

The morphology and mechanism of formation of SiC in C/C-SiC composites fabricated by liquid silicon infiltration

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Carbon fibre reinforced carbon and silicon carbide dual matrix composites (C/C-SiC) are a new type of high performance brake materials. In the present study, C/C-SiC brake composites were fabricated by the combination of chemical vapor infiltration (CVI) with liquid silicon infiltration (LSI). Results show the composite is composed of 55% C, 39% β -SiC, and 6% Si. There exist two different areas of SiC, one zone of coarse micro- β -SiC grains between 5 and 20 μm at the SiC/silicon interface, and this zone usually forms inside the porosity of the carbon fibre reinforced carbon (C/C) preform such as around the fibres and among the C/C bundles. The other zone consists of fine nano-SiC particles with dimensions of 100–800 nm at the pyrocarbon/carbon fibre interface. From these observations, reaction mechanisms governing the siliconization of porous C/C preform are proposed. After an initial reaction of carbon with liquid silicon, an initial continuous SiC layer formed on the silicon/pyrocarbon interface, and the subsequent formation of SiC is controlled by diffusion of carbon atoms and/or silicon atoms through the already formed SiC layer.

Key words: C/C-SiC, Liquid silicon infiltration, Microstructure, Reaction mechanism.

Introduction

Carbon fibre reinforced carbon and silicon carbide dual matrix composites have been developed by the German Aerospace Center (DLR) since the end of the 20 century, originally for space applications [1]. Due to their multiphase matrix composition and the internal SiC, C/C-SiC composites show superior tribological properties in comparison to ferrous metal, powder metallurgy (PM) and carbon/carbon (C/C) composites. In combination with a lower density (about $2.0 \text{ g}\cdot\text{cm}^{-3}$), high thermal shock resistance, ambient conditions such as humidity have nearly no deleterious effect on the material characteristics, excellent impact resistance and higher tensile and flexural strength are shown by these composites [2–3]. For automobiles, the abrasion resistance of the C/C-SiC disks guarantees a service life up to 300,000 kilometers, which is four times greater than that of steel disks. To date China, Germany, America and France have gradually launched their theoretical and applied research on C/C-SiC brake materials [4–6]. Researchers at Stuttgart University and DLR have applied C/C-SiC composites to the friction domain and different sports cars including Porsche, Ferrari and Daimler Chrysler are already been equipped with ceramic brakes, and several companies are currently producing C/C-SiC brake disks

and pads. C/C-SiC brake composites fabricated by P. Xiao of Central South University also have shown great progress, and have successfully been applied in engineering machines and magnetic aerotrains, and in preparation to be applied on the wheel disk of helicopters and brakes of tanks.

In recent years, the chemical vapor infiltration (CVI) process has proven to be a most promising method for fabricating ceramic composites [7]. Despite the long manufacturing time, the primary advantages of this process are the abilities to manipulate and modify the microstructure of the matrix, and to fabricate complex net or near-net shaped components at relatively low temperatures, especially when textile structures are used as a preform. The liquid silicon infiltration (LSI) method was developed by DLR to produce ceramic matrix composites since the 1980s [8–9]. The liquid silicon is infiltrated into the open porosity or cracks of the C/C preform by capillary forces and reacts with the carbon matrix and carbon fibres to form SiC. The LSI process leads to a damage-tolerant ceramic material, but has a significantly lower component fabrication time and therefore reduced component costs compared with other CMC manufacturing processes.

The reaction of carbon with liquid silicon has been studied and lead to some disagreement between the authors in the interpretation of the observed phenomena. Mainly, two mechanisms are proposed: (1) the limiting step is the diffusion of carbon and silicon through SiC [4, 10–11] and (2) a solution-precipitation process. On the other hand, the reactive carbons are mostly glassy carbon and graphite, there are only a few publications which try to

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elucidate the siliconization of pyrocarbon by CVI process [12–13]. The aim of our research is therefore to obtain detailed information on the microstructure and the morphology of the silicon carbide. In the present investigation, the carbon fibre reinforced preforms were produced by the CVI process, then the preforms were infiltrated with liquid silicon that reacts to form SiC and obtain the final C/C-SiC composites. Detailed information about the SiC morphology in the C/C-SiC composites was observed. Also, a model of the liquid silicon reaction with the carbon matrix is offered.

