid and substrate, poor agreement is found between the above wetting theories and experiment [13,14]. Effects that complicate wetting kinetics include; substrate surface diffusion of droplet constituents, dissolution of substrate material into the wetting liquid, diffusion of liquid constituents into the substrate, and chemical reaction between droplet and substrate. These effects, collectively called reactive or chemical wetting, can significantly modify wetting kinetics.

A significant amount of work has suggested that processes collateral to wetting can moderate or retard wetting rate. The wide diversity of processes and their possible combinations suggest that various rate laws should be expected for wetting kinetics. Indeed, Nicholas and Poole [15] have observed that droplet radii exhibit linear kinetics ($r(t) \approx t$), Bailey and Watkins [16] and others [17-19] have seen diffusive kinetics ($r(t) \approx \sqrt{t}$), while the kinetics measured by Kritsalis et al. and Armstrong et al. are exponential in character [20,21]. In this paper, an attempt is made to model the energetics and kinetics of substrate dissolution into a spreading droplet. The technique for constructing the coupled kinetic relationships is classical [22] and a similar approach to wetting kinetics was recently suggested by Wang and Lannutti [23]. The specific example chosen involves a Sn-Bi alloy droplet on a pure Bi substrate and the analysis begins with a characterization of the thermodynamic equilibrium state. This is followed by a description of the total entropy production from which the coupled kinetics follow by inspection [22, 24]. Many approximations are intentionally made to keep the approach as transparent as possible. The dissolutive wetting kinetics are represented by two, coupled differential equations that are solved and compared to experimental wetting data obtained with the Sn-Bi system described above.

Dissolution Controlled Wetting Kinetics

Wetting and spreading of molten metal on solid metal substrates often involves dissolution of the substrate. Dissolution kinetics will be modeled in a very simple manner to emphasize the

inherent coupling of this subsidiary process with inert wetting. Consider a droplet at time, t , small enough to be a spherical cap and, thus, unaffected by gravitational forces. The drop has a height, $h_1(t)$, and radius, $r(t)$, and spreads on a smooth, flat, pure substrate. Let the substrate dissolve into but not react with the droplet and form a spherical depression having depth, $h_2(t)$. The thermodynamic system is one of constant temperature, total volume, and total mass. This problem then entails the evolution of chemical equilibrium between gaseous, liquid, and solid species, in addition to capillary equilibrium as the droplet wets and spreads over the substrate.

The Equilibrium State

The substrate is assumed to behave isotropically such that the solid/liquid interface takes a spherical shape in equilibrium. The configuration shown in Fig. 1 will be employed throughout this analysis. An incremental change in the Helmholtz free energy, F , of the system is given by

$$dF = 0 = \sum_{i,j} \mu_i^j dN_i^j + \sum_k \gamma_k dA_k - \sum_j P_j dV_j$$

where μ represents chemical potential, N is number of moles, γ are surface tensions, A are interfacial areas, P are pressures, V are volumes, and i, j, k refers to specific components, phases, and interfaces, respectively. With the imposed system constraints

$$0 = dT = \sum_{i,j} dN_i^j = \sum_j dV_j$$

and assumed spherical shape, the conditions for thermodynamic equilibrium can be derived. For small drops, unaffected by gravity, chemical equilibrium is described by

$$\mu_1^g = \mu_1^l = \mu_1^s \quad \text{and} \quad \mu_2^g = \mu_2^l = \mu_2^s \quad (1)$$

while capillary equilibrium is described by

$$P_l - P_g \equiv \Delta P = \frac{2\gamma_l}{R_l} = \frac{2\gamma_{sl}}{R_{sl}} \quad (2a)$$

$$\gamma_s = \gamma_l \cos \theta_1 + \gamma_{sl} \cos \theta_2 \quad (2b)$$

$$\gamma_l \sin \theta_1 = \gamma_{sl} \sin \theta_2 \quad (2c)$$

where the R_k are the interfacial radii of curvature, and θ_k are contact angles measured relative to the planar substrate surface. Equations (1) are the Gibbs conditions for heterogeneous equilibrium, eq. (2a) is Laplace's equation for excess pressure at curved interfaces, and eqs. (2b) and (2c) are Neumann's description of three-phase capillary equilibrium [27].

Since the surface tensions in eqs. (2b) and (2c) are, in principal, known or measureable, the contact angles are determined. In addition, from the assumed spherical interface shapes one can show that the equilibrium contact angles are related by the expression

$$V_2 = V_1 \frac{f(\theta_2)}{f(\theta_1)} \quad (3)$$

where V_1 is the volume of liquid residing above the substrate surface, V_2 is the volume dissolved from the substrate, and $f(\theta_i) = \sqrt{\frac{1 - \cos \theta_i}{1 + \cos \theta_i}} \left(\frac{2 + \cos \theta_i}{1 + \cos \theta_i} \right)$. These volumes can be obtained from bulk

thermodynamic data allowing a locus of (θ_1, θ_2) pairs to be computed at every stage of dissolution. This relationship will not, in general, be coincident with the values obtained from the Neumann equations. This dilemma was first recognized by Yoo, et al. [28] who also noticed that after wetting of Sn-Bi solder on Bi appeared to cease, a ridge in the substrate slowly emerged. The ridge was circumferential and located at the wetting line but above the original substrate surface. This suggests that a flat substrate and suspended wetting is a metastable state that eventually yields a ridged, metastable equilibrium state.

To resolve the dilemma identified by Yoo et al. the two methods of calculating the contact angles must be made compatible. First, this can be done by simply recognizing that values of γ_k and θ_i are often confounded by significant measurement error. Compatibility is afforded by

selecting values of θ_1 and θ_2 that are solutions of eq. (3) yet are contained within the envelope of reasonable experimental error. This alternative implies that a true equilibrium state is achieved in contrast to the observations of Yoo et al. A second method is to utilize measured contact angles and force eq. (3) to be coincident with them. If the initial liquid volume and atom fractions are accurately known, the only way to achieve compatibility in this manner is to adjust the saturation atom fraction away from that given by the bulk equilibrium phase diagram. This implies that the equilibrium reached at this point is metastable. A third way of examining this incompatibility is to solve eq. (2c) for $\frac{\gamma_{sl}}{\gamma_s}$ and substitute it into eq. (2b). Potential equilibrium states can be

parameterized by the ratio $g = \frac{\gamma_l}{\gamma_s}$ and plotted as shown by the solid line in Fig. 2. Equation (3)

can be parameterized by the ratio of volumes, $W = \left(\frac{V_1}{V_2}\right)^2$, so that $\cos(\theta_1)$ can be plotted versus

$\cos(\theta_2)$ as shown by the dashed line in Fig. 2. In a true equilibrium state, both of these relationships will be satisfied at the intersection of the two curves. At this intersection γ_{sl} takes a value that ultimately provides compatibility but may differ from measurements made independently. The condition for an intersection, other than at (1,1), is $\frac{V_1}{V_2} > \frac{1-g}{g}$ and if this

inequality is violated, equilibrium involving a flat substrate, as was assumed, is not allowed. It is conjectured that this inequality is a statement that distinguishes true equilibrium from metastable dissolutive equilibrium. That is, if the inequality holds, a flat substrate will persist, but if not, a ridged surface will eventually evolve.

Wetting Kinetics

An alloy of Sn and Bi wetting a pure Bi substrate is a good prototype for this problem because liquid Sn-Bi alloys are nearly ideal [25,26], thermodynamically, which simplifies the analysis. However, Bi is anisotropic and for this reason is not a good choice for the substrate. To construct the kinetic description in the manner suggested by Wang and Lannutti [23], the entropy production must be calculated. With the same system constraints as were used above, and assuming that the

substrate is flat, the entropy production, $\frac{dS}{dt}$, can be written

$$T \frac{dS}{dt} = (P_l - P_s) \frac{dV_l}{dt} - \gamma_l \frac{dA_l}{dt} - \gamma_{sl} \frac{dA_{sl}}{dt} - \gamma_s \frac{dA_s}{dt} \\ - (\mu_{Sn}^s - \mu_{Sn}^g) \frac{dN_{Sn}^s}{dt} - (\mu_{Sn}^l - \mu_{Sn}^g) \frac{dN_{Sn}^l}{dt} - (\mu_{Bi}^s - \mu_{Bi}^g) \frac{dN_{Bi}^s}{dt} - (\mu_{Bi}^l - \mu_{Bi}^g) \frac{dN_{Bi}^l}{dt}.$$

For simplicity, it has been assumed that diffusion of components is rapid relative to the transfer of components across the solid/liquid interface; whereas, Wang and Lannutti explicitly include diffusional processes. This assumption allows a global statement of entropy production that offers a more transparent demonstration of the suggestion of Wang and Lannutti. With use of the spherical shape assumption the entropy production becomes

$$T \frac{dS}{dt} = \left[\frac{\Delta P}{2} (h_1 + h_2) - \gamma_l - \gamma_{sl} + \gamma_s \right] 2\pi r \frac{dr}{dt} \\ + \left[\Delta P \frac{\pi}{2} (r^2 + h_1^2) - 2\pi \gamma_l h_1 \right] \frac{dh_1}{dt} + \left[\Delta P \frac{\pi}{2} (r^2 + h_2^2) - 2\pi \gamma_{sl} h_2 \right] \frac{dh_2}{dt} \\ - (\mu_{Sn}^s - \mu_{Sn}^g) \frac{dN_{Sn}^s}{dt} - (\mu_{Sn}^l - \mu_{Sn}^g) \frac{dN_{Sn}^l}{dt} - (\mu_{Bi}^s - \mu_{Bi}^g) \frac{dN_{Bi}^s}{dt} - (\mu_{Bi}^l - \mu_{Bi}^g) \frac{dN_{Bi}^l}{dt} \quad (4)$$

where

$$P_l - P_g \equiv \Delta P = \frac{4\gamma_l h_1}{r^2 + h_1^2} = \frac{4\gamma_{sl} h_2}{r^2 + h_2^2} + \Delta p \quad (5)$$

and Δp denotes a deviation from capillary equilibrium at the solid/liquid interface. Since the substrate is assumed to be pure Bi and since it has negligible solubility for Sn [29], the terms involving N_{Sn} can be dropped. If evaporation of Sn and Bi is negligible, and upon substitution of eqs. (2) and (5) into eq. (4), it is found that

$$T \frac{dS}{dt} = \{-\gamma_l \cos \theta_1(t) - \gamma_{sl} \cos \theta_2(t) + \gamma_s + h_2 \frac{\Delta p}{2}\} \frac{dA_s}{dt} + A_{sl} \frac{\Delta p}{2} \frac{dh_2}{dt} - (\mu_{Bi}^l - \mu_{Bi}^s) \frac{dN_{Bi}^l}{dt}.$$

