Reactive melt infiltration fabrication of C/C-SiC composite: Wetting and infiltration

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ABSTRACT

Reactive melt infiltration is a fast and economical fabrication process for high performance C/C-SiC composite. In order to help understanding reactive melt infiltration production of C/C-SiC composite by liquid silicon, wetting and infiltration of the porous C/C composite preform by liquid silicon were investigated using a sessile drop technique. The contact angle decreased with the increase of time while the drop base diameter increased. According to the variation of drop base diameter and contact angle as a function of time, four different stages corresponding to the interfacial reaction and infiltration of liquid silicon were identified during wetting of the porous C/C composite preform by the liquid silicon. The infiltration height based on wetting curve linearly increased with time, much smaller than that calculated according to Washburn equation, which strongly indicated the reaction control of silicon infiltration.

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1. Introduction

C/C-SiC composite is a potential candidate for highly demanding engineering applications such as heat shields, structural components for reentry space vehicles, high performance brake discs and high temperature heat exchanger tubes due to its low density, high hardness, excellent oxidation resistance, high strength and thermal shock resistance [1–3]. Reactive melt infiltration (RMI) has been demonstrated to be an effective technique for preparing C/C-SiC composite [4,5]. Its advantages include short fabrication period, low cost and near net shape [6]. During the RMI process, liquid silicon infiltrates into a porous C/C preform under the driving of capillary force. The liquid silicon expands to fill the pores and reacts with the carbon in the porous C/C preform, which ultimately results in a dense carbon and SiC composite matrix. Wetting of the porous C/C preform by liquid silicon is the foundation of RMI process. In the past years, wetting behavior of carbon by liquid silicon has been investigated by several researchers. Li et al. [7] used commercial graphite materials with different surface roughness as substrates and tested the contact angles at 1430 °C. Dezellus et al. [8] performed wetting experiments with molten silicon on glassy (vitreous) carbon and pseudo-monocrystalline graphite. Israel et al. [9] studied the wetting of different graphite substrates by liquid silicon. Whalen et al. [10] reported equilibrium contact angles under vacuum at 1426 °C from 40° to 50° for glassy carbon and 5° to 15° for graphite materials. The contact angles on different carbon substrates and measured values by different researchers have certain differences. Particularly, the above work focuses on the wetting of glassy carbon and graphite substrates with very few pores by liquid silicon. No published information is available on the wetting of porous C/C composite preform with large amount of pores by liquid silicon.

Infiltration of the liquid silicon is critical for the RMI fabrication of C/C-SiC composite. It determines the density of the as-produced composite and therefore greatly affects the composite’s performance. Liquid silicon infiltration is generally described to be a viscous flow with a parabolic trend as predicted by Washburn equation [11–13]. However, the recent work on infiltration of Si–Ni alloy and silicon into graphite material indicated that silicon infiltration is not limited by the viscous flow but by the reaction at the infiltration front with a linear variation process [14,15]. These infiltration experiments were performed with graphite material with few pores (< 15%) and the infiltration was interrupted by the closure of the small pores in the graphite. The infiltration height is very small (1–2 mm) due to the closure of the pores, which is different from the silicon infiltration during RMI fabrication of C/C-SiC composite (several millimeters without pore closure). The silicon infiltration into C/C composite preform with large porosities...
during RMI fabrication of C/C-SiC composite is still not well understood.

The aim of this investigation is to study the wetting and infiltration of a porous C/C composite preform by liquid silicon. The wetting behavior and infiltration process of C/C composite preforms with large porosity (25%) were investigated, which could help to understand RMI production of C/C-SiC composite.

2. Experimental

Porous C/C composite preforms prepared for RMI production of C/C-SiC composite were used as the substrate material. Carbon fiber needle felt was used as the reinforcement of the preforms. The carbon fibers were PAN-based (T300, Toray, Japan). The needle felt was prepared by a three-dimensional needling technique, starting with repeatedly overlapping the layers of 0° non-woven fiber cloth, short-cut fiber web, and 90° non-woven fiber cloth with needle-punching step by step. Pyrolytic carbon was deposited on the surface of carbon fibers by chemical vapor infiltration and the porous C/C composite preforms were obtained. The density of the preforms was approximately 1.3 g/cm³ and the open porosity was about 25%. The substrate surfaces were mechanically ground and polished by diamond paste to a mirror finish. Silicon of electronic purity (less than 20 ppb of total impurities) was cut into small cubic pieces with dimensions of 3 x 3 x 3 mm for wetting experiments. Before the wetting experiment, both C/C composite preforms and silicon were immersed in acetone and ultrasonically cleaned and dried at 100 °C for 2 h. The wetting experiments were performed in a flowing Ar (99.999%) atmosphere using a sessile drop method. Detailed description of the experimental procedure was given elsewhere [16].

