INFLUENCE OF GAS PHASES ON THE PROCESSING OF C/SiC VIA LIQUID SILICON INFILTRATION

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Introduction

The liquid silicon infiltration process (LSI) of C/C is one of three established ways to fabricate carbon fiber reinforced silicon carbide (C/SiC). Relatively short processing times and moderate costs are the main advantages as low infiltration rates (CVI-process) or repeated impregnation/pyrolysis-cycles (polymer-pyrolysis route) can be avoided [1].

A severe drawback which is tightly connected to the LSI process, is carbon fiber degradation. Silicon melt reacts not only with carbon matrix but also with the reinforcing fibers. As a consequence their strength and strain to failure are reduced dramatically. Additionally, the resulting strong interconnection between the two components leads to an excessive fiber/matrix-adhesion and therefore brittle failure behavior. Modifications of the standard LSI-process to overcome these restrictions are described in another contribution [2].

There is a broad agreement about the central importance of the fast reaction between liquid silicon and solid carbon for the formation of the SiC matrix. But some experimental observations suggest that the mechanisms are more complex and gas phase reactions have to be considered, too. Prerequisite for the development of suitable fiber-coatings which can, both preserve the carbon fibers from degradation and allow to control the fiber/matrix-adhesion, is the understanding of the relevant reaction mechanisms before and during the silicon melt infiltration.

Experimental

For the present work 2D C/SiC samples were produced through liquid silicon infiltration of C/C. As shown in Fig.1 phenolic resin is used as carbon matrix precursor. High tenacity (HT) carbon fiber fabrics with twill weaving represent the reinforcing component. The carbonization of the resin matrix was performed at 900°C in flowing argon atmosphere. For the silicon infiltration 1450°C and vacuum conditions were chosen, with the samples embedded in Si powder of $d_{90} < 15\mu$m grain size. A more detailed description of the processing is in [3].

![Diagram of the LSI-process for the production of C/SiC](image_url)

Figure 1. LSI-process for the production of C/SiC

To separate the role of liquid phase from gas phase reactions, additional experiments were made. The same carbon fiber fabrics which were used for the composites were annealed for the same time (1h) under the same conditions as for the silicon infiltration, but direct contact to the silicon melt was avoided. The fabrics were built up of fiber bundles of 12000 single filaments. Afterwards the samples were prepared metallographically to reveal their microstructure. The composites were examined by optical and scanning electron microscopy, the fibers only by SEM. For the investigation of the morphological changes which happened to the exposed fabrics, it was favorable to introduce another preparation step. Through an oxidation treatment at 800°C in air the unaffected carbon fraction of the fibers was removed. Those parts which had contact to Si-containing gaseous species and reacted to SiC are more pronounced then and easily detectable also at lower magnifications.
Results

After liquid silicon infiltration of the carbonized C/C samples within 1h at 1450°C an interconnected SiC matrix fills the space within and between the fiber bundles quite homogeneously. Fig.2 gives an overview of the SiC distribution through the composites cross section.

Figure 2. 2D-C/SiC after liquid silicon infiltration, dark gray: carbon fibers; light gray: SiC.

Not only the former matrix carbon is converted to SiC, but also a significant part of the carbon fibers; Fig.3 shows the typical microstructure in a more detailed view.

Figure 3. 2D-C/SiC, partially converted carbon fiber with SiC shell and core of unreacted carbon; embedded in dense SiC matrix.

The appearance of the matrix is dominated by relatively large, dense SiC crystals with arbitrary orientation. Whereas the SiC layer which surrounds the fiber core consists of significant smaller (100-200 nm in size) grains and contains considerable porosity. Due to the different morphologies of the SiC product, the shape of the original fiber is still clearly recognizable.

In Fig.4(a) the “vacuum” treated fibers are shown. Their surface structure has changed, if compared to untreated, PAN-based carbon fibers. After oxidative removal of the uncombined carbon, the effect of the siliconizing atmosphere is more obvious, as one can see from Fig. 4(b).

Figure 4. Carbon fibers treated at 1450°C, 1h, vacuum, in presence of Si. (a) without any additional treatment, (b) after oxidation at 800°C, 4h.

Tube-like SiC structures are what is left when the residual carbon is removed. Their wall thickness typically is in the range of 200 to 400 nm with a smoother outside and a rougher inside. The SiC tubes appear crystalline and dense with only minor porosity.
Although these morphologies represent the biggest portion of the vacuum high-temperature treated fibers, there is a non-negligible amount of them, located exclusively at the most outward area of the bundles, with dissimilar appearance. From Fig.5 it gets visible that these carbon fibers have been converted to SiC completely. Although no consecutive oxidation treatment was performed here, only a highly porous skeleton is left. It consists of fine grained SiC-crystals of about 100 nm in size. This morphology is in good agreement with those found throughout the composites cross section (see Fig.3). However, it has to be mentioned again that these porous structures are only a minority within the annealed fabric, in contrary to their considerable fraction in the melt infiltrated composites.

Discussion

It is well known that the direct reaction between Si melt or vapor with solid carbon results, at least in the investigated temperature region, in the formation of β-SiC crystals [4, 5]. This explains very well the SiC shell of the fibers exposed to the Si-containing furnace atmosphere. As soon as the Si powder starts melting sufficient amounts of Si-vapor should be available to form crystalline and dense SiC layers. But this cannot explain the presence of highly porous fiber structures in the composites and the pure fabrics. For this a carbon removing reaction has to be involved. SiO is known to form porous SiC material with solid carbon, according eqn.(1) [6].

\[ \text{SiO} + 2C \rightarrow \text{SiC} + \text{CO} \]  

(1)

The formation of porosity is due to the fact that every second carbon atom is removed to form CO. Silicon possesses a high oxygen affinity and therefore always has an oxide layer at the surface (0.7 wt.% O for the used powder). From this source enough SiO could be produced, following eqn.2, to convert the most outward fibers in the fabric but not the complete fiber bundle.

\[ \text{SiO}_2 + \text{Si} \rightarrow 2\text{SiO} \]  

(2)

Also the limited amount of O which is introduced by the Si powder cannot generate enough SiO to form the widespread porous SiC phases around the carbon fiber cores in the infiltrated composites by one simple reaction. The presence of liquid silicon in the composite must play a key role for any possible explanation. This might be found in the combination of two reactions.

\[ \text{SiO} + 2\text{C} \rightarrow \text{SiC} + \text{CO} \]  

(1)

\[ \text{CO} + 2\text{Si} \rightarrow \text{SiC} + \text{SiO} \]  

(3)

The reaction mechanism described by eqn.(3) is proofed for temperatures of 1500°C and higher [6]. When the Si melt infiltrates the composite, pores and cracks become encapsulated areas. SiO which is consumed according to eqn.(1) will be regenerated when the by-product CO reacts with the Si melt, according to eqn.(3). This means also that SiC is formed in the Si melt. Even small amounts of oxygen are able to keep this process running, because they work like catalysts in transportation reactions. In the present case silicon and carbon are transported as monoxides via the gas phase to their reaction partners.

At the same time, of course the direct reaction between Si and C takes place and forms SiC layers on the carbon matrix and the fibers which suppress the full conversion to porous SiC. Furthermore, the porous products are filled with liquid silicon. With increasing holding time their small grains tend to grow by recrystallization processes. As a consequence the fine-grained areas will disappear slowly and transform to the coarser material.

References
