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Wetting and infiltration of carbon by liquid silicon

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The wettability of carbon materials by molten silicon was investigated at 1430°C under vacuum by using the dispensed drop variant of the sessile drop technique. The results are compared with data in the literature and used to contribute to a comprehensive understanding of wetting in the liquid-Si/solid-C system. Consequences on the dynamics of Liquid Silicon Infiltration (LSI) processes are discussed. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

The properties of liquid silicon (Si)/carbon (C) materials interfaces are of particular interest in the field of materials science. Among numerous applications (brazing, liquid containers, silicon carbide growth from the melt...) one of particular interest is the production of silicon carbide based materials for advanced applications using several techniques such as Reaction Bonded Silicon Carbide (RBSC) and Liquid Silicon Infiltration (LSI) [1–3]. These advanced processes have a common step of reactive infiltration of C preformed shapes by liquid silicon to form low-cost ceramic matrix composites.

In the literature, infiltration dynamics is usually described via capillary flow equations assuming that infiltration is non-reactive and controlled by viscous flow. In these models, the only effect of the chemical reaction between liquid silicon and carbon is the pore closure behind the infiltration front [4, 5]. However, for optimization of siliconizing processes, a thorough understanding of the wetting dynamics of liquid silicon on solid carbon substrates is vital. From an overview of the literature, it appears that there are significant differences in results, both for equilibrium contact angles (Table I) and spreading kinetics [6, 7].

In the present study, specific wetting experiments were performed with molten silicon on two different carbon materials (vitreous carbon C_v and pseudo-monocrystalline graphite C_g) to explain the divergent results reported in the literature and to obtain a better understanding of the mechanisms of the spreading kinetics.

2. Experiments

Preliminary wetting experiments were performed in a high-vacuum metal furnace using the classical version of the sessile drop method .With this method, which consists in melting directly a piece of Si on the study substrate, the equilibrium contact angle of Si on vitreous carbon was found to be 35°–40°. However these experiments revealed that in the case of liquid Si the time needed to reach capillary equilibrium and the time required for complete melting are of the same order of magnitude [6]. For this reason the spreading kinetics were studied using the dispensed drop technique which allows the process of melting (in an alumina or graphite crucible) and spreading to be separated so that fully isothermal experiments can be performed [8].

The pressure in the stainless-steel chamber used in the present study can be reduced to 10^{-6} Pa at room temperature and 10^{-5} Pa at working temperature (1430°C). Images were obtained using a CCD camera and recorded on videotape at a film speed of 25 frames per second, enabling measurement of the characteristic dimensions of the drop after 40 ms of contact between the substrate and the liquid.

The experiments were performed both on vitreous carbon (C_v) substrates (V25 grade provided by Le Carbone-Lorraine, France) and pseudo-monocrystals of graphite (C_g). Vitreous carbon is a hard, low-density ($1.6 \times 10^3\ \mathrm{kg \cdot m^{-3}}$) material, which has no open porosity and contains less than 50 ppm impurities. After polishing up to 1 micron diamond paste, the average substrate roughness R_a, characterized with an optical interferometer with a vertical resolution of 0.5 nm, is lower than 5 nm. The pseudo-monocrystals of graphite present a high density nearly equal to the density of monocrystals of graphite ($2.267 \times 10^3\ \mathrm{kg \cdot m^{-3}}$). The average roughness measured on areas of $20 \times 20\ \mu\mathrm{m}^2$ is about 2–4 nm [9].

The liquid silicon used in this study was prepared from pure Si (99.9995 wt%) by melting in an alumina crucible (graphite crucible for a single specific experiment).

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TABLE I Equilibrium contact angles of liquid silicon on carbon materials. The average roughness (R_a) value is indicated when reported by authors

	Whalen and Anderson [6]	Li and Hausner [3–4]	Naidich [5]
Vitreous carbon	40–50°	10–40° $R_a < 0.005\ \mu$m	
Graphite	5–15° (pyrolitic graphite)	$3^\circ - R_a = 3.18\ \mu$m $35^\circ - R_a = 0.005\ \mu$m (graphite N)	15°

After cooling, selected specimens were cut: (i) first half was embedded in resin and polished for optical and SEM observations on the cross section, (ii) a specific acid melt was used to dissolve the metal droplet on the second part of the specimen so that the interfacial area could be observed from above.

