

## FIBER CERAMIC STRUCTURES BASED ON LIQUID IMPREGNATION TECHNIQUE

W. Krenkel, P. Schanz

German Aerospace Research Establishment (DLR)  
Institute for Structures and Design  
Stuttgart, Germany

### Abstract

For future reentry vehicles ceramic matrix composites (CMC) are very favorable materials for hot structures and thermal protection systems. This paper describes the fabrication and evaluation of CMC-components manufactured by the liquid impregnation technique. This process offers the potential for a low-cost CMC production for all components which can be fabricated by resin transfer molding (RTM) or other techniques for reinforcing polymers. The two main fabrication steps, the component shaping and the matrix conversion to ceramics, are described in detail. Experimental data on infiltration parameters as well as mechanical properties and oxidation resistance of the produced fiber ceramics were determined. Emphasis was given on manufacturing real components like panels with integrated stringers to demonstrate the feasibility of the process.

### 1. Introduction

The design of present space transportation systems (e.g. Space Shuttle) is based on the separation of functions between thermal protection systems (TPS) and loadcarrying substructures. All mechanical loads have to be carried by a buckling resistant structure of aluminum. Only parts like the nose cone of the fuselage or the leading edges consist of oxidation protected C/C (carbon fiber reinforced carbon) as so-called hot structures combining both functions, thermal protection as well as load carrying.

For future space transportation systems (e.g. Hermes) or hypersonic airplanes (e.g. S nger) the thermal and mechanical loads are considerable higher and exceed the property spectrum of conventional materials. For large, thinwalled structures there is a need for materials able to withstand temperatures far above the melting point of superalloys.

Besides high specific mechanical properties ceramic materials exhibit high erosion, corrosion and oxidation resistance. The major problem for their application in structural components of flying systems is their inher-

ent brittleness, resulting in an insufficient reliability of the components. By reinforcing with continuous fibers based on carbon or silicon carbide (SiC) the damage tolerance of ceramics can be increased considerably. The key points hereby are the bonding forces in the interface of fibers and matrix. To reach a quasi-plastic behavior a more or less low bonding between fibers and matrix must be achieved. With this, stress peaks don't result in a catastrophical failure of the component but will be locally reduced by microcracks, delaminations and other energy absorbing mechanisms.

Fiber ceramics have been under investigation for more than ten years, namely in France. SEP developed the chemical vapor infiltration (CVI) process to produce fiber ceramics like carbon fiber reinforced SiC (C/SiC) and silicon carbide reinforced SiC (SiC/SiC). This process is well documented in the literature [1], [2], [3] and represents the state of development with the highest mechanical properties of fiber ceramics. The main disadvantage of this process are the low deposition rates, typically 50  $\mu\text{m}$  per day, resulting in component manufacturing time of weeks and months. By application of thermal and pressure gradients over the preform the deposition rates can be increased to some millimeters per day [3], [4], but this process is limited to components of simpler shapes and relatively high porosity.

Processes on the base of polymer pyrolysis promise considerably shorter manufacturing times, resulting in a better economy. By these processes fiber preforms are liquid impregnated with specific polymers (precursors) by common techniques for reinforcing polymers and are subsequently cured under pressure and temperature. These precursors must show a high content of SiC and carbon, respectively, to achieve a high ceramic yield.

Organo-metallic polymers based on polysilane or polysilazane show a ceramic yield of 60-80%, but the inherent high shrinkage of the polymers as a result of the high difference in density between polymers and SiC necessitates several re-infiltration steps [5], [6].

Polymers with a high carbon yield of more than 50% are the base material for the in-house liquid impregnation technique [7], [8], [9], [10], [11], [12]. This process offers the potential for an economical process to produce fiber ceramics in near-net-shape technology. In this paper, manufacturing details to produce structural components as well as microstructural, thermal and mechanical properties of the material are described.

## 2. Materials and Processing Technology

Two classes of fibers are commercially available on the market as continuous reinforcements for applications above 1000°C: carbon and ceramic fibers. Table 1 gives a summary of commercial fibers and fibers on the laboratory scale with their typical properties and thermal range of application. Generally, carbon fibers offer the higher thermal stability, showing high and nearly constant strength values within an inert atmosphere. However, in an oxidative environment pronounced degradation starts at temperatures above 450°C, so oxidation protection rather than thermal stability represents the factor limiting the use of carbon fibers.

High strength (HT) fibers like T300 are comparatively cheap and available in a wide range of modifications and products. High modulus (HM) fibers are more expensive and in particular ultra high modulus (UHM) fibers are not easy to handle because of their high stiffness. Carbon fibers show considerable differences in their thermal stability: high modulus fibers with a carbon content of 100% are very stable and thermogravimetric analysis demonstrates their applicability for temperatures up to 1600°C under inert atmosphere (Figure 1). The measured mass loss for HM fibers of about 1.5% above 300°C only indicates the decomposition of the sizing agent. The same stability can be measured for pitch-based UHM fibers, while HT fibers with carbon contents of about 95% (e.g. T300) already show a mass loss at temperatures above 800°C.

