CF/SIC COMPOSITES BY A NOVEL MANUFACTURING METHOD

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Abstract
A continuous carbon fibre/silicon carbide matrix composite material has been produced by a low-cost manufacturing method. According to this method, the space in a 2-D carbon fibre preform is filled with a SiC powder by a pressure infiltration method. High particle packing densities are achieved within the fibre preform in this way. The compact body is heat treated at 400°C to form a porous framework, which is then infiltrated with a liquid pre-ceramic polymer, CERASET™SN. Subsequently the infiltrated polymer is pyrolysed in argon in the temperature of 1300°C. The densification degree, mechanical and thermal properties of the composite material have been measured and related to the microstructure. The developed C_/SiC/SiC composite is considered to be a promising material for low and high-temperature applications such as brake discs, seals, components of chemical reactors, gas turbines, etc.
SUMMARY

The fast and simple process of manufacturing the C\textsubscript{f}/SiC Composites by pressure infiltration/polymer infiltration method has been developed. The liquid pre-ceramic polymer, CERASET\textsuperscript{TM} SN, was used for infiltration of a green composite body followed by the pyrolysis step in argon at the temperature of 1300°C.

The manufactured material consists from carbon fibres, SiC powders, SiCN glassy phase and pores in quantities of 28.5/43.0/21.1/7.4%, respectively. The CMC material is characterised by the density of 2.329/cm\textsuperscript{3}, bending strength of 105 MPa, fracture toughness of 9.9 MPa.m \(\frac{1}{2}\) and thermal conductivity, of 14 W/m.K. This material can be used for manufacturing of brake disc/pads for rapid train systems/automobiles and also in high temperature devices such as components of heat exchanger, chemical reactors, gas turbines, waste incineration plants, etc.
1. INTRODUCTION

Weight reduction and significant decrease in the manufacturing cost of components are the driving forces for new composites to be developed by a cost-effective method. In the field of ceramic-matrix-composites (CMC), which are potential candidates for applications where a low specific density, high strength and high toughness are required, a significant progress was made in the last two decades. However the major obstacle to a much broader CMC components application in the civil sector of the economy is still their quite high price [1]. CMCs in which continuous C- or SiC fibres are embedded in a non-oxide ceramic matrix have allowed a breakthrough in improving the fracture toughness of ceramic materials [2-4]. Therefore CMCs are ideal candidates for demanding low- and high-temperatures environments (substitutes for conventional ferrous materials and light alloys) like those in brake discs, heat exchangers, gas turbines, and chemical reactors [3].

Several processes, including tape casting/lamination, Chemical Vapour Infiltration (CVI), solid and liquid infiltration followed by hot pressing (HP) or hot isostatic pressing (HIP) have been employed for the fabrication of this new class of materials [2-9]. The hot pressing method employed for the manufacture of composite limits the components to simple plate shapes. Additionally this method will degrade the fibre reinforcement through treatment at high temperatures and pressures. More complex shapes would require very expensive machining. In the CVI method the matrix is formed in a multiple step process by infiltrating 3-D preforms via reaction of gaseous precursors. The isothermal CVI process leads to materials with good mechanical properties but needs a very long manufacturing time, sophisticated equipment and is therefore very expensive. The alternative to the isothermal CVI is the CVI gradient method; it is faster, but limited in shape complexity [3]. Complex shape C/SiC composites are already being manufactured by the infiltration of C preforms using molten silicon, followed by transformation by a reactive sintering process into the dense C/SiC material (Liquid Silicon Infiltration process – LSI) [2-4]. The reaction sintering method leaves residual metal in the product, so the strength decreases at elevated temperatures. Another interesting method is the Liquid Polymer Impregnation (LPI) method based on organometallic preceramic precursors such as silazanes or carbosilazanes [2, 3, 6-9]. Upon pyrolysis the ceramic precursors are converted into a ceramic material yielding a SiCN-glass, SiC, Si3N4 or mixtures of these compounds. Such polymers are used for matrix formation by multiple infiltration of porous fibre preforms followed by the pyrolysis step. Very complex shaped components can be manufactured by this method. However, the high number of infiltration/pyrolysis steps employed for manufacturing a relatively dense material is both expensive and time consuming. The second disadvantage of this manufacturing method is that the low-density amorphous pyrolysis products are converted to the crystalline state at temperatures above 1400°C, which makes precise microstructure control of the CMC composites difficult to achieve. The residual porosity also significantly affects the mechanical properties of the resulting composites.