Experimental

Materials processing

PAN-based carbon fibre (T700) was employed supplied by Toray of Japan, and each yarn contained 12,000 filaments. Silicon powders 37 μm in diameter and contains 99.3% silicon (Da Zelin-silicon Corp., Beijing, China) were used. The processing of the investigated C/C-SiC brake materials included three steps as shown in Fig. 1. The first step involved production of a fabric preform using the three-dimensional braided method, starting with repeatedly overlapping the layers of 0° non-woven fibre cloth, short-cut fibre web, and 90° non-woven fibre cloth with needle-punching step by step. The density of the preform was about $0.6 \text{ g}\cdot\text{cm}^{-3}$. The second step used a gas phase route to manufacture the porous C/C composites, also referred to as chemical vapor infiltration (CVI). The temperature for CVI was about 1000°C for 200–500 h in an argon atmosphere of 0.1 MPa. C_3H_6 was used as a precursor and H_2 as a carrier and diluting gas. The density of the porous C/C composites was about $1.36 \text{ g}\cdot\text{cm}^{-3}$. The final step was a subsequent infiltration of the resulting, porous C/C material with molten silicon at a temperature of 1650°C in a vacuum for 0.5 h. Thereby the silicon reacts with a small amount of the C and forms SiC as the ceramic matrix. The resulting C/C-SiC consists of C or rather C/C bundles (C fibre-reinforced C) embedded in the SiC

matrix. SiC and unreacted silicon are mostly distributed in the short fibre web layers of the material. The density of the resulting C/C-SiC lies below $2.2 \text{ g}\cdot\text{cm}^{-3}$.

Experimental

The open porosity and bulk density of samples were measured by Archimedes' method. Experiments were conducted on the micrometre and submicrometre scales. By etching C/C-SiC specimens with an aqueous solution of 90 volume% nitric acid (HNO_3) and 10 volume% hydrofluoric (HF) for 48 h, it was possible to remove the unreacted silicon and to observe the SiC crystals at the interface of SiC/silicon. The phase identification was performed by means of X-ray diffraction (XRD) (model Rigaku D/max 2550PC, Japan) using $\text{Cu K}\alpha_1$ radiation with Si as an internal standard. The phase compositions, morphology of worn surfaces and wear debris were measured by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDX) (model JSM-6360LV, Japan).

TEM specimens were prepared using resin cross section holders to stabilize the C/C-SiC material during the preparation process. By mechanically cross sectioning the holders 3 mm discs are obtained. Subsequent polishing, dimple grinding and final argon ion milling result in electron transparent samples. The ion beam thinning was performed in a GATAN600 made by USA at an ion energy of 600 kV and an incident angle of 6° . The HRTEM investigations were performed on a JEOL-2010 operated at 200 kV. This instrument has a point resolution of 1.7 Å.

Results and discussion

Phase and Microstructure analysis

The bulk density and open porosity of samples are about $2.20 \text{ g}\cdot\text{cm}^{-3}$ and 2.4%, respectively. The XRD pattern of the C/C-SiC composite is shown in Fig. 2. The phase analysis reveals the presence of carbon, silicon carbide and unreacted silicon in the C/C-SiC composite.