Ceramic fibers based on silicon carbide (e.g. Tyranno, Nicalon) or silicon nitride are fabricated by pyrolysis of organo-metallic precursors. They exhibit an inherent high oxidation resistance but due to free active elements (carbon, oxygen) they degrade at temperatures above 1200°C, in air as well as in inert atmospheres. At present all weavable SiC type fibers are Japanese and major efforts, also in Europe and USA, are in progress to produce more stoichiometric (and therefore more stable) ceramic fibers.

The most common matrix systems for CMC are carbon and silicon carbide, respectively. Regarding the liquid impregnation process the ceramic matrix is fabricated from polymer precursors by chemical conversion and reaction to carbon and silicon carbide matrices. To reach the goal of a low-cost fabrication route only high carbonaceous polymers are suitable to get high carbon yield after pyrolysis. As a result of initial investigations two types of precursors were selected:

- Phenolics FW 435/247
- Thermoset XP-60

Both of them exhibit low viscosity for a good wetting of the fibers and can be cured before carbonization.

In principle, the liquid impregnation process can be divided into two steps

- shaping of CFRP components and
- matrix conversion from polymer to ceramic.

Figure 2 schematically shows the liquid impregnation process. Using common techniques for reinforcing polymers with continuous fibers like resin transfer molding or prepreg technology, the components can be manufactured integrally. Except for the RTM the ceramic yield can optionally be increased by adding graphite or silicon carbide powder to the precursors. After curing, the shape of the components is fixed and the properties of the material are comparable to those of conventional carbon fiber reinforced plastics (CFRP). To get CMC, a thermal treatment and the addition of liquid silicon to convert the matrix to silicon carbide are necessary in separate furnaces. First, the matrix is pyrolysed at temperatures up to 900°C in inert atmosphere. Subsequently, the resulting porous C-matrix partially reacts with molten silicon to SiC. Details of infiltration and reaction are given in the following chapter.

The most time consuming step of the process is the carbonisation of the matrix. To make use of the full potential, only one carbonization step without any re-infiltration of precursors is worth striving for. That means, that the carbon yield of the precursors have to be at least 50% for the chosen phenolics and XP-60. Thermogravimetric analysis were conducted to evaluate the thermal degradation of the material. Nearly the whole mass loss occurs in the range between 400 to 600°C, so the temperature gradient during pyrolysis was adapted to very low values within this range to avoid delaminations. A total furnace time of about 100 hours is sufficient to convert the polymer matrix to carbon.

Siliconizing is a well established industrial process to produce monolithic silicon infiltrated silicon carbide (SiSiC). Due to the high melting point of silicon, the C/C-component must be heated up to 1500 - 1600°C under vacuum in a special furnace. The required in-house installed furnace is depicted in Figure 3, a PC-controlled, water cooled facility for high temperature applications. The C/C heating elements, controlled by pyrometers, allow a fast and homogeneous heating-up under vacuum or in inert atmosphere. Components with dimensions up to 350 x 400 mm can be produced, only restricted in size by the geometry of the heating chamber.

For siliconizing, the C/C components have to be arranged in a bed of silicon powder and fixed by auxiliary supports of dense graphite or boron nitride. All materials must be thermally stable and chemically inert to exclude any influence on the process.

In comparison to the CVI route the processing temperatures are somewhat higher. As a result, the presently available ceramic fibers are not applicable for the liquid impregnation process due to their drastic decrease in strength above 1300°C and their reactivity with silicon. However, HM carbon fibers are very sta-

ble if the chemical attack by silicon can be avoided. This can be realized by a controlled matrix conversion to a microcrack pattern where only the matrix but not the fibers will be partially converted to SiC. So, the microstructure of the C/C material has a fundamental importance for a successful siliconizing.

### 3. Microstructure

The liquid impregnation process makes use of the fact that carbonaceous precursors show a low mass loss after pyrolysis, resulting in a geometrical shrinkage of the former polymer without any microcracks. The precursor XP-60 shows a mass loss of about 30-35% corresponding with a shrinkage in volume of about 40%, i.e. 16% in each direction of the axis. As a result, pure polymers without any shrinkage impediment can be pyrolysed microcrack-free to a dense carbon material.

When embedding anisotropic carbon fibers in unidirectional (UD) orientation into the precursors, a quite different shrinkage behavior can be observed. Perpendicular to the fibers there is no significant impediment and shrinkage occurs in a similar manner to that of pure polymers. The matrix is almost free of voids and densely surrounds the fibers.

In crossply composites, where unwoven UD-layers are alternately orientated to a 0°/90° laminate, dense C/C bundles consisting of some hundreds of filaments form discrete cracks, running parallel to the fibers throughout the whole material. Perpendicular to the layers, i.e. in the thickness direction, no shrinkage impediment and therefore no crack formation occurs.

