

DYNAMICS OF BRAZE SPREADING

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Abstract—Fundamental studies of liquid flow provide a useful framework for analysing the spreading behaviour of brazes. Three stages can be distinguished by analysing kinetic data for the spreading of a reactive Ni–P braze over Fe–Cr workpieces. The first and last stages when the interfacial microstructure is relatively stable can be modelled by mathematical relationships developed to describe the flow of idealised non-reactive systems, while the intermediate stage can be related to the flow kinetics of active metal brazes over ceramics. We discuss the mechanisms responsible and argue that classification of kinetic behaviour could be of value in modelling other systems.

Résumé—Les études de base des écoulements liquides offrent un cadre utile pour l'analyse du comportement des métaux d'apport de brasage fort pendant leur diffusion sur les pièces à joindre. A partir d'une analyse des données cinétiques sur la diffusion d'un alliage réactif d'apport en Ni–P sur des pièces en Fe–Cr on a pu distinguer trois étapes de ce procédé. Le premier et le dernier de ces étapes, pendant lesquels la microstructure de l'interface est relativement stable, se laissent modeler par certaines relations mathématiques qui furent développées pour décrire l'écoulement de systèmes non réactifs idéalisés, tandis qu'on peut rattacher l'étape intermédiaire à la cinétique d'écoulement de métaux d'apport réactifs sur les matières céramiques. Les auteurs discutent les mécanismes qui sont à l'origine de ces observations, et proposent qu'une classification des formes de comportement cinétique pourrait être d'intérêt pour la modélisation d'autres systèmes.

Zusammenfassung—Grundlegende Untersuchungen der Strömung von Flüssigkeiten bieten einen nützlichen Rahmen zur Analyse des Ausbreitungsverhaltens von Hartlotzusatzmetallen an. Durch eine Auswertung der kinetischen Daten zur Ausbreitung eines reaktiven NiP-Zusatzwerkstoffes über zu fugende Teile aus Fe–Cr lassen sich drei Stufen dieses Vorgangs unterscheiden. Die erste und die letzte dieser Stufen, wobei die Gefüge der Phasengrenzfläche relativ stabil ist, können mit mathematischen Beziehungen modelliert werden, die zur Beschreibung der Strömung von idealisierten unreaktiven Systemen entwickelt wurden, während die Zwischenstufe kann mit der Kinetik der Strömung aktiver Zusatzmetalle über keramische Werkstoffe in Zusammenhang gebracht werden. Die Verfasser erläutern die zugrundeliegenden Mechanismen und stellen die Ansicht vor, daß zur Modellierung anderer Systeme eine Klassifikation der Arten kinetischen Verhaltens nützlich sein könnte.

1. INTRODUCTION

Spreading kinetics are important, or at least relevant, for such diverse technologies as brazing or soldering, lubrication, crop spraying, composite infiltration, painting and plasma spraying. Not surprisingly the technical literature contains both experimental descriptions and semi-empirical analyses, albeit often for physically or chemically complex systems. In contrast, most fundamental studies of wetting and spreading have been for simple liquids on smooth, inert substrates. Yet it is clear that fundamental studies have an important role in applied science, especially as a framework in which observations can be characterised or analysed.

In this paper we attempt to analyse observations for a complex reactive system in terms of relationships developed by fundamental studies. The results cited are largely observations of the flow of a Ni–P eutectic braze on substrates of Fe–Cr binary alloys. There is no doubt that the behaviour is more complex than that described in the standard theories: substrate

elements are dissolved into the braze and there is isothermal solidification at later stages, the surface is not ideally smooth, and so on. Yet the framework of theories like that of de Gennes [1] allows us to identify when the braze is behaving as a simple liquid and to characterise, if not yet to understand fully, the behaviour at other times.

2. MODELS OF SPREADING

There is general agreement that an imbalance of surface and interfacial energies is the main driving force for spreading. Gravity can be significant for large drops (typically when the square of the drop radius, $R^2 > \{\gamma/g \cdot \rho\}$ where γ is the surface energy, ρ the density, and g the acceleration due to gravity) though this is not believed significant in our experiments. Viscosity is presumed to be the main retarding force. This picture of flow driven by interfacial energies and limited by viscosity has been verified for the free flow of a wetting liquid in a horizontal

capillary, even in quite complex systems. For example, Latin [2] observed the expected relationships for lead-tin solder flow in tinned copper capillaries.

