

# MECHANICAL AND PHYSICAL CHARACTERISATION OF LOW DENSITY CARBON-CARBON COMPOSITES

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## ABSTRACT

The material investigated in this study is a prototype material, where a porous carbon-carbon composite, termed carbon bonded carbon fibre (CBCF), has been infiltrated with silicon carbide by chemical vapour infiltration (CVI). The CVI SiC CBCF composites have been developed in order to facilitate the usage of CBCF materials within reactive environments. This research is looking to establish whether the incorporation of silicon carbide into the CBCF composites, has indeed improved their performance in reactive conditions and whether there are any other benefits. This paper reports the results of a study of the oxidation and thermal shock resistance. Results thus far have been promising. It has been found that the performance of the CBCF material has improved in oxidising conditions with the incorporation of the silicon carbide coating, and also that the coated material is resilient against thermal shock.

## INTRODUCTION

CBCF materials are low density carbon-carbon composites ( $0.1-0.5 \text{ g/cm}^3$ ) which are very porous. They are composed of three constituents which are virgin carbon fibres, recycled material from the manufacturing process, and a carbon matrix produced from the pyrolysis of a phenolic. Often, the fibrous material within the composite is given an additional coating of carbon using a chemical vapour deposition process. CBCF has been used for many years as insulation for furnaces. However, its usage has been limited within this sector due to oxidation (CBCF begins to oxidize at about  $450^\circ\text{C}$ ) and degradation in other hostile environments (such as  $\text{H}_2$ ). The material, as a consequence of the vacuum molding stage in the manufacturing process, has a layered structure where a high percentage of the solid material is concentrated in parallel layers termed the 'x/y layers'. These layers are held together by a lesser amount of material in the z direction. This layered structure has commonly been referred to as a 2D planar random structure [1], and results in CBCF being anisotropic. The fact that the CBCF has anisotropic thermal conductivity, which is high within the x/y layers and low perpendicular to them, together with its low density and high porosity makes it highly suitable for thermal insulation. Fig 1 is a pictorial representation of the CBCF structure, and figure 2 is a SEM micrograph highlighting the high level of porosity as well as the layering within the composite.

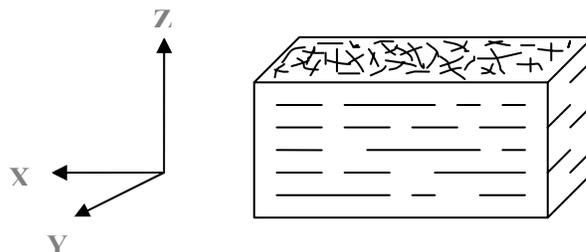


Figure 1. Layered structure of CBCF materials

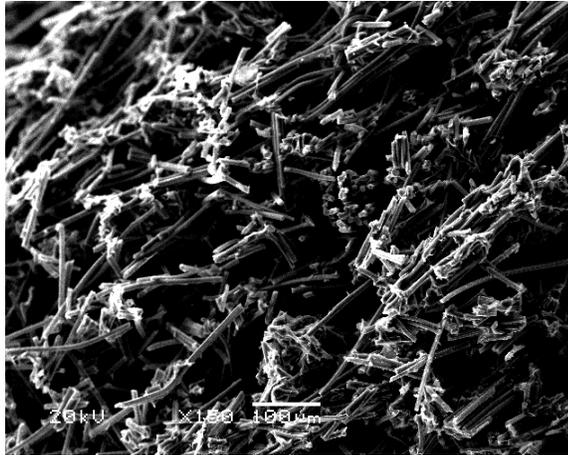


Figure 2. SEM micrograph of silicon carbide coated CBCF. In this image the traces of the x/y layers lie at approximately 45% to the horizontal.

