



KINETICS OF DIFFUSION-LIMITED SPREADING OF SESSILE DROPS IN REACTIVE WETTING

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Introduction

Recent sessile drop experiments on metal/ceramic systems (1,2) have shown that a sufficient condition for improving wetting of a given substrate by a given metal is to alloy the metal with a chemical species which reacts with the substrate to form a dense layer of solid reaction product that is better wetted by the metal than the original solid substrate (3). Such use of chemical reactions between liquid and substrate to promote wetting is frequent (4-7), and generally causes transitions with time in the wetting angle that is measured during a sessile drop experiment. Namely, when the metal drop is first formed on a solid substrate, it deforms rapidly, opposed only by viscous forces, to form an initial wetting angle θ_0 corresponding to the contact angle of the liquid on the original unreacted substrate surface; typically θ_0 is reached within 10^{-2} s for millimeter-sized molten metal droplets (8,9). Thereafter, the droplet spreads while the reaction between metal and substrate progresses, to reach a final stable value, θ_f . Spreading times as long as 10^2 to 10^4 s can be needed for θ to decrease from θ_0 to θ_f ; during this time, the rate at which the droplet spreads is determined not by viscous resistance, but by the rate of reaction product formation at the triple line, movement of which is arrested by the line of substrate material/reaction product contact along the solid surface. The macroscopically observed contact angle θ is then not related to capillary force equilibrium during spreading, but is instead dictated by the radius of the reaction product layer disk formed, and the droplet volume.

When the metal droplet is alloyed with a reactive species, or when interfacial reaction causes enrichment of the droplet with certain solute elements, two limiting cases can be envisaged for the rate of motion of the liquid/solid/gas triple line. In the first limit, local reaction kinetics are rate-limiting, and diffusion within the droplet is comparatively rapid (or non-existent when the droplet is made of the undiluted reacting species). If we restrict attention to cases where the reaction does not change significantly the global drop composition, there is no change in time in the chemical environment near

the triple line: then, the rate of reaction, and hence the triple line velocity, are constant in time. Constant triple line velocities have indeed been observed in several systems using sessile drop experiments: examples include the Al/C system (10), the CuSi/C system (11), CuAg-Ti on alumina at 950°C (12), Ni-P braze alloys on Fe-Cr substrates (13), and Au-Si alloys on SiC (14).

In the second limit, diffusion is rate-limiting: local reaction rates are comparatively rapid, and the extent of local reaction which drives spreading is limited by the diffusive supply of reactant from the drop bulk to the triple line. In contrast with the previous limiting case, the rate of isothermal spreading may then depend on time. Examples of time-dependent spreading rates are found with CuPdTi on alumina and silica substrates (1) and Cu-Ti on alumina (15).

We examine in this article this latter class of systems, focussing on the case where diffusion of only one reactive species to or from the triple line controls the rate of spreading.

Simplified Analysis of Solute Diffusion to the Triple Line

1-Assumptions

We consider a moving wetting front of a liquid binary alloy A-B, component B of which reacts with the solid substrate to form a solid reaction product. We assume that the reaction between B and the substrate is rapid upon initial contact of the liquid with the solid, leading to the rapid formation of a small thickness e of reaction product. Thereafter, the rate of reaction at the interface far from the triple line is assumed to be negligible, namely because of slow diffusion through the solid product layer of thickness e . Since spreading of the liquid requires further reaction at the triple line, spreading in turn requires transport of solute element B through the liquid to (or from) the triple line, Fig. 1.

We seek to calculate the rate of spreading of the droplet when this diffusion process limits motion of the triple line. We thus assume that, comparatively, local reaction kinetics are very rapid, such that the local solute concentration along the triple line equals the equilibrium concentration, C_e , in an A-B alloy contacting the reaction product at the temperature of the experiment. Therefore, during spreading, reaction proceeds at an appreciable rate only at the contact line, where the liquid has direct access to