Gravimetric analysis was employed to determine the

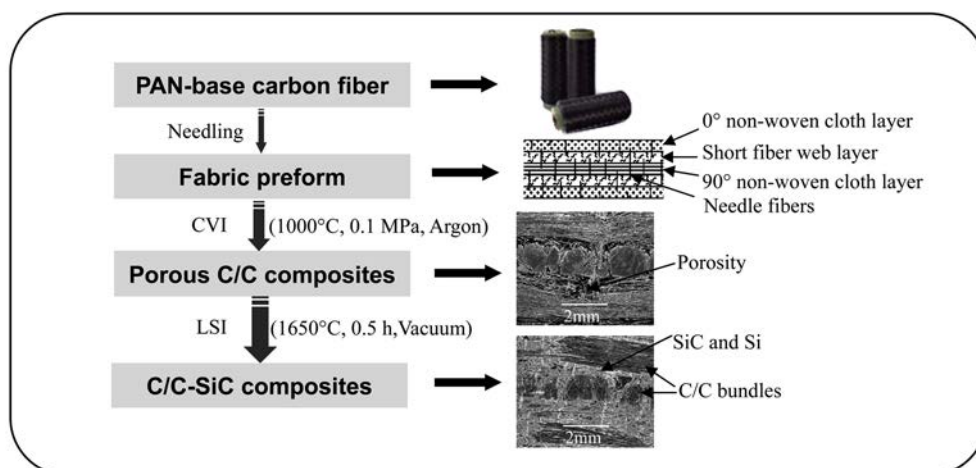


Fig. 1. Schematic representation of the manufacturing process for the C/C-SiC composites.

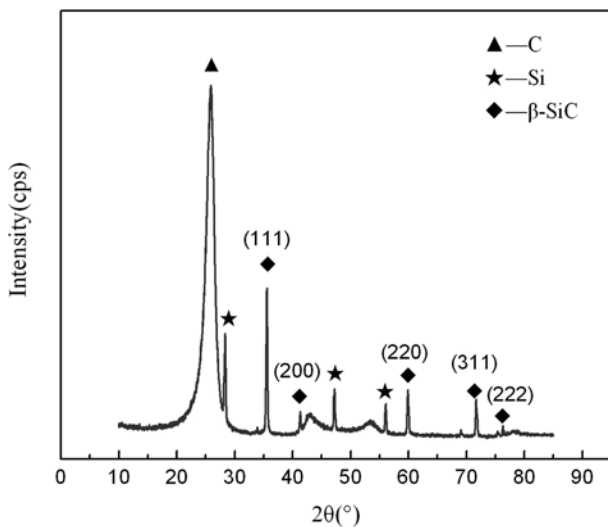
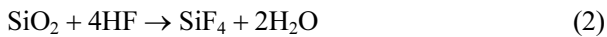
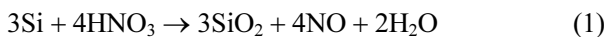


Fig. 2. XRD pattern of C/C-SiC composite.

content of carbon, unreacted silicon, and SiC in the composites. The distribution and morphology of each phase in C/C-SiC composites is visible (as shown in Fig. 3(a)). Unreacted silicon is removed by dissolving the composite in a mixture of nitric acid and hydrofluoric at room temperature for 48 h. During this etching, silicon first oxidizes to silicon dioxide and subsequently reacts to form a stable hexafluoro-complex according to the following equations:



The acids only affect free silicon, whereas carbon and silicon carbide remain stable during etching. Due to the high accessibility of the SiC zones the acid reached all regions of residual free silicon and removed it completely, as shown in Fig. 3(b). The carbon fibre and pyrocarbon matrix is moved by burning it off at 700°C for 10 h in air according to the following equations:



Fig. 3(c) and (d) show the C/C-SiC microstructure after the chemical and thermal treatment. The content of each component can be calculated after weighing the residual mass and the result is shown in Fig. 4. The gravimetric analysis revealed there is little residual silicon but much SiC is produced because of the high activity of the pyrocarbon carbon. A large amount of SiC matrix was formed combined with some residual silicon around the dense C/C substructures in the C/C-SiC composite (Fig. 5), and moreover a large amount of isolated SiC particles scattered in the solidified silicon phase was seen. For the porous C/C materials with high density microstructure, silicon rapidly infiltrates the C/C preform and reacts with the fibre bundle exterior carbon (including thermally decomposed carbon and part of the carbon fibre) form SiC during the LSI process. So the macroscopic holes between the fibre bundles have been filled with SiC, which also can be seen in Fig. 3(c).

