DYNAMICS OF LIQUID DROP SPREADING IN METAL–METAL SYSTEMS

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Abstract—This paper analyses the observed spreading kinetics of drops of a Ni–11P braze and of copper on metal substrates. The observed spreading rates were initially fast but decreased progressively in accord with the de Gennes model in which a surface energy driving force is balanced by a viscous impedance. However, the observed spreading rates depended on the chemistries of the substrates and were usually far slower than those predicted by the de Gennes model. It is suggested that these discrepancies are due to the reactivity of the systems and a concentration of the viscous damping in narrow regions adjacent to the braze/substrate interfaces.

Résumé—Cet exposé présente une analyse de la diffusion superficielle observée de gouttes d'un métal Ni–11P d'apport pour brasage fort, et de gouttes de cuivre, sur des substrats métalliques. On constate une diminution progressive des taux de diffusion qui est conforme au modèle de Gennes, selon lequel une force mortrice d'énergie superficielle se trouve équilibrée par une impédance visqueuse. Cependant les taux de diffusion observés ont varié en fonction de la chimie du substrat, étant pour la plupart beaucoup plus faibles que ne prédict ce modèle. Les auteurs suggèrent que ces différences résultent de la reactivité des systèmes et d'une concentration de l'amorttissement visquex en regions étroites contiges aux interfaces substrat–métal d'apport.

Zusammenfassung—Im vorliegenden Beitrag wird die beobachtete Ausbreitung von Tropfen eines Ni–11P-Hartlot-Zusatzmetalls un Kupfertropfen auf metallischen Unterlagen analysiert. Eine fortschreitende Abnahme der Ausbreitungsraten wird festgestellt, und zwar in Übereinstimmung mit dem Modell von de Gennes. wonach eine Oberflächenenergie-Triebkraft und eine viskose Impedanz sich ausgleichen. Dagagen waren die beobachteten Ausbreitungsraten von der Chemie der jeweiligen Unterlagen abhängig und Grösstenteils viel neidriger als diejenigen, die das de Gennes'sche Modell vorhersagt. Die Verfasser schlagen vor, dass diese Unterschiede ihren Ursprung in der Reaktivität der Systemen und in einer Konzentration der viskosen Dämpfung in begrenzten Beriechen neben den Grenzflächen zwischen Unterlage und Zusatzmetall haben.

1. INTRODUCTION

The wetting behaviour of drops of liquid metals on solids is an important aspect of brazing, soldering, plasma spraying, composite infiltration and other technologies. Both the kinetics of wetting—the rate at which the drop spreads across a solid surface—and the ultimate, or equilibrium, extent of wetting are of practical importance. Equilibrium wetting behaviour has been studied and modelled for a wide range of systems, but models for the kinetics of spreading are a recent development. The approach adopted in analysis of spreading kinetics is exemplified by the de Gennes model [1] which describes the spreading of an inert sessile drop on a smooth and perfectly wetted substrate as a balance between a surface energy drive and a viscosity impedance. This leads to the relationship

$$R_t^{3m+1} = (3m + 1)(C\gamma/\eta)(4/\pi)^m \Omega^m t + R_0^{3m+1} \quad (1)$$

where R_t is the radius of the drop at time t, and R_0 the radius at $t = 0$, γ is the surface energy of the liquid, η is the liquid viscosity, and Ω is the volume

of the liquid drop. The term m lies in the range 3 ± 0.5 and C is a constant equal to 0.02.

One of the authors (Ambrose [2]) has made extensive measurements of the spreading kinetics of a reactive system, drops of Ni–11P braze on iron–chromium substrates, and all three present authors [3] have examined the application of the de Gennes relationship, equation (1), to the spreading of Ni–11P on Fe–20Cr substrates. This spreading displayed a complex three stage behaviour. The initial spreading followed the form of the de Gennes relationship with a deduced m value of approximately 3. Later in the spreading process there was a transitory departure from the form of the de Gennes relationship when the system microstructure was changing due to chemical reactions at the braze–substrate interface. During this stage, the drop radius vs time data were similar to those observed experimentally for reactive brazes spreading on ceramic substrates. Once the system had reverted to a stable microstructure by virtue of having a completely converted interface, the form of the de Gennes relationship was again followed. Flow then

continued until the drop resolidified isothermally due to dissolution of the substrate and consequent dilution of the melting point depressant, phosphorus.

