Development of Advanced CMC Materials for Dual-bell Rocket Nozzles

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The main goal of sub-project D7 is the development of advanced ceramic matrix composites (CMCs) for a dual-bell application. These CMCs are characterized by continuous carbon filaments which are embedded in a silicon carbide matrix (SiC). The process route used for the manufacture of the so called C/C-SiC material is the Liquid Silicon Infiltration (LSI), also called Melt Infiltration (MI). The CMC material is favorable to replace conventional high-density engine alloys due to their outstanding high temperature properties.

In a liquid-fueled rocket engine the material must withstand extreme conditions, e.g. high gas temperatures and high mechanical loads. In a first step the specifications and requirements of a CMC nozzle material have been defined and also the thermal and mechanical loads of a typical launcher system engine (e.g. Vulcain 2-Ariane 5) were described prior to the further development of C/C-SiC.

A central part of the development is the integration of the filament winding process into the LSI route and the characterization of specimens in terms of thermo-mechanical properties by variation of fibre orientation. The analysis of permeability to hot gases and a study on oxidation behavior is planned in the upcoming year. The manufacturing process and the concept of characterizing the CMC material are presented and discussed.

1. Introduction

Since the beginnings of CMC research in the 1970s, space technology has always played a pioneering role in the development of Ceramic Matrix Composites (CMCs). Hot structures with limited lifetime like thermal protection systems for re-entry aerospace systems (e.g Space Shuttle) are well-known application examples. The objective of this work is that CMCs shall substitute heavy metal super-alloys currently used in rocket nozzle extensions in near future. The use of CMCs as a structural component in nozzles will result in a major engine mass reduction, leading to an increase in payload capacity. Furthermore, due to the high temperature properties the operation temperature can be increased. Thus, there is the possibility to simplify the cooling process from active cooling to radiation cooling, which will contribute to the desired weight reduction. The abdication of a active cooling system will also reduce the total costs of the engine.

CMCs represent a relatively new class of quasi-ductile ceramic materials. The well-know bulk ceramics offer high thermal and chemical stability, hardness, and resistance to abrasive wear. However, due to their intrinsic brittleness and low thermal shock resistance, bulk ceramics cannot be used for structural components with high mechanical and thermal loads. The most commonly used approach to improve the fracture behavior

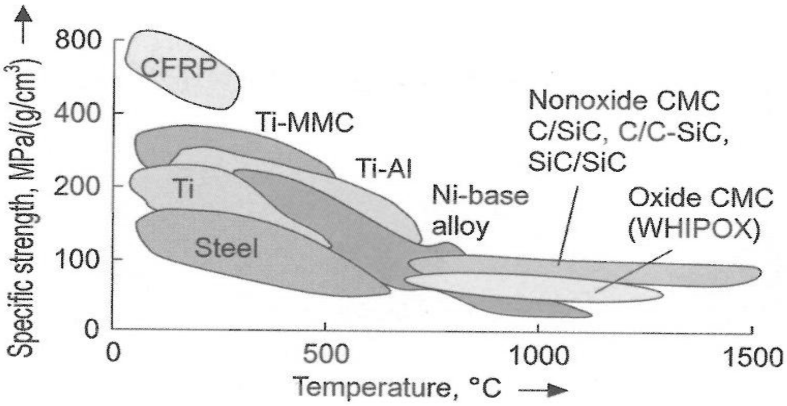

FIGURE 1. Mass-specific strength of structural materials as a function of temperature [1].

of ceramics and to increase the strength of structural parts is embedding of continuous fibers. The strain-to-failure of non-oxide CMCs is up to one order of magnitude higher than in monolithic ceramics and their low densities result in mass-specific properties which are unsurpassed by any other structural material, Fig. 1.