The C/C composite preform substrate was placed horizontally in a vacuum chamber while the small cube of silicon was stored in a stainless-steel tube with a flexible connector on the top of the dropping device outside the chamber. The stainless-steel tube connected an open alumina tube through which the silicon could be delivered to the substrate surface when the desired testing temperature (i.e. 1773 K) was reached, thus enabling the isothermal wetting kinetics to be fully monitored and avoiding the pre-interaction of the wetting couples during continuous heating. The drop profiles during spreading were captured using a high resolution charge-coupled device camera. The contact angles together with drop geometric parameters such as drop base diameter and height were directly calculated from the drop profiles by using an axisymmetric drop shape analysis program based on the Laplace equation. After the wetting experiments, the specimen was embedded in resin, sectioned perpendicular to the interface, and then polished for microstructure observation and phase identification. The morphologies of the specimen were observed by Hitachi-S4800 scanning electron microscope (SEM). The chemical composition was examined by energy dispersive spectroscopy (EDS). The phases of the specimen were identified by X-ray diffraction (XRD, Rigaku D/Max 2550VB-).

3. Results and discussion

Fig. 1 shows the spreading process of liquid silicon on the porous C/C composite preform substrate. The time t=0 refers to

![Fig. 1. Wetting of liquid silicon on the porous C/C composite preform with the increase of time (a) t=0, (b-d) 0 < t < 43s, (e) 43s < t < 70s, (f) 70s < t, and (g) the final morphology of the wetted sample.](http://dx.doi.org/10.1016/j.ceramint.2016.08.007)
the complete melting of the solid silicon. Seen from Fig. 1, the melting silicon droplet gets a regular spherical crown shape on the porous C/C composite preform. The contact angle takes relatively high value at the moment of complete melting but decreases rapidly with time when \( t < 43 s \) and decreases relatively slowly after about 43s. After wetting for about 70s, all the liquid silicon spreads and infiltrates into the porous C/C composite preform, resulting in a uniform and regular spreading circle. This phenomenon is different from that of Li et al.’s work [7]. In their study, they found the spreading process of liquid silicon proceeds in a non-uniform manner and the solid-liquid-vapor three phase line was non-circular and irregular.

Fig. 2(a) shows the drop base diameter and contact angle as a function of time for silicon spreading over the porous C/C composite preform at 1500 °C. The contact angle decreases rapidly with time while the drop base diameter increases. The initial contact angle between the porous C/C composite preform and silicon is 106.7°, a little larger than that between porous graphite and silicon (90°) [9] and that between glassy carbon and silicon (95°) [7]. As can be seen from Fig. 2(b), the rapid spreading of liquid silicon occurs at a nearly constant rate equal to about 30 μm/s. This is several orders of magnitude slower than the spreading rates measured in non-reactive liquid metal/solid systems [17,18] and is about 3.4 times of that of liquid silicon on the porous graphite substrates [9]. According to the variation of drop base diameter and contact angle as a function of time, four different stages as shown in Fig. 2(a) can be identified during the wetting of porous C/C composite preform by liquid silicon. Stage 1 slight decrease of contact angle and slight increase of drop base diameter with time; stage 2 sharp decrease of contact angle and sharp increase of drop base diameter with time; stage 3 slow decrease of contact angle and constant of drop base diameter with time; stage 4 constant of contact angle and drop base diameter.

It is known that carbon reacts with liquid silicon at high temperatures and forms a SiC interfacial layer between carbon and liquid silicon. The interfacial reaction is believed to influence the wetting process of porous C/C composite preform by liquid silicon. Reaction of carbon with liquid silicon indicates that carbon begins to dissolve into the liquid silicon once they contact and a continuous SiC layer is then formed between carbon and liquid silicon in a very short time period [7,19,20]. The variation of drop base diameter and contact angle in the above 4 stages identified in Fig. 2(a) closely relates to the interfacial Si-C reaction process and infiltration of liquid silicon into the porous C/C preform.

At the initial stage of wetting process, silicon is melted and contacts with the solid carbon. Once the solid carbon contacts with the liquid silicon, it begins to dissolve into the liquid silicon, which leads to the spreading of silicon on the C/C composite preform substrate. The solubility of carbon in liquid silicon is very small [7,19] and the dissolution of carbon becomes saturated in a very short time period. Thus, the dissolution of carbon just makes a slight spreading of silicon on the C/C composite preform and lasts for a very short time period, which results in a slight decrease of contact angle and slight increase of drop base diameter for a very short time period, corresponding to stage 1 in Fig. 2(a). Due to the very short lasting time period, stage 1 is hardly seen from Fig. 2(a). However, it can be clearly observed in the logarithmic scale of the contact angle and drop base diameter for time t in Fig. 2(c).