After equating the geometric description of V_2 to its solution thermodynamic description, and differentiating with respect to time, an independent equation containing the above time derivatives may be obtained. Multiplying this expression by Δp and substituting into the above representation of the entropy production gives

$$T \frac{dS}{dt} = \{\gamma_s - \gamma_l \cos \theta_1(t) - \gamma_{sl} \cos \theta_2(t)\} \frac{dA_s}{dt} - (\mu_{Bi}^l - \mu_{Bi}^s - \bar{V}_{Bi}^l \Delta p) \frac{dN_{Bi}^l}{dt}$$

where it is recognized that the surface tensions are now functions of time since they are dependent upon the mole fraction of Bi which is changing as dissolution occurs. It is also assumed that the partial molar volumes of Bi in solid and liquid phases are equal ($\bar{V}_{Bi}^l = \bar{V}_{Bi}^s$). The Gibbs-Thomson effect of interfacial curvature on solubility can also be inserted at this point. To do this, appropriate pressure terms are added to the chemical potentials and combined with the term $\bar{V}_{Bi}^l \Delta p$ giving

$$T \frac{dS}{dt} = \{\gamma_s - \gamma_l \cos \theta_1(t) - \gamma_{sl} \cos \theta_2(t)\} \frac{dA_s}{dt} + \left[RT \ln \frac{X_{Bi}^l|_m}{X_{Bi}^l} + \bar{V}_{Bi}^l \left\{ \left(\frac{2\gamma_l \sin \theta_1}{r} \right) \Big|_m - \frac{2\gamma_{sl} \sin \theta_2}{r} \right\} \right] \frac{dN_{Bi}^l}{dt}$$

where $|_m$ indicates evaluation at the metastable or equilibrium state as the case may be and RT has its usual significance. Taken individually, the terms within the curly and square brackets approach zero as the system approaches equilibrium. Calculations have shown that the term containing $\bar{V}_{Bi}^l$ is negligible compared to that containing RT which causes it to approach equilibrium very slowly. This suggests that the metastable equilibrium state is one that satisfies eqs. (1) and (2b) but not (2a) and (2c). By neglecting the term containing $\bar{V}_{Bi}^l$, and with minor algebraic rearrangement, the entropy production can be written

$$T \frac{dS}{dt} = \left\{ 1 - \frac{\gamma_l}{\gamma_s} \cos \theta_1(t) - \frac{\gamma_{sl}}{\gamma_s} \cos \theta_2(t) \right\} \gamma_s \frac{dA_s}{dt} + \frac{RT}{\bar{V}_{Bi}^l} \ln \left(\frac{X_{Bi}^l|_m}{X_{Bi}^l} \right) \frac{dV_l}{dt}. \quad (6)$$

Since entropy production given in eq. (6) must be positive definite it is possible to immediately write out the kinetic expressions in the manner of Onsager [22]

$$\frac{dA_s}{dt} = L_{11} \left\{ 1 - \frac{\gamma_l}{\gamma_s} \cos \theta_1(t) - \frac{\gamma_{sl}}{\gamma_s} \cos \theta_2(t) \right\} + L_{12} \ln \left(\frac{X_{Bi}^l|_m}{X_{Bi}^l} \right) \quad (7a)$$

$$\frac{dV_l}{dt} = L_{21} \left\{ 1 - \frac{\gamma_l}{\gamma_s} \cos \theta_1(t) - \frac{\gamma_{sl}}{\gamma_s} \cos \theta_2(t) \right\} + L_{22} \ln \left(\frac{X_{Bi}^l|_m}{X_{Bi}^l} \right) \quad (7b)$$

where the L 's are the Onsager coefficients. One limitation of this technique is that the expansion is to first order and applies only to processes close to equilibrium. It should be noted that the dissolution rate given by eq. (7b) is not proportional to the surface area of the dissolving region as is often assumed [30]. The advantage of this technique, as mentioned by Wang and Lannutti [23], is that it demonstrates the possible kinetic coupling between the capillary and dissolution processes. Following their suggestion it would be possible to construct a similar model that specifically includes diffusion in the liquid as well as other effects.

Solution of Onsager Rate Equations

To solve eqs. (7), expressions that relate X_{Bi}^l and $\cos \theta_i$ to A_s and V_l must be formulated. By definition, the atomic fraction of Bi is $X_{Bi}^l(t) = \frac{N_{Bi}^l}{N_{Sn}^l + N_{Bi}^l}$

where N_{Bi}^l is related to the total volume of liquid through

$$N_{Bi}^l = \frac{V_l - N_{Sn}^l \bar{V}_{Sn}^l}{\bar{V}_{Bi}^l}.$$

The temporal contact angles can be obtained from the relation

$$\cos \theta_i = \frac{A_s - \pi h_i^2}{A_s + \pi h_i^2}$$

and the description of the volumes

$$V_i = \frac{\pi}{6} h_i \left(\frac{3}{\pi} A_s + h_i^2 \right), \quad (8)$$

both expressions following from the assumption of spherical geometry. Since the V_i and A_s are known by integration of eqs. (7), the h_i can be determined as positive, real roots of eqs. (8).

These roots are given by $h_i = S_i - \frac{A_s}{\pi S_i}$

where

$$S_i = \left[\frac{6}{\pi} V_i + \left\{ \left(\frac{6}{\pi} V_i \right)^2 - \left(\frac{A_s}{\pi} \right)^3 \right\}^{1/2} \right]^{1/3}.$$

The surface tensions γ_l and γ_{sl} must also be expressed in terms of X_{Bi}^l . The surface tension of the liquid was approximated with a Langmuir adsorption isotherm [30] and literature values for $\gamma_{Sn}^l = 555 \text{ mJ/m}^2$ [31], $\gamma_{Bi}^l = 380 \text{ mJ/m}^2$ [32], and $\gamma_l = 440 \text{ mJ/m}^2$ at 65 weight percent Bi [33]. These data yielded the approximation $\gamma_l = 380 - 142.4 \ln(0.293 + 0.707 X_{Bi}^l) \text{ mJ/m}^2$. Because Bi has a very small solid solubility for Sn, it was assumed that the interface between solid and liquid is saturated throughout the wetting event. The surface tension of this interface could then be calculated from $\gamma_l(X_{Bi}^m)$ and the measured contact angles with use of the Neumann equations. The value for $\gamma_s = 550 \text{ mJ/m}^2$ was found in Murr [33]. Partial molar volumes were obtained by simply dividing molecular weight by density at 240°C, the test temperature. The initial conditions were taken to be those consistent with an initial solder volume V_1 , contact angles $\theta_1 = 90^\circ$ and $\theta_2 = 0^\circ$, and $X_{Bi}^l(0) = 0.43$ (the eutectic composition).

As a consequence of the nonlinearities in the right hand side of eqs. (7), a numerical integration of the dynamical system was performed. A fourth order Runge-Kutta algorithm with adaptive stepsize control [34] provided the solution trajectories for the range of parameters used for this system.

Experimental Procedure

The Bi material used in this study was 99.99% pure and was melted at $\sim 300^\circ\text{C}$ and cast into a shallow, aluminum mold, allowed to cool for several minutes, and then dropped into a bath of cool tap water. The Bi bars were then machined into substrates $\sim 3\text{mm}$ thick and $\sim 1\text{cm}^2$ in area with a hole in one side for a thermocouple. The substrates were polished to a $0.05 \mu\text{m}$ surface finish, ultrasonically cleaned in acetone, then isopropyl alcohol, dried in a stream of nitrogen gas, and stored in lint-free paper. The eutectic alloy composition (43Sn-57Bi weight percent) was made by

weighing out the appropriate amount of Sn and Bi, placing the mixture into a glass test tube, and then immersing the test tube into a container of Sn at $\sim 350^{\circ}\text{C}$ until the mixture was fully melted. The test tube was then cooled, the alloy removed from the test tube, and the casting cut into ~ 10 mg pieces. The pieces were then reflowed at $\sim 350^{\circ}\text{C}$ in a petri dish containing a small amount of mildly activated rosin flux. The resulting spherically shaped specimens were then ultrasonically cleaned in isopropyl alcohol for 3 minutes, allowed to air dry, weighed, and stored in plastic bags.

All wetting experiments were performed in a nitrogen atmosphere containing less than 25 ppm oxygen. The flux used in the study was a non-activated rosin flux and the heat source was a Cu block on a hot plate. The hole in the side of the substrate was filled with thermally conductive grease and a thermocouple was inserted to establish the substrate temperature. It was found that the flow temperature could be maintained at 240°C to within $\pm 1^{\circ}\text{C}$ during the course of each wetting event.

To perform the wetting experiment, a Bi substrate was placed onto the heated Cu surface and a controlled amount of flux was applied. After the substrate reached the flow temperature, a controlled amount of flux was again applied evenly to the surface. The substrate was allowed to equilibrate for an additional 20 seconds. Four experiments were performed to obtain metastable equilibrium contact angle measurements. Four additional experiments were recorded on video tape for subsequent analysis of wetted area versus time. After adjusting the video system for optimal contrast, several seconds of a calibration reticule (10mm by 10mm) were recorded for use in calibrating the image data acquisition system. This system is used for measuring the area of solder spread. The substrate was removed to an aluminum cooling block after wetting appeared to have stopped. All specimens were then cleaned, metallographically prepared, and polished through a diametrical plane. This permitted measurement of the contact angles in a scanning electron microscope.

Results and Discussion

The eight contact angles measured on four identically processed specimens are shown as open squares in Fig. 3. Eight additional values, shown as filled diamonds, were obtained from the specimens used in the dynamic wetting experiments. The contact angle data cluster around an average of $\bar{\theta}_1 = 8.57^{\circ}$ and $\bar{\theta}_2 = 63.32^{\circ}$ with standard deviations of $\sigma_1 = 4.32^{\circ}$ and $\sigma_2 = 6.21^{\circ}$, respectively. Some of this contact angle dispersion can be attributed to preferred grain boundary penetration that could be observed in the metallographically prepared crosssections. The Bi substrates were observed to have large grain size as a result of the solidification process and additional scatter was caused by pronounced anisotropic dissolution behavior. A scanning electron micrograph of one of the cross-sections is shown in Fig. 4. Measurement of contact angles on this particular specimen was straight forward. In other cases, it was more difficult to determine the location of the solid/liquid interface which lead to subjective interpretation of contact angle values. The expression for the liquid surface tension, given above, was used to evaluate the parameter $g = 0.72$ for the equilibrium atom fraction $X_{Bi}^e = 0.84$ estimated from the phase diagram. This equilibrium atom fraction, initial solder mass and composition, and the ideal solution assumption were then used to compute the parameter $W = 0.123$ for the plots shown in Fig. 5. Superimposed are the cosines of the measured contact angles shown in Fig. 3. Notice that the curves do not intersect which suggests that the eutectic composition wets into a metastable equilibrium state. It is also clear that the data fall a significant distance from either curve. This evidence suggests that the contact angles are characteristic of a metastable equilibrium state. The parameters g and W can be modified such that an intersection occurs at the cosines of any measured pair of contact angles but the results may be unrealistic.

Figure 6 shows the results of the dynamic wetting experiments on four specimens which were analyzed to investigate repeatability. Clearly, all show convergence to a final wetted area but with some variation from specimen to specimen, especially at later times. One source of variation is due to small differences in initial solder mass but several other reasons, such as surface roughness, are also likely. All evidence seems to indicate that the eutectic alloy approaches a metastable state with

a wetting rate near zero. To simulate the kinetics for one of the dynamic experiments, the parameters g and W were selected to yield an equilibrium state at the measured contact angles as shown in Fig. 7. The average values of the contact angles on the chosen specimen were $\bar{\theta}_1 = 7.55^\circ$ and $\bar{\theta}_2 = 63.95^\circ$. The calculated atom fraction Bi required in saturation was $X_{Bi}^l|_m = 0.946$, which seems extraordinarily high, and is most likely due to the inappropriate assumption of spherical shape. In the metastable states that were examined metallographically, the solid/liquid interface was nonspherical, having a shape somewhat between a coin and a sphere. The measured contact angles and the spherical assumption, force an increase in the dissolved volume over that actually observed, which effectively decreases W and increases $X_{Bi}^l|_m$. The required surface tension of the solid/liquid interface, needed for the third means of reconciliation, was $\gamma_{sl} = 76.45 \text{ mJ/m}^2$ which compares favorably with the measurements of Gunduz and Hunt [35] for Sn-Pb alloys on Sn and Pb substrates.