In the case of woven fabrics there is an additional shrinkage impediment caused by the bending of the fibers, analogous to the effect of a weak 3D-reinforcement. In addition to the crossply crackpattern continuous cracks between each fabric layer are created. Generally, the cracks are smaller and the distribution looks quite homogeneous. Figure 4 illustrates by SEM micrographs the different crackpattern for unidirectional, crossply and fabric reinforcement after pyrolysis. As a result, the C/C material consists of compact bundles of carbon filaments, embedded in a dense carbon matrix, surrounded by three dimensional orientated continuous cracks. It is essential to notice, that no matrix separation from filaments occurs. During the carbonization the macroscopic shrinkage of the laminates in the fiber direction is close to zero, but in the thickness direction it shrinks about 10%, depending on the fiber content. The in-house developed liquid impregnation process now takes advantage of this morphology to create an internal oxidative protection of the carbon fibers by siliconizing.

The siliconizing can be divided into two principal effects, the physical infiltration of silicon into the laminate and its chemical reaction with a part of the C-matrix to SiC [13].

On the assumption that all cracks are extending through the total dimension of the laminate and that the molten silicon can penetrate these cracks lengthwise, the process of infiltration can be described by the effect of capillarity. The driving force of capillarity  $F_c$  depends on crack width and the physical properties

of the carbon/silicon interface such as surface stress and wetting angle (Table 2).

Generally, the larger the crack width the higher the force and the higher the infiltration velocity, i.e. the shorter the infiltration time. The viscosity of silicon at melting temperature is very low, lower than water at room temperature, so a fast and homogeneous infiltration within the cracks is possible. Normally, the mean widths are 10 to 20  $\mu\text{m}$  and a laminar pipe flow can be assumed, so the infiltration time and the maximum distance of infiltration is calculated in the range of a few minutes and a few meters, respectively. These theoretical values correspond very well with the experimental data measured with 0°/90° C/C fabric laminates.

Infiltrating the C/C perpendicular to the layers, i.e. in direction of the laminate's thickness, the infiltration leads to infiltration times which are orders of magnitude longer in comparison to the longitudinal infiltration. As a result, the arrangement of the components in the sinter furnace has to ensure that the impregnation of silicon can occur in the fiber direction. On contact with the C-matrix at the walls within the cracks the silicon reacts immediately to form a thin layer of  $\beta$ -SiC. The following exothermal reaction between C and Si is controlled by diffusion: Si-atoms diffuse into the matrix, reacting to SiC and resulting in an increase of volume and a slow closing of the cracks. The goal of a complete reaction and impregnation of the cracks requires

- high purity of silicon (99.99%)
- stoichiometrical dosage of silicon
- dense matrix within the C/C-bundles
- crack widths 10-30  $\mu\text{m}$
- high homogeneity of the C/C

This process is very complex and determines the furnace parameters, e.g. temperature, time and pressure. So, the siliconizing step has to be a compromise between the requirement for a complete reaction which leads to high temperatures and longer times and the protection of the fibers which requires shorter processing times.

The state of development today is thus, that no attack and no pronounced degradation of the carbon fibers occur and all cracks are filled with SiC, the bigger ones containing a small amount of free silicon.

As a result, each C/C bundle and each fabric layer is protected against oxidation by SiC. Thus, the oxidation protection takes place in the whole volume around each bundle and between each fabric layer. The 3D model of Figure 4 demonstrates this characteristic microstructure of the C/SiC material, showing SEM micrographs of a 1.5mm thick laminate. Typically, these fiber ceramics consist of one third in mass of SiC and two thirds of carbon (fiber and residual matrix), for an adjusted fiber content of about 50%.

In practice, the morphology of the C/SiC material can be adjusted in a wide range by varying the reinforcements and precursors, respectively. Fiber content, weaving mode and type of fiber as well as the carbon yield of precursors determine the crack pattern and therefore the thermal and mechanical behavior of the C/SiC.

To evaluate the crack pattern before siliconizing, a suitable method is to measure the open porosity by water absorption. There exists standards for porous materials like concrete or monolithic ceramics which can be adapted to C/C. Typical values for laminates with fiber contents of 50% are 17-23% open porosity after carbonization, corresponding with a matrix mass loss of 30 - 35% and a shrinkage in thickness of about 10%. These porosity data lead to the siliconizing parameters described above. Lower porosities than 15% should be avoided due to considerable increase in infiltration time.

#### 4. Mechanical and Thermal Behavior

This chapter describes the results of mechanical and thermal investigations carried out on C/SiC with XP-60 as the precursor. As mentioned above phenolic resins could be applied in the same manner as XP-60. However, a relatively high solvent content, the polycondensation reaction when curing and the subsequent bubble formation complicated the use of phenolics. Their application requires further investigations.

Table 3 summarizes the properties of C/SiC at room temperature. The specimens were cut out of C/SiC plates, which were fabricated of HT fabric (plain weave) with 0°/90° balanced fiber orientation and XP-60 as precursor.

The tensile tests showed a relatively brittle fracture behavior with only 0.22% fracture strain. The tensile strength amounted to 90 MPa on average with a secant modulus of 49 GPa. The bending strength was determined to be 160 MPa. The interlaminar shear strength (ILSS) reached the relatively high value of 23 MPa, based on a strong fiber/matrix bonding.