Therefore it is required to develop process routes for low-cost ceramic-matrix composite materials. Such an attempt has been made and a novel low-cost manufacturing method has been developed, primarily for manufacturing of the C/Si3N4 composite [10]. In this method, a long 2-D carbon preform is mounted on a filter within a die cavity. A small quantity of the ceramic slurry is homogeneously distributed on the surface of carbon ply of fabric, the next ply of fabric is layered and infiltrated with the ceramic slurry, etc. The number of steps is repeated to reach a designed composite thickness. Then a pressure is exerted on the dispersed slurry to cause the majority of the water to be squeezed out of the green composite body and the ceramic particles to be trapped at the filter and build a consolidated layer within the fibre preform. The slurry is formulated such that the particles are repulsive with respect to themselves and the fibres. The particles are also smaller than the fibre diameter to ensure good particle packing. After
removing the liquid via evaporation, the powder is strengthened by infiltrating the composite with a liquid pre-ceramic polymer, followed by pyrolysis step. After pyrolysis, the precursor polymer molecules form an inorganic amorphous (glassy) material that bonds the particles together and also bonds the particles to the fibres.

The objective of this paper is to develop a simple and fast process leading to materials able to compete with C/SiC composites obtained by the chemical vapour infiltration, liquid polymer infiltration and liquid silicon impregnation methods. The material obtained is characterised in terms of its porosity, microstructure, thermal and mechanical properties and compared to the properties of CMC materials manufactured by other methods.
2. EXPERIMENTAL PROCEDURE

The 2-D ceramic fibre plain weave supplied by Amoc P25 Carbon FMI Composites Ltd, Scotland, was used in the preparation of the fibre preform. Silicon carbide powder, UF 15, from Starck, Germany, with an average particle size of 0.5 µm and specific surface area of 14-16 m²/g was used as the major component of the slurry for the pressure impregnation process. Sodium hydroxide (NaOH) from Merck, Germany was added to the slurry as a dispersing agent, Glydol from Brunchwig Chemie, Germany as a wetting agent and demi-water as a solvent. From the large variety of possible organometallic polymers, CERASET™ SN pre-ceramic polymer, made by Commodore Polymer Technologies, Inc., USA, was selected due to its high ceramic yield and formation of SiC or Si₃N₄ compounds after pyrolysis. The solvent-free polymer has a low viscosity, can be processed in an ambient air environment and, which is equally important, it is available in large quantities at a relatively low cost [11, 12]. By pyrolysis in a nitrogen or argon atmosphere in the temperature range of 1000-1300°C, the polysilazane decomposes into amorphous silicon carbonitride compound (SiCN glass) with a ceramic yield of 70 wt%.

