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## DIFFUSION-LIMITED REACTIVE WETTING: SPREADING OF Cu-Sn-Ti ALLOYS ON VITREOUS CARBON

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### Introduction

Wetting of a solid by a liquid can be significantly improved by addition to the liquid of appropriate alloying elements which, by reaction with the solid, cause the formation of an interfacial layer of a compound which is better wetted by the liquid than the original unreacted solid surface. Titanium is a frequently used such alloying addition for wetting of carbon-containing substrates: reaction then leads to the formation of TiC, which by virtue of its partly metallic character is relatively well wetted by many metals and alloys [1,2].

When wetting is promoted by interfacial reaction, the rate at which the liquid spreads over the solid substrate is controlled by the rate at which the well-wetted interfacial reaction product can be formed along the liquid/solid/atmosphere triple line. If this interfacial reaction involves a reactive alloy addition to the liquid, the rate of spreading can be limited by two possible phenomena [3]:

- (i) local reaction kinetics at the triple line, leading to constant spreading rates, or
- (ii) the rate of supply of reactant from the drop bulk to the triple line, itself generally limited by the rate of diffusion of solute through the liquid, leading to time-dependent spreading rates.

A simplified analysis of diffusion-limited reactive spreading [4], based on the assumption that the interfacial reaction is strictly localised at the triple line, has led to the conclusion that the velocity of a sessile drop triple line  $dR/dt$  (where  $R$  is the radius of the drop base and  $t$  is time) varies in direct linear proportion to the instantaneous contact angle  $\theta$ :

$$\frac{dR}{dt} = \frac{2DF_{(t)}}{en_v}(C_o - C_e)\theta, \quad (1)$$

otherwise exhibiting no significant explicit time-dependence. In Eq.(1),  $D$  is the diffusion coefficient in the liquid phase,  $n_v$  is the number of moles of reactive solute per unit volume of the reaction product,  $e$  is the reaction product thickness at the triple line,  $C_o$  is the nominal (far-field) drop reactive solute concentration,  $C_e$  is the concentration of reactive solute in equilibrium with the reaction product (such that  $C = C_e$  at the triple line), and  $F_{(t)}$  is a function of time  $t$  which varies very little, and can thus be considered constant with a value near 0,04 in usual sessile drop experiments [4].

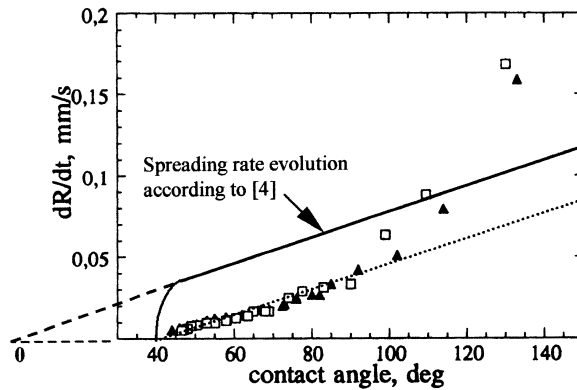


Figure 1. Experimental triple line velocity as a function of instantaneous contact angle  $\theta$  for Cu-1at.%Cr on vitreous carbon at 1150°C [5] and spreading rate according to Eq. (1), Ref. [4].

This relation was compared with spreading kinetics measured for Cu-Cr alloys sessile drops on vitreous carbon (Fig. 1), which spread by formation of chromium carbide along the liquid/solid interface [5]. This comparison confirmed several of the predictions of the above analysis: the spreading rate is indeed found to be directly related to  $\theta$ , and to vary linearly with the drop nominal solute concentration  $C_o$ , confirming that spreading is indeed governed by solute transport for this system. Also, it was found that for  $\theta < 90^\circ$ ,  $dR/dt$  does vary linearly with  $\theta$ ; however, there are two discrepancies between data and theory for this system:

- (i) for  $\theta > 90^\circ$ , there is an upward deviation in the spreading rate from the linear relation observed at lower angles, and
- (ii) for  $\theta < 90^\circ$ , the intercept of the line of  $dR/dt$  versus  $\theta$  with the  $\theta$  axis was not at the origin ( $\theta = 0$ ), but rather near the final equilibrium contact angle  $\theta_e$ , of about  $40^\circ$ .