Expressions for the kinetics of spreading contain at least two components. One is geometric; for a droplet of known shape and constant volume, Ω , there is a relationship between Ω , R and the contact angle, ϕ ; other relationships can be obtained in terms of the height, h , of the droplet. Usually the shape is assumed to be a cap of a sphere, and we shall follow that view here. For small contact angles, the expressions reduce to the following

$$\Omega \approx \pi h R^2 / 2 \tag{1}$$

$$h \approx R \phi / 2 \tag{2}$$

$$\Omega \approx \phi R^3. \tag{3}$$

The second component concerns dynamics. We shall distinguish two main classes of behaviour. In Class I behaviour, the dynamics are determined only by unchanging liquid properties: viscosity, surface and interface energies, and by gravity or thermal effects when these apply. For Class II behaviour, however, chemical effects are involved: the liquid may react with the substrate, or it may dissolve species from the substrate so that the system changes during the spreading process. It is not always clear that the two classes are independent, yet recognising a distinction between non-reactive and reactive systems is often helpful in contrasting different systems or different regimes of behaviour.

2.1. Non-reactive (Class I) flow of liquid drops

Some approaches to non-reactive (Class I) flow behaviour attempt to analyse the velocity distribution within the drop, and hence to estimate the viscous drag explicitly. Thus the Yin [3] treatment of the spreading of a spherical cap lead to a prediction that, within appropriate limits, the drop radius varies with time approximately as $(t)^y$, with $y = 0.2$. The constant of proportionality is a simple multiple of the ratio $S_{(t)}/\eta$, with $S_{(t)}$ given by

$$S_{(t)} = \{ \gamma_s - \gamma_{LS} - \gamma_L \cos \phi_{(t)} \} \tag{4}$$

where γ_s is the solid surface energy, γ_{LS} is the liquid/solid interface energy and γ_L is the liquid surface energy. There is an additional factor depending on the drop volume

$$dA/dt = \{ (4\pi/\eta)(3\Omega/\pi)^{1/3} \} S_{(t=0)} I_{(t)} \tag{5}$$

where $I_{(t)}$ is a dimensionless integral and η is the viscosity. Experimental support comes from the data of Schonhorn *et al.* [4] for organic liquids flowing on aluminium, mica and teflon, which confirmed that the drops did remain spherical caps, and that the rates did scale with the ratio of drop surface energy to viscosity.

A quite different approach was followed by de Gennes [1], who took instead the empirical relationship found by Hoffman [5] for liquids pumped through a channel. The contact angle was distorted at high speeds, with an empirical relationship holding

$$U = C(\gamma/\eta)\phi^m \tag{6}$$

where C is a constant equal to 0.02 rad^{-3} and U is the velocity of the liquid front. The power term m lies in the range 3 ± 0.5 for values of liquid velocity (advance of droplet perimeter in our case) up to a few metres a second.

De Gennes assumed that the Hoffman relationship applied to the instantaneous contact angle, $\phi_{(t)}$, of droplets approaching their equilibrium shape. This yields the basic equations

$$dR/dt = (C\gamma/\eta)\phi^m = (C\gamma/\eta)\Omega^m R^{-3m} \tag{7}$$

$$R^{3m+1} = (3m+1)(C\gamma/\eta)\Omega^m t + G \tag{8}$$

$$\phi = \Omega \{ (3m+1)(C\gamma/\eta)\Omega^m t + G \}^{-3/(3m+1)}. \tag{9}$$

Note that if, at a given time when R has a particular value, m were to rise, then the spreading rate given by equation (7) would fall more rapidly. Similarly, if the constant of integration, G , is negligible, we can write

$$A = \{ \pi(3m+1)^{2/(3m+1)}(C\gamma/\eta)^{2/(3m+1)} \} (t)^n \cdot (\Omega)^p$$

where A is the contact area, $n = 2/(3m+1)$ and $p = 2m/(3m+1)$. Experimental values of n equal to 0.20 have been reported by Summ *et al.* [6], of 0.22 by Hyppia [7], of 0.21 by Tanner [8] and of 0.16 to 0.32 by Lelah and Marmur [9], as compared to the predicted 0.2 when m is 3. Similarly, the experimental results of Lelah and Marmur indicate a volume power, p , of $2/3$ close to the predicted 0.6.