A sequence of spreading events were simulated for different values of the Onsager coefficients, L_{ij} , and compared with the chosen dynamic experiment in Fig. 6. The measured contact angles and the parameters given above were used in the solution of eqs. (7). Good agreement with experimental measurements was obtained with the values $L_{11} = 20$, $L_{12} = L_{21} = 0$ (all cm^2/sec) and $L_{22} = 0.002 \text{ cm}^3/\text{sec}$ as shown in Fig. 8. The same values of the Onsager coefficients that gave a good fit to the measured area of spread were used to simulate the evolution of X_{Bi}^l to its metastable equilibrium value and the contact angles to their measured values. These calculations are shown plotted in Fig. 9.

It should be emphasized that even though the off-diagonal coefficients are set to zero, there is still coupling between the area of spread and the total liquid volume. This is due to the compositional dependence of γ_l and the geometric dependence of θ_2 on h_2 . It appears from Fig. 9 that $\cos(\theta_2)$ approaches its metastable equilibrium value quickly ($\sim 50 \text{ sec}$) indicating that dissolution is rapid. At first glance, the rate equations suggest that dissolution can be slowed by simply adjusting L_{22} to smaller values. However, the inherent coupling of the equations makes the solutions sensitive to small changes in L_{22} as shown in Fig. 10. Such changes destroy the quality of fit to the experimental data. If the initial atom fraction of Bi is set equal to $X_{Bi}^l|_m$ simple inert spreading is recovered from the model. A rate saturation effect has also been observed. For a fixed value of one of the diagonal coefficients (say $L_{22} = 0.002$), increases of L_{11} beyond approximately a certain value (in this case $L_{11} = 0.02$) have little effect on the area of spread kinetics as shown in Fig. 11. Calculations have shown this observation to be symmetric in the L_{ii} suggesting a rate dependence that is, in effect, proportional to the ratio $\frac{L_{11}L_{22}}{L_{11} + L_{22}}$. The form of this

ratio of rate coefficients is characteristic of two rate processes in series. A study of the influence of off-diagonal rate coefficients was judged to be beyond the scope of this work, so little can be said of their importance. It could be argued that the interfacial work terms are vectorial in character [36] and should not yield interaction effects with scalar processes such as dissolution. Interactions between forces of mixed tensorial character are explicitly ruled impossible by the Curie-Prigogine theorem [37]. On the other hand, gradients of chemical potential that drive diffusion are vectorial and may exhibit interaction. Careful consideration should be given to the possibility of interactions in any future work.

Conclusions

Thermodynamic equilibrium conditions were described for a spreading droplet that is simultaneously dissolving a solid substrate. The conditions for contact angle equilibrium were shown to be incompatible with those obtained from the bulk equilibrium phase diagram and

reasonable shape assumptions. A technique for restoring compatibility was employed and an expression for the entropy production was derived. From this, the kinetic equations for wetting were established in the manner of Onsager. The rate equations were solved numerically and compared with experimental data. It was found that good agreement can be obtained with use of this technique for describing wetting kinetics in the Sn-Bi on Bi system. Time varying quantities, such as atom fraction Bi dissolved in the liquid, were found to converge to the values expected from the metastable equilibrium analysis. To obtain a compact model of these kinetics, the model explicitly neglects diffusion and any form of convection in the liquid. The model assumes that spherical caps are sufficient geometric descriptions of the interfaces and that the liquid is an ideal solution. To relax these assumptions, more detailed models, employing the same Onsager methodology, could be constructed. Additional difficulties are possible if preferred dissolution occurs at grain boundaries in the substrate, the substrate is inherently anisotropic, and if the flux efficacy is strongly time dependent.

References

1. P. G. de Gennes, *Rev. Mod. Phys.* **57**, 827 (1985).
2. L. H. Tanner, *J. Phys. D* **12**, 1473 (1979).
3. P. Neogi and C. A. Miller, *J. Colloid Interface Sci.*, **86**, 525 (1982).
4. P. J. Haley and M. J. Miksis, *J. Fluid Mech.*, **223**, 57 (1991).
5. P. Ehrhard and S. H. Davis, *J. Fluid Mech.*, **229**, 365 (1991).
6. T. D. Blake and J. M. Haynes, *J. Colloid Interface Sci.*, **30**, 421 (1969).
7. B. W. Cherry and C. M. Holmes, *J. Colloid Interface Sci.*, **29**, 174 (1969).
8. T. D. Blake, in *Wettability*, edited by J. C. Berg, Marcel Dekker, Inc., New York, NY (1993).
9. R. L. Hoffman, *J. Colloid Interface Sci.*, **94**, 470 (1983).
10. L. M. Hocking, *J. Fluid Mech.*, **239**, 671 (1992).
11. A. Cazabat, *Contemp. Phys.*, **28**, 347 (1987).
12. M. D. Lelah and A. Marmur, *J. Colloid and Interface Sci.*, **82**, 518 (1981).
13. J. C. Ambrose, M. G. Nicholas, and A. M. Stoneham, *Acta metall. mater.*, **40**, 2483 (1992).
14. J. C. Ambrose, M. G. Nicholas, and A. M. Stoneham, *Acta metall. mater.*, **41**, 2395 (1993).
15. M. Nicholas and D. M. Poole, *Trans. Met. Soc. AIME*, **236**, 1535 (1966).
16. G. L. J. Bailey and H. C. Watkins, *J. Inst. Metals*, **80**, 57 (1951).
17. F. W. Spiers, *Phil. Mag.* **7**, 1048 (1933).
18. T. Alty and A. R. Clark, *Trans. Faraday Soc.*, **31**, 648 (1935).
19. X. Chen, A. F. Sprecher, and H. Conrad, in *Materials Developments in Microelectronics Packaging: Performance and Reliability*, edited by P. J. Singh, ASM International, Materials Park, OH (1991).
20. P. Kritsalis, L. Coudurier, and N. Eustathopoulos, *J. Mater. Sci.*, **26**, 3400 (1991).
21. W. M. Armstrong, A. C. D. Chaklader, and D. J. Rose, *Trans. Met. Soc. AIME*, **227**, 1109 (1963).
22. L. Onsager, *Phys. Rev.*, **37**, 405 (1931).
23. G. Wang and J. J. Lannutti, *Met. and Mat'l. Trans. A*, **26A**, 1499 (1995).
24. I. Prigogine, *Introduction to Thermodynamics of Irreversible Processes*, 3rd Edition, Interscience Publishers, New York, NY (1967).
25. B. Lee, C. Oh, and J. Shim, *J. Elect. Matls.*, **25**, 983 (1996).
26. U. R. Kattner and W. J. Boettinger, *J. Elect. Matls.*, **23**, 603 (1994).
27. F. Neumann, *Vorlesungen uber die Theorie der Capillaritat*, Teubner, Leipzig, (1894).
28. Y. Yoo, C. A. Handwerker, W. J. Boettinger, M. Williams, and L. Smith, unpublished research.
29. T. B. Massalski, editor, *Binary Alloy Phase Diagrams*, Vol. 1, p.540, American Society for Metals, Metals Park, OH (1986).
30. A. Adamson, *Physical Chemistry of Surfaces*, 5th edition, John Wiley and Sons, Inc., New York, NY (1967).
31. A. E. Schwaneke, W. L. Falke, and V. R. Miller, *J. Chem. and Eng. Data*, **83**, 298 (1978).

32. C. C. Addison and J. B. Raynor, *J. Chem. Soc. (A)*, 965 (1966).
33. L. E. Murr, *Interfacial Phenomena in Metals and Alloys*, Addison-Wesley, Reading MA, 105 (1975).
34. W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling, *Numerical Recipes in C*, Cambridge University Press, New York, NY (1988).
35. M. Gunduz and J. D. Hunt, *Acta metall.*, **33**, 1651 (1985).
36. D. W. Hoffman and J. W. Cahn, *Surface Science*, **31**, 368 (1972).
37. A. Katchalsky and P. F. Curran, *Nonequilibrium Thermodynamics in Biophysics*, Harvard University Press, Cambridge, MA, 88 (1965).

Fig. A-1. The thermodynamic system consists of constant mass, temperature, and volume and contains Sn and Bi liquid and vapor and a pure Bi substrate that dissolves/evaporates into the liquid/vapor.

Fig. A-2. The equilibrium contact angles may be calculated from the Neumann equations (solid line) and also obtained through utilization of the equilibrium phase diagram (dashed line). These methods of computing equilibrium contact angles will yield a true equilibrium state if the lines intersect.

Fig. A-3. Contact angles as measured for eutectic Sn-Bi alloy on pure Bi substrate. Four specimens yielded 2 measurements each (shown as filled circles) of the contact angles. Four additional specimens were used for dynamic measurement of wetted area. Contact angles on these specimens are shown as filled diamonds.

Fig.A-4. A metallographically prepared cross-section of the Sn-Bi eutectic alloy in metastable equilibrium with a solid Bi substrate. The contact angles measure approximately $\theta_1 = 9.5^\circ$ and $\theta_2 = 58.0^\circ$.

Fig. A-5. The parameters for the eutectic Sn-Bi alloy, chosen for the dynamic wetting experiments, do not yield an intersection and a true equilibrium state. Contact angle data fall a significant distance from either curve.

Fig. A-6. Area versus time for all four specimens used for dynamic wetting measurements.

Fig. A-7. By alteration of the parameters g and W , any data point can be treated as an equilibrium point. However, significant deviations from the expected parameters may result.

Fig. A-8. Comparison of the numerical solution of eqs. (7) and kinetics data from one of the specimens used for dynamic wetting experiments. Off-diagonal Onsager coefficients are set to zero.

Fig. A-9. Evolution of the contact angles and atom fraction Bi as a function of time for the Onsager coefficients chosen for the calculation shown in Fig. 8.

Fig. A-10. The Onsager coefficient L_{22} cannot be modified significantly without losing the quality of fit.

Fig. A-11. Calculations have shown that when L_{11} becomes more than a order of magnitude larger than L_{22} the kinetics become saturated as if being controlled by L_{22} in a series process. This effect has been found to be symmetric in the L_{ii} .

METASTABLE AND EQUILIBRIUM WETTING STATES IN THE Bi-Sn SYSTEM

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Abstract

Sessile drop experiments involving a variety of Bi-Sn alloys on solid Bi substrates were performed. Substrates prepared from small and large-grained polycrystals and single crystals were used to measure equilibrium and metastable contact angles and estimate the surface tension and equilibrium contact angle of the solid-liquid interface. The substrates were also used to investigate the coupling of the dissolution and wetting processes and to investigate the effect of substrate grain size on wetting. It was determined that the equilibrium wetting geometry is independent of linear scale and that grain size has little influence on wetting or dissolution in the Bi-Sn system.

Introduction

During the long history of wetting science, Young's equation has been modified in many ways to account for a large variety of subsidiary effects. Gibbs [1] recommended that an energy term, associated with the three-phase contact line of a sessile drop, be considered in describing capillary equilibrium. This suggestion has given rise to much recent experimental work directed at measuring the "line tension" [2,3]. By including this term it has been shown that the equilibrium contact angle is dependent upon droplet size. Surface roughness and chemical heterogeneity were accounted for in work by Wenzel [4] and Cassie [5], respectively, and these resulted in useful modifications of Young's famous equation. Evaporation and condensation of liquid constituents are reported to give rise to an equilibrium spreading pressure that leads to a modification of Young's equation [6]. Modifications have also been constructed for thin solid substrates that are elastically deformed by liquid surface tension [7,8]. Certain chemical effects have led to modifications, especially in ceramic systems [9]. The capillarity of one liquid wetting another has a lengthy history [10-13]. Incomplete wetting of this sort entails the formation of a liquid lens and three contact angles θ_1 , θ_2 , and θ_3 as shown in Fig. 1. This equilibrium capillary configuration was carefully analyzed with use of calculus of variations in 1894 by Neumann [12, 13] and is partially described by what are now called Neumann's equations. These can be written as

$$\gamma_l \cos \theta_1 + \gamma_{sl} \cos \theta_2 = \gamma_s \cos \theta_3 \quad (1a)$$

$$\gamma_l \sin \theta_1 - \gamma_{sl} \sin \theta_2 = \gamma_s \sin \theta_3 \quad (1b)$$

In these equations γ_l , γ_{sl} , and γ_s are the surface tensions of the liquid-gas, solid-liquid, and solid-gas interfaces, respectively.