These CMCs combine the outstanding performance of bulk ceramics with novel properties that are unusual for ceramics:

- Quasi-ductile fracture behavior
- High fracture toughness
- Extreme thermal shock resistance
- Low coefficient of thermal expansion (CTE)
- Low density

The main issue in developing nonbrittle CMC materials is the interface bonding between the fibers and the brittle matrix. Weak interfaces enable the fibers to locally separate from the matrix, and the CMC material can capitalize on the typically high tensile strength ($\sigma > 2000\,MPa$) and fracture elongation ($\varepsilon > 1.5\,\%$) of the fibers, that are significantly higher than those of bulk ceramics (SiC: $\sigma = 400\,MPa$; $\varepsilon > 0.05\,\%$). This leads to high crack resistance and pseudoplastic material behavior, due to the energy-dissipating effects of crack bridging, crack deflection, fiber fracture, interface debonding and fiber pull-out, Fig. 2. In contrast to monolithic ceramics, where cracks lead to catastrophic failure, in CMCs, arising cracks are stopped at fiber-matrix interfaces or at microcracks within the matrix [1].

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2. Liquid Silicon Infiltration (LSI)

The LSI process is derived from the manufacture of monolithic SiSiC materials and was further developed to an advanced method for economical manufacture of carbon fiber reinforced C/C-SiC or C/SiC materials. The significant difference to all the other CMC manufacturing processes (Chemical Vapor Infiltration (CVI), Polymer Impregnation and Pyrolysis (PIP) and isostatic pressing) is the fact that the SiC matrix is built up by a chemical reaction of molten silicon with a porous carbon/carbon (C/C) preform.

The LSI process can be subdivided into three main steps, Fig. 3:

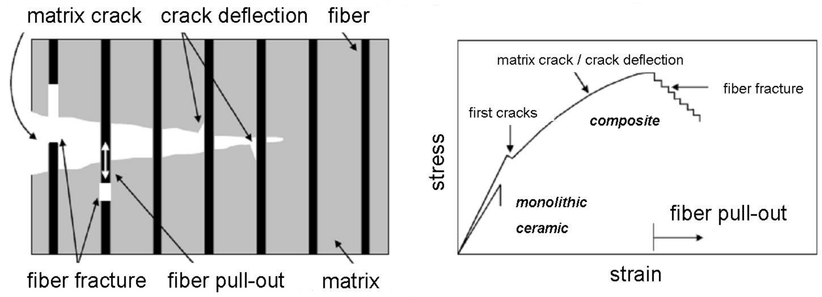

FIGURE 2. Fracture behavior (left) and stress-strain-diagram (right) of a CMC and a monolithic ceramic.

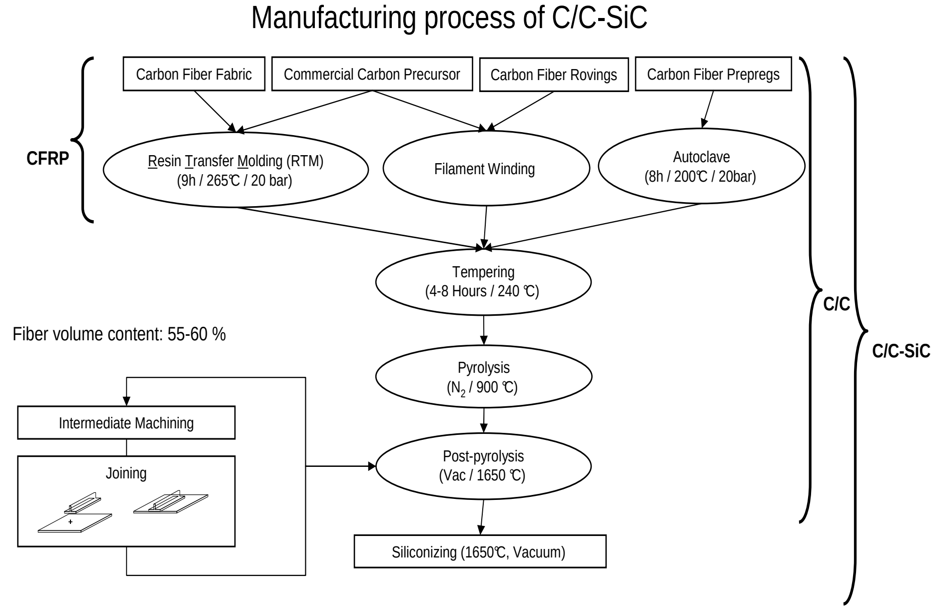

FIGURE 3. Schematic overview of the manufacture of C/C-SiC materials by LSI process.

(*a*) Manufacture of a carbon fiber reinforced polymer (CFRP) preform.

(*b*) Pyrolysis of the CFRP preform to give a porous carbon/carbon (C/C) preform.