2.2. Reactive (Class II) flow of liquid drops

The modelling of reactive (Class II) behaviour is less well developed. However a look at recent published experimental data for the spreading of reactive alloys on ceramics (Tomsia *et al.* [10] for Si_3N_4 , and Kritsalis *et al.* [11] for Al_2O_3) shows that the power-law behaviour of Class I flow, equation (9), is not applicable. Instead, we find that their data, Fig. 1, can be fitted empirically by an exponential form

$$(\phi - \phi_\infty) = \text{Const} \times \exp(-t/\tau) \tag{10}$$

which, for a spherical cap, implies that

$$R_{(t)} = \text{Const} \times \exp(+t/3\tau) \tag{11}$$

where ϕ_∞ is the stable contact angle value assumed after a long time. Clearly the R dependence cannot be valid at long times, when the assumption of a spherical cap will surely fail. Yet the exponential rule is sensible for use over limited time ranges, for which a

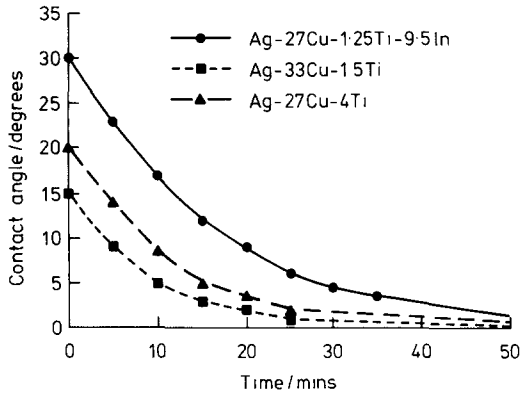


Fig. 1. Si_3N_4 wetting data of Tomsia *et al.* [10]. The data can be described by an exponential decay to respectable accuracy.

single characteristic time (τ) is appropriate even though there is no guidance as to the process responsible.

The brazes used by Tomsia *et al.* [10] that wetted fully ($\phi_\infty = 0$) contained Ti as the reactive component. Their contact angles fell exponentially with time, with a τ value of 16 min characterising the data for a Ag-27Cu-9.5In-1.25Ti alloy and of 12 and 10 min characterising those for Ag-33.5Cu-1.5Ti and Ag-26.7Cu-4.5Ti alloys. Similar analysis of the data of Kritsalis *et al.* [11] for the partial wetting of Al_2O_3 by Cu-7.5Ti using a ϕ_∞ of 25° yielded a τ of 0.6 min. Thus the exponential relationship is not restricted to fully wetting systems, and there is some evidence that τ values are a function of braze reactivity.

3. EXPERIMENTAL OBSERVATIONS OF Ni-P FLOW ON Fe-Cr SUBSTRATES

The data were taken from experimental observations of braze flow using a small evacuable hot stage chamber fitted to an optical microscope. Details of the method are reported elsewhere (Ambrose *et al.* [12]). Briefly, small discs of Ni-11P braze foil with a radius of 0.5 mm and a thickness of 0.038 mm were melted on polished substrate coupons of Fe-10Cr,

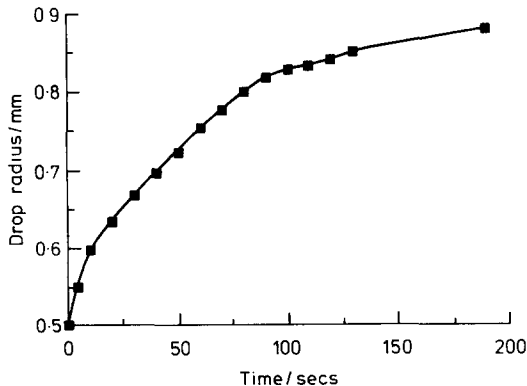


Fig. 2. Radius of a circular drop of Ni-11P braze on Fe-20Cr at 930°C [13].

