ABSTRACT

Originally, the demands in space technology played the decisive role in the DLR’s development of melt-infiltrated ceramic matrix composite (C/C-SiC) materials. High mass-specific characteristics and extreme temperature resistance are important selection criteria for materials used in jet engines and thermal protection systems in new spacecraft and rockets. Within the last few years, the properties and the manufacturing methods of C/C-SiC materials were consistently improved, so that particularly the brake industry can now share the profits of this new class of material. Brake disks and pads made of C/C-SiC offer great advantages for high performance vehicles as well as emergency brake systems. Mainly based on carbon and silicon carbide these braking materials show high and stable coefficients of friction and low wear rates. Prototypes of originally sized pads as well as disks have been manufactured and were successfully tested by the respective brake system manufacturers or end-users. After seven years of development, C/C-SiC braking materials are now entering the market in high performance cars, trains, and lifts. Their main advantages lie in the reduced mass, their non-fading characteristics, their improved coefficient of friction, and their extremely low wear rates.

INTRODUCTION

For non-oxide CMCs three processing methods are currently used for space applications: The chemical vapour infiltration (CVI), the liquid polymer infiltration (LPI or PIP), and the liquid silicon infiltration (LSI). Table 1 gives an overview of material data for SiC ceramics with bi-dimensional reinforcement (C and SiC fibres), derived from these three processes of different European manufacturers [1-4].

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Table 1: Properties for SiC ceramics with bi-dimensional reinforcement.

The synthesis of the ceramic matrix of CMCs manufactured via the liquid silicon infiltration process is carried out by liquid-phase infiltration of molten silicon into porous carbon fibre preforms, followed by a chemical reaction to silicon carbide (Fig. 1). As the end product of the three-step process, C/C-SiC materials consist of load-bearing carbon fibres, amorphous carbon, residual silicon, and crystalline silicon carbide as the most important matrix components.

![Fig. 1: Overview of the fundamental processing steps for the manufacture of C/C-SiC components.](image-url)
C/C-SiC composites were originally developed for high temperature and short term applications such as aircraft engine parts or thermal protection for spacecraft. They show a considerably low open porosity (less than 5 %), a low density (about 2 g/cm³), and a SiC ceramic matrix content of at least 20 % in mass.

HOT STRUCTURES

Space transportation systems are exposed to temperatures of up to 1,700 °C during the re-entry phase into earth’s atmosphere. Aside of the nose-area of the fuselage and of the wings, the surfaces of the steering control units and the shingles of the Thermal Protection System (TPS) are thermomechanically, highly loaded structures, which are preferably made of CMC materials.

In 1998 DLR started the development of the LSI process and evaluated C/C-SiC composites with respect to space applications in various arc jet facilities. Further efforts concentrated on inflight verification and material samples were integrated into the ablative heat shield of Russian FOTON capsules in 1992 and 1994. A hot structure experiment called CETEX has been developed and tested during the EXPRESS mission in 1995.

The hot structures of X-38, which was originally planed to serve as a technology carrier for a new Crew Return Vehicle (CRV) of the International Space Station (ISS), are regarded as an example for the current stage of TPS development, Fig. 2. In a joint program with the German space industry, different CMC structures based on CVI-, LPI- as well as LSI-processes were designed, manufactured, and tested. DLR has been responsible for the nose cap system and fabricated C/C-SiC prototypes via the LSI- process.

![Fig. 2: C/C-SiC nose cap for X-38 (left) and C/C-SiC jet vanes for solid fuel rockets (right).](image)

The nose cap is particularly exposed to extreme temperature and stresses upon re-entry due to its exposed location directly in the stagnation region of the vehicle. Surface temperatures of up to about 1,750 °C are expected during the re-entry
phase, which lasts approximately 20 minutes.

The connection of the C/C-SiC nose shell to the fuselage consists of altogether eight individual mounting braces, which are also made of C/C-SiC, or respectively, in the cooler areas of a metal alloy resistant to high temperatures. This lever-type fastening system guarantees high durability against mechanical stress, and it also allows an unhindered thermal expansion of the shell, which may amount to as much as three millimeters at a mean diameter of 700 mm, at the expected temperature level [5].