This paper is focused on the second discrepancy. This discrepancy was attributed to the presence of continuing drop/substrate chemical reaction behind the triple line [5]. Such reaction causes added solute to be consumed along the liquid/solid interface, in turn reducing, by diversion, the total flux of solute which reaches the triple line from the drop bulk. This interpretation was in particular reinforced by the fact that final measured chromium carbide interfacial reaction layers were relatively thick in the Cu-Cr/C system (several micrometers), and by the observation that the final reaction layer thickness increases significantly in this system with the total liquid/solid contact time, which suggests continued reaction after wetting.

A test of this interpretation could be provided by observation of a system for which the reaction layer is sufficiently impervious for the liquid/solid interaction to be effectively stopped behind the triple line. In what follows we present results for the Cu-Sn-Ti/ $C_v$  system, which satisfies this criterion. Indeed, at temperatures close to 1100°C the diffusion coefficient of carbon in solid TiC, which is the reaction product in the above system, is 1–2 orders of magnitude lower than in chromium carbide [6,7].

### Experimental Procedures

A substrate of vitreous carbon (V25 vitreous carbon, heat treated at 2773K and featuring no open porosity, provided by Le Carbone-Lorraine, France) was mechanically polished to a  $1 \mu\text{m}$  diamond

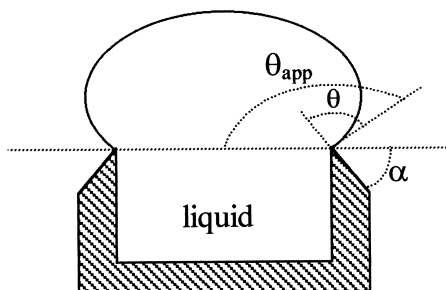


Figure 2. Principle of a large-drop experiment after Naidich *et al.* [2]. The use of a sharp-edged cup leads to an apparent contact angle  $\theta_{app} = \theta + \alpha$  where  $\theta$  is the true contact angle of liquid on the cup material.

paste. Height variations along the polished substrate surface were measured to be of amplitude between 1 and 2 nm and wavelength between 10 and 20  $\mu\text{m}$ ; the surface roughness of these substrates is thus sufficiently low not to influence wetting angle data. The metal drops were prepared from 99.999% pure copper and tin, and 99.7% purity titanium by alloy formation upon melting of elemental metals. The composition investigated is Cu-15at.%Sn-3at.%Ti.

The sessile drop experiments were conducted within a stainless steel cold wall furnace under a static purified helium atmosphere. The spreading process was filmed by a video-camera and recorded on videotape at a film speed of 25 frames per second. After the experiments, the measured contact angle,  $\theta$ , as well as the drop base radius,  $R$ , were computed from the recorded drop profile with an accuracy of  $\pm 2^\circ$  for  $\theta$  and  $\pm 2\%$  for  $R$ . The transferred drop technique, described in more detail in Ref [5], was used: in this technique, the drop is first formed and homogenized over an inert, non-wetted, substrate, and then raised until it contacts the carbon substrate from below. The drop then spreads, and detaches from the lower substrate; this causes an abrupt change in the contact angle during the experiment. Thereafter the drop remains suspended under the carbon substrate, over which it continues spreading until the equilibrium contact angle on the reaction product is attained.

A difficulty encountered in this study was to find a ceramic substrate that is at the same time non-reacting with the Cu-Sn-Ti alloy and poorly wetted by it (indeed, Ti-containing alloys react and wet most usual ceramics). To overcome this difficulty we used, instead of a flat substrate, an alumina support having the shape of a cup with sharp edges. This geometry makes it possible to produce apparent contact angles,  $\theta_{app}$ , that are much higher than the true contact angle  $\theta$  of the melt on the substrate material (Fig. 2). This technique, used to measure the surface tension of metals and alloys [8,9], led for the Cu-15at.%Sn-3at.%Ti alloy to values of  $\theta_{app}$  exceeding ninety degrees, thus making it possible to transfer the drop upon contact with the carbon substrate.