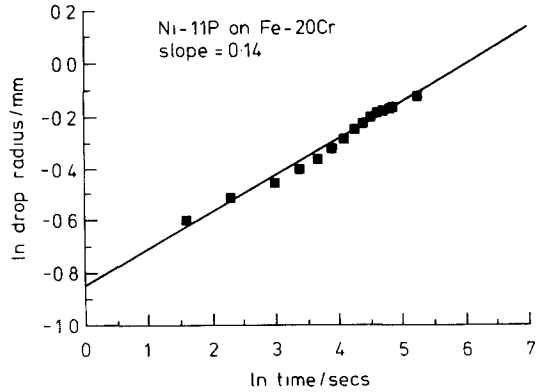


Fig. 3. Log-log plot of the Fig. 2 data. There are systematic trends from simple linear behaviour.

Fe-15Cr and Fe-20Cr and held at a constant temperature higher than the 880°C at which the braze melts. The samples were viewed from above the magnification of about $100\times$ using the microscope optics. This permits direct measurement of the radius of the drop as a function of time, as well as a detailed view of the effects of roughness, surface oxide films, and other complexities. These data have been reported in detail elsewhere (Ambrose [13]), but the principal observations can be summarised:

(i) The melting of the Ni-P braze was rapid, occurring in less than 0.04 s. Clearly the first few measurements were influenced by melting dynamics and the ramping to the experimental temperature, but the main part of our data was unaffected. The shortest time for which reproducible data can be measured approached 5 s.

(ii) The surfaces of the Fe-Cr substrates were initially covered by oxide films which prevented metal-metal contact. As the experiments continued, so these oxide films were undermined and the braze advanced to approach its equilibrium configuration. There were no optical signs of a precursor film advancing ahead of the bulk of the braze.

(iii) The initial contact angle assumed by the molten braze was about 0.25 rad, but this decreased progressively to a value approaching zero. The spreading rate defined by dR/dt was at first similar for all the Fe-Cr substrates but decreased with time, Fig. 2. Experimentally determined instantaneous rates slowed from about $10\ \mu\text{m/s}$ after a few seconds to about $0.1\ \mu\text{m/s}$ after 10 min or more. The decreases were most marked for the Fe-20Cr substrate. These rates temporarily increased if some physical impediment to spreading such as a groove in the substrate surface parallel to the braze front was overcome, and decreased dramatically with the onset of isothermal solidification.

(iv) Microstructural examination showed that the substrates were eroded and chemical analyses showed that Cr and Fe dissolved in the braze from the substrate, but braze elements were not taken into the substrate. One effect of this was to increase the

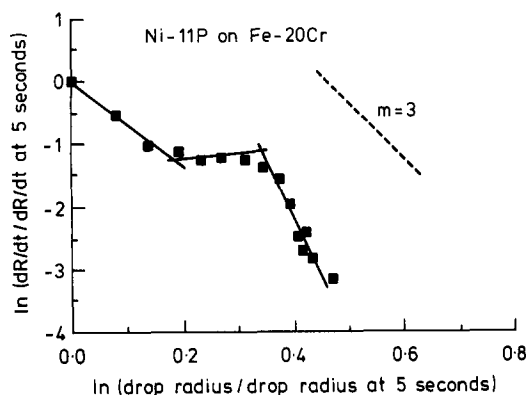


Fig. 4. Test of the de Gennes model, our equation (12). Note that the initial and final regions behave broadly similar to that given by Hoffman and by de Gennes. The central section, apparently anomalous, is fitted by a small negative value of m .

volume of the liquid drop progressively with spreading until the onset of resolidification.

(v) The braze resolidified at the constant experimental temperature, typically in the range of 920 to 950°C. This was related to the uptake of Cr and Fe. The braze drops prior to the onset of solidification were typically 2 to 4 mm in diameter and 0.02 mm deep at their centres. The diffusion constant, D , for a solute in a liquid metal is typically $10^{-8} \text{ m}^2 \cdot \text{s}^{-1}$, so that diffusion distances, $\sqrt{(Dt)}$, of 0.1 mm in 1 s are possible, i.e. all of the droplet should be affected rapidly by the changes in composition.

(vi) Resolidification of the braze did not stop spreading completely; slow spreading occurred by spilling over the top of the solidified edge.