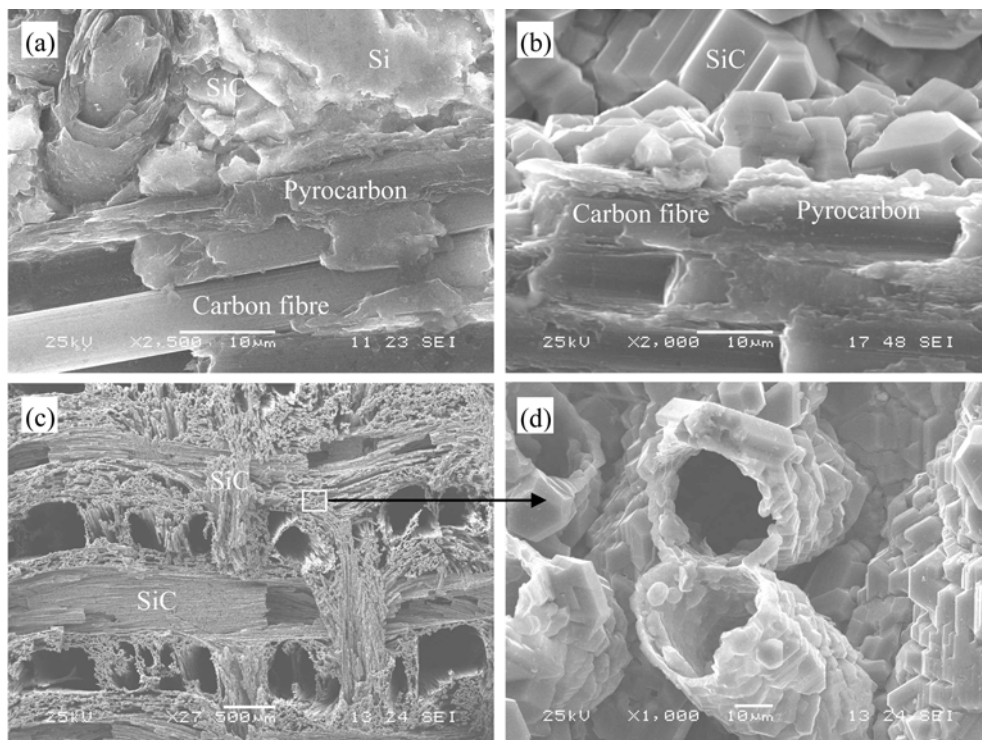


Fig. 3. Micrographs of the C/C-SiC composite during the gravimetric analysis process for (a) C/C-SiC composite, (b) after dissolving Si, (c) and (d) after oxidation.

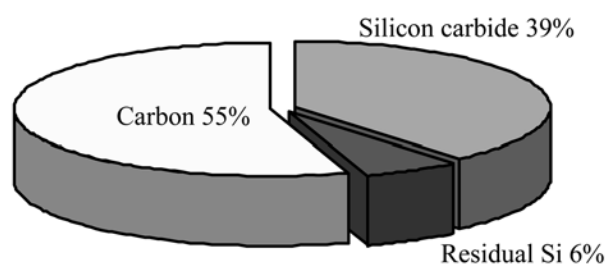


Fig. 4. Phase composition of the C/C-SiC composite.

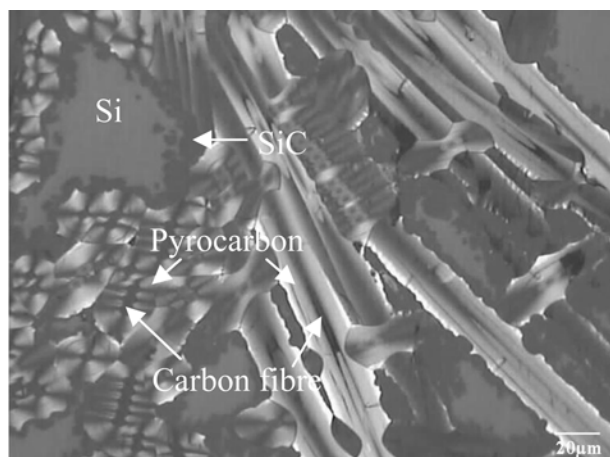


Fig. 5. Optical micrograph of the C/C-SiC composite.

