Development and Characterisation of Novel C/C-SiC Material using LSI Method and Effective Fibre Preform Techniques for Rocket Nozzle Extensions

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The main goal of sub-project D7 is the development of novel ceramic matrix composites (CMCs) for nozzle structures. These CMCs are characterized by continuous carbon filaments which are embedded in a carbon-silicon carbide matrix (C-SiC). The process route used for the manufacture of the so called C/C-SiC material is the Liquid Silicon Infiltration (LSI) process. A central part of the development is the integration of effective preform techniques like filament winding and braiding of carbon fibres into the LSI route as well as the characterisation of specimens. This CMC material is favourable to replace conventional high-density superalloys in nozzle extensions of liquid fuelled rocket engines due to their outstanding high temperature properties.

In this report, an overview of the progress and findings from sub-project D7 is given. Results from the manufacture of C/C-SiC via braiding technique are presented and compared to filament winding based C/C-SiC material. Furthermore, the manufacture of the first C/C-SiC nozzle demonstrator is described. Critical aspects within the filament winding process of such a axis-symmetric structure were identified and measures for coping with these challenges for future CMC nozzle structures are presented and discussed.

1. Introduction

Carbon-fiber-reinforced silicon carbide matrix composites are still considered to be one of the most promising material candidates to replace heavy refractory superalloys in future rocket propulsion applications, e.g. rocket nozzle extensions, due to their excellent thermal and mechanical properties in high temperatures and its much lower material density [1–9].

In the last decades the CMC development based on fabric fibre preform with a variety of different processing routes, like chemical vapor infiltration (CVI), liquid polymer infiltration (LPI, PIP) and reactive melt infiltration (RMI) has been studied intensively [10–22]. In the field of carbon-fiber-reinforced silicon carbide matrix composites for future rocket nozzle structures the DLR focuses on the development of C/C-SiC material using the liquid silicon infiltration route (LSI) and effective fibre preform techniques like filament winding and braiding, which are indispensable for axis-symmetric structures. The possible use of adapting fibre orientations as well as the influence of different fibre preforms, like filament winding or braiding, result in novel LSI-based C/C-SiC materials with dif-
different final microstructures and mechanical properties which will be compared and discussed [23].

The presented work is divided into two parts. In the first part the material characterization of braided C/C-SiC using biaxial and triaxial preforms is presented and compared to the results from filament winding based C/C-SiC material. In the second part the manufacture of the first basic, sub-scale C/C-SiC nozzle structure using simple filament winding architectures is described.

2. Material characterisation results - Comparing C/C-SiC based on filament winding and braiding technique

A central part of the work done in sub-project D7 was the manufacture and characterisation of C/C-SiC materials based on filament winding and braiding preforms, respectively. The variation of the fibre orientation and the preform techniques eventually result in different microstructures of the final composite material. The influence on mechanical properties was studied.

The fabrication method and preliminary characterisation results of these materials were presented in previous SFB/TRR 40 Annual Reports [24, 25]. In this annual report essential findings for both material types are described, compared and discussed. The study on the influence of different carbon fibre types on the mechanical performance was described also in the previous annual report form 2011. It was shown that C/C-SiC materials using T800 carbon fibres surpassed all other materials types in terms of mechanical performance and quality of the resulting microstructure. For this reason the presented characterisation results are based on C/C-SiC plate material which was fabricated with T-800 carbon fibre (12K, 12000 single carbon filaments per roving) and a phenolic resin with the internal abbreviation JK 60. The fibre volume fraction of all tested composites was in the range of about 50–60%.

2.1. Mechanical properties

C/C-SiC plates were manufactured for mechanical and micro-structural analysis. Figure 1 gives a compact overview on the mechanical characterisation results. The presented charts show average values for tensile strength, initial Young's modulus, strain to failure and flexural strength for three selected typical fibre orientations, $\alpha = 0/90^\circ$, $\pm 45^\circ$ and $\pm 15^\circ$. Drawings at the bottom of the chart bars represent the tested fibre orientation. Black lines represent the main fibre directions and red lines the third fibre orientation of triaxial specimens.

The study showed that the biaxial braided material is very similar to the filament winding based material. The much higher amount of undulations of fibre rovings had no significant influence on the final composite compared to the filament winding based material with a much lower amount of roving undulations. Differences observed in the presented mechanical properties result from different fibre volume fractions. This was clearly noticeable when looking at the triaxial braided material. Here the total fibre volume fraction accumulates from three fibre orientations which lead to a lower fibre volume fraction in loading direction at $0/90^\circ$ and $\pm 15^\circ$ reducing ultimate strength values, see Figure 1(a) and 1d. At $\pm 45^\circ$ the triaxial fibre orientation lead to an increase of the Young's modulus and a reduction of the strain to failure, due to the dominant fibre characteristic in C/C-SiC composites, see Figure 1(b) and 1(c). Generally speaking, the triaxial material showed a more quasi-isotropic material characteristic than their biaxial
counterparts. Ultimate composite strengths of the studied C/C-SiC material can be increased to values well above 200 MPa (tensile test) and 400 MPa (flexural test) when fibres are oriented in loading direction.