These properties were measured on a C/SiC material with the open porosity of 5% on average, with density of 2,000 kg/m<sup>3</sup> and a fiber content of 55%. In a high temperature dilatometer the mean coefficient of thermal expansion was measured to be  $2 \cdot 10^{-6}$  1/K.

In the absence of standard tests for fiber ceramics different specimen geometries were investigated based on aviation standards and the German Industrial Standards (DIN). Presently, international efforts are going ahead to prepare test standards for CMC with continuous reinforcements [14].

The investigations aimed to develop a specimen geometry as simple as possible. Tensile specimens with load initiation by the principle of geometrical locking were out of question because of the higher manufacturing costs. The following tapered tensile specimens showed the highest tensile strength:

- length of the cross section      40 mm
- specimen width                      15 mm
- aspect ratio of taper                3:2
- transition radius                    100 mm

Within one material batch the tensile strength scattered 10%, at maximum.

Applying different types of bonded laminate tabs did not increase the measured tensile strength values. The

shear stress peaks at the ends of the tabs mostly caused failure close to the load initiation.

Variations of the total length and width of the specimens exhibit no influence on the tensile strength. With tapered tensile specimens failure always occurred at the cross section. However, the machining of the cut edges had an effect on the strength values. Grinding and sawing with diamond tools, respectively showed better results than water jet cutting which caused deep grooves. Hence it follows that cut edges of tensile specimens should be ground or sawn.

Also the bending tests with HT fibers generally exhibited a brittle fracture behavior. The material morphology - characterized by a certain open porosity, a conspicuous microcrack pattern and a lot of phase boundaries - had no critical effect on the bending strength despite the variation of the following parameters:

- specimen size
- rate of load application
- test method (3 point bending / 4 point bending)

Initial tests with HM fabric showed a tendency towards a quasi-plastic fracture behavior. Figure 5 summarizes bending tests with untreated HT fabric and specially treated HM fabric. At nearly the same bending strength of 150 MPa the HM fabric exhibits a conspicuous fracture toughness in contrast to the more or less linear-elastic behavior of the HT fabric. Enclosed SEM micrographs confirm the measurements. In contrast to the HT fabric the HM fabric shows a clear fiber bundle-pull out. The results indicate one way to improve the damage tolerance of our material.

After initial fatigue tests on C/SiC at room temperature, this material appeared to be suitable for future applications under cyclic loadings. Tensile loads at a range up to 70% of the static tensile strength ( $R=0.1$ ) could be cycled  $10^8$  times at 180 Hz without failure of the specimens.

For quality assurance purposes and further improvement of the manufacturing technology suitable NDE procedures were investigated. Plates in the CFRP state were examined by ultrasonic scanning to determine existing voids and local delaminations.

After siliconizing, X-ray analysis was used to assess the regularity of the silicon carbide content in this material. The currently available material quality exhibits a very regular SiC distribution, even in parts of 300 x 300 mm size and a thickness up to 16mm.

The high temperature application of fiber ceramics requires investigations to examine the oxidation resistance. For these tests specimens are used with dimensions 80 x 30 x 3 mm. These samples were placed into a furnace. While increasing the temperature the heating chamber was flushed by inert gas. When the desired test temperature was reached the scavenger gas was replaced by air. After the exposure time the cooling down was again carried out under inert gas. The mass loss - a criterion for the decrease of oxidation resistance - was determined by weighing the samples before exposure and afterwards.

First tests were carried out with uncoated C/SiC specimens. After one hour of exposure time at the range from 1000 to 1400°C the samples showed high mass

loss values of 12 to 14 %. That means a still insufficient oxidation resistance, especially pronounced at the cut edges.

To improve the behavior in oxidative atmospheres the C/SiC specimens were coated with a silicon carbide layer by chemical vapor deposition technique (CVD). Prior treatments of the samples were necessary: cleaning of the specimens and subsequently etching off the small amount of free silicon which occurred during the siliconizing. The oxidation protected C/SiC specimens were subjected to the same procedure as the nonprotected samples. The mass loss after different exposure times at 1400°C is summarized in the following table:

Time of Exposure	1 h	10 h	100 h
Mass loss at 1400°C in air	0.1%	0.1%	4.2%

These initial oxidation tests can be summarized as follows: uncoated C/SiC exhibits an insufficient oxidation resistance. However, supplementary external SiC coating shows a high oxidation stability. Further improvements are on the way.

One of the most critical requirements for the application of C/SiC as a TPS material are low erosion rates during the reentry. To get information concerning the applicability of fiber ceramics, samples were investigated under simulated reentry conditions. Disk specimens of 25 mm in diameter and 2-3 mm thickness were positioned in a plasma flow (rate 2.5 g/sec, 80% N<sub>2</sub> / 20% O<sub>2</sub>). The duration of each test was about 15 minutes, corresponding to one reentry operation at constant surface temperatures, measured by a spectral pyrometer. By weighing the samples before and after the test, the specific erosion rate (related to exposed area and exposure time) were determined. Some results of these erosion tests are depicted in Figure 6.