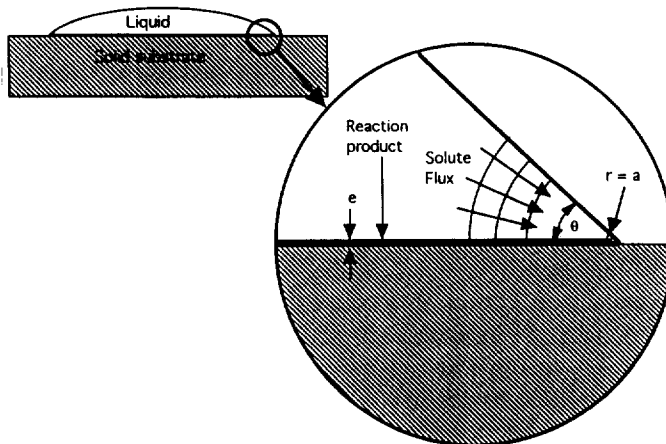


Figure 1. Schematic description of the advancing triple line driven by localized chemical reaction requiring solute diffusion in the liquid.

the solid: we assume that this “pseudo-steady state” has been reached, and do not treat the first transient of chemical interaction along the initial contact interface.

We assume that the experiment is isothermal, and that the liquid drop is sufficiently large for its bulk to be treated as an infinite medium with constant concentration C_o far from the triple line. We neglect the influence of curvature along the liquid/solid interface, and thus model the liquid region near the triple line as a straight wedge of angle θ , Fig. 1. In the liquid, solute is transported by convection and diffusion; the governing equation is Fick’s second law written in the referential of the moving contact line:

$$D \Delta C + \mathbf{u} \cdot \nabla C = \partial C / \partial t \tag{1}$$

where \mathbf{u} is the local velocity in the liquid.

We assume that, near the triple line, diffusion is the dominating mechanism for solute transport, and hence neglect the second term on the left-hand side of Eq. (1). This should be a reasonable assumption (16) when the diffusion problem envisaged takes place within a small volume of width $L \ll D/u$, corresponding to values of the solutal Peclet number $Pe = L \cdot u \cdot D^{-1} \ll 1$, where D is the diffusion coefficient in the liquid phase. For a particular alloy, the convective velocity \mathbf{u} in the liquid can be roughly estimated by the analysis in Ref. (17).

2-Derivation of the Solute Flux to the Triple Line

This diffusion problem is simply solved by noting that, with the above assumptions, both the liquid/solid and the liquid/vapor interfaces are no-flux lines from the standpoint of diffusion. Boundary conditions are then, in cylindrical coordinates (r, Φ) :

$$\text{at } r = a, C = C_e \tag{2}$$

$$\text{at } r \rightarrow \infty, C \rightarrow C_o \tag{3}$$

$$\text{at } \Phi = 0 \text{ and } \Phi = \theta(t), \partial C / \partial \Phi = 0 \tag{4}$$

where a is a (small) radius of volume along the triple line near the site of reaction where C can be taken equal to C_e , and $\theta(t)$ is the contact angle at time t . Parameter a is somewhat arbitrary, but is necessary for convergence of the solute profile near $r = 0$ (somewhat analogously to the strain field surrounding a dislocation, which can only be predicted using continuum elasticity up to a finite distance from the geometric dislocation line).

Having neglected all influence of convection on solute transfer within the liquid, according to boundary conditions (2) to (4), the concentration C in the liquid wedge near the triple line depends only on radial distance from the triple line, r . The concentration in the liquid is then given by analogy with the thermal conduction problem solved in Ref. (18). The solute flux at $r = a$ is thus approximately equal to:

$$D \left(\frac{\partial C}{\partial r} \right)_{r=a} = \frac{2(C_o - C_e) D}{a} \left\{ \frac{1}{\ln(4T) - 2\gamma} - \frac{\gamma}{[\ln(4T) - 2\gamma]^2} - \dots \right\} \tag{5}$$

for values of $T = D t a^2$ greater than 100, and where γ is Euler’s constant, equal to 0.57722.