3. Results

A typical variation in drop base radius R and contact angle θ versus time for a dispensed drop experiment conducted at 1420°C with pure liquid silicon on vitreous carbon is given in Fig. 1. Spreading occurs between $\theta = 180^\circ$ and a final or steady contact angle θ_F close to 35° is obtained.

The spreading regime between 180° and the first measured contact angle of about 146°, noted θ_0, was too fast to be monitored by the CCD camera used in this study. In other words, the time t_0 corresponding to θ_0 was different from but very close to zero. The equilibrium contact angle was reached after a spreading time of 50 s.

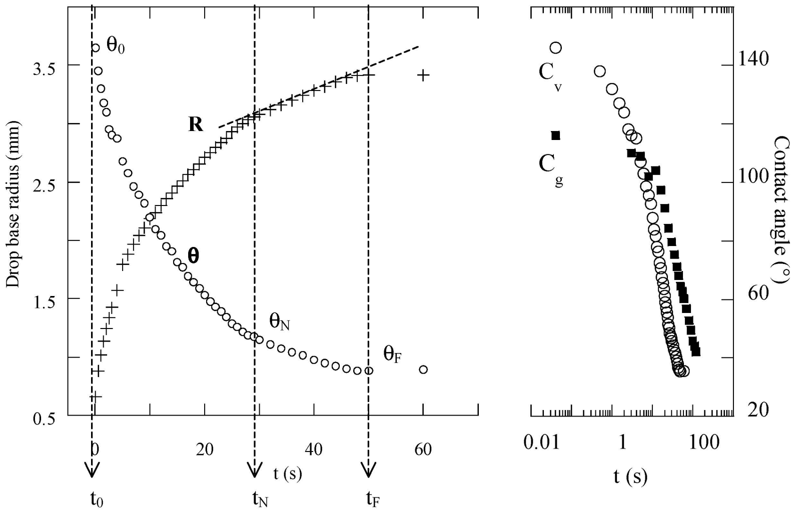
On the $R(t)$ curve between $t_0 \approx 0$s and t_F two kinetic stages can be distinguished (Fig. 1a). In the first stage ($t_0 < t < t_N$, where t_N denotes the contact angle θ_N at which the sharp change in the slope of R versus t curves occurs—see Fig. 1a, the spreading rate $U = dR/dt$ decreases *continuously* with time, first rapidly, then much more slowly. For this reason, spreading between t_0 and t_N is called decreasing rate spreading (DRS) [10].

In contrast to the first stage in Fig. 1a, the second stage (between t_N and t_F) is strictly linear. This stage, during which the change in contact angle is very limited (about twenty degrees), takes place at a spreading rate two times lower than in the DRS stage. The transition between the DRS and linear stages is abrupt. Similar spreading curves have been obtained for some metal-silicon alloys on C_v substrate [10] for which strictly linear spreading follows an initial DRS stage of comparatively rapid spreading.

The SEM observations of the interface performed on a cross section and from above after dissolution of the silicon in an acid mixture show that a continuous SiC reaction layer with an average thickness of about 3 to 4 microns was formed during spreading. The microstructure of this layer in the center of the interface consists mainly of individual particles of SiC with a diameter which can reach tens of microns. Moving away from the center of the drop, the microstructure changes progressively from equiaxial to mainly columnar (see Fig. 2) and the SiC dendrite growth direction is close to the direction of the triple line movement. Note that for contact angle values lower than θ_N, the microstructure of the SiC reaction layer changes suddenly and becomes fully equiaxial with a diameter of SiC particles of a few microns.

The plot variation for contact angle versus time for an experiment performed at 1430°C with pure liquid silicon on C_g is given in Fig. 1b (full square). Note that at $t = 120$ s it is obvious that liquid silicon infiltrated the C_g substrate. The liquid disappeared progressively and percolated through the graphitic leaf of the pseudo-monocrystal of graphite.

Comparison with the spreading kinetics obtained on C_v substrates indicates two main differences: (i) first, the initial contact angle on C_g ($\theta_0 = 120^\circ$) is 26° lower than in the case of vitreous carbon, (ii) second, the spreading rate is about one order of magnitude lower on C_g than on C_v. After cooling, no silicon is visible



(a)

(b)

Figure 1 (a) Time-dependent variation in drop base radius (R) and contact angle (θ) observed in the Si/C_v system at 1430°C. (b) Logarithmic representation of θ versus time in the case of respectively C_v (open circles) and C_g (full squares) substrates.