For C/SiC a quasi-linear increase of mass loss to about 10% was measured at a temperature range from 1150 to 1500°C. For higher temperatures, the slope became steeper, and at 1800°C the mass loss had grown to about 9 kg/m<sup>2</sup>h, corresponding to a decrease of sample thickness of about 1 mm. In case of SiC/SiC the specific erosion rate is quite similar, even though the curve is equidistantly shifted to lower values.

To determine the upper limit of oxidation effects, non-protected C/C specimens were tested. As expected, the level of mass loss is very high over the whole temperature range and, compared to C/SiC and SiC/SiC, considerably higher erosion rates were evaluated.

To improve this relatively good behavior, additional tests were investigated with coated specimens. Preliminary tests used mullite as coating. Experiences with former mullite coatings on C/C could be applied. C/SiC samples on one side coated with mullite were examined in the same test facility and under the same conditions. Results of these erosion tests are also shown in Figure 6. At temperatures ranging from 1500 to 1800°C, a constant mass loss of about 1 kg/m<sup>2</sup>h was

measured, indicating that mullite coating could be an effective protective layer. Further investigations must be done.

With regard to the applicability of C/SiC at considerably higher temperatures, as occurring during capsule reentry (EXPRESS, [15]), there is little known. A few tests have been carried out at a pressure of about 8 mbar and a plasma mass flow rate of 8.5 g/sec (N<sub>2</sub>/O<sub>2</sub>) to investigate this problem. The temperature reached up to 2200°C and the specific mass loss rated about 30 kg/m<sup>2</sup>h. The present results point out, that erosion rates do not increase exponentially with rising temperature. The specimen temperature temporarily reached 2400°C at the surface, and times of exposure amounted from 3 to 6 minutes. That means: for short time exposure essentially higher temperatures can be sustained. Thus, C/SiC has properties in reserve for reentry applications.

## 5. Component Fabrication and Design Aspects

From the beginning the institute's aim was to demonstrate the feasibility of the liquid impregnation process to produce structural components. From the present point of view fiber ceramics are the unique materials for structures like leading edges, nose cones and rudders in future space transportation systems and flaps or nozzles in airbreathing engines of future hypersonic systems.

As a first application a ramjet nozzle with an integrated secondary combustion chamber was fabricated and successfully tested up to the material's thermo-mechanical limits at a ramjet test facility [16]. In addition, preliminary design and manufacturing studies were carried out to fabricate highly integrated stringer stiffened flaps for the intake of a jet engine. Using one flap configuration as an example, the in-house process will be described from the designers point of view and some generally valid aspects for fiber ceramics will be deduced.

One of the major design requirements is to achieve high integration to minimize supplementary machining and joining of the ceramics, that means the CFRP manufacture has to be a near-net-shape technology. Technical feasible CMC materials need to have at least two dimensions of fiber reinforcements. Usually, the composites are fabricated by conventional layup constructions where plies of prepreg tapes and fabrics are stacked and subsequently consolidated and cured in an autoclave.

Nevertheless, the resin transfer molding method offers the best possibilities for net-shape composites, providing

- complex shaped components
- three dimensional reinforcements
- dimensional reproducibility
- no human contact with toxic vapors.

Generally, RTM involves placement of dry reinforcement fiber in a closed mold which is subsequently injected with low viscosity resins. Besides high rheological properties, the resin should be a one-part liquid. The selected phenolics and in particular the XP-60 show the desired property profile.

The goal of the processing technique is to produce uniform, void free composites with variable fiber volume fractions. A two-chamber mold of steel was used (Figure 7), heated by electric cartridge heaters to reach the curing temperature of the precursors.

For XP-60, the RTM process can be described as follows: The mold is heated up to 210°C to melt the pulverized polymer to a liquid with a very low viscosity of 30 mPas. A vacuum is pumped to remove entrapped air and any other volatiles. By decreasing the vacuum on the preform chamber the resin is soaked into the fiber preform. After impregnation, the XP-60 is cured in the mold over 8h with pressures up to 18bar to avoid volatiles during the polycondensation reaction.

By inserting mandrels the mold can be adapted easily to different requirements in shape and dimension. As an example, Figure 8 shows the preform lay-up sequence for a stringer stiffened panel. The fabrics were cut by water jet, dried and inserted in a balanced lay-up to avoid distortion after removing the cured laminate from the tool.

The reinforcement of fabrics leads to a characteristic anisotropy in thermal and mechanical properties of the fiber ceramics, similar to other composites. Due to the different thermal expansion coefficients perpendicular to the fibers and parallel to the fibers, non-restrained edges show spring-forward phenomena when heating up or cooling down from the solidification temperature. In restrained edges like tubes, this phenomena leads to frozen in stresses and reduces the allowable strength level. Generally, for fiber ceramics this effect is more pronounced caused by the higher difference between manufacturing and application temperature.