Droplet Spreading Kinetics

Writing a mass balance at the triple line:

$$D\theta a \left(\frac{\partial C}{\partial r} \right)_{r=a} = en_{v,B} \frac{dR}{dt} \quad (6)$$

where $n_{v,B}$ is the number of moles of B per unit volume of the reaction product, concentration C is in moles per unit volume, and R is radius of the drop/substrate contact, we deduce:

$$2(C_o - C_e)\theta D \left\{ \frac{1}{\ln(4T) - 2\gamma} - \frac{\gamma}{[\ln(4T) - 2\gamma]^2} \right\} = en_{v,B} \frac{dR}{dt} \quad (7)$$

and by integration:

$$\int_{\frac{D_e}{a^2}}^{\frac{D_t}{a^2}} \left\{ \frac{1}{\ln(4T) - 2\gamma} - \frac{\gamma}{[\ln(4T) - 2\gamma]^2} \right\} dT = \frac{V^{1/3} en_{v,B}}{2(C_o - C_e) a^2} \int_{R(\epsilon)V^{-1/3}}^{R(t)V^{-1/3}} \frac{d(RV^{-1/3})}{\theta_{(RV^{-1/3})}} \quad (8)$$

where V is the droplet volume, ϵ is a time sufficiently long that Eq. (5) be a good approximation of the flux near the triple line, and R_ϵ is the contact perimeter radius at time ϵ . If a is sufficiently small, ϵ can be taken such that $R_\epsilon \approx R_o$, the initial contact perimeter at $t = 0$; otherwise, the full expression given in Ref. (18) for all T must be integrated. $\theta_{(RV^{-1/3})}$ is the contact angle corresponding to a given position of the triple line, R. Taking V to be constant (*i.e.*, assuming that $e \ll R$), R and θ are linked by (19):

$$\frac{3\sin^3(\theta)}{2 - 3\cos(\theta) + \cos^3(\theta)} = \frac{\pi R^3}{V} \quad (9)$$

Integration of Eq. (8) is eased considerably by noting that:

$$F(T) = \frac{1}{\ln(4T) - 2\gamma} - \frac{\gamma}{[\ln(4T) - 2\gamma]^2} \quad (10)$$

varies little with T for $T > 10^5$, Fig. 2. Knowing (i) that in liquids, D varies roughly between 10^{-8} and $10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$, (ii) that a must be on the order of a few atomic jumps in the liquid, typically 10^{-9} m , and (iii) that t will vary between 1 and 10^3 s in sessile drop experiments, T is expected to vary at most between $10^{18-8+3} = 10^{13}$ and $10^{18-9} = 10^9$. $F(T)$ is thus comprised between 0.05 and 0.03, a very small range of variation indeed, especially in light of the usual uncertainty that exists in system parameters such as D. Furthermore, for a given train of experiments, t will not vary by more than three orders of

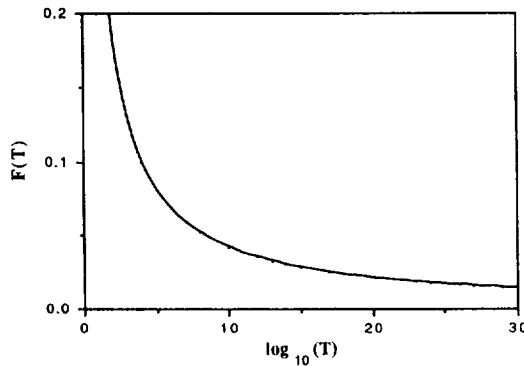


Figure 2. Plot of the function $F(T)$ defined in Eq. (10).

magnitude: $F(T)$ will thus with good precision remain constant over the course of a given series of experiments. Eq. (7) then becomes the very simple relationship:

$$\frac{dR}{dt} = \frac{2F(T)D}{en_{v,B}} (C_o - C_e)\theta \tag{11}$$

where $F(T)$ is now a constant close to 0.04. Knowing that the time ϵ required for T to exceed about 100 (and thus for Eq. (5) to be valid) is very short on the time-scale of a sessile drop experiment, and inserting Eq. (9), Eq. (8) becomes:

$$\frac{2F(T)D(C_o - C_e)t}{V^{1/3}en_{v,B}} = \int_{\theta_0}^{\theta} \frac{6\cos(\theta) - 3\cos^2(\theta) - 3}{(2 - 3\cos(\theta) + \cos^3(\theta))^{4/3}} \frac{d\theta}{\theta} \tag{12}$$