While this analysis of the spreading of the nickel braze on Fe–20Cr substrates showed that the de Gennes relationship applied when the system was microstructurally stable, the actual rates of spreading were far slower than those predicted because, it is thought, the viscosity was not the only factor to impede spreading. Thus for drops of Ni–11P braze spreading on iron–chromium substrates, it is necessary for the advancing braze front to remove unwetted or poorly wetted oxides from the substrate surface. This was achieved by progressive dissolution of the substrate at the braze periphery to undermine the oxide films and disperse them by floating away up the surface of the braze drop.

The aim of the work reported in this paper is to determine whether the de Gennes relationship can be used to describe the *initial* spreading behaviour of other liquid metal–solid metal systems for which experimental data are available or were determined for this specific purpose. These include the spreading of drops of Ni–11P braze on other iron–chromium substrates and also of copper on nickel or tungsten.

2. EXPERIMENTAL METHOD AND OBSERVATIONS

The observations of the liquid metal drops spreading out on their substrates were made directly using a small evacuable heating chamber fitted to the stage of an optical microscope. The details of this method are reported elsewhere [2]. In brief, a small disc of braze foil, usually 1.0 mm in diameter and 0.038 mm thick, was melted on a polished substrate, 5 mm in diameter and 0.5 mm thick, positioned on a stainless steel anvil in which was buried a thermocouple. The samples were heated to and held at a constant temperature higher than that needed to melt the metal foil. For each individual experiment, the temperature quoted is that recorded by the thermocouple and maintained once the metal foil had melted. This stable temperature was 930–1010°C for Ni–11P on iron–chromium substrates, 1020°C for Ni–11P on nickel, 1100°C for copper on nickel and 1140°C for copper on tungsten. Since the heating rate was ap-

proximately 0.8 K s^{-1} (50 K min^{-1}), the temperature of the molten sample was rising—or at least the temperature of the buried thermocouple was rising—during the early stages of spreading. However, the rate of heating was similar for each experiment so that the kinetics of spreading for the individual experiments can be compared.

The samples were heated in a vacuum, the pressure being 2×10^{-6} mbar at the start of the experimental run and never rising to more than 1×10^{-5} mbar at any time during an experiment. The samples were viewed from above usually at a magnification of 100 times. The microscope images were also video-taped to enable measurements of the radius of the liquid metal drops to be made later with an accuracy of about $\pm 5 \mu$m. Not all the liquid drops remained circular as they spread out, in which case measurements were made of the advance in a specific radial direction.

The experimental observations made for individual systems are described below and some characteristics are summarised in Table 1. Certain aspects of the behaviour observed were common to all the systems:

(i) Melting of copper and of the Ni–11P braze was almost instantaneous;
(ii) The spread drops were initially circular and had smooth peripheries, but these ideal features were lost later in some systems;
(iii) Spreading ultimately ceased, and in chemically reactive systems this was associated with isothermal resolidification;
(iv) Most spreading was achieved before the onset of isothermal resolidification.

2.1. Ni–11P on iron–chromium substrates

The Ni–11P discs melted within 0.02 s and the radii of the molten drops increased on average during the first 10 s after melting by 50 μm on a Fe–20Cr substrate and by 58 μm on a Fe–15Cr substrate. These initial spreading rates slowed progressively, Fig. 1, while the drops expanded over the substrate surfaces as near perfect circles with smooth peripheries until isothermal resolidification ended the first

Table 1. Summary of experimental observations

| System	Stable temperature (°C)	Experiment duration (s)	Onset of resolidification (s)	Radius at onset (mm)	Final radius (mm)
Cu on Ni	1100	500	30	0.54	0.55
Ni–11P on Fe–20Cr	930	500	120	0.84	0.90
Ni–11P on Fe–20Cr[a]	1010	500	87	0.58	0.68
Ni–11P on Fe–15Cr	985	900	125	0.83	1.10
Ni–11P on Fe–10Cr	955	1000	240	1.22	1.34
Ni–11P on Fe–5Cr	990	1300	440	1.42	1.68
Ni–11P on Fe–2Cr	975	1500	685	1.57	1.62
Cu on W	1140	500	—	—	0.61
Ni–11P on Ni	1020	7900	7000	1.56	1.58