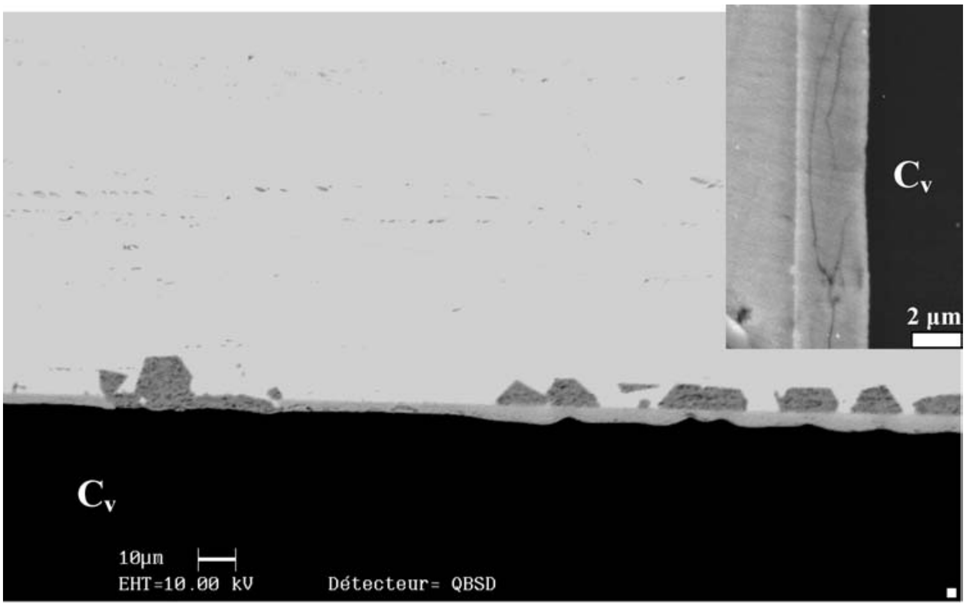


Figure 2 Liquid Si on C_V at 1430°C under vacuum. SEM micrographs of a cross-section in an area belonging to the beginning of the DRS stage. The inset shows the interface area of the DRS stage characterized by a mainly columnar growth of the SiC layer.

on the C_g substrate, indicating that the liquid has fully infiltrated the substrate.

A specific experiment was performed to study the effect of the carbon content of the liquid on the initial stages of the wetting process on C_V. Silicon was melted in a graphite crucible, instead of an alumina one, and held at 1430°C for 2 h. Then the liquid was extruded from the crucible as in a classical dispensed drop experiment. Both the initial contact angle value (found equal to 148°) and the initial spreading rate were nearly the same with the values measured using alumina crucibles. Therefore, the initial carbon content of the liquid does not have a significant effect on the spreading kinetics and the main source of carbon for SiC growth is the dissolution of the carbon substrate.

Note that a curious result was observed during an experiment when an equilibrium contact angle as low as 10° was obtained. Because this result was not consistent with the others, the furnace was carefully inspected and a microleak was found on a window. After changing the window, an equilibrium contact angle close to 35° was again measured. This confirms reports in the literature of the high sensitivity of the surface properties of liquid silicon to the oxygen partial pressure [11], which can have a significant effect on wetting.

4. Discussion

4.1. Characteristic contact angles

The first stage in discussing reactive spreading is to determine the meaning of the initial and final contact angles. Because of the rapid change in contact angle during the very first moments of wetting, the initial contact angle θ_0 can be determined more accurately using a logarithmic scale for time t. An example of a $\theta(\log t)$ curve is given in Fig. 1b. When the time tends towards zero, the contact angle tends towards a constant value θ_0 close to 150°. This non-wetting value is consistent with other values found for Cu-Si alloys on vitreous carbon [10] and is identified as the contact angle of molten silicon on an *unreacted* vitreous carbon surface. Note that the specific experiment performed with a liquid saturated in carbon indicates that the C content of the liquid has no significant effect on θ_0. The difference between C_g and C_v (θ_0 is 26° degrees lower in the case of C_g) can be satisfactorily interpreted assuming the predominance of Van der Waals interactions at the *unreacted* interface between Si and carbon substrate [12]. Indeed, the increase in the atomic density in the case of the pseudo-monocrystals of graphite led to an increase in the number of interactions per unit area between the liquid and the solid.