2.2. Microstructures

All fabricated materials types have been analysed by means of scanning electron microscopy (SEM) to identify major differences in the resulting microstructures. The evolution of a characteristic micro-crack pattern during carbonisation is very important for the C/C-SiC manufacture. Material properties, such as pore and crack distribution, and the amount of fibre degradation during siliconisation are as equally important to the final material performance as the earlier mentioned fibre volume fraction. The main objective during pyrolysis is the development of dense C/C. At the same time a homogeneous channel system is required to ensure proper liquid silicon infiltration. Figure 2 and Figure 3 give an overview on typical microstructures of polished surfaces observed with SEM. All analysed micrographs showed a suitable typical C/C-segmentation with channels of silicon carbide (SiC) and residual silicon (Si). Nevertheless some differences were identified comparing the different fibre architectures.

For biaxial material the formation of the C/C-blocks tends to be more equally formed and distributed than its triaxial counterpart. Moreover the triaxial material exhibits more residual silicon clusters in undulation areas. The channel width is significantly influenced
by the third fibre orientation at ±15°. Due to the impediment of the shrinkage parallel to the third fibre orientation, the resulting channels are wider compared to the biaxial micrograph at ±15°, see Figure 2(e) and Figure 2(f). At the biaxial material with a fibre orientation of ±15° almost no residual silicon was detected.

The microstructure of filament winding based C/C-SiC is typically described by a very regular formation of C/C-segments with laminar and trans-laminar silicon carbide channels showing very few undulations, see Figure 3(a). At ±15° the formation of the channel system is rather randomly orientated consisting of thin SiC channels and bigger pores that are filled with residual silicon which has not been transformed to SiC.
a) Filament winding - $\pm 45^\circ$.
b) Filament winding - $\pm 15^\circ$.

**Figure 3.** Overview on typical microstructures of C/C-SiC material (T800/JK60) using filament winding technique for different fibre orientations.

<table>
<thead>
<tr>
<th>Preform technique</th>
<th>Filament winding</th>
<th>Braiding</th>
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<tbody>
<tr>
<td>Advantages</td>
<td>- fast CFRP processing (one process step: wet filament winding)</td>
<td>- third fibre orientation possible (quasi-isotropic laminate)</td>
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<td></td>
<td>- great variety in terms of fibre architectures</td>
<td>- low porosity in CFRP state (&lt;3%)</td>
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<td>- fibre volume fraction adjustable</td>
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<tr>
<td>Disadvantages</td>
<td>- high porosity in CFRP state (5-10%)</td>
<td>- time-consuming 2 step process for CFRP</td>
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<tr>
<td></td>
<td>- limited adjustment of fibre volume fraction</td>
<td>- 1st: dry braiding of fibre preform</td>
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<tr>
<td></td>
<td></td>
<td>- 2nd: costly VARI or RTM process necessary</td>
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<tr>
<td></td>
<td></td>
<td>- limited variety of fibre architectures</td>
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**Table 1.** Advantages and drawbacks of filament winding and braiding technique.

2.3. **Assessment of filament winding and braiding technique with regard to C/C-SiC nozzle manufacture**

Within the work done in sub-project D7 new knowledge has been gathered concerning the manufacture of C/C-SiC with advanced fibre preform techniques. The major advantages and disadvantages of both preform techniques used in this study are presented in Table 1.

The characterisation of braided C/C-SiC material shows no significant improvement in terms of mechanical performance in contrast to the filament winding route, see Section 2.1. Moreover the complex and time-consuming two step CFRP process as well as the restricted freedom of variation of possible fibre architectures are drawbacks using braiding technique. At this point the filament winding technique seems to be more suitable for the development of novel CMC nozzle structures.
3. Manufacture of first C/C-SiC nozzle structure using filament winding technique

Within the scope of the first phase of SFB/TRR 40, D7 set the objective to demonstrate the fabrication of a basic, sub-scale C/C-SiC nozzle structure. The manufacture of the first nozzle structure based on filament winding technique is described in the following section.

In order to manufacture a nozzle structure with a complex inner wall contour, consisting of changing diameters over the axial length direction, a sophisticated software is essential to simulate the desired fibre architectures. D7 is using the latest version of Cadwind V9 Expert filament winding software. The fibre preforms were generated using a basic two-axis filament winding machine made by Waltrisch & Wachter.

First step in the manufacturing process was the development of a suitable fibre architecture using Cadwind software, Figure 4(a). With the contour geometry of the mandrel provided to the software, Cadwind is able to create single fibre layers with specific fibre orientations within the rules of filament winding. The nozzle mandrel contour was a simple parabolic contour with a exit diameter ($D_{exit}$) of 150 mm, an initial diameter ($D_i$) of 50 mm and a total length of about 140 mm. On both sides of the mandrel pin adapters were established to additionally secure the roving from slipping. There are two types of winding techniques, geodesic winding and non-geodesic winding, respectively. Geodesic winding is described by a winding path, where theoretically no slippage of the fibre roving occurs, regardless of the friction coefficients between fibre and surface. When using non-geodesic winding technique, the possible fibre path is calculated upon friction coefficients. Here the non-geodesic winding technique was used. Hence, the amount of possible fibre architectures and the amount of surface coverage were increased in contrast to geodesic winding.