The lens configuration is also known to exist when the wetting liquid has finite solubility for a solid substrate, here called dissolutive wetting. This situation would exist, for example, if a water droplet were to be placed on a flat salt or sugar surface. Many examples also exist amongst metal/metal systems of interest. Thermodynamic equilibria of this sort involve not only the capillary energetics, as described above, but also chemical energy exchange due to dissolution of the solid substrate into the droplet and potential reactions between certain components of the liquid and solid to form new phases. The additional chemical energetics may lead to a sequence of metastable states since each of the capillary and chemical processes has its own kinetics. Some of these processes are rapid, such as fluid flow and some are especially slow such as solid surface reconstruction.

In the work reported here, seven Sn-Bi alloys were allowed to wet and dissolve the surface of polycrystalline and single crystal Bi substrates. Contact angles and interfacial profiles were characterized as a function of alloy content. The existence of metastable states along the path to complete thermodynamic equilibrium will be discussed. It will be shown that the equilibrium contact angles at the solid-liquid interface can be predicted from the experimental data even though thermodynamic equilibrium is not complete. Experimental indications suggest that the liquid-vapor

interface is in equilibrium and this allows the measured contact angle, θ_1 , to be identified with its equilibrium value. The equilibrium value of θ_2 can then be computed with eqs. (1) and compared with the measured or metastable value. The effect of substrate grain size is also investigated and discussed in the context of the Neumann equations.

Equilibrium Conditions For Dissolutive Wetting

Consider a droplet of known volume, containing Sn and Bi in known atomic fractions, X_{Bi} . Let the substrate be a Bi-Sn alloy, saturated in Sn, which can dissolve into the liquid until the droplet is saturated at atomic fraction, X_{Bi}^{sat} . The thermodynamic system is assumed to be one of constant temperature, total volume, and chemical potentials. The system free energy, Ω , is given by

$$\begin{aligned}\Omega = & \int_0^{r_o} \left\{ \frac{\rho_l g}{2} \psi^2 + \gamma_l (1 + \dot{\psi}^2)^{1/2} + \lambda_l \psi \right\} 2\pi r dr \\ & + \int_0^{r_o} \left\{ \frac{(\rho_s - \rho_l)g}{2} \zeta^2 + \gamma_{sl} (1 + \dot{\zeta}^2)^{1/2} + (\lambda_s - \lambda_l) \zeta \right\} 2\pi r dr \\ & + \int_{r_o}^R \left\{ \frac{\rho_s g}{2} \eta^2 + \gamma_s (1 + \dot{\eta}^2)^{1/2} + \lambda_s \eta \right\} 2\pi r dr + \text{constants}\end{aligned}$$

where ψ , ζ , and η are the profiles shown in Fig. 2, g is the acceleration due to gravity, ρ 's are mass densities, γ 's are appropriate surface tensions, λ 's are Lagrange multipliers to maintain constant phase volumes, r_o is droplet radius, and R is a radius large enough that $\eta = \dot{\eta} = 0$ at $r = R$. Minimization of this energy yields three Euler-Lagrange (or Laplace) equations for the profiles

$$0 = \rho_l g \psi - \gamma_l \left\{ \frac{\dot{\psi}}{r(1 + \dot{\psi}^2)^{1/2}} + \frac{\ddot{\psi}}{(1 + \dot{\psi}^2)^{3/2}} \right\} + \lambda_l \quad (2a)$$

$$0 = (\rho_s - \rho_l) g \zeta - \gamma_{sl} \left\{ \frac{\dot{\zeta}}{r(1 + \dot{\zeta}^2)^{1/2}} + \frac{\ddot{\zeta}}{(1 + \dot{\zeta}^2)^{3/2}} \right\} + \lambda_s - \lambda_l \quad (2b)$$

$$0 = \rho_s g \eta - \gamma_s \left\{ \frac{\dot{\eta}}{r(1 + \dot{\eta}^2)^{1/2}} + \frac{\ddot{\eta}}{(1 + \dot{\eta}^2)^{3/2}} \right\} + \lambda_s \quad (2c)$$

and two end-point [14] or transversality conditions [15], which are the Neumann equations.

As a measure of the importance of g in determining capillary equilibria, it can be seen that if $\rho_l g r_o^2 \ll \gamma_l$, then the influence of gravity is negligible and equilibrium is dominated by the liquid surface tension. In cases involving metal droplets with $r_o \sim 0.1$ cm this inequality is often obeyed. For example, Sn-Pb [16] and Sn-Bi [17] alloys have mass density ~ 8.0 gm/cm³ and surface tension ~ 400 ergs/cm², so if $g \sim 980$ cm/s², the inequality is obeyed [16]. This same inequality holds in eq. (2c) which, after neglecting gravity, becomes

$$0 = -\gamma_s \left\{ \frac{\dot{\eta}}{r(1 + \dot{\eta}^2)^{1/2}} + \frac{\ddot{\eta}}{(1 + \dot{\eta}^2)^{3/2}} \right\} + \lambda_s$$

thus demanding that the substrate have constant mean curvature (the quantity in curly brackets) in capillary equilibrium. In the context of this problem, the only surface satisfying this requirement is a flat surface such that $\lambda_s = 0$. Thus for many problems of interest $\theta_3 = 0$ and the Neumann equations become

$$\gamma_s = \gamma_l \cos \theta_1 + \gamma_{sl} \cos \theta_2 \quad (3a)$$

$$\gamma_l \sin \theta_1 = \gamma_{sl} \sin \theta_2. \quad (3b)$$

Since gravity is negligible compared to the surface tensions, γ_l and γ_s , the equilibrium profiles are portions of spheres, which are also constant mean curvature surfaces. Whereas γ_{sl} is often considerably smaller than γ_l and γ_s , the density difference, $\rho_s - \rho_l$ in eq. (2b), is also much smaller than either density and gravitational effects are negligible in eq. [2b] as well.

Experimental Procedure

In order to study the effect of liquid composition on wetting, seven Sn-Bi alloy compositions were prepared: 100Sn-0Bi, 75Sn-25Bi, 43Sn-57Bi, 35Sn-65Bi, 27Sn-73Bi, 20Sn-80Bi, and 10Sn-90Bi in weight percent. All Bi and Sn used in this study were 99.99% pure. The alloys were created by weighing out the appropriate amount of Sn and Bi, placing the mixture into a glass test tube, and immersing the test tube into a container of $\sim 350^\circ\text{C}$ Sn until the mixture was fully melted. The test tube was allowed to cool, and the alloy was removed and cut into ~ 10 mg pieces. The solder pieces were then reflowed at $\sim 350^\circ\text{C}$ in a Pyrex dish containing Alpha 611 mildly activated rosin (RMA) flux. The resulting spherically shaped solder balls were then ultrasonically cleaned in isopropyl alcohol (IPA) for 3 minutes, allowed to air dry, weighed, and stored in plastic bags.

Three different types of Bi substrates were examined in this study: fine and coarse grained polycrystals, and two single crystals. The large-grained substrates were prepared in the following manner: Bi was melted at $\sim 300^\circ\text{C}$, poured into rectangular forms (held at room temperature), allowed to cool for several minutes, and transferred into a bath of cool tap water. The resulting bars were then machined into substrates approximately 10 mm square with a thickness of ~ 3 mm. A hole was drilled into one side to accept a thermocouple. The substrates were polished to a root-mean-square 50 nm finish, ultrasonically cleaned in acetone, rinsed with IPA, blown dry with nitrogen, wrapped in lint-free wipes, and stored in a dessicator until the experiments were performed.

The small-grained substrates were prepared as follows: The Bi was melted at $\sim 300^\circ\text{C}$, and poured into a rectangular depression machined into a large copper cylinder (9 cm dia. by 10 cm long) which served as a heat sink. Prior to the pour, the cylinder was cooled in a bath consisting of an IPA and dry ice slurry. The Bi substrates were then machined to approximately 25 mm square with a thickness of ~ 5 mm. A hole was drilled into one side to accept a thermocouple and the substrates were polished, cleaned and stored as described above. The single crystal substrates used in this study were 20 mm in diameter, ~ 3 mm thick and had a (111) orientation. The crystal substrates were drilled, polished, cleaned, and stored in the same manner as were the polycrystalline substrates.

All experiments were performed in a nitrogen atmosphere containing less than 25 parts per million oxygen. The flux used in the study was Alpha 100, a non-activated rosin flux and the heat source was a hot plate. The Bi substrates were placed on the hot plate and brought to a nominal temperature of 240°C after which the following steps were performed:

- a. A controlled amount of flux was applied evenly to the substrate surface
- b. the substrate temperature was allowed to return to 240°C
- c. a controlled amount of flux was again applied evenly to the substrate surface
- d. the substrate temperature was allowed to return 240°C
- e. the video recorder was turned on and a solder ball was placed on the substrate and
- f. the wetted substrate was removed to an Al cooling block after a predetermined time.

After a series of experiments, the substrates were bagged, labeled, and stored. The substrates were metallographically sectioned and polished through a diametral plane, thus permitting the measurement of the quantities shown in Fig. 3. All measurements were made in a JOEL JSM 6300V scanning electron microscope (SEM). The contact angles, θ_1 and θ_2 were measured on both sides of each sectioned droplet. For each solder alloy and polycrystalline substrate studied, four droplets were sectioned and measured. A total of eleven droplets were measured on the single crystals. All wetting events were recorded on video tape with use of a Sony SVHS Video Recorder. After adjusting the video system for optimal contrast, several seconds of a calibration reticule (10 mm by 10 mm) were recorded for use in calibrating an ImagePro image analysis

system. Grain size was measured using the intercept method [18]. The fine-grained substrates had a grain size of approximately 0.85 mm and the large-grained substrates had a grain size of approximately 1.71 mm.

Results

Small-grained Substrates

The solder drops were observed to wet and slowly spread over a time span of 480 seconds which was sufficient time for all motion to cease on each specimen. Typical cross-sections are shown in Fig. 4a-c. In Fig. 4a, the initial solder alloy was pure Sn and resulted in significant dissolution and spreading. Figure 4b shows the result of using the eutectic alloy, which also resulted in significant dissolution and spreading. An alloy containing 83.6 at.% Bi, a composition near the saturation concentration of 84 at.% Bi at 240°C, is shown in Fig. 4c. This alloy spread to an average final contact angle of $\theta_1 = 24.1^\circ$ without appreciable dissolution, as would be expected from a nearly saturated alloy. Since only sparse, localized dissolution was observed, θ_2 for this alloy was taken as zero. With the exception of this alloy, dissolution occurred uniformly with little preferential penetration of substrate grain boundaries.