Even shorter operational times are demanded for rocket jet vanes, which are used to divert the direction of thrust in solid fuel rockets, but they are loaded by considerably higher stresses than those occurring during re-entry, Fig. 2. The controllable vanes provide an increased maneuverability of the rockets, primarily during the low-speed phase immediately after take-off. Only a few seconds of endurance are required, but these few seconds impose upon the material the utmost demands regarding thermomechanical stability and resistance to abrasion.

The vanes were manufactured of C/C-SiC composites with a two-dimensional fibre reinforcement. The surfaces are additionally coated with a protective ceramic coating (e.g. CVD-SiC) in order to be able to withstand the immense blast of particles (e.g. Al₂O₃) occurring as the solid fuel burns away. At the same time, the ceramic content of the structure material must be at such a high level, and thus the unavoidable burn-up consumption takes place only gradually, so that a sufficient residual vane surface is available during the complete burning period. The formulation of the microstructure of the C/C-SiC composites consequently requires an optimization of the conflicting demands for high fracture toughness (high C contents) and high resistance to abrasion (high SiC contents).

Due to their low coefficient of thermal expansion, their high thermal conductivity, and moderate modulus, C/C-SiC materials show an excellent thermal shock stability. They retain their strength level at elevated temperatures, similar to carbon/carbon materials. Moreover, their high temperature strength is superior to the level at room temperature, i.e. the higher the temperature, the higher the strength.

Typically, C/C-SiC composites for hot structures are made of bi-directionally woven fabrics, which are stacked together and wound to the desired thickness. An orthotropic behaviour results for the technical as well as for the thermophysical properties, which show considerable differences between the in-plane and the through-thickness direction. The constitution of the matrix and the material's microstructure mainly depend on the choice of matrix precursor and fibre structure, the processing parameters, and the fibre/matrix interface. One main advantage of the LSI process lies in the possibility to vary these parameters in a wide range leading to different qualities of C/C-SiC materials [3].

ADVANCED FRICTION SYSTEMS

Tribological tests to investigate the coefficient of friction (COF) and the wear resistance of C/C-SiC composites started seven years ago, and have been
conducted on test facilities of brake system manufacturers. In first tests, bi-directionally reinforced C/C-SiC disks were pressed in stop brakings and fading tests against pads of the same ceramic material. As a result, high and nearly identical wear rates were measured for the disk as well as for the pads [6]. Also, the COF of this complete CMC tribosystem showed a certain degree of instability and high surface temperatures due to the low transverse thermal conductivity of these 2D-composites. The use of conventional organic or sinter-metallic based pads improved the COF stability, but in these early high performance brakings, the non-ceramic pads overheated and showed an unacceptably low wear resistance.

Generally, high ceramic contents within the C/C-SiC composite increase the transverse conductivity as well as wear resistance. This has been achieved for example by reducing the fibre volume content resulting in a higher silicon uptake and SiC formation during the siliconizing step. Short fibre reinforced C/C-SiC composites with their nearly isotropic fibre architecture offer more than doubled values for the silicon carbide content and for the thermal conductivity in comparison to woven fabric reinforced C/C-SiC materials (Table 2).

High SiC levels and low carbon contents also influence the mechanical properties and decrease the damage tolerance of the brake component. As high ceramic contents are mainly necessary in the region of the friction surfaces, two approaches for a further wear improvement can be pursued:

- Gradient C/C-SiC composites with a gradual increase of SiC from the centre of the component to the surfaces
- Homogeneous C/C-SiC composites with additional SiC layers on the surfaces