Stacks of 12 sheets of 2-D woven fibres in the shape of discs 150.0 mm in diameter were pressed together in a steel mould and infiltrated with a SiC slurry under a pressure of 20 bar for 60 min. (Figure 2.1). The slurry contained 66.2 wt% SiC. The relative viscosity of the slurry was 8.5 ±0.3 cPa.s and pH =9.5 at 20°C. After the infiltration process the green body was dried overnight at ambient temperature and calcinated at 400°C for 1 hour. Then the calcinated material was infiltrated with a liquid pre-ceramic polymer containing 0.1wt% dicumyl peroxide initiator at a temperature of 80°C for 24 hours. The plate disc was removed from the pre-ceramic polymer, wiped free of excess resin, and then cured at 160°C for 1 hour. The consolidated material had a remaining open porosity of 0.1%. The thickness of the manufactured component was 6.0 ±0.1mm. Pyrolysis of samples was first performed in a resistance-heated laboratory furnace at a temperature of 700°C for 2 hours while the samples were kept under a pressure of 1 MPa, to prevent plate delamination, and then at a temperature of 1000 or 1300°C under a flowing argon atmosphere (0.1 MPa) for a further 2 h. The flow diagram of this novel processing route is presented in Figure 3.1. The manufactured C/SiC composites were characterised according to their density and residual porosity, microstructure, phase identification, strength in bending, fracture toughness, elasticity, thermal expansion and thermal conductivity. The density and open porosity was evaluated using the water immersion technique and the latter parameter also by nitrogen porosimetry.
Figure 2.1 Set-up for pressure infiltration process

The microstructure of the sintered samples was analysed by SEM. The room-temperature flexural strength of composite samples was measured on bars of 3.5 x 4.5 x 50 mm$^3$ in 4-point bending tests (4-PBT), span 40/20 mm and a crosshead speed of 0.1 m/min. The load versus displacement curves were recorded and the maximum of the curve gives the flexural strength $\delta$ and the slope $d\delta/de$ when $e$ is small gives the elastic modulus. The average values of flexural strength and Weibull modulus were calculated from 10 measurements. The fracture toughness ($K_{IC}$) was determined by the chevron notch beam method and the result is reported as an average of three measurements. The coefficient of thermal expansion (TCE) was measured parallel to the fibre orientation in the temperature range of 20-1000°C. The thermal diffusivity was characterised with a laser flash technique and then the thermal conductivity was calculated from the equation:

$$k = \nu \times \rho \times C$$  

where: $k$ - thermal conductivity, $\nu$ - thermal diffusivity, $\rho$ - density, $C$ - heat capacity of the specimens. The bulk density was measured using Archimedes’ method and the constant pressure specific heat, $C$, was taken from the literature [2].
3. RESULTS AND DISCUSSION

The preparation of the C/SiC composite material from the carbon pre-form by pressure impregnation with the SiC slurry resulted in the formation of a porous sample exhibiting relatively poor mechanical properties. The porous material after calcination at 400°C was characterised by a high particle packing density within the fibre pre-form (Fig 3). Filling the interstices with a powder increases the composite density and also limits the size of crack-like voids within the matrix. The pore size distribution measured by mercury porosimetry showed that the majority of pores are in the range of 20-100 nm, with the average pore diameter of 67 nm (Figure 3.3). The measured porosity of the compact, 27.9%, was very close to the theoretically calculated value, 28.5%. The composition of the green compact calculated from densities of separate components in a given volume of the mould was as follows:

- Carbon fibres - 28.5 vol.%
- SiC powder - 43.0 vol.%
- Total porosity - 28.5 vol.%

![Flow diagram of a novel processing route for the C/SiC composite production](image)

Figure 3.1 *Flow diagram of a novel processing route for the C/SiC composite production*
The size of (nano)pores homogeneously distributed in the whole volume of the compact had a significant influence on the time of the polymer infiltration process. This time was prolonged to nearly 24 h and was in a very low degree related to the pressure of infiltration. The porous compact was infiltrated only once with the CERASET™ SN polymer at the temperature of 80°C for 24 h under a pressure of 4 bar. Under these conditions the porous C/SiC preform was fully infiltrated with polymer which was confirmed on the cross section of the infiltrated sample. The up-take of the polymer into the open structure of calcinated C/SiC composite was up to 14.8 wt%. The density of the green composite body cured at 160°C was 2.25 g/cm³. The density decreased slightly after pyrolysis at 700°C (2.20 g/cm³) due to the evaporation of gaseous decomposition products at temperatures between 400-700°C. After the pyrolysis at 1300°C the density increased again to the value of 2.26 g/cm³. The open porosity of the product was 4.3 %. The SEM investigation showed that some residual pores exist in the composite body pyrolysed at 1000 and 1300°C originating from long microcracks formed in the SiC matrix (SiC powder bonded with SiCN glass) (Figure 3.4A) and also delamination to the matrix/fibre interface is visible (Figure 3.4B). The microcracks are formed due to the shrinkage process of the matrix and the stiff structure of the carbon preform. The length of microcracks is comparable with the thickness of the matrix layer, from hundred to a few hundred micrometres. The second type of delamination, circular in shape, are formed due to the high shrinkage of carbon fibres in diameter, approximately 10% at 1300°C, and the thermal expansion mismatch of fibres and the matrix (-1.3x10⁻⁶ 1/°C to 4.0x10⁻⁶ 1/°C, respectively). The matrix, except for these two types of microcracks, is non-porous, with the SiC particles homogeneously embedded into the SiCN glass (Figure 3.4C).