This expression has the additional advantage over Eq. (8) of removing the weak dependence on parameter α of the functional dependence of θ on time. It can be easily shown that for θ less than about 60° , Eq. (9) is closely approximated by:

$$\theta = \frac{4V}{\pi R^3} \tag{13}$$

Eq. (12) is then easily integrated, to yield:

$$R^4 - R_o^4 = \frac{2^{11/3}F(T)D(C_o - C_e)}{\pi^{4/3}en_{v,B}} Vt \tag{14}$$

Hence, in diffusion-limited reactive wetting, at small angles and with assumptions made above, plots of the difference in the fourth power of contact radius R versus the product of droplet volume V and

time t are predicted to yield a straight line. This behavior is to be contrasted with that found for reaction-kinetics limited spreading (R proportional to $V^0 t$), and that found at small θ for viscous spreading ($[R^{10} - R_0^{10}]$ proportional to $V^3 t$) (20).

Discussion

The main result from the present derivation is that the time-dependence of the unsteady diffusion process which limits the rate of spreading can be neglected: for all practical purposes, the diffusion-limited rate of motion of the triple line is independent of the time that has elapsed since initial contact of the fluid with the substrate. As a consequence, the spreading rate given by Eq. (11) depends, for a given system, essentially only on the configuration of the triple line or, in other words, only on the instantaneous contact angle θ .

At small r and large T , the solute concentration profile can with good precision be assimilated to the cylindrically symmetric steady-state solute distribution between $C = C_e$ at $r = a$, and $C = C_o$ at $r = b$, for which:

$$C = \frac{C_e \ln\left(\frac{b}{r}\right) + C_o \ln\left(\frac{r}{a}\right)}{\ln\left(\frac{b}{a}\right)} \quad (15)$$

As T increases, the value of b corresponding to the time-dependent solute distribution increases; at given T , the appropriate value of b is found by equating the solute flux at $r = a$ for both concentration profiles, to deduce $b = a \exp [1/F(T)]$. It is, then, clearly apparent why the solute flux to the triple line is essentially independent of time: as time increases, b increases slowly, and furthermore its value exerts little influence on the solute gradient near the triple line, given the logarithmic dependence of C on both r and b (calculation of the elastic energy surrounding a dislocation, results of which depends little on the value of the outer cut-off radius used in calculations provided realistic values are used, provides again a good analogy).

This steady-state approximation of the solute field near the triple line also provides a necessary condition for validity of the present calculation: the bulk of the drop must be little affected by diffusion near the triple line, and must retain a homogeneous concentration C_o , as was assumed. Estimating that the far-field boundary condition used is realistic if R exceeds b significantly, a necessary condition for validity of the present analysis in the absence of convection is that R exceed $10^4 a$. Taking $a \cong 1$ nm, the condition becomes $R > 10 \mu\text{m}$, which is always satisfied in classical sessile drop experiments. Also, if significant convection (for example due to gravity) is present in the droplet, its influence may be accounted for by appropriately reducing the value of b , as is done in the derivation of the Burton-Prim-Schlichter equation which is used to predict solute partition in crystal growth with convection in the melt (21).

Finally, we emphasize that many simplifying assumptions have been made in the present derivation, regarding in particular the shape of isoconcentrates, the role of convection near the triple line, and that of continued interfacial reaction behind the triple line: the latter two have been entirely neglected. In practice, some level of reactivity will often persist behind the triple line, and some deviations from the spreading laws derived here must to be expected in practical situations; however, we expect that the

functional dependence of spreading rate on contact angle only will be retained even though these assumptions are somewhat violated.

Conclusion

Simple laws are derived for the isothermal spreading of a sessile drop driven by liquid/substrate chemical reaction limited by solute diffusion to the triple line. It is shown that the spreading rate is independent of time and droplet volume, proportional to the contact angle, and linearly dependent on the droplet solute concentration. Exponents n and p in the relationship $R^n = K V^p t$ are shown to be 4 and 1, respectively, for $\theta \leq \pi/3$.

Comparison of these predictions with experimental data will be presented in a future publication.

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