As previously detailed, the major limiting factor with the CBCF is its reactivity within hostile environments, which is why the material was given a silicon carbide coating using CVI. This paper will detail work carried out in order to ascertain the level of protection offered by the silicon carbide coating to the CBCF composite. Experiments conducted include testing the coating using thermo gravimetric analysis by heating to high temperatures in air whilst monitoring weight loss. This was done using differential thermal analysis (DTA) equipment. Due to size restrictions on the DTA samples, ‘bulk oxidation’ tests have also been performed where the conditions of the DTA experiments were reproduced as closely as possible within a standard furnace. This facilitated the use of larger samples. The idea behind these two experiments was simply to gauge the effectiveness of the silicon carbide coating in acting as a barrier between the oxygen and the carbon. Thermal shock tests were conducted from various temperatures up to 1100°C. These provided a measure of how the composite is affected by the difference in coefficient of thermal expansion between the coating and the substrate CBCF material.

## EXPERIMENTAL PROCEDURE

Thermo gravimetric analysis (TGA) was conducted for both the CBCF and the silicon carbide coated CBCF (1 sample each) using a Stanton redcroft STA 780 series differential thermal analyser. The samples for the TGA were blocks of size 2×2×3 mm<sup>3</sup> and were cut using a fine hacksaw. The tests were conducted to 900°C in air, at a heating rate of 10°C/min. The reference material was alumina.

The results from the thermo gravimetric analysis led to the conduction of bulk oxidation tests, which basically made an attempt to replicate the TGA test conditions within a standard furnace, so that larger samples could be studied. These samples had approximate sizes of 20×20×20 mm<sup>3</sup>. The furnace was set to heat up to 1200°C at 10°C/min. The samples had to be removed at incremental temperatures (mostly 100°C) and weighed on a balance. When removed for weighing, the samples were allowed to sit for 10 minutes in order for them to become cool enough for weighing. During this time the temperature within the furnace was kept constant. Once the sample/s had been weighed, they were placed back into the furnace and heated to the next increment at 10°C/min. Three samples were tested for both the CBCF and the silicon carbide coated CBCF material.

The thermal shock tests were conducted for the silicon carbide coated CBCF and involved heating the samples to temperatures ranging from 200 to 1100°C at 10°C/min. Once at the required temperature, the samples were removed from the furnace and quenched in water. The samples remained within the water for 2 minutes. The samples were then placed in a desiccator to remove excess water, and their flexural residual strength evaluated using 3 point bend testing. Samples had dimensions of 5×10×60 mm<sup>3</sup> which has been shown to be an effective sample size for obtaining flexural failure with CBCF materials [2]. Both the x/y and z orientations were studied, with 3 samples being tested at each temperature. The shocked samples

were examined using scanning electron microscopy (SEM) and images were taken of any damage present. An attempt was made to quantify the damage present by counting the regions which were deemed to be damaged within a constant area for the various samples. Regions which were taken as being damaged included those where the coating was visibly cracked, or had fragmented/spalled (as in figure 7), or where the texture of the coating was visibly different. Images were also taken where entire fibres had cracked.

## RESULTS/ DISCUSSION

The results from the TGA of the CBCF and silicon carbide coated composite are shown in fig 3. As can be seen these results seem to imply that the silicon carbide coated composite was not providing any protection to the CBCF composite from oxidation, as both materials were burning off at the temperature, under the conditions of the experiment.

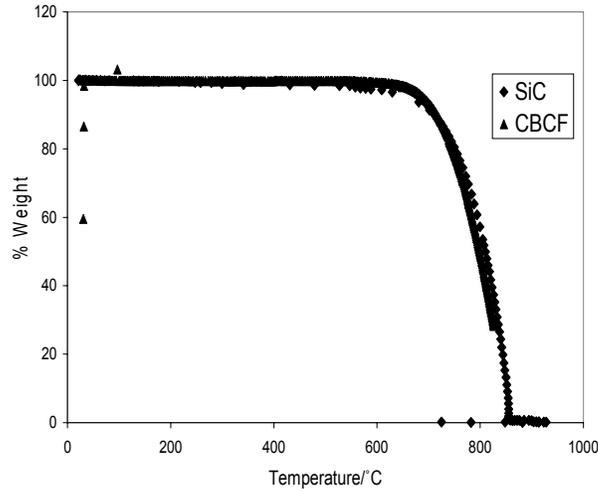


Figure 3. DTA results for CBCF and SiC coated CBCF.