4. ANALYSIS OF BRAZE FLOW; TIME DEPENDENCE OF R AND dR/dt

The simplest empirical description of the Ambrose data for the flow of a Ni-P braze on Fe-Cr substrates is obtained by plotting $\log R$ vs $\log t$. If the description of Yin [3] holds, the slope should be 0.2, while according to the de Gennes analysis the slope will be 0.1 if the constant of integration, G , in equation (8) is negligible and the power term m is equal to 3. On the other hand, if there is reactive Class II flow, we would expect a non-linear log-log plot. Experimentally, we obtain approximately linear plots with slopes of 0.13–0.16 from log-log plots of flow data for the Ni-P braze on Fe-Cr substrates as illustrated in Fig. 3. However, the plots are not perfectly linear but have characteristic curvatures, suggesting complicated behaviours.

To analyse the braze flow data we follow first the ideas of de Gennes [1] and of Hoffman [5] for non-reactive systems using equations which implicitly assume perfect wetting, that ϕ_∞ is 0° . This seems reasonable for a metal-metal system and in specific accord with observations for systems with a high degree of mutual solubility such as Fe-Ni. There are

in fact two quite different ways to apply the ideas of de Gennes and Hoffman, both of which could shed some light on the type of behaviour, if not the underlying mechanisms at an atomic scale. The first way is to assume changes with time are due to changes in the phenomenological parameter m , perhaps because the character of the liquid flow pattern is altering. The second way is to assume that it is some material property, like the braze viscosity or surface energy (or V^* , the ratio of γ/η), which varies with time as substrate dissolution proceeds.

Finally we test the applicability of the Class II reactive flow relationships to a stage of the braze flow that cannot be described adequately by the de Gennes and Hoffman relationships.

4.1. Approach I: Class I flow with time dependent “ m ” values

This approach is presentational, rather than associated with a specific interpretive model. It allows us to identify where, if at all, the de Gennes analysis appears to be valid. We start from the differential form of equation (7), rewriting it as

$$\ln(dR/dt) = a + s \ln(R) \quad (12)$$

so that the slope s is equal to $-3m$, and the term a , equal to $\ln(C\gamma/\eta) + m \ln \Omega$, is treated as a constant—which it will be for an inert system. The slope at time t gives a snapshot of the value of m .

For each substrate the behaviour is qualitatively similar, with differentiation of braze flow behaviour into three stages being particularly marked for flow on Fe-20Cr substrates as illustrated in Fig. 4. In this plot the instantaneous values of R and dR/dt are normalised using 5 s data because of experimental uncertainties about the zero time values. There is first a region of high slope (relatively large m), a flat region (m apparently close to but somewhat less than zero) and then a return to a larger value of m . The initial and final stages have slopes equivalent to m values of approximately 2.5 and 4.5 rather than the

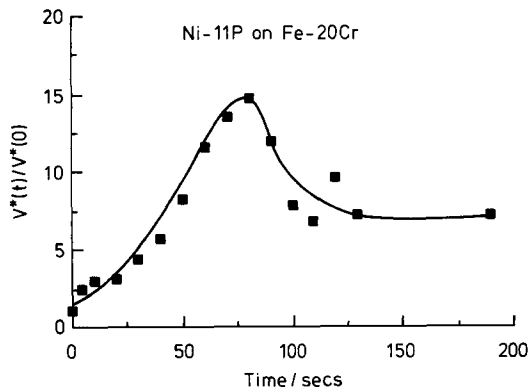


Fig. 5. Test of the de Gennes model, our equation (13). This fit (with $m = 3$) would imply a massive decrease in viscosity until about 80 s. Such a change is implausible. Merely choosing another value of m does not avoid the problem.

3 predicted by the de Gennes model. These discrepancies may reflect the complex role of the hidden Ω term in equation (12); $\Omega_{(t)}$ increases during the first stage due to dissolution of the substrate, so that m must be smaller to keep a as a constant. In contrast, $\Omega_{(t)}$ decreases from an initially large value during the final stage as the molten braze isothermally resolidifies, so that m must be more than 3 to keep a as a constant.

Thus the two regimes of simple behaviour occur when the braze composition is as yet not significantly changed by substrate dissolution, and when the melt has an unchanging saturated composition. The middle low m section then could relate to the production of a new phase at the braze/substrate interface.