(*c*) Siliconization of the porous C/C preform by capillary infiltration of molten silicon and simultaneous build up of SiC matrix by chemical reaction of Si and C.

As mentioned before, in C/C-SiC the weak fiber matrix interface is essential to obtain a quasi-ductile fracture behavior. Additionally, the fibers must be protected against direct contact to the high reactivity of the molten Si to obtain characteristic CMC properties, such as high strength, fracture toughness, and thermal shock resistance. Time consuming and costly fiber coatings via polymer impregnation of fibers and pyrolysis (PIP) and CVI of fibers are not necessary if particularly suitable precursors are used for manufacture of the CFRP preform to provide an in-situ fiber protection. These precursors offer a strong fiber matrix bonding in the CFRP preform, leading to a segmentation of each fiber bundle into dense C/C bundles during pyrolysis, Fig. 4 (left). During the subsequent MI, only the fibers on the outer surface of the C/C bundle are contacted to the Si and trans-

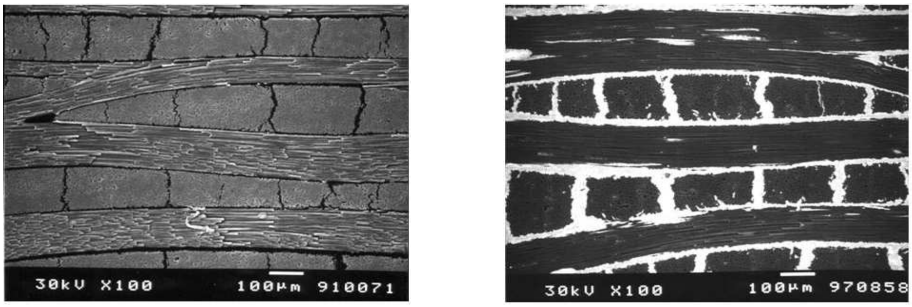

FIGURE 4. Left: Porous C/C preform. Right: Protected fibers in a dense C/C bundle (black), embedded in SiC matrix (grey).

Properties	**Unit**		**XB**	**XD**	**XS**
Composition	-		Fabric	Fabric	Fabric
Density	$10^3\ kg/m^3$		1,9	2,3	1,9
Porosity	%		3,5	1,0	2,0
Interlaminar shear strength	MPa		28	-	-
Bending strength	MPa		160	80	160
Tensile strength	MPa		80	30	120
Strain to failure	%		0,15	0,04	0,25
Youngs modulus	GPa		60	100	60–85
CTE	$10^{-6}\ 1/K$	$100\ ^{\circ}\mathrm{C} \parallel$	$-1{,}0$	1,5	0,43–2,5
(reference temperature: $25\ ^{\circ}\mathrm{C}$)		$100\ ^{\circ}\mathrm{C} \perp$	2,5	4,5	-
Thermal conductivity	W/mK	$200\ ^{\circ}\mathrm{C} \parallel$	18,5	33,7	-
		$200\ ^{\circ}\mathrm{C} \perp$	9,0	18,2	15,3
Specific heat	J/kgK	$25\ ^{\circ}\mathrm{C}$	750	720	720

TABLE 1. Typical material properties of fabric based LSI-C/C-SiC materials with different micro-structures.

formed to SiC, whereas the fibers inside the C/C bundle are well protected, Fig. 4 (right). This cost-efficient method is the basis of the LSI process, which has been developed at the DLR and which has already been transferred to Nammo Raufoss AS for rocket motor applications as well as to FCT Ingenieurkeramik GmbH for serial production of friction materials. Similar processes are used by Schunk Kohlenstofftechnik (SKT), SGL and the joint venture Brembo SGL Carbon Ceramic Brakes S. p. A.

In Table 1 typical microstructures and mechanical as well as thermal properties of two dimensional fabric reinforced CMC materials, manufactured via LSI are compared. These material properties will serve as a reference for future CMCs developed via filament winding technique.

3. CMC Material Requirements

In order to develop a novel CMC material, the conditions in an operating liquid-fueled rocket nozzle must be known to define the CMC material requirements. Therefore a specifications sheet has been compiled which gives an overview on typical conditions and requirements. It covers the main demands, such as thermal, mechanical and chemical loads.