[a] 0.6 mm diameter disc.
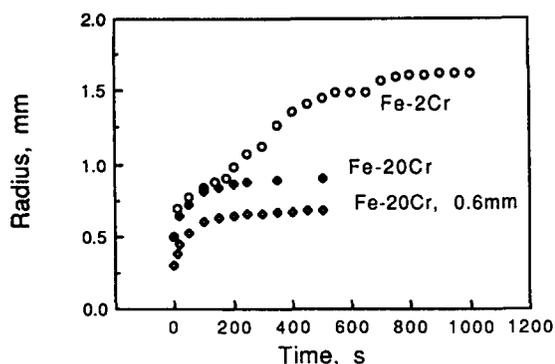
Fig. 1. Radii of drops of Ni–11P on iron–chromium substrates.

stage of spreading after 120 s for Fe–20Cr substrates and 125 s for Fe–15Cr substrates.

Decreasing the chromium contents of the substrates to less than 15% accelerated the spreading of the Ni–11P drops. However, decreasing the chromium contents also distorted the spreading process due to effects caused by grain boundary grooving. The grain sizes were larger for low chromium substrates—60 μm on average for Fe–2Cr substrates as compared to 20 μm for Fe–10Cr substrates—and grain boundaries emerging at substrate surfaces formed deeper grooves as they assumed equilibrium configurations at the high temperatures used in our experiments. Grooves oriented normally to the advancing braze fronts provided easy routes for liquid flow, while those approximately parallel to the fronts impeded flow in the later stages of spreading when the molten drops were very shallow, as illustrated in Fig. 2. The effect of this was to produce a jerky advance in any one radial direction as illustrated in Fig. 1.

Spreading on all the iron–chromium substrates ultimately stopped because of isothermal resolidification which was first observed at the drop peripheries, Fig. 2. The data in Table 1 show that the onset of this resolidification occurred after shorter times as the chromium contents of the substrates were increased or the volume of the braze drop was decreased.

2.2. Ni–11P on nickel

In this system, liquid drop spreading progressed at appreciable rates for about 800 s, to cause a tenfold increase in area, but spreading thereafter was negligible. The liquid braze drop was circular in shape and its edge was smooth for the first minute of spreading. After this, however, the edge of the braze drop became irregular because of the effect of grain boundary grooving of the substrate surface. The overall effect of the grain boundary grooving was to cause the advance of the liquid front to be jerky, as can be seen in a plot of one radial direction in Fig. 3. Some evidence of isothermal resolidification of the braze was observed with this substrate after about 7000 s, but it was not initiated at the drop edge.
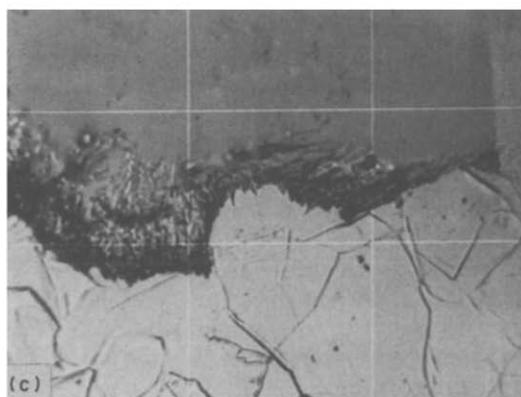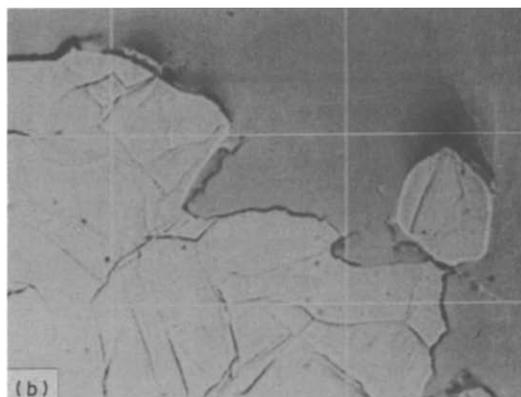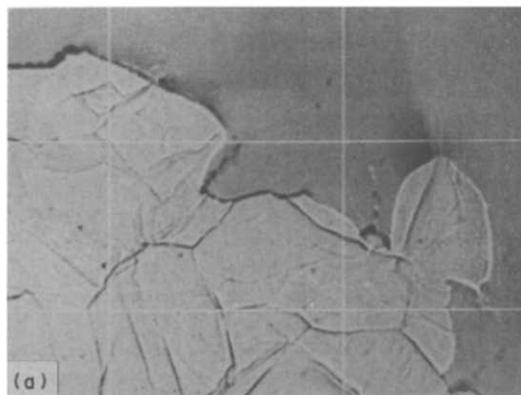