<table>
<thead>
<tr>
<th>Material Properties</th>
<th>Unit</th>
<th>C/C-SiC Silica XB</th>
<th>C/C-SiC Silica SF</th>
<th>C/SiC SIGRASiC</th>
<th>C/C Hitco/SGL</th>
<th>C/C Carbon Industrie</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reinforcement Fibre architecture</td>
<td>woven fabric orthotropic</td>
<td>short fibre nearly isotropic</td>
<td>short fibre nearly isotropic</td>
<td>short fibre nearly isotropic</td>
<td>3 D preform isotropic</td>
<td></td>
</tr>
<tr>
<td>Fibre content [%]</td>
<td>60</td>
<td>50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Density [g/cm³]</td>
<td>1.9</td>
<td>2.0 - 2.1</td>
<td>2.4</td>
<td>1.72 - 1.8</td>
<td>1.65 - 1.86</td>
<td></td>
</tr>
<tr>
<td>Open Porosity [%]</td>
<td>3.5</td>
<td>&lt; 3</td>
<td>&lt; 1</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SiC / Si content [mass %]</td>
<td>30 / 2</td>
<td>50 - 55 / 2.3</td>
<td>60 / 10</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Flexural Modulus at RT [GPa]</td>
<td>60</td>
<td>50 - 70</td>
<td>30</td>
<td>50</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Flexural Strength at RT [MPa]</td>
<td>160</td>
<td>90 - 140</td>
<td>80</td>
<td>140 - 170</td>
<td>90 - 150</td>
<td></td>
</tr>
<tr>
<td>Therm. Conduct. (transverse) [W/mK]</td>
<td>10</td>
<td>25 - 30</td>
<td>40</td>
<td>4.6 / 7.5</td>
<td>10 - 90</td>
<td></td>
</tr>
<tr>
<td>(transverse) [10⁶ K⁻¹]</td>
<td>-1 / 2.5</td>
<td>0.5 / 3.5</td>
<td>1.8 / 3.0</td>
<td>0.3 / 1.14</td>
<td>-1 to 2</td>
<td></td>
</tr>
<tr>
<td>CTE (in plane) 100 °C / 1400 °C</td>
<td>100 °C / 1400 °C</td>
<td>RT / 1200 °C</td>
<td>100 °C / 800 °C</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTE (transverse) [10⁶ K⁻¹]</td>
<td>2.5 / 6.5</td>
<td>1.0 / 4.0</td>
<td>5 / 10</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Table 2: Mechanical and thermal properties of bi-directionally reinforced C/C-SiC (Silca XB) and short fibre reinforced C/C-SiC (Silca SF) compared to commercial products of carbon/carbon [7–9] and C/SiC [10]</td>
<td></td>
<td></td>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

DLR concentrated its research work on the latter approach. First investigations showed that coatings of pure silicon carbide, deposited via chemical vapour
deposition (CVD) on the friction surface of C/C-SiC brake disks, decrease the wear rates drastically by 90%. These SiC coatings lead to a very wear resistant and robust tribosystem and therefore only small thicknesses of 0.1 to 0.2 mm, achievable by CVD, are sufficient for long term applications. However, CVD-SiC coatings are expensive and need a separate manufacturing step, which increases the costs of CMC braking materials considerably.

To overcome this restriction, DLR developed a ceramic coating, which can be deposited on the friction surface without any additional manufacturing step. During siliconizing, the last processing step of the C/C-SiC composite manufacture, additional silicon as well as carbon are added to the surfaces. By varying the type of carbon source, the amount of shares of the two materials and the processing conditions, a ceramic layer containing only silicon and silicon carbide, permanently and strongly bonded with the C/C-SiC substrate, has been achieved by complete chemical reaction of carbon with silicon to SiC.

A high portion of free silicon in the protective coating is necessary to maintain toughness and elasticity. Therefore, the portion of silicon is given in an overstoichiometrical ratio to carbon prior to siliconizing to achieve a Si-rich SiSiC coating. Fig. 3 shows SEM-micrographs of such a coating on a short fibre reinforced substrate (fibre length between 130 – 200 mm). The light grey areas represent free silicon (about 70% in mass) whereas the dark grey areas show silicon carbide (about 30% of the coating’s mass).