Since the specimens were examined after solidification some distortion of the liquid surface was unavoidable. In some specimens a small "pimple" of exuded liquid was found and concluded to be due to the curious expansion property of Bi alloys during solidification. Nevertheless, contact angle measurements and other shape observations have been made from SEM photomicrographs such as these. Note that the surface of the liquid is close to being spherical in overall appearance, but that the solid-liquid interface is distinctly different from that of a sphere. This shape suggests that rapid spreading was followed by a slower dissolution process. This observation prompted Warren et al. [19] to model the evolution of this interface as a slow diffusion controlled process. Since the liquid surface is very mobile, eq. (2a) will successfully describe this state of equilibrium and measured values of θ_1 should be close to true equilibrium values if the dissolution process is complete. Equation (2b) will certainly not describe the observed solid-liquid interface shape since, in equilibrium, it should be spherical as well. Since the solid surface appeared flat in all of our specimens and since the effects of gravity were shown to be negligible, eqs. (3a) and (3b) are assumed to adequately describe contact angle equilibrium.

The experimental contact angle data for the fine-grained substrates is shown in Fig. 5 plotted versus the initial composition, X_{Bi} , of the solder alloy droplet. The location of the plotting symbols represents the mean value of 8 measurements (2 contact angles from each of 4 specimens) and the error bars represent $\pm$ one standard deviation. The contact angle, θ_1 , remains at or below approximately 10° for all alloys except that containing 83.6 at.% Bi. This alloy is nearly saturated in Bi and its wetting behavior seems to be impaired by it being marginally liquid. The averages of contact angles, θ_2 , remain above approximately 53° for all alloys except the nearly saturated alloy. Note also that the measurements of this contact angle have a larger standard deviation. The error observed with the alloy containing 51.3 at.% Bi is large enough to suspect the reliability of this particular set of data. The increased error in making θ_2 measurements is partially due to difficulty in identifying the precise path of the solid-liquid interface.

Since the final liquid composition should be X_{Bi}^{sat} in all seven sets of experiments, the fact that a trend of contact angles is observed is cause for reflection. If the system was in complete thermodynamic equilibrium, the measured contact angles should be independent of initial solder composition and the drop configurations should vary only in linear scale. If dissolution was complete, the upper contact angle, θ_1 , would be determined by eq. (2a) and, be independent of initial solder composition. The only remaining process necessary for the system to then reach true equilibrium is the ripening of the solid-liquid interface into a spherical shape. To probe the extent of the dissolution process the volume of the dissolved material was estimated by fitting a polynomial to the observed solid-liquid profile. The polynomial was of the form

$$f(r) = -h_2 + ar^m + br^n$$

where h_2 is the measured dissolution depth, m and n are positive integers, while a and b were determined such that $f(r_o) = 0$ and $f'(r_o) = \tan \theta_2$ and r_o is the measured drop radius. The volume of dissolved material estimated in this manner is given by

$$V_m = 2\pi r_o^3 \left(\frac{h_2}{2r_o} - \frac{ar_o^{m-1}}{m+2} - \frac{br_o^{n-1}}{n+2} \right).$$

An example of such a fit is shown in Fig. 6 which is the eutectic alloy also shown in Fig. 4b. The exponents chosen for this fit were $m = 4$ and $n = 22$. These volumes were then compared to the dissolved volumes, V_i , that would be expected if the final composition was X_{Bi}^{sat} (see Appendix) and plotted in Fig. 7. Slight differences in the values of V_i are due to minor differences in volume of the initial solder alloy droplets. The data are highly suggestive that dissolution is nearly complete since a linear least squares fit yielded a slope of 0.93. For given values of γ_s , γ_l , and θ_1 , eqs. (3a) and (3b) enable calculations of γ_{sl} and θ_2 . For this purpose a value of $\gamma_s = 550$ ergs/cm² was found in Murr [20], while the data of Drath and Sauerwald [17] and the compilation of Iida and Guthrie [21] were used to obtain a linear, least squares fit ($R=99.13$) that represents liquid surface tension behavior at 240°C, $\gamma_l = 509.9 - 158.3X_{Bi}$ (all surface tension data are in ergs/cm²). Because the liquid surface appeared spherical and dissolution was nearly complete, $X_{Bi} \approx X_{Bi}^{sat}$, the measured values of θ_1 should be equilibrium values so it was assumed that $\gamma_l = 509.9 - 158.3X_{Bi}^{sat}$ for these calculations. The resulting predicted values of γ_{sl} and θ_2 are listed in Table 1. The solid-liquid surface tension for the nearly saturated alloy was computed from Young's equation, while the others were determined from Neumann's equations, as were values of θ_2 . Considering the wide range of alloys examined, and the errors involved in the measurements,

TABLE B-1. Predicted equilibrium values of contact angles and solid-liquid surface tension.

Atomic % Bi	θ_1 (degrees)	θ_2 (degrees)	γ_{sl} (ergs/cm ²)
0.0	5.16	10.97	177.9
15.9	7.35	15.31	182.7
43.0	9.43	19.12	188.6
51.3	8.16	16.83	184.8
60.6	7.8	16.16	183.8
69.4	6.2	13.08	179.9
83.6	24.1	0.00	205.3

the predicted values were quite uniform. Excluding the alloy at 83.6 at.% Bi, the average solid-liquid surface tension was 182.9 ergs/cm² (standard deviation = 9.3 ergs/cm²) and the average θ_2 was 15.25° (standard deviation = 2.88°). The average drop radius versus alloy content is shown in Fig. 8, which shows that wetting improves, if judged by areal coverage, as tin content increases. Thus, the process of dissolution produces improved wetting by increasing the available fluid, not by decreasing the contact angles. It should be noted here that surface tension values are very sensitive to fluxes used in their measurement [22-24] and the values used and computed in this study should not be considered absolute.

Large-grained and Single Crystal Substrates

The wetting line will advance on a dissolving substrate if the total interfacial energy decreases. Since grain boundaries contribute to the total interfacial energy, it is conceivable that wetting may be influenced by the energy and density of grain boundaries. While not observed in these experiments, dissolution may also cause a roughening of the solid-liquid interface due to the formation of grain boundary cusps, as illustrated in Fig. 9. According to the rough surface premise established by Wenzel [4] this may also affect the extent of wetting in a dissolving system.

Consider a droplet that dissolves a polycrystalline substrate having grain size, $\bar{\ell}$. The droplet radius, r_o , is taken to be larger than $\bar{\ell}$. The total grain boundary area removed in this process is equal to the grain boundary area per unit volume [18], $S_v = \frac{2}{\bar{\ell}}$, multiplied by the volume of substrate dissolved such that the total grain boundary energy lost by the system will be $E_b = \frac{2\gamma_b V_t}{\bar{\ell}}$ where γ_b is grain boundary energy. This energy and the associated roughened interface could be used to derive modifications to eqs. (3a) and (3b). However, the experimental results on large-grained substrates do not seem to warrant this effort.

Typical cross sections, all utilizing solder drops with eutectic composition, are shown in Fig. 10 a-c. Figure 10a shows a small-grained substrate, 10b a large-grained substrate, and 10c a single crystal substrate. Whereas the solder microstructure varies, due to different solidification rates, the wetting configurations are similar. A summary of the contact angle behavior on large-grained substrates is shown in Fig. 11. The large-grain data is shown as boxes (open and filled) and the single crystal data are shown as circles (open and filled). Judging from this data, it was concluded that little effect of grain size can be discerned. The wetting behavior of the nearly saturated alloy was particularly poor. The drops were not all spherical in shape and in some cases showed contact angles greater than 90° . Measured values of θ_1 were large and showed excessive scatter and this was again interpreted as an effect of marginal liquidity. Because of local and sparse dissolution, it was again decided to set $\theta_2=0$, as was done for the small-grained specimens. In contrast to the behavior on the small-grained substrates, wetting measurements of the alloy containing 51.3 at.% Bi possessed typical scatter indicating that the small-grained data taken on this alloy was, indeed, corrupt. The contact angle, θ_1 , observed on the single crystal substrates was more typical of the behavior of the small-grained substrates than of the large-grained substrates. This would also indicate that there was little effect of substrate grain size on wetting behavior.

Discussion and Conclusions

The stability of a metastable state depends critically upon the frequency and magnitude of system perturbations of this state. The growth or decay of the perturbations are determined by local mobilities, diffusion coefficients, and rate constants as well as the driving forces for physico-chemical processes that can disturb the system. If this stability is characterized by the relative time spent in that state, then a sequence of metastable wetting states of widely varying stability have been observed in the Bi-Sn system. The complete description of thermodynamic equilibrium of Bi-Sn alloy droplets on a solid Bi substrate saturated in Sn requires equality of chemical potentials in vapor, liquid and solid phases. It also requires three interfacial shape functions (Laplace equations) and two Neumann equations to specify capillary equilibrium. Chemical and capillary equilibria are necessarily coupled through the chemical dependence of surface tension. If one or more of the equilibrium requirements are not met, the system is metastable.

Early in the dissolutive wetting process, none of the above requirements are met and the system follows a sequence of short-lived metastable states in which the Laplace equation for the liquid-vapor interface is the only requirement even close to being met. Under slow wetting conditions the liquid surface is likely to be spherical, but the curvature of this interface will depend on the extent of dissolution. It was shown in this work that long after wetting and spreading stops, the liquid-solid interface has still not reached equilibrium, judging from its nonspherical shape, even though substrate dissolution is sensibly complete. The Laplace requirement for this interface is not met, so the system is metastable and will remain so for a long period of time. Estimation puts the required time for this coarsening process at approximately one year [19]. This period of time makes measurement of the equilibrium contact angle of this interface untenable and inefficient. It was demonstrated that it may be possible to estimate the true equilibrium contact angle when dissolution is complete and the Laplace condition for the liquid-vapor interface is met. For the Bi-Sn system at 240°C , this angle is approximately 15° and the solid-liquid surface tension is approximately 183

ergs/cm². To compute θ_2 and γ_{sl} , values for γ_s and γ_l were selected from the literature and not measured in these experiments. It is likely that the flux used in these experiments influenced the reported results, so computed values should not be used out of this context. It was shown that the predicted equilibrium contact angle θ_2 is relatively constant, as was the contact angle θ_1 , over a wide range of alloy compositions. Although the drop diameter increased with increasing Sn content, it did so because more fluid was made available by the dissolution process. The equilibrium wetting configuration should be and was experimentally shown to be scale invariant.

The solid-vapor interface appeared to be flat in all of the experiments. It was shown that gravitational forces are too small to cause any distortion of this interface near the wetting line. There have been some indications, however, that distortion is possible[25]. This suggests that other forces, not included in the Neumann analysis, should be considered. No significant wetting effect due to substrate grain size was found and there did not appear to be any significant preferential dissolution at emerging grain boundaries. The wetting of single crystal substrates appeared to be very similar to wetting of small-grained substrates. This behavior is certainly not to be expected in general, since evidence to the contrary has been reported in the literature for decades[26].