The evolution of the winding angle $\alpha$ with changing diameters $D$ follows the basic law of filament winding. The law named Clairaut equation is defined as:

$$ C_{CL} = D_x \cdot \sin \alpha_x = D_1 \cdot \sin \alpha_1 $$

transformed to

$$ \alpha_x = \arcsin \left( \frac{D_1}{D_x} \sin \alpha_1 \right) $$

with the condition

$$ \sin \alpha_1 < \frac{D_x}{D_1} $$

Generally speaking, from a starting diameter (here $D_{exit}$) and a starting winding angle $\alpha$, the winding angle increases with decreasing mandrel diameter to a point where it becomes 90° and returns back to the starting position. The combination of transverse fibre placement and mandrel rotation creates the typical cross winding fibre architecture, as depicted in Figure 4(a).

The most important input parameter to calculate the winding path is the winding angle or fibre orientation at a specific diameter. The fibre layup structure and its starting fibre orientations of the C/C-SiC nozzle are summarized in Table 2. This fibre layup structure was selected on the one hand to create a balanced fibre architecture and on the other
hand to study the limits and challenges coming with the filament winding technique when manufacturing nozzle structures.

After cross checking the producibility of fibre layers using dry winding, Figure 4(b), the actual wet winding process was performed using HTA 6K carbon fibre and a phenolic precursor, Figure 4(c). The wet wound preform was then cured to the CFRP state. Then standard C/C-SiC processing was done, including carbonisation (pyrolysis) and siliconization. Due to shrinkage effects during pyrolysis special measure had to be made
to avoid any type of contour deformation. This was done by supporting the inside and outside of the CRFP nozzle preform with graphite support cores, preventing any ovalisation effects. This procedure lead to a full axis-symmetric inner contour with no signs of deformations, Figure 4(d). After siliconization, Figure 4(e), the C/C-SiC structure was examined by means of CT-analysis to look for any delaminations or other characteristic flaws, like pores. Figure 5 shows a series of axial CT images extracted from the C/C-SiC nozzle. In addition to the detection of imperfections, like pores and delaminations, CT-analysis is also useful to provide an accurate determination of the wall thickness for changing diameters. The left image of Figures 5 shows the full nozzle, the picture in the center and on the right show cuts at the middle and near the end of the nozzle. It clearly visualises the wall thickness growth. The wall thickness of the nozzle ranges from 3.6 mm at $D_{Exit}$ to about 12 mm at $D_i$. The growth of wall thickness is a result of the decreasing nozzle diameter. At a diameter of 150 mm fibre rovings are rarely overlapping, covering the surface for 100%. With decreasing nozzle diameters the same amount of fibres have to be placed on the surface, resulting in an fibre roving overlapping which leads to a increase in wall thickness. This typical winding characteristic and its impact on the resulting composite microstructure will be studied in more detail in the following programme of SFB/TRR 40. The fabricated sub-scale C/C-SiC nozzle structure will serve as a exhibit and reference part for the upcoming investigations and developments. The exhibition of this sub-scale C/C-SiC nozzle, as depicted in Figure 4(f), is planned for the SFB/TRR 40 assessment in Braunschweig, August 2012.

The material density and open porosity are important parameters during the entire manufacturing process. Table 3 presents the material density and open porosity of the reference C/C-SiC nozzle for each process step. In the CFRP state the structure exhibited a noticeable high value of open porosity. The sub-scale nozzle was fabricated at the time were only two winding axis had been available leading to a very basic fibre lay-up
structure as well as a limitation of optimizing the fibre placement and fibre architecture adaption.

Within 2012 the existing filament winding machine was upgraded to a three-axis winding machine to improve the fibre placement on the mandrel and to expand possible fibre architectures to intensify the development of novel adapted C/C-SiC materials for nozzle structures.

From the material processing point of view the following issues should be met for future nozzle material development:

- full fibre coverage of the surface
- fibre layup structure with decreasing fibre angles for every consecutive layer desirable; reduced affinity of delaminations [24]
- balanced fibre architecture throughout the entire layup structure to carry radial, axial and circumferential stresses
- open porosity of CFRP < 10%

4. Summary and Outlook

Within the last year the fundamental material characterisation on C/C-SiC materials fabricated using filament winding and braiding technique has been completed. Challenges and opportunities resulting from both preform techniques have been identified and evaluated. As a result future studies concentrate on the development of adapted C/C-SiC materials based on filament winding technique. Sub-project D7 demonstrated the feasibility of manufacturing a basic sub-scale C/C-SiC nozzle structures based on filament winding technique. Nevertheless, the sub-scale nozzle showed the necessity of further development of adapted fibre architectures for future C/C-SiC nozzle structures. Future studies will focus on a optimized CFRP manufacture and the development of different fibre architectures and their influence on the material performance.

Acknowledgments

Financial support has been provided by the German Research Foundation (Deutsche Forschungsgemeinschaft – DFG) in the framework of the Sonderforschungsbereich Transregio 40.
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