Figure 3.2 Cross section of the C-fibre preform infiltrated with the SiC slurry under a pressure of 20 bar and calcinated at 400°C for 1 h. The total porosity of the calcinated compact was 27.9 % and average pore size was 67 nm
The crystallisation of the polymer-delivered amorphous phase to nanocrystalline SiC starts above 1260°C, resulting in a high shrinkage of the ceramic matrix and further formation of microcracks [12]. The majority of cracks run perpendicular to the carbon fibre direction, which means that the shrinkage of the matrix is bigger in the direction parallel to the carbon fibre plane. Therefore the temperature of thermal treatment was kept so low as 1300°C, to avoid the even more excessive formation of microcracks in the composite at higher temperatures. Nevertheless, a larger number of microcracks was detected in products sintered at the temperature of 1300°C than in those sintered at 1000°C. More cracks were also observed in the plane direction than in the direction perpendicular to the fibre plane.

The composite material pyrolysed at 1300°C was selected for testing mechanical and thermal properties. The physical, mechanical and thermal properties of the C/SiC composite fabricated by mixed process of Pressure ceramic Slurry Infiltration followed by Liquid Polymer Infiltration (PSI-LPI) are compared with the properties of C/SiC composites manufactured by three other routes in Table 3.1 [2].
Figure 3.4 Polished cross-section of a $\text{C}/\text{SiC}_p/\text{SiCN}_{am}$ composite:
(A) Microcracks in the SiC/SiCN glass matrix; (B) Circular decohesion microcracks formed around the C fibres; (C) Dense SiC/SiCN matrix formed from the SiC particles embedded into the SiCN glass.
Table 3.1 Properties of the C/SiC composite manufactured by PSI-LPI method, pyrolysed at 1300°C, in comparison to properties of the composites manufactured by other methods according to A. Mühlratzer [2]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>PSI-LPI* C/SiC</th>
<th>CVI* C/SiC</th>
<th>LPI* C/SiC</th>
<th>LSI* C/C-SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibre content vol. %</td>
<td></td>
<td>28-30</td>
<td>42-47</td>
<td>42-47</td>
<td>55-65</td>
</tr>
<tr>
<td>Density g/cm³</td>
<td></td>
<td>2.32</td>
<td>2.1-2.2</td>
<td>1.7-1.8</td>
<td>1.8-1.95</td>
</tr>
<tr>
<td>Porosity %</td>
<td></td>
<td>7.4</td>
<td>10-15</td>
<td>15-20</td>
<td>2-5</td>
</tr>
<tr>
<td>Coefficient of thermal expansion (20-1000°C)</td>
<td>10⁻⁶ K⁻¹║ 3.0</td>
<td>3</td>
<td>3</td>
<td>1-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>4.0</td>
<td>5</td>
<td>4-6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14</td>
<td>15</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7</td>
<td>2.1</td>
</tr>
<tr>
<td>Bending strength (RT*) MPa</td>
<td></td>
<td>105±11</td>
<td>450-500</td>
<td>430-450</td>
<td>210-320</td>
</tr>
<tr>
<td>Weibull modulus</td>
<td></td>
<td>7.2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fracture toughness MPa.m¹/²</td>
<td></td>
<td>9.9</td>
<td>22</td>
<td>8-17</td>
<td>7</td>
</tr>
<tr>
<td>Young’s modulus GPa</td>
<td></td>
<td>27±3</td>
<td>90-100</td>
<td>60-80</td>
<td>50-70</td>
</tr>
</tbody>
</table>