Appendix: Volume of Dissolved Substrate, V_i

For ideal solutions such as Bi-Sn [27,28], the total volume of initial liquid can be written

$$V_o = m \left(\frac{x_{Bi}}{\rho_{Bi}^l(T)} + \frac{1-x_{Bi}}{\rho_{Sn}^l(T)} \right)$$

where m is the mass of a solder droplet, x_{Bi} is weight percent Bi (known from alloy preparation) and $\rho_i^l(T)$ are mass densities in the liquid[21]. The atomic fraction of Bi can be computed from x_{Bi} and is by definition

$$X_{Bi}^l = \frac{N_{Bi}^l}{N_{Bi}^l + N_{Sn}^l}$$

where N_i^l are moles of i in the initial liquid and are given by

$$N_{Bi}^l = \frac{X_{Bi}^l}{X_{Bi}^l \bar{V}_{Bi}^l + X_{Sn}^l \bar{V}_{Sn}^l} V_o$$

and

$$N_{Sn}^l = \frac{X_{Sn}^l}{X_{Bi}^l \bar{V}_{Bi}^l + X_{Sn}^l \bar{V}_{Sn}^l} V_o$$

where, for ideal solutions, $\bar{V}_i^l = \frac{M_i}{\rho_i^l(T)}$ and M_i is the atomic weight of i . The substrate is imagined

to be solid Bi saturated in Sn at 240°C such that its atomic fraction, according to the equilibrium phase diagram, is very close to 1.0. The volume of dissolved material is given by

$$V_i = (N_{Bi}^{sat} - N_{Bi}^l) \bar{V}_{Bi}^s + (N_{Sn}^{sat} - N_{Sn}^l) \bar{V}_{Sn}^s$$

where N_i^{sat} are moles of i in the saturated liquid,

$$N_{Bi}^{sat} = N_{Sn}^{sat} \frac{X_{Bi}^{sat}}{1 - X_{Bi}^{sat}},$$

and X_{Bi}^{sat} is the atomic fraction Bi in the saturated liquid which is also known from the equilibrium phase diagram. Bi has negligible solubility for Sn so, $N_{Sn}^{sat} \cong N_{Sn}^l$ and

$$V_i \cong (N_{Sn}^{sat} \frac{X_{Bi}^{sat}}{1 - X_{Bi}^{sat}} - N_{Bi}^l) \bar{V}_{Bi}^s$$

Since the substrate is nearly pure Bi, the partial molar volume can be written

$$V_{Bi}^s = \frac{M_{Bi}}{\rho_{Bi}^s(T)}$$

where $\rho_{Bi}^s(240^\circ\text{C})=9.75 \text{ gm/cm}^3$ is the mass density of solid Bi [29] at the test temperature.

References

1. J. W. Gibbs, *The Collected Works of J. Willard Gibbs*, **1**, Yale University Press, New Haven, (1957).
2. J. Drelich and J. D. Miller, *J. Coll. and Interface Sci.*, **164**, 252 (1994).
3. D. Duncan, D. Li, J. Gaydos, and A. W. Neumann, *J. Coll. and Interface Sci.*, **169**, 256 (1995).
4. R. N. Wenzel, *Ind. Eng. Chem.*, **28**, 988 (1936).
5. A. B. D. Cassie, *Disc. Faraday Soc.*, **3**, 11 (1948).
6. J. C. Berg, *Wettability*, ed. J. C. Berg, Marcel Dekker, Inc., New York, 76 (1993).
7. G. R. Lester, *J. Colloid Sci.*, **16**, 315 (1961).
8. M. E. R. Shanahan, *J. Phys. D: Appl. Phys.*, **20**, 945 (1987).
9. M. W. Barsoum and P. D. Ownby, *Mater. Sci. Res.*, **14**, 457 (1980).
10. C. G. Lyons, *J. Chem. Soc.*, 623 (1930).
11. N. F. Miller, *J. Phys. Chem.*, **45**, 1025 (1941).
12. F. Neumann, *Vorlesungen uber die Theorie der Capillaritat*, Teubner, Leipzig, (1894).
13. B. V. Toshev, *Comptes Rendus de l'Academie bulgare des Sciences*, Vol. 33, No. 8, 1980, pp.1095-1098.
14. R. Weinstock, *Calculus of Variations*, McGraw-Hill Book Company, New York, 1952, p. 38.
15. M. J. Forray, *Variational Calculus in Science and Engineering*, McGraw-Hill Book Company, New York, 1968, p. 52.
16. A. E. Schwaneke, W. L. Falke, and V. R. Miller, *J. Chem. and Eng. Data*, **83**, 298 (1978).
17. G. Drath and F. Sauerwald, *Zeitschrift fur Anorg. Chem.*, **162**, 301 (1927).
18. R. T. DeHoff and F. N. Rhines, *Quantitative Microscopy*, McGraw-Hill Book Company, New York, 235 (1968).
19. J. A. Warren, W. J. Boettinger, and A. R. Roosen, submitted for publication in *Acta mater.*
20. L. E. Murr, *Interfacial Phenomena in Metals and Alloys*, Addison-Wesley, Reading, MA, 124 (1975).
21. T. Iida and R. I. L. Guthrie, *The Physical Properties of Liquid Metals*, Clarendon Press, Oxford, 134 (1988).
22. L. S. Goldmann and B. Krall, *Rev. Sci. Instrum.*, **47**, 324 (1976).
23. F. H. Howie and E. D. Hondros, *J. Mater. Sci.*, **17**, 1434 (1982).
24. R. J. Klein-Wassink, *Brazing and Soldering*, No. 12, 5 (1987).
25. Y. Yoo, C. A. Handwerker, W. J. Boettinger, M. Williams, and L. Smith, unpublished research.
26. E. R. Parker and R. Smoluchowski, *Trans. ASM*, **35**, 362, (1944).
27. B. Lee, C. Oh, and J. Shim, *J. Elect. Matls.*, **25**, 983 (1996).
28. U. R. Kattner and W. J. Boettinger, *J. Elect. Matls*, **23**, 603 (1994).
29. Y. S. Touloukian, R. K. Kirby, R. E. Taylor, and P. D. Desai, *Thermal Expansion, Metallic Elements and Alloys*, IFI/Plenum, New York, 33 (1975).

Fig. B-1. The thermodynamic system showing three phases and three equilibrium contact angles.

Fig. B-2. Three shape functions that define the axisymmetric, equilibrium lens profile.

Fig. B-3. Illustration of the drop cross section and the measurements made from them.

a.

b.

c.

Fig. B-4. Typical droplet cross sections showing
 a. the wetting behavior of an initially pure Sn droplet
 b. the wetting behavior of a droplet initially comprised of eutectic composition
 c. the wetting behavior of a droplet that was nearly saturated in Sn when placed on a small-grained Bi substrate.

Fig. B-5. Experimental contact angle behavior of a variety of Bi-Sn alloys on small-grained Bi substrates. Excellent wetting was observed in all but the alloy containing 83.6 at.% Bi.

Fig. B-6. An example of a simple polynomial fit to the cross section of a wetted droplet. The fit was used to estimate the volume of substrate dissolved by the Bi-Sn solder alloys.

Fig. B-7. A comparison of the volume of Bi dissolved by molten Bi-Sn alloys. V_m represents the volume estimated by the fitting procedure described above while V_t represents the same volume predicted by equilibrium solution thermodynamics. The data are highly suggestive that the dissolution process is nearly complete.

Fig. B-8. The average drop radius versus initial solder composition. The data show that the extent of wetting decreases as saturation of the droplet is approached even though the equilibrium contact angles remain constant.

Fig. B-9. An illustration of potential sources of wetting dependence on substrate grain size.

a.

b.

c.

Fig. B-10. Typical droplet cross sections showing initially eutectic Bi-Sn alloys on **a.** a small-grained substrate **b.** large-grained substrate and **c.** single crystal substrate. No significant difference in wetting behavior is perceived.

Fig. B-11. Summary of wetting behavior on large-grained and single crystal substrates. Wetting behavior is similar to that observed on small-grained substrates.

THE TRIPLE LINE IN REACTIVE WETTING

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Introduction

In a recent publication Landry et al. [1] discussed the question of the wetting or triple line configuration in reactive wetting systems. Their main objective was to resolve "...which interfacial energies determine the final contact angle θ_F of the system." In this discussion, θ_F is the contact angle between the liquid and the plane of the substrate as shown in Figs. 1a and b. In the Figures v designates vapor, l liquid, p reaction product, and s the substrate. Their use of the word "final" and their search for the appropriate characterization of contact angles implies that they are attempting to describe the equilibrium state. The contact angle descriptions they consider are

$$\cos \theta_F = \frac{\gamma_{sv} - \gamma_{pl}}{\gamma_{lv}} \quad (1a)$$

$$\cos \theta_F = \frac{\gamma_{pv}}{\gamma_{lv}} \quad (1b)$$

$$\cos \theta_F = \frac{\gamma_{pv} - \gamma_{pl}}{\gamma_{lv}} \quad (1c)$$

where the γ_i 's are surface tensions. These equations can be understood and surmised from examination of Figs. 1a and b. The purpose of this paper is to, first, point out that eqs. (1a) and (1b) are insufficient descriptors of the reactive wetting equilibrium state. Second, a complete description of the equilibrium state will be derived which will include a characterization of the contact angle in question. Finally, a discussion of metastable wetting configurations and the complexity of actual wetting configurations will be presented.

Equilibrium Analysis

Consider a liquid wetting a solid substrate and simultaneously reacting with it to produce an intermetallic phase that adheres to the substrate. An equilibrium vapor consisting of components A , B , and C and their partial pressures surrounds all phases in the system. Let temperature, volume, and mass be held constant and the substrate be comprised of A saturated in the components B and C of the liquid. The components react such that $xA + yB \rightarrow A_xB_y$, while component C remains unreacted in the liquid. An example would be the Sn, Bi, Ag ternary system [2] in which the compound Ag_3Sn forms and Bi is the counterpart of C . In this equilibrium thermodynamic state, it will be assumed that gravitational effects are negligible and all surface tensions are isotropic. Except for the substrate-vapor interface spherical interfaces are an equilibrium requirement under conditions of negligible gravitational effects. The substrate-vapor interface will be flat unless other forces, not considered here, are included in the analysis.

The configuration shown in Fig. 2 will be employed throughout this analysis. An incremental change in the Helmholtz free energy, F , of the system is given by

$$dF = 0 = \sum_{i,j} \mu_i^j dN_i^j + \sum_k \gamma_k dA_k - \sum_j P_j dV_j \quad (2)$$

where μ represents chemical potential, N is number of moles, γ are surface tensions, A are interfacial areas, P are pressures, V are volumes, and i, j, k refers to specific components, phases, and interfaces, respectively. With the imposed system constraints

$$0 = dT = \sum_{i,j} dN_i^j = \sum_j dV_j$$

the conditions for thermodynamic equilibrium can be derived. Substituting the constant mass constraint into eq. (2) yields

$$\mu_i^v = \mu_i^l = \mu_i^p = \mu_i^s \quad i = A, B \text{ and } C \quad (3)$$

which are the Gibbs conditions [3] for chemical equilibrium and substituting the remaining two constraints yields

$$0 = -(P_s - P_v)dV_s - (P_p - P_v)dV_p - (P_l - P_v)dV_l \\ + \gamma_{lv}dA_{lv} + \gamma_{pl}dA_{pl} + \gamma_{ps}dA_{ps} - \gamma_{sv}dA_{sv}.$$

Under negligible gravitational conditions the substrate is flat and $P_s = P_v$. Substitution of the appropriate spherical descriptions for dV_j and dA_k , collecting terms in the increments dr and dh_k , and setting each multiplier of these increments to zero yields

$$P_l - P_v = \frac{4\gamma_{lv}h_{lv}}{r^2 + h_{lv}^2} \quad (4a)$$

$$P_p - P_l = \frac{4\gamma_{pl}h_{pl}}{r^2 + h_{pl}^2} \quad (4b)$$

$$P_p - P_s = \frac{4\gamma_{lv}h_{lv}}{r^2 + h_{lv}^2} + \frac{4\gamma_{pl}h_{pl}}{r^2 + h_{pl}^2}. \quad (4c)$$

Along with $P_s = P_v$, eqs. (4) represent four Laplace conditions [4] on the four interfaces. The above process also yields, after some algebraic manipulation, two conditions on the contact angles

$$\gamma_{sv} = \gamma_{lv} \cos \theta_F + \gamma_{pl} \cos \theta_{pl} + \gamma_{ps} \cos \theta_{ps} \quad (5a)$$

$$\gamma_{lv} \sin \theta_F + \gamma_{pl} \sin \theta_{pl} = \gamma_{ps} \sin \theta_{ps} \quad (5b)$$

which are the Young-Neumann conditions [5] for capillary equilibrium.