While distortions caused by the anisotropic thermal behavior are reversible the shrinkage in thickness of about 10% during the carbonization as described in chapter 3 leads to irreversible spring-forward effects which are additionally of a higher order of magnitude. To maintain the geometry and shape during the pyrolysis the component's contour has to be suitably fixed. For the illustrated stringer panel of Figure 8 mandrels of graphite are inserted to suppress the spring-forward of the edges during cooling. One other possibility to maintain the correct geometry is to adapt the RTM mold according to the shrinkage behavior.

Generally, the machining of ceramics should be reduced to a minimum. The material's hardness require special tools of hard metal or diamond resulting in high machining costs and time. By the near-net-shape technology of the liquid impregnation process only few machining steps are necessary, which can be mainly done in the polymer stage, where all tools for CFRP machining can be used. Nevertheless, traditional tooling methods like cutting, drilling and eroding are under investigation for the finish of CMC components. Due to the relatively high carbon content machining parameters are similar to C/C tooling and no essential problems occurred. Laminates with a thickness up to 4 mm can be roughly cut by water jet with pressures up to 3500 bar and cutting velocities of 200 mm/min, for higher qualities and bigger components eroding by wire and sparking is applicable with good results as well as usual diamond cutting tools.

To date, different C/SiC components have been fabricated from laminates with 1 to 16 mm thickness and

up to 300 mm length. Their application range comprises nozzles and stringer stiffened flaps for aeronautical structures as well as disks for braking systems in high speed trains. Figure 9 shows an assembly of some of these in-house fabricated components. While the nozzle has already demonstrated its applicability in a real gas test, the stringer and double walled panels are feasibility studies for the institute's activities on the German HYTEX programme. There, a highly integral, thin walled intake flap as a demonstration component for Sanger will be designed, manufactured and tested at temperatures up to 1200°C in air.

## 6. Summary

C/SiC fiber ceramics, fabricated by the liquid impregnation process, take advantage of the quasi-ductile damage tolerance behavior of carbon/carbon in combination with the high temperature stability of silicon carbide. The internal protection by discrete SiC layers leads to low erosion rates under simulated reentry conditions but by supplementary anti-oxidation coatings the oxidation resistance can be improved further. However, these fiber ceramics are still limited life structures due to the oxidative attack on the carbon components.

Resulting from a high number of processing parameters, a large variety in material behavior can be achieved. The mechanical properties can be considered as design values for structural components. All tests were conducted with standard material, i.e. no optimization concerning treatment, SiC content or process management were conducted. So chemical and physical bondings at the fiber-matrix interface are still too high to achieve high damage tolerance.

First structural applications showed the feasibility of the process for a fast, low-cost CMC fabrication route. Complex shaped structures with dimensions only limited by the geometry of the furnaces can be manufactured in near-net-shape technology by liquid impregnation within two weeks. Generally, this process offers enormous potential for lightweight structures not only for applications in the aeronautical industry.

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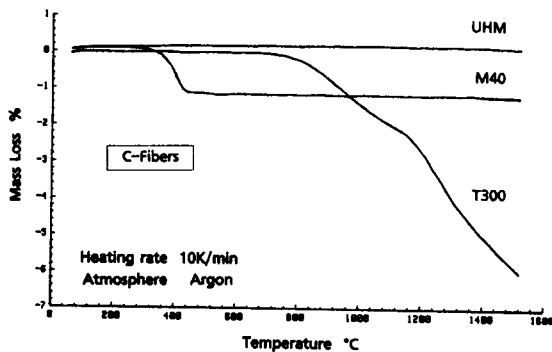


Figure 1. Thermogravimetric Analysis of Carbon Fibers

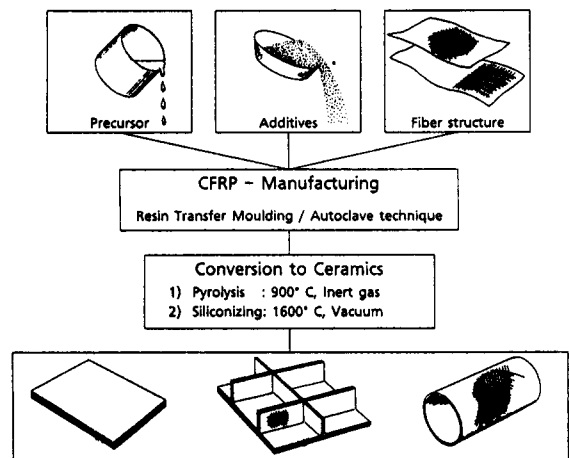
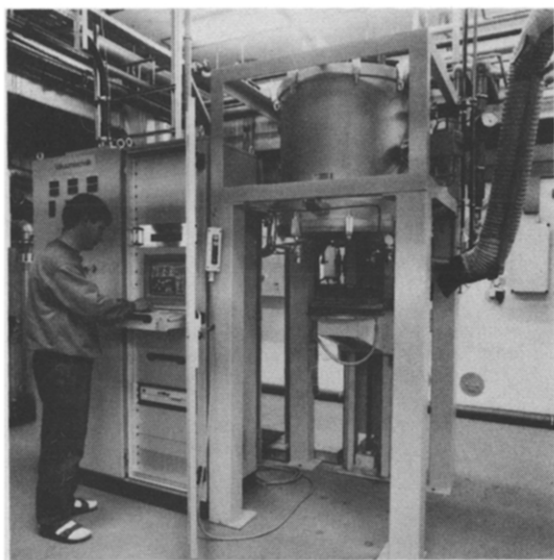