Fig. 2. Video frames showing the spreading of drops of Ni–11P braze on Fe–2Cr substrates. The magnification is 176X. (a) 100 s after melting. (b) 130 s after melting. (c) 1000 s after melting.

2.3. Copper on tungsten or nickel

In contrast to the Ni–11P/nickel system, spreading in the copper–tungsten system was over in a few seconds and the extent of spreading was modest. Most of the increase in the drop radius occurred in the first 0.5 s after melting and ceased after about 11 s, see Fig. 4. There was no evidence of isothermal resolidification of the copper before the run was ended 500 s later.

The spreading of copper on nickel was even less than that on tungsten; the drop radius was only 0.536 mm 50 s after the copper had started to melt on
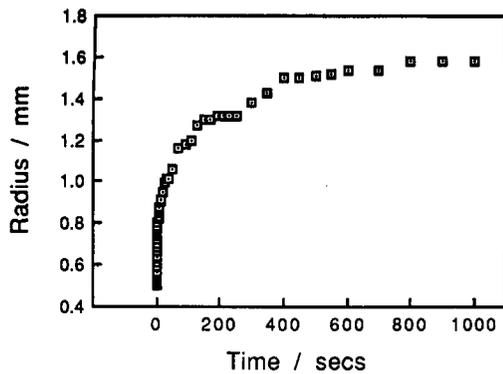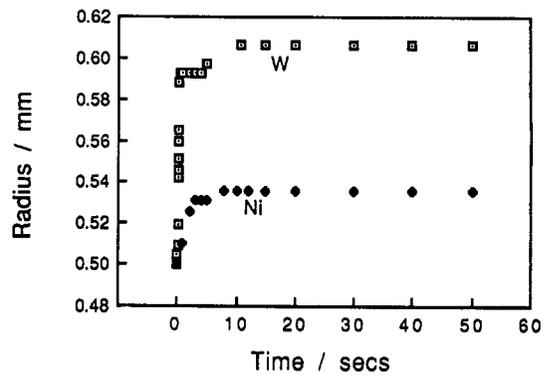
Fig. 3. Radius of a drop of Ni-11P on nickel.

Fig. 4. Radii of drops of copper on nickel and tungsten.

the nickel as compared to 0.606 mm for copper on tungsten. The rate of spreading of the copper was slower on nickel than on tungsten, Fig. 4, and spreading stopped because the copper started to resolidify. This resolidification started to occur at the edge of the drop and first became apparent 30 s after melting began.

3. EXPERIMENTAL DATA ANALYSIS

The experimental data for the initial spreading have been analysed to determine how well they fit the de Gennes model which predicts a radius time dependence of the form

$$R^{3m+1} = Kt + R_0^{3m+1}. \qquad (2)$$

In these analyses, it has been assumed that the power term, m, is equal to 3; de Gennes deduced that m could range from 2.5 to 3.5 so the mid-point value was chosen. In fact, curve fitting the experimental data for the early stages of spreading gave m values in the range 2.3–3.14, Table 2. Assuming m is indeed 3 for all the data sets, however, enabled direct comparisons to be made between data sets for the rate constant, K.

A summary of the experimental data analyses are shown in Table 2. Two values of K are quoted for each system; a measured value, K_m, and a predicted

value, K_p. The measured values were determined using the experimental data characterising spreading prior to the onset of isothermal resolidification or evidence of grain boundary groove effects, and Fig. 5 shows that for Ni-11P on nickel, for example, the fit of experimental data by a curve generated using the de Gennes relationship with $m = 3$ and $K = K_m$ is reasonable.