Results and Discussion

In addition to the usual Gibbs conditions for equilibrium in a reactive system, the simple reactive wetting problem considered here requires four Laplace conditions and two Young-Neumann conditions to completely specify thermodynamic equilibrium. With the assumptions made above, the Laplace conditions require that each interface have constant mean curvature. For the sessile drop geometry this requirement implies either a flat or spherical shape. The substrate will most likely be flat, the product phase will have a lens shape with spherical caps, and the liquid interface will also be a spherical segment.

If $\theta_{pl} = \theta_{ps} \equiv 0$ in eq. [5a] there is some resemblance between it and eq. [1a] and [1b]. The magnitudes of γ_{pl} and γ_{ps} determine which of eqs. [1a] or [1b] is the more correct in the classical sense. Equation [1c] will be valid if $\gamma_{pv} = \gamma_{sv}$ or $\gamma_{pv} - \gamma_{pl} = \gamma_{sv}$. Landry et al. did not discuss a vertical capillary force balance as embodied in eqs. [5b].

It should be noted that the classical approach to capillary problems ignores microstructure and defects. It contains the implicit assumption that all phases of the system are homogeneous and structureless which, of course, bears no resemblance to reality except for systems that are totally liquid. Wetting structures that appear as depicted in either Figs. 1 or Fig. 2 are virtually nonexistent. Real interfaces assume a wide variety of configurations such as that illustrated in Fig. 3 with a scalloped product phase [6]. Analysis of this wetting problem should consider, for example, grain boundaries in the substrate and reaction product phases in addition to phase interfaces. Such a structure is metastable and will only evolve to that shown in Fig. 2 after a very long period of time, if ever. This points to the need for a more appropriate method of characterizing these real, but complex, capillary configurations. One approach might be to systematically seek microstructures that evolve very slowly. These configurations will have low, but not necessarily minimal, energy and very small mobilities and driving forces such as gradients of interfacial mean curvature. The scalloped interface, a result of nucleation and growth, can

easily be visualized as such. Other features, such as cusps in dissolving grain boundaries, might also be considered in this way. Much more complicated structures can also be expected if more components and more reactions occur which will make the search for true equilibrium states even more superficial. In any case, one must be careful to recognize metastable microstructures, and cite conclusions drawn from these microstructures, only in this context.

Conclusions

The classical method for specifying the conditions of capillary equilibrium has been used to describe the wetting line in a simple reactive system. The results, being Young-Neumann equations for the contact angles, are compared to suggestions made by Landry et al. [1]. It was shown that under specific circumstances the suggestions made by Landry et al. agree with the classical approach. A discussion was also presented regarding the complexity of real capillary microstructures and their very simplistic theoretical description. An approach that considers microstructural defects and can distinguish metastable and true equilibrium states in complex systems is needed.

Acknowledgment

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References

1. K. Landry, C. Rabo, R. Voitovich, and N. Eustathopoulos, *Acta mater.*, **45**, No. 7, 3079 (1997).
2. U. R. Kattner and W. J. Boettinger, *J. Electronic Mat'ls*, **23**, No. 7, 603 (1994).
3. J. W. Gibbs, *The Collected Works of J. Willard Gibbs*, **1**, Yale University Press, New Haven, (1957).
4. H. M. Princen, *Surface and Colloid Science*, **2**, Wiley-Interscience, New York, (1969).
5. F. Neumann, *Vorlesungen uber die Theorie der Capillaritat*, Teubner, Leipzig, (1894).
6. H. K. Kim, H. K. Liou, and K. N. Tu, *Appl. Phys. Lett.*, **66**, 2337 (1995).

Fig. C-1. Two illustrations of potential wetting line configurations in a reactive wetting system. The vapor phase is designated s, the liquid phase l, the reaction product p, and the substrate s.

Fig. C-2. Illustration of the classical depiction of the wetting line in a simple reactive wetting system. This configuration is used for the analysis in the paper.

Fig. C-3. Illustration of potential microstructural configurations in a reactive wetting system.

Molecular Dynamic Studies of Wetting in Ag-(111) Cu EAM Systems

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Abstract

Continuum models of wetting generally employ solutions to the Navier-Stokes equations with a boundary condition that sets the fluid velocity to zero at solid-liquid interfaces. However, this leads to an inconsistency in wetting and spreading models that require liquid motion or slip at the wetting line. To investigate the atomic behavior of liquids at interfaces during wetting, we simulated wetting in the Ag-Cu system using molecular dynamics with EAM potentials and observed both atomic dynamics and structural correlations at the liquid-solid interface. We found that spreading is prompted by interactions between the liquid and the substrate surface that cause the liquid layer in contact with the substrate to take on some of the symmetry of the substrate surface and result in the formation of a liquid monolayer that extends beyond the major part of the liquid droplet. This study thus provides insight into the atomistic processes that control spreading kinetics.

Introduction

Complete wetting in a solid-liquid-vapor system occurs when the solid-vapor surface energy exceeds the sum of the liquid-solid interfacial energy and the liquid-vapor surface energy, that is, when $\gamma_{SV} > \gamma_{SL} + \gamma_{LV}$, where γ_{SV} is the solid-vapor surface energy, γ_{SL} is the solid-liquid interfacial energy, and γ_{LV} is the liquid-vapor surface energy. In partial wetting, liquid droplets attain an equilibrium wetting angle θ , given by $\gamma_{LV} \cos \theta = \gamma_{SV} - \gamma_{SL}$, as illustrated in Figure 1. As the spreading of a drop progresses, the wetting angle diminishes until the equilibrium wetting angle is reached. The equilibrium shape of liquid droplets on uniform substrates has been well established, and computer models can successfully predict equilibrium shapes for liquid droplets on non-uniform substrates [1,2].

Certain spreading models employ the Navier-Stokes equations, which use liquid parameters such as density and viscosity, to describe the kinetics of liquid spreading under the driving forces for minimization of interfacial and gravitational potential energies. An assumption commonly used in the solution of these equations is that the fluid velocity with respect to the substrate approaches zero at the liquid-substrate interface, as shown in Figure 2. This leads to an apparent paradox as applied to wetting, since it implies that liquid cannot flow at the edge of the droplet and that spreading can not occur. Other models [3,4] assume that in a region close to the wetting line, liquid slips against the substrate thus allowing flow and wetting to continue. These make use of an ad-hoc relationship between the contact angle and the slip velocity. Beyond this, little is said regarding the nature of the slip process.

The aim of this study is to elucidate the liquid behavior at the wetting line by using a model that incorporates liquid/solid interactions that are not subject to the constraints imposed by the boundary conditions on the Navier-Stokes equations. Previous studies by Landmann and Luedtke [5] using the molecular dynamics (MD) simulation technique have shown that small solid clusters can spread on a substrate via a dislocation mediated settling process termed "solid-on-solid settling." Here we use MD to examine the atomistic dynamics of a liquid on a substrate at the wetting line. It will be demonstrated that "liquid" atoms near the wetting line are positionally correlated with the substrate lattice and that dislocations in this correlated region allow for an analogous "liquid on solid settling" that underlies the slip process during wetting.

Procedure

Molecular dynamics is a computational simulation technique that uses semi-empirical interatomic potential functions to predict the atomic dynamics of systems consisting of thousands to millions of atoms over a period of tens of picoseconds. It records a complete history of the atomic system over a period of time that can be used to determine cooperative behaviors that could not be otherwise predicted. Thus, this technique is ideal for studying how correlations between liquids and substrates affect the atomistic spreading behaviors and kinetics of liquids on substrates. In this study, we used MD to simulate the spreading of liquid silver on solid copper substrates.

Molecular dynamics requires an appropriate set of potential functions to give the simulated system an identity. In our simulations, we used the "Universal" embedded atom method (EAM) potential set of Foiles et al. [6] that covers the fcc metals Cu, Ag, Au, Ni, Pd, Pt, and their alloys. These potentials couple an atom-density dependent embedding potential with a simple pairwise potential to model the energy of an atom in a metallic system where each atom interacts with the overall electron gas as well as the atoms in its vicinity. Foiles [7] demonstrated the applicability of this potential set for modeling liquid phases in addition to the solid phases for which they were developed. This potential set gives melting temperatures for Ag and Cu as 1170 K and 1340 K [8], as compared to accepted experimental values of 1234 K and 1358 K, respectively.

We simulated spreading on substrates having both free and constrained top surfaces (x - y plane facing positive z -direction), constrained bottom surfaces (x - y facing negative z -direction), and periodic bulk boundaries in x - and y -dimensions. Allowing free atomic motion on top in some cases enabled simulations of liquids spreading on thermally active substrates, while constraining atomic motion on the bottom in all cases prevented relaxation effects that would reveal the limited thickness of the substrate to the dynamic atoms on top. The sizes of the substrates and the constrained regions within were such that in the dynamic substrate case, all the bulk atoms with which the surface atoms could interact were dynamic, and in all cases, all dynamic atoms were beyond the interaction range of the bottom surface. The periodicity in the x - and y - dimensions prevented edge effects that would have revealed the limited size of the substrate.

After creating the substrate structure, we placed a block of the liquid on top. To avoid spreading over the whole substrate surface with a minimum amount of substrate area and to minimize the number of liquid atoms required, we simulated the spreading of a line in the x -dimension rather than of a round droplet in both x - and y -dimensions. This results in the area covered by liquid increasing linearly rather than quadratically with drop dimension. We formed this line of liquid by creating a liquid block that spanned the y -periodic dimension. In all subsequent discussion, we will refer to this line as a drop. The resulting geometry (after assumed spreading) is shown in Figure 3. With this geometry, we found system sizes of about 5000 atoms to be sufficient to provide both the area of substrate and the volume of liquid required to allow spreading unconstrained by geometry to occur on realizable time scales. Simulation dimensions were generally about $130\text{\AA} \times 30\text{\AA} \times 40\text{\AA}$ in the x -, y - and z -dimensions, respectively.

We performed wetting simulations at a temperature of 1250 K, between the EAM melting temperatures of Ag and Cu, using both static and dynamic substrates. We found that 40 ps simulations were sufficient to elucidate the spreading behavior in these systems.

We analyzed spreading behavior in several ways. Visual analyses of systems revealed whether or not the liquid was melting, visibly ordering, and/or spreading. Spreading kinetics were determined from the width of the drops over time. Atom correlations in the z -dimension were calculated to determine the presence of layering in the liquid near the substrate. Time-averaged in-plane Fourier transforms of atomic positions were calculated to provide meaningful time-averages of spatial occupation in 2-D that were comparable to data obtained by diffraction techniques and could distinguish between correlations caused by interactions between substrate and liquid atoms and those caused by the presence of a simple wall constraint. Finally, we examined visual images of atom positions within the bounding planes to determine the presence of dislocations in these planes.

Results and Discussion

A representative picture of the system after 40 ps of spreading on a static substrate is shown in Figure 4. Note the precursor foot-like feature at the edge of the spreading liquid that appears to be a monolayer of liquid on the substrate surface. Previous atomistic Monte-Carlo simulation studies using similar EAM potentials have shown that there is segregation of Ag to Cu surfaces in Ag/Cu alloys, [9,10] which may explain the presence of this feature. The presence of this monolayer may prevent this from being a textbook example of wetting on the atomic scale. However, it is not clear what textbook examples of wetting can be obtained in an atomistic model. Thus, we will continue with our analysis, bearing in mind that the behavior observed here may not be universal.