The density of the C/SiC composite infiltrated with pre-ceramic polymer was a little bit higher than the density of the composites manufactured by other methods, due to a lower content of C fibres (28.5 vol.%) and a higher content of the SiC powder (43.0 vol.%). The existence of micro-cracks and the residual porosity had a negative influence on the thermal conductivity parameter. The measured thermal conductivity of the developed composite, 14 W/m.K, was significantly lower than the values reported for the separate components of the composite. The values of 22 W/m.K for carbon fibres Amoco P25 and 110 W/m.K for silicon carbide monolithic ceramics have been reported [3]. As expected the coefficient of thermal expansion (CTE) of the tested composite depends on the direction of layered fibres. The CTE measured for the C/SiC composite perpendicular to the fibre orientation was 30% higher then that measured for the parallel direction. This is due to the marked anisotropy of the CTE of the carbon fibres reported by the manufacturer. The room temperature flexural strength of the composite material, above 100 MPa, is lower than the values of the mechanical strength reported for the C/SiC composites made by the multiple infiltration process with pre-ceramic polysilazane polymers and silicon infiltration method [2, 4, 7]. In the composites manufactured by CVI and LPI the matrix surrounding the fibres is very strong and limits the stress concentration at the fibre surface. In the powder-filled composite, the matrix is composed of two materials, the SiC powder and the pyrolysed polysilazane. The 7% porosity remaining is also dispersed in a non-homogenous way across the composite. It is assumed that the temperature of pyrolysis, 1300°C, is still too low for a strong bonding between the SiC grains and between the SiC grains and the pyrolysed polysilazane. The mechanical properties of this matrix network are quite poor and this leads to the low mechanical resistance of the composite. To improve the mechanical resistance of the matrix, the bonding between the powder grains and the powder grains and pyrolysed polysilazane must be increased [13]. This could be done by the introduction of sintering additives such as boron, boron carbide and active carbon (carbon resin) to the matrix, increasing the fibres content, increasing the quantity of infiltrated polysilazane, or increasing the temperature of sintering. However, the two latter options have to be carefully implemented because of the possibility of creating a higher porosity and there is also a risk of fibre damage. Therefore, the two former options are preferred. The much higher value of the flexural strength, 200 MPa, was measured for the C/SlN₄ composites manufactured by this same method [10]. However, the content of C fibres, 44.0 vol.%, was much higher in the C/SlN₄ than in the C/SiC composite and also a mixture of alumina and yttria compounds was added to the matrix as a sintering additive. The temperature of sintering was 1350°C and the sintering atmosphere...
consisted of a mixture of nitrogen and ammonia. These differences in the composition of composites and in the processing procedure had a strong influence on the elastic properties; the Young’s modulus of the C/Si₃N₄ material was 120 GPa and for the SiC only 27 GPa.

Fracture toughness. It is well known that the mechanical behaviour of fibre-reinforced composites depends dramatically on the characteristics of the interface between the fibres and the matrix. A weak interface leads to energy-dissipative mechanisms such as fibre pull-out and de-bonding which increase the energy required for the propagation of the cracks and lead to a high toughness [5, 13-14]. Both phenomena were realised in the manufactured composite body. The fracture toughness of the developed composite material, relatively high - 9.8 MPa.m^1/2, may be further improved by increasing the content of fibres or by applying better quality carbon fibres coated with a BN or pyrolytic carbon nanolayer. The content of carbon fibres, 28-30 vol%, is far below the average content of fibres used in the composites fabricated by the CVI and LPI processes (40-45 vol%). The load-deflection curves at room temperature for the C/SiC composite is shown in Figure 3.5.