The predicted values of K were calculated using the de Gennes relationship so that

$$K_p = (3m + 1)(C\gamma/\eta)(4/\pi)^m \Omega^m. \qquad (3)$$

As already stated, m was taken as 3 and C was equated to 0.02, following de Gennes. The volume of the drop was taken as that of the solid foil disc multiplied by a factor of 1.038 to allow for expansion on melting [4]. Literature values for the viscosity of copper and Ni-11P (4.34 × 10⁻³ Pa s and 15 × 10⁻³ Pa s respectively) and for the liquid surface energy for copper (1.3 J m⁻²), were used [4, 5]. The liquid surface energy for Ni-11P is not available but a value of 1.5 J m⁻² was taken as being reasonable [3].

The ratio K_m/K_p in Table 2 shows the relative sizes of the measured and predicted values of K for each system and hence is a measure of how close the experimental spreading rates were to those predicted by the de Gennes relationship. This ratio varied from 7.4 × 10⁻⁵ for copper spreading on nickel to 0.041 for Ni-11P spreading on nickel.

Table 2. Values of the spreading rate constant K. K_p is the predicted value derived using equation (3) and K_m is the measured value

| System	Stable temperature (°C)	Best fit (m)	K_p, (m¹⁰s⁻¹) (× 10³⁰)	K_m, (m¹⁰ s⁻¹) (× 10³⁰) if $m = 3$	K_m/K_p
Cu/Ni	1100	2.30	4.35	3.22 × 10⁻⁴	7.4 × 10⁻⁵
Ni-11P/Fe-20Cr	930	2.41	1.45	4.68 × 10⁻⁴	3.2 × 10⁻⁴
Ni-11P/Fe-20Cr[a]	1010	2.72	0.066	0.13 × 10⁻⁴	1.9 × 10⁻⁴
Ni-11P/Fe-15Cr	985	2.36	1.45	5.19 × 10⁻⁴	3.6 × 10⁻⁴
Ni-11P/Fe-10Cr	955	2.71	1.45	4.13 × 10⁻⁴	2.8 × 10⁻⁴
Ni-11P/Fe-5Cr	990		1.45	5.96 × 10⁻⁴	4.1 × 10⁻⁴
Ni-11P/Fe-2Cr	975	3.14	1.45	21.0 × 10⁻⁴	1.4 × 10⁻³
Cu/W	1140	2.45	4.35	89.9 × 10⁻⁴	2.0 × 10⁻³
Ni-11P/Ni	1020	2.49	1.45	603 × 10⁻⁴	4.1 × 10⁻²

[a]0.6 mm disc.
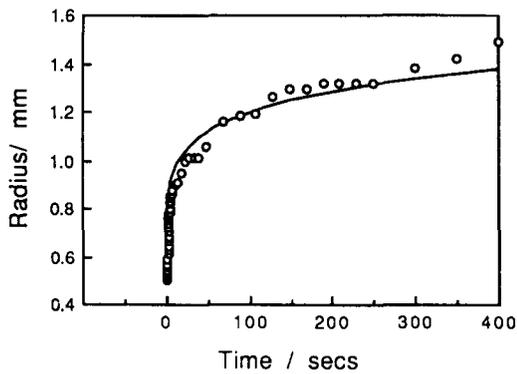
Fig. 5. Re-plot of some of the Ni–11P on nickel data shown in Fig. 3. The line is a plot of the de Gennes relationship with $m = 3$ and $K_m = 603 \times 10^{-34}\,\mathrm{m^{10}\,s^{-1}}$ and $R_0 = 5 \times 10^{-4}\,\mathrm{m}$.
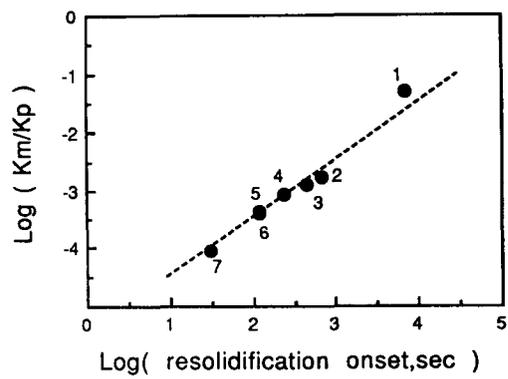

Fig. 6. Comparison of resolidification and spreading rate characteristics. The numbers identify particular systems: (1) Ni–11P/nickel; (2) Ni–11P/Fe–2Cr; (3) Ni–11P/Fe–5Cr; (4) Ni–11P/Fe–10Cr; (5) Ni–11P/Fe–15Cr; (6) Ni–11P/Fe–20Cr; (7) copper/nickel. The original braze diameter was 1 mm for all the samples. The dotted line has a slope of 1.00.