Morphology of silicon carbide

The aim of there investigations is to obtain detailed information on the morphology of the SiC areas, the

pyrocarbon/silicon carbide and silicon carbide/silicon interface that may elucidate the mechanisms governing the siliconization of carbon/carbon preforms.

After 1 h reaction time, some faceted, hexagonal, shaped SiC crystals appear at the pyrocarbon/silicon carbide surfaces (Fig. 6(a)). The size of these SiC crystals is between 5 and 20 μm , with a high density of twins and sometimes there are very large crystals, and some of the grains have grown around others. The interface between SiC and pyrocarbon is shown in Fig. 6(b). The thickness of the SiC layer between the residual silicon and pyrocarbon is between 5 and 15 μm , as shown in Fig. 6(c) and Fig. 5. The continuous SiC layer seems to be a rough monolayer of SiC crystals randomly arranged onto the pyrocarbon surface. Furthermore, it seems that there are cracks between SiC grains or through single grains (Fig. 6(d)). This is because the metal silicon is different from most of metallic materials: the volume of liquid silicon does not contract but expands during the solidification process (the volume expansion reach to 8%). At the temperature decreases during the process of the liquid silicon infiltration, the volume expansion causes stresses to be generated locally and this leads to the cracks.

Further investigations were conducted using transmission electron microscopy. Fig. 7 represents the interface of pyrocarbon/carbon fibre and their EDS patterns. There are nano-SiC crystallites with a mean crystal size between 100 and 800 nm. Furthermore, it seems to have been established that neither the pyrocarbon matrix nor the carbon fibres are preferred reaction sites. Instead siliconization leads to a steady conversion of both fibre and matrix.

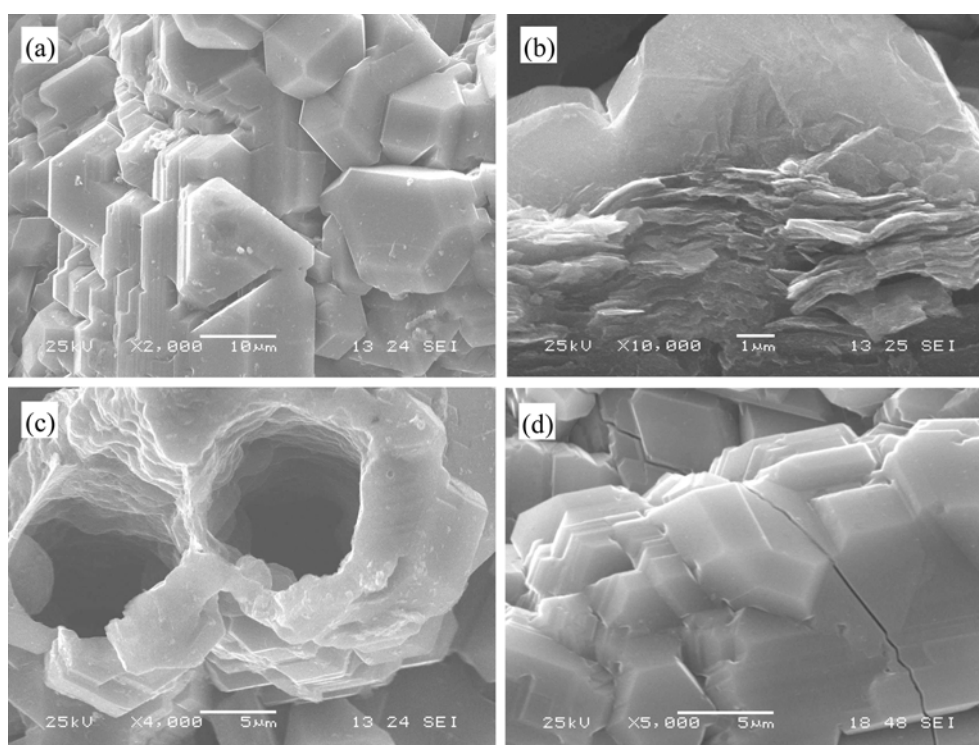


Fig. 6. SEM micrographs of etched an C/C-SiC specimen revealing grains at the SiC/silicon interface.