The value of the initial contact angle of molten silicon on vitreous carbon, measured after 40 ms of contact, is 50° higher than the value reported by Li and Hausner [6]. These authors measured the first contact angle only after 1 s of contact (compared with 0.025 s in our experiments—see Fig. 1b, and thus because of the high initial spreading rate (close to 0.4 $\text{mm} \cdot \text{s}^{-1}$) spreading had already started, leading to an underestimated θ_0 value.

It has been shown previously that the final contact angle is characteristic of liquid silicon on the silicon carbide formed at the interface [10] with a slight but significant effect of the reaction layer roughness. Moreover, the value obtained in the present study ($\theta_F = 35°$) for the liquid-Si/solid-C_v system is consistent with the equilibrium contact angles in the literature measured for liquid Si on SiC substrates (from 30° to 45°) [13].

In the case of other graphite materials (monocrystal, pyrolitic graphite, or polycrystalline graphite), the equilibrium contact angle value should be the same as in the case of vitreous carbon because it is characteristic of the liquid silicon on the SiC reaction product layer. However, most studies in the literature performed with carbon materials (polycrystalline graphite or pyrolitic graphite) [7, 14, 15] report equilibrium contact angles of between 5° and 35°. The experimental value of θ_F found in the present study is in agreement with the high values given in the literature. Note that low θ_F

values are explained by: (i) the average roughness R_a of polycrystalline graphite that can be several hundreds of nanometers (it is well known that for wetting liquids an increase of roughness promotes wetting) [16, 17]; (ii) as seen in the present study and reported elsewhere [7], liquid silicon can infiltrate the porosity in the substrate thereby decreasing the volume of liquid remaining above the surface. Therefore, in this case, receding rather than advancing contact angles are measured.

Wetting experiments on vitreous or glassy carbon materials, whose surface can be easily polished to an average roughness of less than 10 nm, are easier to compare. The agreement between the equilibrium contact angle values obtained by Whalen and Anderson [7] under vacuum at 1426°C (from 40° to 50°) and our results $\theta_F = 36°$ is acceptable. Li and Hausner [6] have also reported equilibrium contact angle values of about 40° in the case of in-situ experiments, but they indicate a value of about 10° for capillary experiments. These results indicate high sensitivity of the wetting process to the experimental conditions. All of Li and Hausner's experiments were performed in an atmosphere of argon (purity of 99.998%) at a total pressure of 1 atm [6]. Such an atmosphere is characterized by a high oxygen partial pressure and, as shown in the present study, wetting of liquid silicon is highly sensitive to O pollution [11].

Pollution by oxygen may also be produced by the interactions between molten Si and the alumina crucible used in the dispensed drop technique. However the equilibrium contact angles on C_v obtained during this study by the dispensed drop technique and by the classical sessile drop technique (direct melting of Si on the C_v substrate) are nearly the same. This result clearly indicates that in our experiments the pollution of Si from alumina crucible is negligible.

4.2. Spreading kinetics

From the discussion on the characteristic contact angles it is clear that pure Si does not wet an unreacted C surface, and that good wetting is obtained because of the formation of a continuous layer of SiC at the liquid-Si/carbon interface. The rate at which the Si droplet spreads is limited by the rate of the interfacial reaction (to form SiC) itself. Moreover, the local reaction kinetics at the triple line controls the interfacial reaction rate and therefore the spreading rate.

Because of the infiltration of liquid through the C_g substrate, spreading kinetics are discussed in detail only in the case of liquid-silicon on vitreous carbon.

The plot variations for drop base radius and contact angle versus time of a liquid silicon droplet on vitreous carbon show two kinetic stages (see Fig. 1). The first (DRS stage) is controlled by the dissolution process of the carbon substrate at or close to the triple line [10]. The spreading rate dependence $U(\theta)$ is rather complex but indicates that the spreading rate varies roughly as the cosine of the instantaneous contact angle, with opposite sign:

$$\frac{U}{F(\theta)} = k\left(\frac{3V}{\pi}\right)^{1/3} \cdot (\cos\theta_F - \cos\theta) \qquad (1)$$

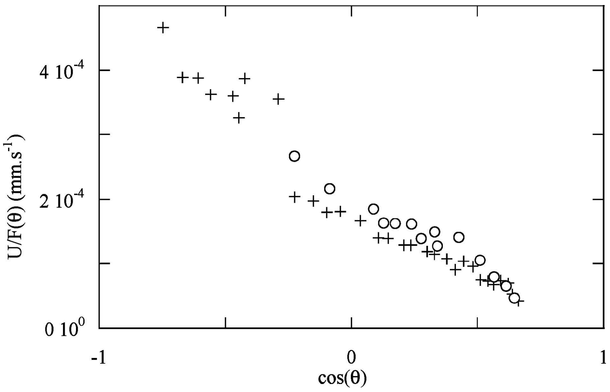


Figure 3 Experimental results of spreading rate $U(\theta)$ divided by the function $F(\theta)$ (see Equation 1) versus the cosine of contact angle during the DRS stage for two experiments performed with liquid silicon on vitreous carbon substrates at 1430°C under vacuum.

where $F(\theta)$ is a function of θ [10] and k a kinetic constant related to the process of carbon atom transfer occurring at the carbon/silicon interface.