DISCUSSION

4.1. Qualitative features

The present observations and those made during previous work by one of the authors [2] show that for a wide range of liquid metal–solid metal system the first stage of braze spreading is phenomologically similar; a monotonic decrease in spreading rate as the braze front advances. This was the only behaviour observed for the copper–nickel and Ni–11P/nickel systems although it was associated with isothermal resolidification during the later stages of the experiments. It was also the only stage observed for the copper–tungsten system before spreading ceased after a few seconds without the onset of isothermal resolidification. The behaviour of the Ni–11P/iron–chromium systems was more complex, but even for these, the first stage accounted for the bulk of the spreading that occurred, Table 1. Thus understanding this stage should provide insight into the dominant spreading behaviour for a number of widely differing metal–metal systems.

The prime conclusion that can be drawn from the spreading rate data presented in this paper is that the de Gennes model [1], provides a satisfactory basis for describing the observed form of first stage spreading behaviour. The radii of braze drops increase with time in the manner predicted by the de Gennes model as exemplified by equation (1). If the de Gennes model as well as the form of the predicted time dependence is applicable to our systems, then extra insight is provided into the effects of a number of process and material factors on the spreading rate constant, K. Thus we have observed that with Fe–20Cr substrates, decreasing the diameter of the solid braze disc of Ni–11P from 1 to 0.6 mm caused the measured value of K, K_m, to decrease by 97%, in good agreement with equation (3) which suggests a decrease of 95%. The effects of other volume variations, therefore, can be anticipated with some confidence. The de Gennes model also provides guidance to the likely effect of temperature on flow rates through the effect of temperature on the γ, η and Ω

terms. Thus for a drop of molten copper that was originally a 1 mm diameter disc, raising the temperature from 1083 to 1183°C should increase K_p from 1.83×10^{-31} to $2.05 \times 10^{-31}\,\mathrm{m^{10}\,s^{-1}}$. The effect of this variation on the predicted extent of spread is minor, the difference during the first 100 s of spreading does not exceed 16 μm. Therefore the 1100–1140°C temperature range used in this work with drops of copper (or the 930–1020°C used with the Ni–11P braze) should not have a noticeable effect on our measurements made with a accuracy of $\pm 5\,\mu$m.

4.2. Quantitative aspects

In contrast to these agreements, Table 2 shows that the ranking of K_m values differs from that of K_p, and demonstrates that the substrate materials have a very definite influence on spreading rates even though they do not play any active role in the de Gennes model. Even more remarkable is the fact that the absolute values of K_m are about 10–10,000 smaller than those predicted for K_p. Clearly not all the assumptions of the de Gennes model are satisfied.

The de Gennes model assumes that the substrates are perfectly smooth, which is a virtual impossibility in practice. Isotropic roughening of substrate surfaces can decrease the extent of equilibrium wetting of iron–chromium alloys by Ni–11P [6], but effects on spreading rates are unclear. All the metal substrates used in this work were polished to a metallographic finish, so roughness effects should have been small and similar for all the systems. However, it is noteworthy that even grain boundary grooves can impede flow when they are aligned parallel to the liquid front.

The de Gennes model also assumes that the substrates are perfectly wettable, but in our work the contact angle did not fall to 0° even after long hold times. The prime reason for this lack of perfection is the presence of unwettable or poorly wettable oxides on the substrate surfaces. Thermodynamic calculations predict that NiO will dissociate in our

evacuated environment, but the oxides on the Fe–Cr alloys and W should be relatively stable. However disintegration of the oxide film can be caused also by dissolution of oxygen in the substrates and Table 3 summarises some relevant solubilities.