4.2. Approach II: Class I flow with time dependent viscosity and surface energy values

The second approach again uses the differential form of equation (7), but puts all the anomalies of behaviour into a time dependence of the braze property V^* , the ratio (γ/η)

$$V_{(t)}^* = V_{(0)}^* \{R_{(t)}^{-3m} dR_{(t)}/dt\} / \{R_{(0)}^{-3m} dR_{(t=0)}/dt\}. \quad (13)$$

The power term m is held constant at a value of 3. Smaller values of m lead to more constant values of V^* , but the qualitative features change little. We note that the $t = 0$ value of V^* appears to be a property of the braze alone, with no dependence on the substrate, in accord with the experimental observation of Ambrose [13] that the initial spreading rates are similar for a range of Fe–Cr substrates. Whether the observations of Ambrose are in quantitative agreement with the predictions of the de Gennes model cannot be tested because there seems to be no measurement of surface energy for Ni–11P. However, one might guess a value of 1.5 J/m², somewhat less than that for Ni at its melting point (1455°C) of 1.78 J/m² [14], since Ni–11P has a lower melting temperature (880°C). The viscosity of Ni–11P at its melting point is 15 mPa · s [15], so the value of $V_{(0)}^*$ is about 100 m · s⁻¹ and the predicted instantaneous velocity of the drop periphery— U in equation (6)—is about 30 mm · s⁻¹ at zero time.

Qualitatively what emerges from this analysis is a striking time dependence of V^* , Fig. 5. Accounting for the observed changes in the instantaneous spreading rates requires large variations in V^* , in the viscosity or surface energy of the braze. In particular, V^* needs to increase 15 times to account for the instantaneous spreading rate on Fe–20Cr after 80 s at temperature if the power term m is assumed to remain equal to 3. There is then an apparent slowing that probably begins as isothermal solidification starts and a gradual fall that continues until the experiment ends. While these variations in V^* satisfy the arithmetic requirements, there is no experimental evidence or theoretical basis for expecting such dramatic changes in surface energy or viscosity values.

4.3. Approach III: Class II flow of reactive systems

Here we test the extent to which Class II reactive flow behaviour can describe the anomalous intermediate stage of braze flow behaviour illustrated in Fig. 4 when m is apparently slightly less than zero. Differentiation of the empirical equation (11) leads to the conclusion that dR/dt is proportional to R , a conclusion that can be reached also by using the de Gennes model, equation (7), provided m is $-1/3$. The middle portion of Fig. 4, therefore, has behaviour similar to that displayed by the data of Tomsia *et al.* [10] and Kritsalis *et al.* [11] for the spreading of chemically reactive alloys on ceramic substrates. The exponential behaviour, equation (10), may well be typical of a broader class of spreading liquids where reactions occur with the substrates.

While it is not clear exactly what is happening, for the systems used by Tomsia *et al.* and Kritsalis *et al.* there appears to be a single characteristic time and a single process, presumably controlled by chemical reaction or subsequent diffusion. In the case of the Ambrose data, matters are more complex. No doubt particular time intervals could be fitted to a similar exponential, but this would not necessarily add value or insight. Nevertheless, even in the more complicated system, we see only two distinct regimes of behaviour.

5. CONCLUSIONS

1. The fundamental theories of wetting dynamics give a useful reference case for comparison, as well as providing a helpful framework when analysing the behaviour of real and complex systems.
2. Even for complex systems, there are some regions for which the simple (Class I) behaviour is observed, e.g. the initial and final stages of braze spreading observed by Ambrose [13].
3. The time dependent characteristics of reactive spreading (Class II behaviour) implies effects of composition changes on dynamics. It also shows that the spherical cap model must fail, so that there is a need to measure drop shape (or at least the contact angle) as well as the drop radius.
4. Variations in the power term m in equation (6) rather than the braze specific ratio of the surface energy to viscosity, V^* , can account more easily for experimental observations of Ni–P braze flow. This implies that two differing mechanisms, Class I and Class II, can describe the different stages of braze spreading as the interfacial and liquid chemistries change.
5. Even the complex spreading phenomena after the onset of isothermal solidification are more easily characterised by application of the fundamental analyses, which suggest that the remaining braze has reached a steady state composition and once more behaves like a simple liquid.

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