This unexpected result was that due to the small sample size, and hence the large surface to volume ratio, which meant that a significant proportion of the carbon fibres were exposed to the atmosphere and were open to attack. Thus in order to test the effectiveness of the coating, larger samples needed to be investigated. Therefore bulk oxidation tests were conducted, the results of which are shown in figure 4.

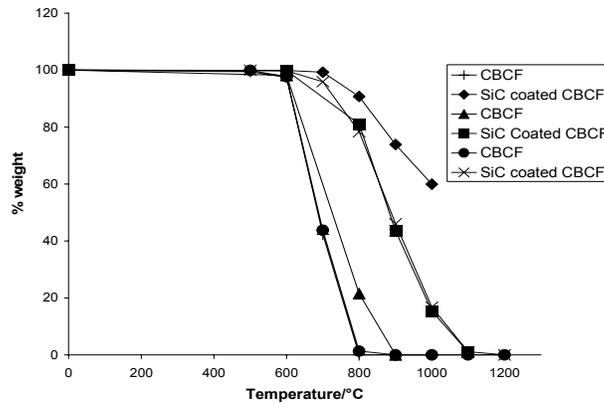


Figure 4. Bulk oxidation test results for the CBCF and SiC coated CBCF.

From these results it can clearly be seen that the silicon carbide coating provides a good level of protection to the CBCF composite within oxidizing environments. There is a sharp drop in the weight of the CBCF samples at 700°C whereas the silicon carbide coated samples remain unaffected at this temperature. Degradation with the silicon carbide coated samples commences at around 800°C and is not as drastic as that which occurs with the CBCF at 700°C. Two of the CBCF samples had combusted completely by 800°C and the other by 900°C. Whereas all three silicon carbide coated materials retained some integrity to much higher temperatures.

The results of the thermal shock experiments described earlier are shown in figures 5 and 6, where figure 5 shows the flexure strength for x/y direction samples, and figure 6 for the z direction. The values shown at the temperature of zero are the mean flexure strengths for the unshocked materials.

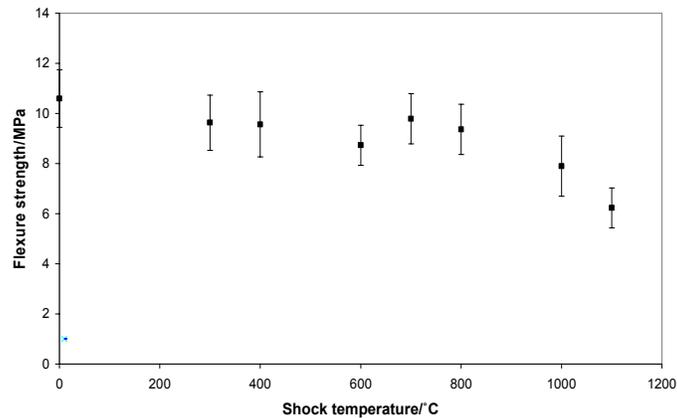


Figure 5. Residual flexural strength results for x/y orientation thermal shock specimens

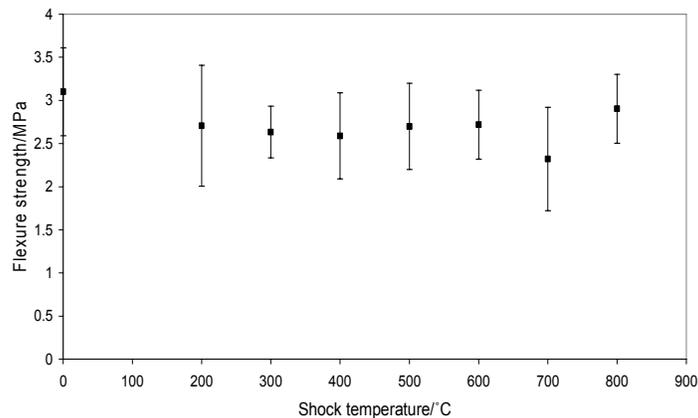


Figure 6. Residual flexural strength results for z direction thermal shock specimens