These comments relate to equilibrium conditions which are not satisfied during our experiments because of the rapid heating rates and relatively short dwell times used. Many of the substrates, therefore, will have been at least partially oxide coated. At least for the Ni–11P/iron–chromium system, spreading over such surfaces is effected by dissolution of the substrate to undermine the oxide which can then float away on the braze surface [2]. The kinetics of this dissolution will control the spreading and ultimately cause it to cease when the braze liquid is so alloyed with substrate material that resolidification occurs. This undermining by dissolution will be even slower if the liquid is being consumed by diffusing into the substrate. Interdiffusion data are not readily available for the liquid braze–substrate systems of direct interest, but some guidance can be gleaned from the solubilities summarised in Table 3. These range from the negligible (copper in tungsten) to the substantial (copper in nickel) or total (nickel in iron or nickel).

Reviewing the K_p and K_m data summarised in Table 2, it is apparent that the deviation between the measured and predicted rate constants can be related to both the likely presence of oxide films on the substrate surface and particularly to interdiffusion across the liquid–solid interface. The most deviant system is copper–nickel for which the solubility of the liquid in the substrate is very large. The behaviour of the Ni–11P/iron–chromium systems is also markedly deviant, although the solubility values for nickel will vary with the chromium contents of the substrates. The K_m value for Ni–11P/Fe–2Cr is relatively high, but this could be due also to the relative instability of Cr_2O_3 films on low chromium substrates. Similarly, the copper–tungsten system is very insoluble and hence the discrepancy between K_p and K_m could be a reflection of a stable oxide film. Finally, the modest deviation of the Ni–11P/nickel system is consistent with both the limited scope for interdiffusion in a chemically similar braze and substrate and the relative instability of NiO.

4.3. Extending the de Gennes model

Clearly some guidance to a semi-quantitative ranking of the spreading kinetics of a range of liquid metal–solid metal systems can be achieved by applying the de Gennes model and relating the non-ideality of the systems to their solubility and oxide stability characteristics. A more direct guide to the non-ideality of the particular systems used in this work is provided by the onset of isothermal resolidification, and comparison of the resolidification times and the K_m/K_p ratios shown in Fig. 6 reveals a clear correlation. This provides support for assuming that the main, but not only, cause for deviation of spreading rates from those predicted by the de Gennes model is interdiffusion, and as such the correlation identifies a direction for further development of a model describing the spreading behaviour of reactive systems.

Any further development of the de Gennes model must account for three striking results. First, the kinetics of spreading for short times fit the equations derived from the de Gennes theory qualitatively very well; the complications are largely those discussed in our earlier paper [3], where we found evidence for a second spreading mechanism at intermediate times. Secondly, there is a profound quantitative disagreement between predicted and observed spreading rates, in some cases by as much as 10^4. Thirdly, the factor by which spreading is slower than predicted depends on the chemistry of the substrate and is directly proportional (with reasonable accuracy) to the onset of isothermal resolidification.

We can understand these results by extending the de Gennes analysis. He considered a perfectly wetting system in which the spreading drop had the form of a shallow cap surrounded by an extremely thin precursor film; in our work, this precursor can be equated to the liquid undermining the oxide film ahead of the main drop. In his study, the spreading rate is predicted by equating two expressions for the rate of doing work. One expression comes from the work done by the interfacial energies, and is the product of the non-compensated Young force, equal to $(\gamma_S - \gamma_{SL} - \gamma \cos \theta)$ where γ_S and γ_{SL} are the energies of the surface of the solid substrate and the liquid–solid interface and θ is the contact angle of the drop. The force consists of two parts; of these, only that which varies with the contact angle need concern us for, as de Gennes argues, all the remainder is dissipated in the precursor film and does not contribute to the spreading rate. The second expression for the rate of doing work relates to viscous damping. Here de Gennes evaluates the velocity profile in a film of a normal liquid of constant thickness and derives the rate of doing work from an approximate integral; he then generalises this to give the rate of doing work in a wedge of liquid, such as the advancing front of a drop.