Thermal Loads

The material temperature of a radiation-cooled nozzle extension will be in the range of 1300 − 1700 °C [2]. Heat fluxes of about 5–8 MW/m^2 are expected. Due to the high temperature gradients from the inner wall temperatures to the outer wall temperatures, the material has to withstand high thermo-mechanical stresses.

Mechanical Loads

During operation a series of mechanical loads act on the structure of the nozzle extension. During start-up of the engine high side-loads are induced, due to flow transitions inside a TOC-nozzle (thrust optimized contour nozzle) [3, 4]. These side loads can be as high as 3 % of the specific vacuum thrust and range from 75-120 kN. Furthermore, there is the risk of buckling loads due to the high pressure gradients from ambient to inner wall pressure during the start. An other mechanical load is created by the so called buffeting. These are fluctuating forces with moderate frequencies of about 20 Hz during the trans-sonic ascent.

Chemical Loads

A big issue is the protection of CMCs from oxidation. A serious drawback of carbon fiber reinforced ceramics is that carbon in any form will react with oxygen at temperatures as low as 500 °C. The main reaction product in liquid fueled rocket engines (LOX/LH2) is water vapor (mt. 95–97%). Water vapor at high temperature ($>$600 °C) does not only react with carbon fibers and matrix, it also leads to an accelerated SiC recession by oxidation at high water-vapor pressures [5, 6]. The oxidation leads to significant mass loss and consequently weakens the material strength properties. Protection coatings like environmental barrier coats (EBC) and thermal barrier coats (TBC) are inevitable and have to be evaluated in terms of erosion resistance and their adherence to the substrate.

The following properties are required for a CMC rocket nozzle material:

(*a*) Thermal-shock resistance
(*b*) Oxidation resistance in oxygen conditions at high temperatures ($>$1300 $^\circ C$)
(*c*) Oxidation resistance in water vapor conditions at high temperatures ($>$1300 $^\circ C$)
(*d*) Erosion resistance to exhaust gases
(*e*) Moderate fracture toughness
(*f*) High temperature strength
(*g*) Sufficient durability for typical operation lifetimes

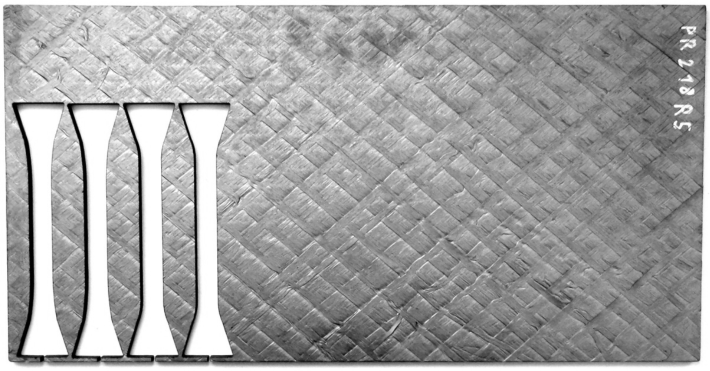

FIGURE 5. Example of a C/C-SiC panel via filament winding and LSI route.

4. Studies

Due to its cylindrical form the nozzle structure will very likely be manufactured via filament winding technique or braiding technique. In the first phase of sub-project D7 the goal is to manufacture a series of C/C-SiC specimens (panels and cylinders) via filament winding technique. In this part of the work the winding technique will be integrated into the LSI process. In a later stage thermo-mechanical studies will be performed to evaluate the material properties. During the CFRP manufacture a variety of process parameters can influence to microstructure and material properties of the final CMC.

Therefore the following winding process parameters will be investigated:

- Winding angle
- Winding pattern
- Roving size
- Carbon fiber type
- Winding speed
- Resin-bath temperature

Different geometries are available for sample generation and preparation. Panels and cylindrical specimens will be manufactured in different dimensions. Panels are used to provide specimens for determination of mechanical properties. Fig. 5 shows a CMC panel used for tensile test specimens. The tensile specimens are cut in different orientations to determine strength values for different fiber orientations. One objective is a material database which will give information on how to set the winding process parameters to receive a desirable CMC material. Typical winding angles for mechanical testing are ± 15, ± 30, ± 45, ± 60 and ± 75 degrees.