Once the dissolution of carbon in the liquid silicon becomes saturated, an interfacial SiC layer is thought to be formed on the solid carbon by the reaction between carbon and silicon, which can be demonstrated by the cross-section morphology of C/C composite preform reacting with the liquid silicon for 35 s (Fig. 3). Both EDS and XRD analysis indicate the formation of SiC layer on the solid carbon at the substrate and liquid silicon interface. The reaction between silicon and carbon greatly improves the wetting between carbon and silicon and thus, spreading of silicon proceeds at a rather high speed rate as shown in Fig. 2(b). The contact angle sharply decreases and drop base diameter sharply increases, i.e. the stage 2 in Fig. 2(a). Stage 3 has constant drop base diameter, which means the wetting spreading of silicon has stopped. However, the contact angle decreases with time, which should be caused by the infiltration of silicon into the porous C/C composite preform. After infiltrating of silicon for a certain time, the liquid silicon completely infiltrates into the porous C/C composite preform. The contact angle becomes 0° and the wetting and infiltration of silicon completes, corresponding to the stage 4 in Fig. 2(a) with constant of contact angle and drop base diameter.

Fig. 4 shows the infiltration height as a function of time during the wetting of C/C composite preform by the liquid silicon. The infiltration height was calculated according to the method in reference [14] based on the wetting curve in Fig. 2(a). As seen, the infiltration height linearly increases with infiltration time, strongly suggesting that infiltration is governed by the interfacial-reaction formation of SiC on the pore walls at the infiltration front, rather than the viscous flow. This is consistent with the results from silicon infiltration of graphite material with few pores [14,15]. In order to further confirm the silicon infiltration kinetics, the infiltration height as a function of time based on viscous flow of liquid silicon was calculated according to Washburn equation [12],

\[
h^2 = \frac{\eta r \cos \theta}{2\mu} t
\]

where \( \eta \) and \( \mu \) are the surface tension and viscosity of the liquid silicon, \( \theta \) the equilibrium contact angle of the liquid silicon on the solid carbon and \( r \) the effective pore radius characteristic of the preform.

Pore-size distribution of the C/C composite preform substrate was determined using a mercury porosimetry. The pore size
distribution of the C/C preform is shown in Fig. 5. As can be seen, the pore diameter mainly ranges from 8 μm to 100 μm. The median pore diameter on the basis of volume is 19 μm. Thus, the effective pore radius, $r$, is 9.5 μm based on the median pore diameter. Other parameters [7,13,21,22] used in the Eq. (1) are listed in Table 1. Substituting these parameters into Eq. (1), the infiltration height for different time based on viscous flow of liquid silicon can be calculated. The calculated results are also shown in Fig. 4. As can be seen, the infiltration height at different time based on viscous flow of liquid silicon is much larger than that in present work. The calculated infiltration height for 10 s can reach about 240 mm, which is far from the facts. All the above information distribution of the C/C preform is shown in Fig. 5. As can be seen, the pore diameter mainly ranges from 8 μm to 100 μm. The median pore diameter on the basis of volume is 19 μm. Thus, the effective pore radius, $r$, is 9.5 μm based on the median pore diameter. Other parameters [7,13,21,22] used in the Eq. (1) are listed in Table 1. Substituting these parameters into Eq. (1), the infiltration height for different time based on viscous flow of liquid silicon can be calculated. The calculated results are also shown in Fig. 4. As can be seen, the infiltration height at different time based on viscous flow of liquid silicon is much larger than that in present work. The calculated infiltration height for 10 s can reach about 240 mm, which is far from the facts. All the above information
Physical properties of liquid silicon.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (Kg/cm³)</td>
<td>2330</td>
</tr>
<tr>
<td>Viscosity (Kg/ms)</td>
<td>6.4 x 10⁻⁴</td>
</tr>
<tr>
<td>Contact angle on carbon (°)</td>
<td>20</td>
</tr>
<tr>
<td>Surface tension (N/m)</td>
<td>0.82</td>
</tr>
</tbody>
</table>

confirms the governing of silicon infiltration by the interfacial reaction formation of SiC on the pore walls at the infiltration front.

4. Conclusions

Wetting and infiltration of the porous C/C composite preform by liquid silicon was investigated using a sessile drop technique. The contact angle decreased with time while the drop base diameter increased. The initial contact angle between the porous C/C composite preform and liquid silicon was 106.7° and finally reached 0° due to the complete infiltration of silicon into the porous preform. The infiltration height linearly increased with time, which strongly indicated the reaction control of silicon infiltration.

References