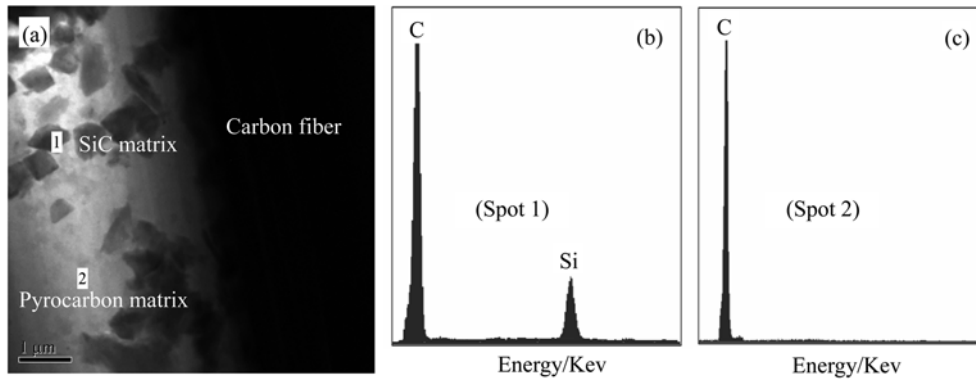


Fig. 7. TEM images of C/SiC interface and EDS patterns for (b) spot 1 and (c) spot 2 of the C/C-SiC composite.

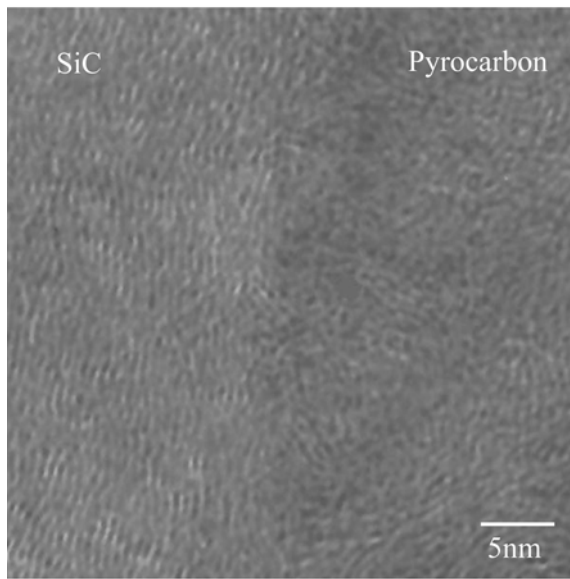


Fig. 8. The pyrocarbon/SiC interface on the atomic scale.

In Fig. 8, a cross section through a SiC/pyrocarbon interface is shown. On the left side of the micrograph SiC can be seen. In this image the fiber axis runs into the image plane so that the crystal lattice of the pyrocarbon can be detected easily in the right part of the image. As mentioned earlier the pyrocarbon shows the typical microstructure of turbostratic carbon in its cross-section. Note that at the SiC/pyrocarbon interface no interphase can be observed.

On the basis of the above analysis and the remarks of other researchers [4, 10-13] a two-stage mechanism for liquid silicon infiltration mechanisms is proposed (as shown in the Fig. 9). Firstly, the dense fibre bundles are hardly accessible to the silicon but the cracks within both the inter-bundles and inter-ply regions could act as a communicating channel system with high capillary forces for liquids of low viscosity. The microcracks and pores within the short-cut fibre webs are convenient for molten silicon to be retained and dispersed within these regions (Fig. 9(a)). Secondly, the wetting angles of liquid silicon on silicon carbide and pyrocarbon are 30~45° and 0~30°,