Figure 2. Schematic Illustration of the Liquid Impregnation Process



Heating chamber	Diameter 350 mm
	Height 400 mm
Operating temperature	2200 °C
Atmosphere	Inert gas or Vacuum
Heating system	CMC - Heating strips
Heat insulation	Graphite felt
Control device	Pyrometry by PC
Water cooling	70 l/min, 6 bar
Power	90 kVA

Figure 3. Furnace for Siliconizing

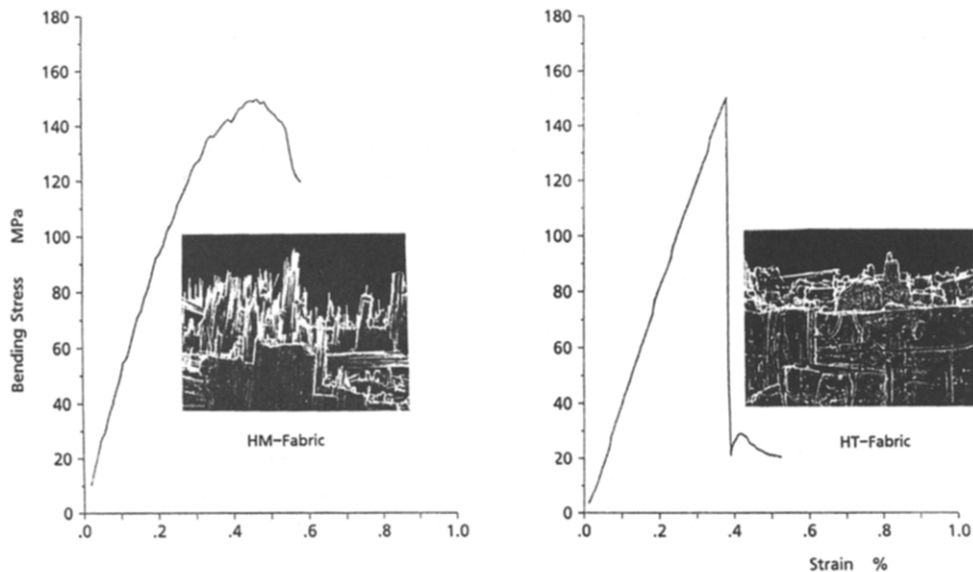


Figure 5. Failure Behavior of C/SiC

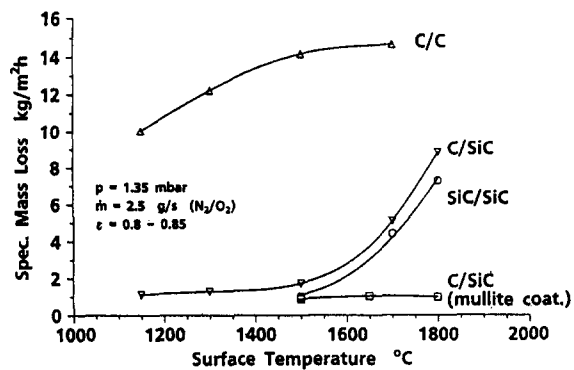
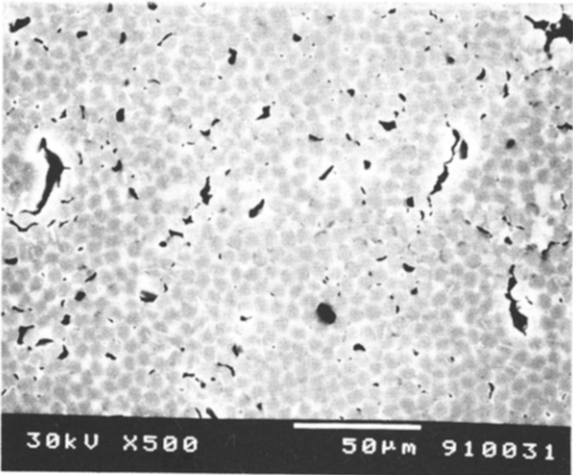
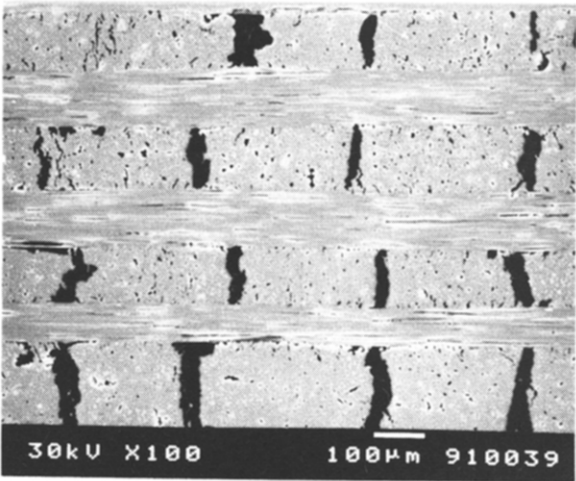