The liquid atoms of the first monolayer seem to be able to diffuse in the plane parallel to the interface more readily than those in higher layers. This may be because atoms within the liquid that obtain enough kinetic energy to escape the drop can move over atomistically smooth substrate surfaces more readily than if they had to undergo collisions with other liquid atoms within the drop. Likewise, atoms that attempt to escape the drop on the second monolayer must travel over the loosely bonded, like-atom monolayer, which could quickly absorb the excess kinetic energy of the escaping atom. Such an atom would drop into the first pocket of excess volume (a "vacancy") encountered in the monolayer, placing more pressure on the monolayer to extend, but not extending the monolayer directly. In these simulations, we find that the precursor foot forms rapidly, but extends more slowly as it widens, indicating that the extension of the foot may occur by a random-walk of vacancies from the edge of the foot to the edge of the bulk droplet where they are filled by atoms from the droplet.

In our analysis of layering in the system, we find significant interlayer correlations in the liquid more than four layers deep, as shown in Figure 5. These correlations clearly show that these layers differ from bulk liquid, but did not elucidate the atomic interactions between the substrate and the liquid. For example, it has been shown that layering occurs in a Lennard-Jones vapor in contact with a hard wall where an external potential applied to all vapor atoms provides an effective vapor-substrate interaction [11] where there is no explicit correlation between vapor atoms and substrate atoms.

The Fourier transform (FT) of planar atomic positions also show correlations between the liquid and the substrate, as shown in Figure 6. The figure shows contour maps of the Fourier transforms of atomic positions in both the surface plane of the substrate and the first plane of the liquid. It should be noted that the major peaks appear in the same locations in both. Because the substrate correlations are greater, significant satellite peaks having a rectangular symmetry are seen in the substrate FT map that indicate the periodic boundaries of the MD cell. These correlations show that, on average, liquid atoms in the first layer above the substrate share a preference for the same symmetry as the atoms in the surface of the substrate. Both maps have the same numeric range (0.1 - 0.3), indicating that correlations in the first layer of liquid are significant with respect to the correlations in the surface layer of the substrate.

An illustration of the differences in spreading behavior caused by the use of a dynamic substrate is shown in Figure 7, where we see significant mixing of the Cu substrate atoms with the Ag-rich liquid. This observation agrees with the experimentally derived phase diagram for the Ag-Cu system. This system exhibits significant solubility of Cu in Ag-rich liquid and only limited solubility of Ag into Cu-rich solid at this temperature. [12] We find that there is significant layering into the liquid, exceeding that in the static substrate case, as shown in Figure 5. Also, we find significant Fourier space correlations in the dynamic substrate case, as shown in Figure 8. The numeric range (0.1 - 0.3) of the Fourier space correlation map for the first liquid layer shows surprisingly strong correlations for a liquid on a dynamic substrate. The double peaks in the Fourier space profile maps show that there are two domains of order on both the surface of the substrate and in the first layer of liquid. Figure 9 shows what appears to be edge dislocations in the surface of the substrate. Here, the top layer of the Cu substrate is modified by both the atomic substitution of Cu by Ag and the injection of vacancies from the Ag liquid. The resulting local strain is relieved by a random array of edge dislocations that locally remove or add planes of atoms. Overall, we observe that the dislocations cancel as required in a filled periodic space, where the sum of Burgers vectors over the periodic cell must be zero. Figure 10 shows the

dislocations in the first liquid layer. Because this layer does not completely fill the periodic cell, there is no requirement for a cancelling of dislocations. Here the major feature is a single, uncancelled, edge dislocation in the center of the liquid layer. Edge dislocations can interact elastically to become an array of dislocations equivalent to a low-angle "grain" boundary. Such a boundary effectively separates domains or "grains" having slightly different crystallographic orientation, as is visible in both the Fourier space profile maps of Figure 8 and the real space image of Figure 10.

Spreading Kinetics

A comparison of spreading kinetics gives an overview of system behaviors, as shown in Figure 11. In general, the systems with dynamic substrates had the highest rates of spreading. One may note that the spreading rates shown here are large compared to those seen experimentally. We see rates ranging from 100 m/s for the slowest spreaders to 500 m/s for the fastest spreaders. This discrepancy is probably due to the time and length scales at which we observe the process. We observe spreading in the regime where the equilibrium width of the precursor foot has not yet been reached. We expect that the precursor foot may initially grow very rapidly, as liquid atoms from the main drop escape and spread ballistically over the smooth surrounding substrate. This ballistic behavior is believed to be the cause of the large computed spreading rates. However, as the precursor foot forms, two things happen. First, atoms escaping from the drop can no longer travel ballistically as they leave the drop. An escaping atom either has to push an atom in the precursor foot outward or travel over it, both of which will likely absorb the escaping atoms' kinetic energies before the precursor foot is advanced. Secondly, the precursor foot is sufficiently well bound that ballistic escape from its edge is more difficult than directly from the liquid drop. The precursor foot then advances non-ballistically by, for example, slow incorporation of "vacancies" at the edge of the foot and subsequent diffusion of these "vacancies" to the edge of the liquid droplet, and this process slows as the precursor foot gets wider.

In addition, there is reason to believe that the dislocations seen in our computed structures exist in real solid-liquid interfaces and are glissile. If the slip process is assumed to occur within an effective thickness, δ , the strain rate in this region is approximated by

$$\frac{d\epsilon}{dt} = \frac{1}{\delta} \frac{dr}{dt} \quad (1)$$

where r is the droplet radius and t is time. If viscous behavior is assumed, we may also write

$$\frac{d\epsilon}{dt} = \frac{\sigma}{\eta} \quad (2)$$

where σ is shear stress and η is the effective viscosity in the correlated region of the solid-liquid interface. Thus, the wetting rate becomes

$$\frac{dr}{dt} = \delta \frac{\sigma}{\eta} \quad (3)$$

and if the shear stress is equal to the total wetting force [13] divided by the wetted area we find

$$\frac{dr}{dt} = 2 \frac{\gamma \delta}{\eta r} (\cos \theta_0 - \cos \theta) \quad (4)$$

where γ is liquid surface tension, θ_0 is the equilibrium contact angle and θ is the temporal contact angle. This expression for wetting rate is similar to that proposed by Tanner [14] and de Gennes [15]. If glide of the interfacial dislocations, shown above, controls the rate of wetting, the strain rate would be

$$\frac{d\epsilon}{dt} = b\rho v \quad (5)$$

where b is an effective Burger's vector, ρ the density of glissile dislocations, and v is the dislocation velocity. By assuming that this velocity is proportional to the shear stress, the viscosity can be shown to scale as $(b\rho)^{-1}$. Thus, conditions that induce the formation of interfacial dislocations will, in effect, reduce the effective viscosity and speed the wetting process.

Conclusions

We simulated the spreading of liquids on substrates in several metallic systems using both EAM and MEAM potential functions to study the atomistic processes involved in wetting. We analyzed the structures of the liquid droplets during spreading with use of visual images, layer correlations in the liquids, and in-plane Fourier space correlations of substrates and contacting liquids. These analyses showed varying degrees of correlation in the different systems. All systems showed layering in a liquid in contact with a substrate to varying degrees, while some systems also exhibited in-plane atomic correlations. Systems with in-plane atomic correlations between the liquid and the substrate tended to form a precursor foot, a monolayer of liquid atoms extending beyond the bulk of the drop, whereas systems without such correlations did not. Systems that formed such a precursor foot had enhanced spreading kinetics as compared to those that did not. It is concluded that the ability of a system to form such a foot determines the spreading kinetics of that system. A dynamic substrate also enhances spreading kinetics as compared to a static one.

In this work we have shown that, in certain systems, a region of high spatial correlation exists in the liquid near the solid-liquid interface. This correlated region is produced by mutual kinetic and potential interactions of the liquid and solid atoms. Dislocations and other defects were found in this region that may influence wetting kinetics by allowing a mechanism for slip of liquid over the substrate near the wetting line. A relationship for wetting rate and effective viscosity was derived based upon the existence of glissile dislocations. The derived wetting rate is nearly identical with that attributed to Tanner [14] and de Gennes [15] and the effective viscosity behaves in a reasonable manner. Careful study of the interfacial defects observed here may reveal important information on the nature of slip in wetting systems, but is beyond the scope of this study.

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References

1. K. Braake, *Experimental Mathematics*, **1**, 141 (1992).
2. F. M. Hosking, F. G. Yost, E. A. Holm, and J. R. Michael, *J. Elect. Mat.*, **25**, 1099 (1996).
3. V. E. B. Dussan, *Ann. Rev. Fluid Mech.*, **11**, 371 (1979).
4. P. Ehrhard and S. Davis, *J. Fluid Mech.*, **229**, 365 (1991).
5. W. D. Luedtke and U. Landman, *Phys. Rev. Lett.*, **77**, 569 (1994).
6. S. M. Foiles, M. I. Baskes, and M. S. Daw, *Phys. Rev. B*, **33**, 7983 (1986).
7. S. M. Foiles, *Phys. Rev. B*, **32**, 3409 (1985).
8. S. M. Foiles and J. B. Adams, *Phys. Rev. B*, **40**, 5009 (1989).
9. Y. Liu and P. Wynblatt, *Surf. Sci.*, **240**, 245 (1990).
10. J. P. Rogers, III, P. Wynblatt, S. M. Foiles, and M. I. Baskes, *Acta Mater.*, **38**, 177 (1990).
11. S. M. Foiles and N. W. Ashcroft, *Phys. Rev. B*, **25**, 1366 (1982).
12. T. B. Massalski, et al., *Binary Alloy Phase Diagrams*, 2 ed., ASM Intern., Materials Park, OH, 1990.

13. W. Y. Lau and C. M. Burns, *Surf. Sci.*, **30**, 497 (1972).
14. L. H. Tanner, *J. Phys. D*, **12**, 1473 (1979).
15. P. G. de Gennes, *Rev. Mod. Phys.*, **57**, 827 (1985).

Fig. D-1. The wetting angle of a liquid on a solid.

Fig. D-2. The usual boundary condition when solving the Navier-Stokes equations for liquid flow in contact with a solid is to set the liquid velocity at the liquid-solid interface to zero.

Fig. D-3. The simulation geometry used in these spreading simulations. The system is periodic in the horizontal plane, effectively simulating an infinite array of infinitely long lines on an infinite substrate plane. The dotted line on the edge of the substrate signifies the transition plane between the static and dynamic parts of the substrate.

Fig. D-4. Visual image of Ag spreading on a static Cu substrate. The appearance of a precursor foot at the edges of the spreading liquid is typical of spreading in all Ag on Cu and Au on Ni systems modeled with the "universal" EAM potentials.

Fig. D-5. Layer correlations in the liquids of the EAM systems.

Fig. D-6. In-plane Fourier space correlations for the Ag-Cu system in surface layer of substrate (a) and in first layer of liquid (b). Note the strong correlation between substrate and liquid.

Fig. D-7. Visual image of Ag spreading on a dynamic Cu substrate at 80 ps.

Fig. D-8. In-plane Fourier space correlations for the Ag-dynamic Cu system in surface layer of substrate (a) and in first layer of liquid (b). Note the strong correlation between substrate and liquid and the appearance of double peaks indicating two domains of ordering rotated with respect to each other.

Fig. D-9. Dislocations in the top layer of the Cu substrate in the Ag-Cu system. Note balance of dislocations required by periodic boundary conditions of the space-filling plane, i.e., the net Burger's vector for the entire plane is zero.

Fig. D-10. Dislocations in the first layer of Ag liquid in the Ag-Cu system. In this case, the plane does not fill the periodic dimensions, so a balancing of dislocations is not required. Note the relative tilt on opposite sides of the dislocation that gives rise to the double peaks in the FT maps.

Fig. D-11. The slopes of the line widths give the spreading kinetics of the various systems. Note the spike in the curve for the Ag on static Cu system that indicates temporary dewetting.

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W. L. Hermina	0826	9111
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