After cooling of the drop, the interfacial reaction product chemistry and morphology were characterized by scanning electron microscopy.

A plot of the variations in time of the contact angle  $\theta$  and the droplet base radius  $R$  for an experiment conducted at 1020°C is given in Fig. 3: it is seen that, aside from a perturbation observed at the moment of drop transfer and occurring around 50°, continuous curves are obtained. In agreement with [2], the Cu-15at.%Sn-3at.%Ti alloy wets very well vitreous carbon, the final contact angle being as low as 10°. Moreover, the  $R(t)$  curve displays a time-dependent spreading rate, indicating that local interfacial reaction kinetics do not govern the rate of spreading. Deriving from these data the triple line velocity  $dR/dt$  and plotting this quantity as a function of the contact angle  $\theta$ , one obtains the curve in Fig. 4. As for the Cu-Cr/Cv couple, when  $\theta < 90^\circ$  the resulting data points lie roughly along a straight line; however, in the present system the resulting straight line through the data passes through the origin, the spreading rate falling abruptly to zero at the final, equilibrium, contact angle of the alloy on the reaction

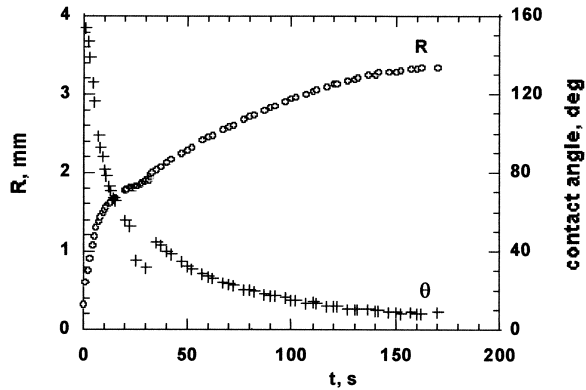


Figure 3. Contact radius  $R$  and contact angle  $\theta$  as a function of time for Cu-15at.%Sn-3at.%Ti on vitreous carbon at 1020°C. The perturbation at  $t \approx 25$  seconds is due to the detachment of the drop.

product, near 10°. Note that for  $\theta > 90^\circ$ , the spreading rate deviates above the straight line in similar fashion to what was observed with the Cu-Cr/C system in Ref. [5].

A cross section of the interfacial region near the center of the drop is given in Fig. 5 (characterization of the interface near the triple line was unfortunately not possible because thermal stresses built-up during cooling of the drop caused interfacial failure, breaking up the drop and the substrate into many small fragments). It was found that the interface is composed of a thin and dense reaction layer of TiC, of average thickness slightly below 500 nm.

A second experiment was performed with the same alloy at 1100°C instead of 1020°C. The contact angle was again found to decrease from an initial value of 160° to a final or equilibrium contact angle of about 10°; however, in this case, the detachment of the drop produced a strong perturbation of the  $R(t)$  curve, such that only the part of the curve after detachment can be used to plot the triple line velocity versus instantaneous contact angle curve, Fig. 6. As for the data at 1020°C, shown also in this figure for comparison, the data points lie on a straight line which passes through the origin. Unfortunately, mechanical failure of the drop along the interface during cooling to room temperature destroyed the interfacial reaction layer, precluding its microstructural characterization.

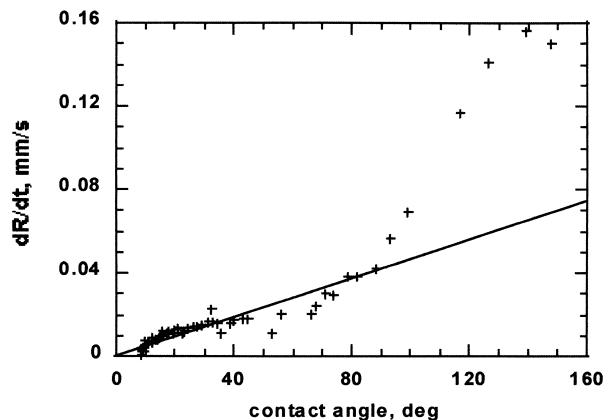


Figure 4. Triple line velocity as a function of instantaneous contact angle  $\theta$  for Cu-15at.%Sn-3at.%Ti on vitreous carbon at 1020°C.