The determination of the mechanical properties, such as tensile strength and Youngs modulus, are also carried out at high temperatures ($>$1000 °C) and after thermal aging in an oxidizing atmosphere.

In addition to the comprehensive thermo-mechanical testings, the C/C-SiC specimens undergo further material testing to determine the erosion resistance in high velocity gas flows at high temperatures. Test campaigns are planned at the cooperating institutes DLR Köln and DLR Lampoldshausen. At DLR Lampoldshausen hot-firing passenger tests are planned at the M11 test facility for summer 2010. Panels are placed into the exhaust gas flow which is containing about 10 % of water vapor. The temperature is assumed to be above 1000 ˚C [7].

In a second test campaign at the high-enthalpy wind tunnels at DLR Köln further testing is conducted on erosion and oxidation resistance behavior. The campaign will be performed in the first half of 2010. Temperatures of about 1000 ˚C and Mach number of 7–8 of hot air flow are the expected test conditions.

Both test campaigns will give a good overview on the materials erosion resistance at moderate temperatures. The main objective is to study and estimate mass loss rates of C/C-SiC.

It is attempted to reduce the open porosity of the CMC material to a minimum. Thus, the permeability will be studied. The Darcy-Forchheimer coefficients (k_d,k_f) which describe the permeability behavior of a porous material are tested at DLR Stuttgart.

The mechanical damping behavior of C/C-SiC is an additional aspect which will be investigated later in this research period.

As mentioned before in section 3, the oxidation behavior of C/C-SiC is an essential aspect in this research. The thermo-chemical kinetics have to be understood in order to provide an adequate protection system. In a first step unprotected C/C-SiC reference samples were used to determine the mass loss in air at different temperatures. Thermogravimetry analysis was used to measure the mass loss over time. Fig. 6 shows the results of the TG-analysis. It is clearly visible that weight loss increases with raising temperatures. Depending upon exposure time mass loss stops when all free carbon has dissipated, leaving the SiC-matrix behind. This led to a total weight loss of about 55 % causing strength degradations. This basic experiment shows the sensitivity of standard uncoated C/C-SiC to oxidizing atmospheres. A protection layer in terms of environmental barrier coatings (EBC) or thermal barrier coatings (TBC) are indispensable for a rocket nozzle application with moderate lifetimes of about 1–2 hours including testing times. The reduction of oxidation rates is the main objective for a protection coating system. Thus, diffusion rates of oxygen into the material have to be reduced. In addition the silicon based ceramics must be protected against accelerated attack by water-vapor environments through oxidation and volatilization reactions.

Beside the material development of C/C-SiC via winding technique there is great attention to evaluation of adequate coating systems. Topcoat materials must be stable in water-vapor pressurized environments at high temperatures. Also, it is important that the thermal expansion coefficient is similar to that of the substrate. In addition, the erosion resistance as well as the bond of the coating to the substrate has to be tested. Well known examples for topcoats are CVD-SiC and yttria-stabilized zirconia (YSZ) or multi layer coatings consisting of mullite and BSAS-systems (barium-strontium-alumina-silicate) [8, 9].

In order to compare the mass loss behavior of uncoated and coated C/C-SiC samples in oxidizing environment at high temperature, thermogravimetric measurements (TGA) with CVD-SiC topcoat on C/C-SiC samples were conducted. Fig. 7 depicts CT-images of the sample at which the topcoat is clearly visible. The thickness of the CVD-SiC protection coat was about 200 μm. A first comparison of un-coated C/C-SiC and coated CVD-SiC C/C-SiC is shown in Fig. 8. The TG measurement was conducted at 1500 ˚C and a constant air flow of 100 ml/s. The sample dimensions were 10x10x10 mm^3. No severe weight loss is recognized at the CVD-SiC coated samples. The uncoated sample in contrast suffered a major mass loss (35 %) within two hours of the test. Further