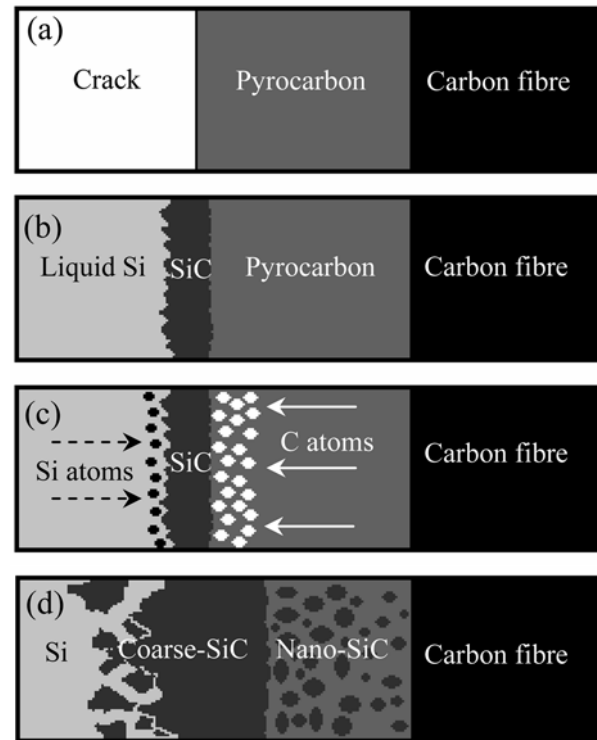


Fig. 9. Schematic representation of a model of liquid silicon infiltration.

respectively. So when the melting point of silicon (1410°C) is exceeded, silicon rapidly infiltrates the C/C preform because of capillary forces and reacts with pyrocarbon to form silicon carbide. The heterogeneous nucleation and growth of SiC leads to the formation of a continuous polycrystalline SiC layer (Fig. 9(b)). The formation of this initial continuous SiC layer is very rapid, and the subsequent growth is controlled by diffusion of carbon atoms and/or silicon atoms through the SiC layer (Fig. 9(c)). The diffusion of the silicon melt in the silicon carbide layer can be expressed by:

$$C = C_0 \left[1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right] \quad (6)$$

where C_0 is the concentration of silicon outside the

silicon carbide layer, C is the concentration of silicon at a distance x from the outside towards the inside, D is the diffusion coefficient of silicon in silicon carbide ($\sim 10^{-17} \text{m}^2 \text{s}^{-1}$), $\text{erf}(x/2\sqrt{Dt})$ and is the Gaussian error function. Studies of the diffusion of carbon and silicon in polycrystalline β -SiC have been carried out by Hon and Davis [14, 15] who suggest that the lattice self-diffusion coefficient for carbon is 50-100 times higher than for silicon. It is likely that the SiC layer growth proceeds by migration of carbon through SiC and the subsequent reaction at the SiC/silicon interface (Fig. 9(d)). Several mathematical models have been presented to describe the kinetics of the reaction, and for all of the models the limiting step is the diffusion of carbon and silicon through SiC [4, 10-11].

Conclusions

C/C-SiC composite samples prepared by a combination of chemical vapor infiltration with liquid silicon infiltration were investigated by SEM, TEM and by XRD. It was established that the composite is composed of 55% C, 39% β -SiC, and 6% Si by means of gravimetric analysis. The β -SiC usually forms inside the short-cut fabric, around the needing fibres and among the C/C bundles in the non-woven web with much porosity or cracks, and unreacted silicon is located among coarse SiC grains. It was found that during siliconization of C/C preforms SiC develops in two morphologies, a zone of coarser SiC grains between 5 and 20 μm in size at the SiC/silicon interface, and a fine nano-SiC particles with dimensions of 100-800 nm at the pyrocarbon/carbon fibre interfaces. A model of the siliconization of porous C/C preform is proposed. After an initial reaction of carbon with liquid silicon, an initial continuous SiC layer formed on the liquid silicon/pyrocarbon interface, and the subsequent formation of SiC is controlled by

diffusion of carbon atoms and/or silicon atoms through the already formed SiC layer.

Acknowledgements

The authors gratefully acknowledge the financial support for this study provided by the National Hi-Tech Research Development Program of China (2006AA03Z560), Excellent Youth of Hunan Province, China (06JJ1007) and the Graduate degree thesis Innovation Foundation of Central South University.

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