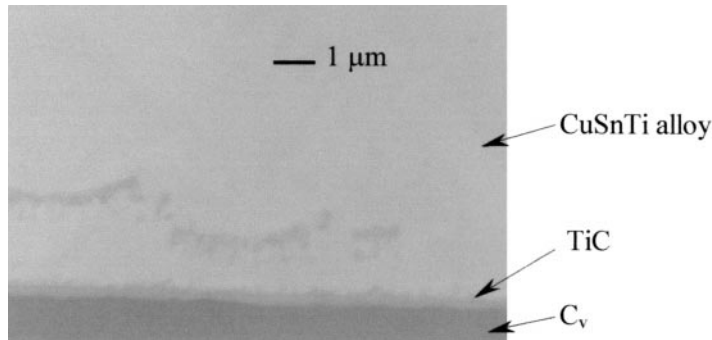


Figure 5. Micrograph of drop-substrate interface for Cu-15at.%Sn-3at.%Ti alloy on vitreous carbon at 1020°C showing titanium carbide formation.

### Discussion

Unlike copper-chromium alloys, Cu-15at.%Sn-3at.%Ti thus displays the simple linear relationship between  $dR/dt$  and  $\theta$  predicted by Eq. (1). The slope of the line through the data at 1020°C for  $\theta < 90^\circ$  is  $2.7 \cdot 10^{-5} \text{ m}\cdot\text{s}^{-1}\cdot(\text{radian})^{-1}$ . Taking  $n_v = 8.26 \cdot 10^4 \text{ moles}\cdot\text{m}^{-3}$ ,  $(C_o - C_e) \approx C_o = 1640 \text{ moles}\cdot\text{m}^{-3}$ , and using an estimated value of  $D \approx 5 \cdot 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ , this slope corresponds, according to Eq. (1), to a thickness  $e$  of the TiC reaction layer formed at the triple line of 300 nm. This is close to the observed reaction layer thickness, found at 1020°C to be slightly below 500 nm. The expected difference between  $e$  (the thickness of the reaction layer formed at the triple line during spreading and deduced from spreading kinetics using Eq. (1)) and its final value at the end of the experiment can be estimated knowing the diffusion coefficient of C in bulk TiC ( $D_C$ ). This quantity is a function of stoichiometry of  $\text{TiC}_y$  which in turn depends on the activity of Ti in the alloy,  $a_{\text{Ti}}$ . For Cu-15at%Sn-3at%Ti,  $a_{\text{Ti}} = 2 \cdot 10^{-3}$  [10], corresponding to  $y = 0.8$  [11], from which we deduce that  $D_C = 1.6 \cdot 10^{-17} \text{ m}^2\cdot\text{s}^{-1}$  at 1020°C and  $9.7 \cdot 10^{-17} \text{ m}^2\cdot\text{s}^{-1}$  at 1100°C [6] (for  $y = 1$ ,  $D_C$  is lower, equalling  $2.6 \cdot 10^{-18} \text{ m}^2\cdot\text{s}^{-1}$  at 1020°C). It can then be estimated that during the time of spreading of the drop (150 s at 1020°C and 50 s at 1100°C), the reaction layer can only grow, starting from an initial thickness of 300 nm, by only an additional 25 and 35 nm at the center of the drop/substrate interface, at 1020 and 1100°C respectively (and by less elsewhere since the time of contact is shorter). The data are, thus, fully consistent with the assumptions of Ref. [4] and reinforce the suggestion made in Ref. [5] that the

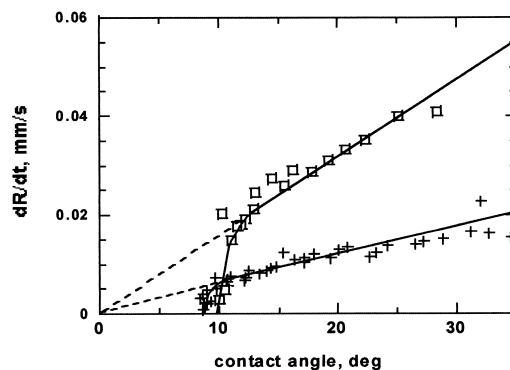


Figure 6. Triple line velocity as a function of instantaneous contact angle  $\theta$  in the low contact angle range for Cu-15at.%Sn-3at.%Ti on vitreous carbon at 1100°C ( $\square$ ) and 1020°C (+).