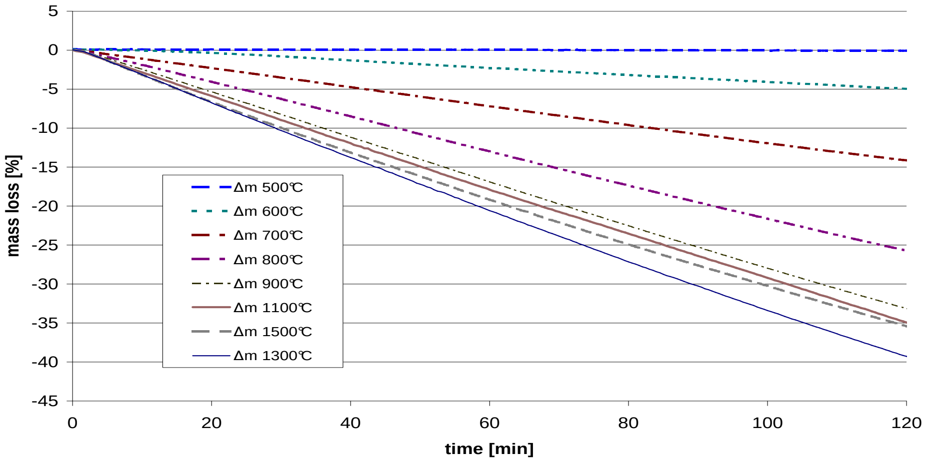

FIGURE 6. Mass loss of C/C-SiC as a result of oxidation. TG-measurement of 10x10x10 mm^3 samples at different temperatures. Air flow 100 ml/min.

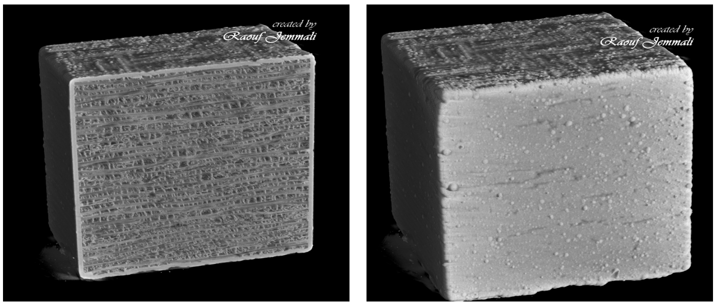

FIGURE 7. CT images of a CVD-SiC coated C/C-SiC sample used for oxidation tests.

testing on coating systems in water vapor conditions at high temperatures and studies on erosion resistance are planned.

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5. Conclusions

Carbon fiber reinforced SiC matrix (C/C-SiC) composites are one of the most promising materials for high temperature structural applications such as rocket nozzles. On going studies have to be intensified to improve the current performance of this kind of CMCs. In the work of sub-project D7 the LSI manufacturing process via filament winding is being verified. Process parameters for ultimate material properties like high strength and moderate fracture toughness are being investigated.

Besides material qualification and generation of a material database consisting of thermo-mechanical properties there is a major interest in evaluating overall coating systems for oxidation protection. Dedicated studies on oxidation and erosion behavior of uncoated and coated C/C-SiC samples in hot gas passenger tests are planned at cooperating institutes within the DLR in 2010.

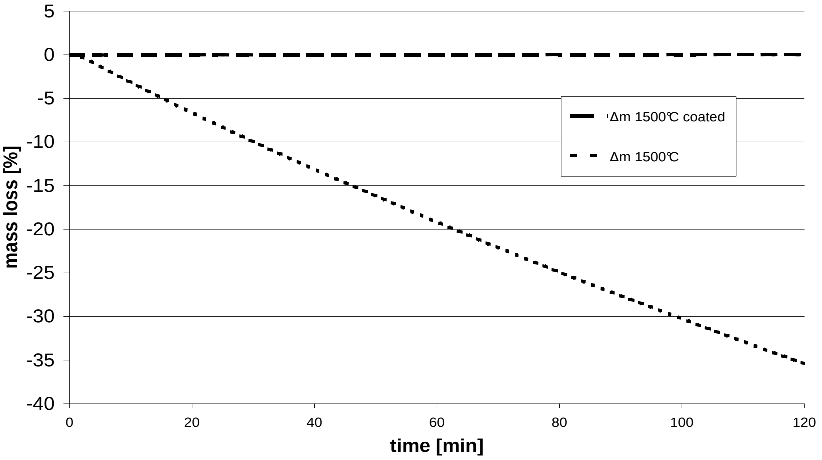

FIGURE 8. Comparsion of mass loss of CVD SiC coated C/C-SiC and uncoated C/C-SiC via TG-measurement.

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