We shall follow this argument with as few changes as possible, though we are aware that there is a need to examine some of the assumptions in more detailed modelling; this we hope to do in due course. Thus we shall retain the prediction of the rate of work done by that part of the spreading force which varies with the contact angle. We shall also retain the equating of the

Table 3. Solubility data, at.%, Refs [7, 8]

Solute	Fe	Ni	W
Cu	6.5	95	0
Ni	100	100	1.5
O	<0.01	0.05	~0

At 1100°C for Cu–Ni and Cu–W, and at 1000°C for the other systems.

rate of work in a layer of liquid to that in a wedge, thereby making certain gross approximations in our case. However, we shall change significantly the velocity profile (and hence the integral involved in estimating viscous damping) in the layer of liquid.

Our assumption is that all the important viscous losses take place in a narrow region close to the resolidification front, initially the original braze–substrate interface. This change has two effects. The narrow region contains dissolved substrate material which can increase the viscosity. This effect we assume to be modest, but possibly significant in the case of the spreading of Ni–11P on nickel which most closely approaches the de Gennes predictions. The main effect of the change is due to the narrowness of the region of the liquid which dominates viscous dissipation. The width of this region we take to be given by the so-called Stefan problem [9]; in a steady state, this width for an interface advancing with a velocity v can be equated to the characteristic length d given by D/v, with D the controlling diffusion constant.

It is now easy to see what happens. The effective viscosity (i.e. the value which, when used in the de Gennes theory, would give the correct dissipation) is multiplied by a term of the order of magnitude h/d where h is the thickness of the liquid layer. But h/d can be written as hv/D, and v can be approximated to h/t_s where t_s is the time at which isothermal resolidification is first observed. Thus the ratio K_m/K_p is a function of Dt_s/h^2; the ratio of the measured and predicted rate constants should be proportional to the time at which resolidification commences.

We can hazard an estimate of the actual extent of slowing, of K_m/K_p, by substituting values for h, D and t_s. The data in Table 1 indicate that the average thickness, h, of a drop of Ni–11P spreading on iron–chromium substrates is about 10^{-5} m. Taking K_m/K_p for those systems as typically 7×10^{-4}, this implies that d is 7×10^{-9} m. Now K_m/K_p is also equal to Dt_s/h^2, therefore taking t_s as typically 300 s, D will be about 2×10^{-16} m^2 s^{-1}. Similar substitutions of data for the spreading of Ni–11P on nickel and of copper on nickel, at 1100°C, yield D values of 4.3×10^{-16} and 2.7×10^{-16} m^2 s^{-1} respectively. These values are reasonably consistent and much lower than the diffusion coefficients for liquid nickel or copper which have been estimated by Iida and Guthrie [4] as 3.9×10^{-9} and 4.0×10^{-9} m^2 s^{-1} respectively. The D values, however, are close to those reported for the self diffusion in solid iron, 5×10^{-15} m^2 s^{-1} at 1000°C, and nickel, 3.7×10^{-16} m^2 s^{-1} at 1000°C and 2.55×10^{-15} m^2 s^{-1} at 1100°C [10]. While at first sight surprising, such a similarity is at least consistent with the estimated ex- treme thinness, only about 10 atom layers for Ni–11P on iron–chromium, of the viscous damping region.

5. CONCLUSIONS

1. The first stage spreading behaviour of the braze–substrate systems studied in this work are phenomenologically similar and can be described by a power relationship

$$R_t^{3m+1} = Kt + R_0^{3m+1}.$$

2. The power term m is approximately equal to 3 in accord with the de Gennes model, which describes spreading behaviour as the resultant of imbalanced Young forces and viscous damping. The de Gennes model also accounts for the observed effect of changing the braze volume and for the relative insensitivity of spreading rates to temperature changes.

3. Quantitative agreement between observed spreading rates and those predicted by naive application of the de Gennes model is poor; the observed rates can be as much as 10^4 times smaller.

4. The deviation between the de Gennes predictions of spreading constants and our measured values can be related to the reactivities of the systems as manifested by isothermal resolidification times, and this can be rationalised by a generalisation of the de Gennes model. It seems, however, that oxide stabilities can also play a role as exemplified by the relatively low K_m/K_p ratio for copper–tungsten.

5. This work suggests directions for the development of models describing the spreading behaviour of reactive systems. A first approach of assuming that viscous damping is confined to a narrow region adjacent to the braze–substrate interface shows promise.

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