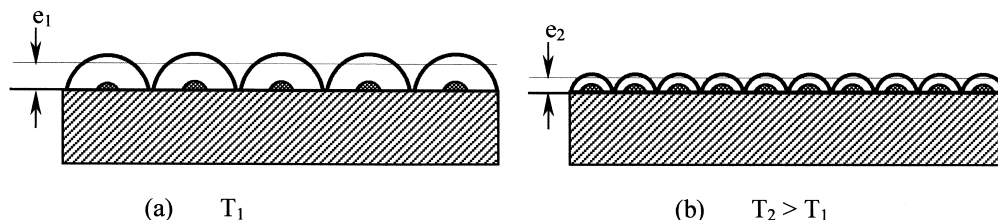


Figure 7. Illustrating how an increase in the nucleation rate with increasing temperature will cause a decrease in the average interfacial layer thickness  $e$  upon formation of a continuous layer.

discrepancy observed for the Cu-Cr/C<sub>v</sub> system between Eq. (1) and small-angle data in Ref. [5] is likely to be caused by a continuation of chemical reaction between the substrate and the liquid behind the triple line, causing diversion of solute diffusion lines away from the triple line and, in turn, slowed spreading. This diversion is important for the Cu-Cr/C<sub>v</sub> wetting couple for which diffusion through the reaction layer is faster,  $D_C$  being one to two orders of magnitude higher [6,7], leading to final carbide layers several micrometers thick.

As the temperature is increased from 1020 to 1100°C, the slope of the line through the data in Fig. 6 increases by a factor of 2.5. At both 1020 and 1100°C,  $C_e \ll C_0$ , such that the variation in  $C_0 - C_e$  is negligible in this temperature range; similarly,  $n_v$  undergoes no significant change. The activation energy for diffusion of Ti in the molten alloy is at most 50 kJ.mole<sup>-1</sup> [12]; hence, increasing the temperature from 1020 to 1100°C will cause an increase in the value of  $D$  by a factor 1.3 at most. Thus, the increased rate of spreading of the triple line as the temperature increases from 1020 to 1100°C is explained by Eq. (1) only if we admit that the thickness of reaction product at the triple line,  $e$ , decreases by a factor near 2 as the temperature increases by 80°C. This, in turn, indicates that the reaction layer growth mechanism must undergo a significant change as the temperature is increased in this range; unfortunately this could not be checked due to destruction of the interface after cooling from 1100°C. We note, however, that since  $e$  is the average thickness of the individual reaction product grains when a continuous layer is formed at the interface, such a decrease in  $e$  could be explained by an increase in the rate of nucleation of reaction product grains at the interface along the triple line. Indeed, the activation energy of nucleation is far higher than that of diffusion in the liquid, such that increasing the temperature from 1020 to 1100°C could cause a significant increase in the surface density of TiC grains along the interface, causing in turn a correspondingly high decrease in  $e$  as illustrated in Fig. 7.

### Conclusion

- The addition of 3at.%Ti to Cu-15at.%Sn leads to very good wetting on vitreous carbon, the final contact angle being close to 10°. This is due to the formation, at the interface, of a continuous layer of TiC of thickness slightly below 0.5 μm. Curves of the drop base radius versus time do not present a linear domain, indicating that spreading is not controlled by the local kinetics of interfacial reaction, but rather by diffusion of Ti from the drop bulk to the triple line.
- For contact angles lower than 90°, spreading kinetics of Cu-15at.%Sn – 3at.%Ti on vitreous carbon agree fully with the analysis of Ref. [4]. This agreement is attributed to the impervious nature of the reaction layer behind the triple line.
- For contact angles above 90°, spreading kinetics of Cu-15at.%Sn-3at.%Ti on vitreous carbon show the same enhancement in spreading rate as in Cu-Cr/C data of Ref. [5]. The causes of this enhancement will be analysed in a future publication.

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