![Load-deflection curve at room temperature of the C/SiC/SiCN composite sintered at 1300°C](image)

The SEM investigation of the sample used for measuring the bending strength demonstrated qualitatively the damage-tolerant behaviour of the composite, showing pull-out lengths of single fibres from the matrix between 10-20 μm (Figure 3.6). The crack deflection is generally achieved by a “weak” interface between the carbon preform and the matrix (SiC powder bonded with pyrolysed polymer residue). In some cases the interface may even be debonded during the sintering process. This allows for the crack to be deflected between the fibre and the matrix. Much higher results for the mechanical strength of the C/SiC composite manufactured by the multiple polymer infiltration process using CERASET™SN as a pre-ceramic polymer, even up to 575 MPa, were reported by Mühlratzer and Tanaka [2,9]. It is obvious that it would be possible to reach much better values of the thermal and mechanical properties of the developed composites by a further optimisation of the manufacturing process (introduction of sintering additives such as elementary boron, boron carbide and carbon resin). The sintering temperature, 1000-1300°C, is too low for this type of composite sintered without any additives. The Weibull modulus of the tested composite was relatively low, 7.1, probably due to the non-homogenous structure of the material and to the presence of long microcracks having a negative influence on
the mechanical strength of the composite. The value of Young’s modulus was also quite low, 27 GPa, due to the presence of elongated and circular microcracks in the SiC matrix.

Figure 3.6  SEM observation of the fracture surface of the C/SiC/SiCN composite sintered at 1300°C. The tip of the chevron notch with extensive fibre pull-out is shown

The manufacturing method of CMC composites, which is still far from full optimisation, proved that it is possible to produce the C fibres-ceramic matrix composites in an inexpensive way, avoiding the expensive hot pressing step as well as the time and energy-consuming multiple infiltration process or chemical vapour infiltration. However, the process using submicron silicon carbide powder to fill the fibre preform prior to the precursor impregnation leads to composite materials with a lower mechanical strength and elastic modulus than those manufactured by CVI or LPI routes. The application of these materials can be, therefore, in components where the strength is not the most important parameter but other properties, such as wear coefficient, determine their potential application, i.e. in brake pads and discs.
4. CONCLUSIONS

The performed work has demonstrated several features about processing of CMC materials by a novel manufacturing method PSI-LPI:

- The method of manufacturing the C/\text{SiC} composites by a single infiltration technique with a polysilazane polymer on a C/\text{SiC} porous pre-form allows for an economical fabrication of the CMC components in comparison to other methods involving hot pressing, multiple pre-ceramic polymer infiltration or chemical vapour infiltration. This fabrication concept can be applied to various fibre/matrix systems.
- According to this method, the space between the fibres is first filled with a ceramic powder, which is subsequently strengthened with an inorganic amorphous phase synthesised from an infiltrated pre-ceramic polymer.
- A pre-ceramic polymer viscosity of approximately 2.0 mPa.s at 80\textdegree C is sufficient for the infiltration of porous composite materials, however, a further improvement of the infiltration process is necessary to speed-up this process.
- Crack bifurcation at fibre-matrix interfaces and fibre pull-outs have been observed in the manufactured CMC material.
- The mechanical properties, especially the bending strength and elastic modulus, are still low and far away from the expected values. Two factors are responsible for this problem: lower quantity of introduced carbon fibres than in an usual composite body and low-strength bonding between the elements constituting the matrix, SiC particles and SiCN glass. The solution to this problem can be an increase in the carbon fibres content to the composite material and an introduction of the sintering additives to the SiC matrix.
- The application of the developed composites is restricted mainly to temperatures not exceeding 1300\textdegree C due to the crystallisation process of the ceramic matrix above 1260\textdegree C and hence a high shrinkage of the ceramic matrix followed by an intensive cracking of the whole composite body.
REFERENCES