Fig. 3 presents two plot variations for the spreading rate U divided by $F(\theta)$ versus the cosine of the instantaneous contact angle during the DRS stage in the case of liquid silicon on vitreous carbon for experiments performed at 1430°C. The data agree with the linearity predictions of Equation 1 in a wide range of contact angles from $\theta \sim 102°$ to $\theta_N \sim 50°$. Extrapolation to zero spreading rate gives a θ_F around 30°, which is in good agreement with the equilibrium contact angle values measured for molten silicon on SiC [13]. In the case of C_g substrates, this graphic representation cannot be made because of the roughness effect and liquid infiltration. However, in agreement with the slower spreading kinetics (see Fig. 1b) and with the results of Whalen and Anderson [7], the value of the kinetic constant should be lower than for vitreous carbon. Note that this conclusion disagrees only with the experimental results of Li and Hausner [6], which could be explained by the effect of oxygen pollution as discussed above (see Section 4.1).

In contrast to the DRS stage in Fig. 1, in the second stage (between t_N and t_F) the $R(t)$ curve is strictly linear. This stage, during which the change in contact angle is limited (about 15°), is characterized by a constant spreading rate that is slower than the DRS stage. The transition between the DRS and linear stages is abrupt and is also characterized by a change in the microstructure of the SiC reaction layer. Similar results were obtained for metal-silicon alloys [8]. The origin of the transition between coupled (DRS stage) and non-coupled (linear stage) reactive spreading will be discussed in a future paper.

4.3. Consequences on LSI processes

Several studies have presented a model to describe liquid silicon infiltration into porous carbon or carbon preforms [4, 5]. The simulation of fluid penetration assumes that: (i) non reactive capillary infiltration is limited only by the viscous flow, (ii) and SiC formation only affects the permeability of the porous solid by pore closure.

As shown in the present study, the contact angle characterizing a non-reacted liquid-silicon/carbon interface (150° on C_v and 120° on C_g) does not allow the non-reactive infiltration of carbon preforms. Silicon carbide formation is necessary to obtain the low contact angle values essential for LSI processes. The results of the present study have also shown the very important influence of the interfacial reaction on the spreading rate. Spreading of molten silicon on carbon materials is coupled with the rate of formation of SiC at the triple line: advancement of the triple line and the reaction front are not dissociable. Therefore, to describe and understand reactive melt infiltration, it is necessary to take into account not only pore closure due to thickening of the SiC reaction layer behind the infiltration front but also the formation reaction at the triple line. Thus, capillary infiltration is not limited by viscous flow but by the kinetics of the chemical reaction between liquid Si and carbon at the reaction front. This is the main reason why the experimental infiltration rate is much lower (by a factor 100) than the theoretical infiltration rate limited by viscous flow.

5. Conclusion

The wettability of carbon materials by molten silicon was investigated at 1430°C under vacuum by using the dispensed drop version of the sessile drop technique. Spreading occurred in two main steps: The first (from $\theta = 180°$ to $\theta_0 = 150°$ on vitreous carbon and $\theta_0 = 120°$ on pseudo-monocrystals of graphite) was non-reactive. The θ_0 values are characteristic of Van der Waals interactions established at an *unreacted* liquid-silicon/carbon interface. The second step (from θ_0 to θ_F) involved reactive wetting and the low equilibrium contact angle value characterized the chemical interactions across the liquid-silicon/SiC interface. The spreading kinetics were coupled to the reaction of SiC formation at the triple line. The structure of the carbon materials influenced both the characteristic contact angles and the spreading kinetics.

These results give a new interpretation to Liquid Silicon Infiltration processes: models based upon capillary pressure and viscous flow cannot accurately describe infiltration rate and height because the primary driving force of infiltration is the formation of a SiC wettable layer at the triple line of the infiltration front.

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