The coefficient of thermal expansion (CTE) for the ceramic coating is in the range of 3 to 4*10^{-6} 1/K whereas the C/C-SiC substrates show normally lower values. Depending on this CTE mismatch, a more or less microcracked surface occurs as a result of the tensile stresses within the coating during cooling after processing. This SiSiC coating is called SiCralee and although it is microcracked, it shows an extremely good adhesion on C/C-SiC substrate surfaces even under thermal shock conditions.

Fig. 3: Views on the top (left) and on the cross section (right) of a SiCralee-coated short fibre reinforced C/C-SiC composite (Silca SF)
The formation of the microcrack pattern depends on the fibre architecture of the substrate to be protected. The most pronounced crack pattern with plenty of randomly orientated cracks can be observed for bi-directionally reinforced C/C-SiC composites whose thermal shrinkage during cooling is close to zero. Short fibre reinforcements with their higher CTE can lead to nearly crack-free surfaces.

Cracks within the coating run preferentially perpendicular to the fibre orientation of the protected substrate because of the high shrinkage impediment in fibre direction during cooling. Some designs of brake disks require a non-uniform fibre orientation, e.g. a higher amount of circumferentially oriented fibres in the load introduction area and a more homogenous orientation in the centre of the disk. As a result, the SiCralee coating reflects this fibre architecture by a corresponding microcrack pattern (Fig. 4).

The width of the microcracks depends on the thickness of the SiCralee coating. In general, the thicker the coating, the wider the surface cracks. During braking, when the coating is heated up, the cracks get narrower as the coating expands more than the substrate. All cracks normally run through the total thickness of the coating, but stop at the surface of the C/C-SiC substrate and no breakage of the fibres has been observed.

SiCralee coated C/C-SiC disks were tested against organic as well as sinter-metallic pads for automotive applications. It was found that the wear rates of the disks (outer diameter 280 mm, thickness of the disk 13 mm with coatings on both sides, each 1 mm thick) after 300 stop brakings against organic series pads were essentially lower (minus 50\%) in comparison to brake disks of grey cast iron. Due to the high thermal conductivity of the SiCralee coatings no overheating of the pads was observed although the pad’s material was not specially adapted to ceramic brakes.

![Fig. 4: Partial view of brake disks (Silca SF) with preferred fibre orientations in circumferential direction at the inner and outer section with (right) and without (left) SiCralee coating](image-url)
The coefficient of friction for this system in comparison to grey cast iron disks with the same organic pads was somewhat lower, but showed a higher stability with respect to initial surface temperature and pressure (Fig. 5).

Fig. 5: Coefficient of friction for grey cast iron (GG) and SiCralee coated C/C-SiC brake disks in combination with organic pads. Sliding velocity between 3.2 and 8.5 m/s

Fig. 6: Fading tests of SiCralee coated C/C-SiC brake disks (repeated brakings on hot surfaces)
In general, high temperatures during repeated brakings of conventional metallic disks cause brake fade and this places operating limits. Therefore, fading tests of SiCralee coated C/C-SiC brake disks with sinter-metallic pads have been performed for passenger cars by braking the vehicle several times from 134 km/h to 44 km/h to investigate the thermal stability of this tribosystem. Although the surface temperature of the disk increases over the number of brakings from room temperature to about 650 °C, the COF remains between 0.4 and 0.5 and demonstrates the high stability of C/C-SiC composites against fading (Fig. 6).

SUMMARY

C/C-SiC composite materials were originally developed for high temperature applications such as heat shields or thermal protection systems for spacecraft. They are manufactured via the melt infiltration of silicon into carbon/carbon and show a multiphase matrix composition of high abrasive resistance. Within the last ten years, DLR has reached a high level of system competence in the development of TPS and hot structures, and manufactured different structural C/C-SiC components successfully as flight hardware.

C/C-SiC composites show superior tribological properties in comparison to grey cast iron or carbon/carbon. In combination with their low density, high thermal shock resistance, and good abrasive resistance, C/C-SiC composites are promising candidates for advanced friction systems. High improvements in wear resistance were achieved by SiCralee ceramic coatings. Almost wear-free brake disks in combination with acceptable low wear rates for pads promise a high potential for lifetime brake disks in passenger cars.

REFERENCES


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