As can be seen there is virtually no degradation in residual flexural strength when the silicon carbide coated CBCF material has been shocked from temperatures of up to 800°C for both orientations. For the higher temperatures investigated for the x/y direction, reduction in strength has occurred. However these reduced strength values are still considerably greater than the flexural strength values for the unshocked CBCF material (1-2 MPa). The fact that the silicon carbide coated CBCF material is retaining its strength after being thermally shocked at these temperatures is due to the fact that the coefficient of thermal expansion of the silicon carbide is similar to the thermal expansion coefficient of carbon and the small size of the structural unit within this porous material. This means that during rapid cooling, the

stresses being generated are not sufficiently large to cause major damage to the coated fibres within the material. Nevertheless, there were regions within the samples that had been damaged such as the region shown in fig 7. Here a portion of the silicon carbide coating has fragmented. A possible explanation as to why damage was occurring in certain regions but not in others is variations in coating thickness and in SiC-substrate interfacial strength. The stresses generated as a result of the thermal expansion mismatch between the two materials in a particular area, would be proportional to the thickness of the silicon carbide coating within that area and the extent of spalling would depend on the interfacial strength.

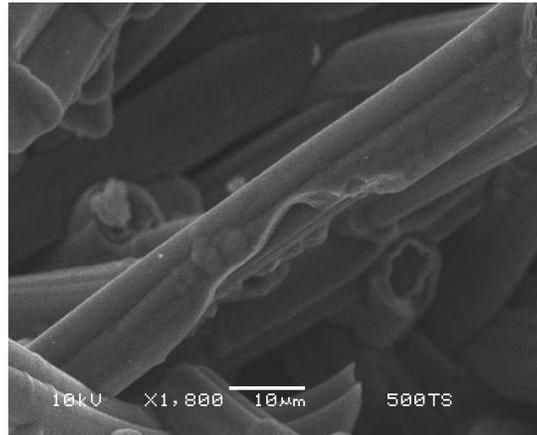


Figure 7. SEM micrograph showing damage caused by thermal shock at 500°C

Quantification of the damage by SEM demonstrated that there was a gradual increase in the amount of damage with increasing shock temperature. This is an expected result as the higher the thermal shock temperature, the greater the thermal gradient and thus the greater the stresses generated. It is proposed that the most critical form of damage with respect to the residual strength of the material, was complete cracking of the coating and the underlying fibre. The reason being that it is the coated fibre network/structure that is responsible for giving the composite its strength. Thus a cracked coated fibre is likely to have a greater effect on the residual strength of the material than any small localised damage of just the coating. The fact that this particular form of damage was the least common is probably why there was little effect on the residual strength of the material due to thermal shock.

## CONCLUSIONS

The results from this study have shown that the silicon carbide coating does indeed provide protection to the CBCF composite in an oxidizing atmosphere. This could mean that in the future, CBCF could be used for medium temperature applications (up to 600°C) within an oxidizing atmosphere. Also, it has been seen that the material performs well after being thermally shocked from temperatures up to 1100°C in air. Again, this is a promising result as it means that the silicon carbide coated CBCF may be rapidly cooled from the CVI processing temperature and has potential for use in applications involving rapid changes in temperature. Future work will include a study of the silicon carbide coated material in other atmospheres such as H<sub>2</sub>, as well as an investigation of the thermal cycling and thermal ageing behavior of the silicon carbide coated material within an oxidizing environment.

## REFERENCES

- [1] Davies, I. J., Rawlings, D. R., J. Mat. Sci., volume 29, 1994, pages 338-344
- [2] Davies, I. J., Rawlings, D. R., Carbon, volume 32, issue 8, 1994, pages 1449-1456