Figure 6. Erosion Rates vs Temperature of Coated and Uncoated Fiber Ceramics

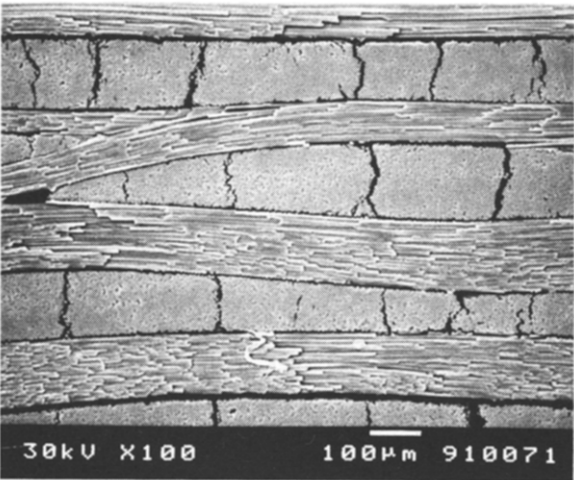




a.



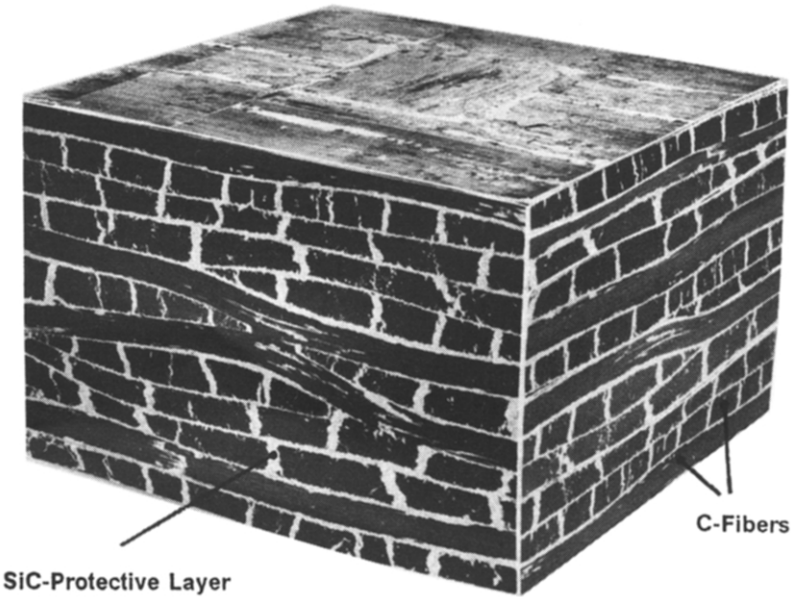
b.



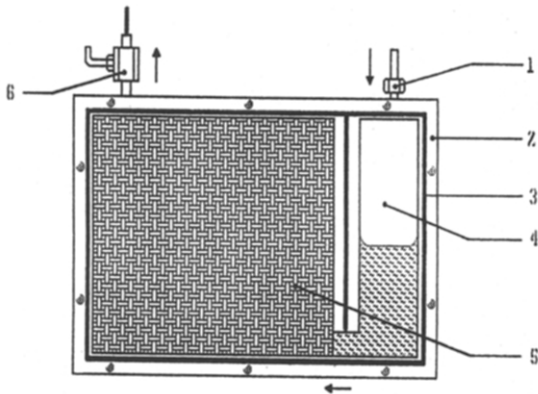
c.

- a. Unidirectional Reinforcement
- b. Crossply 0°/90°
- c. Fabric
- d. C/SiC 3D-Model

Figure 4. C/C-Microstructure for Different Reinforcements



d.



1. Inlet of gas 2. Mold 3. Sealing  
4. Resin chamber 5. Fiber structure 6. Valve

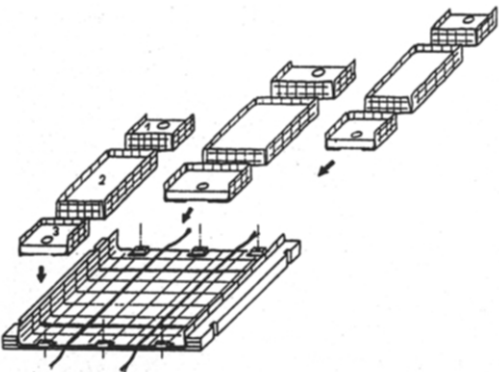


Figure 8. Tooling Process for Stringer Stiffened Panels



Figure 9. In-House Fabricated C/SiC Components

	Unit	HT (T300)	HM (M40)	UHM	Pitch	Nicalon (NL-200)	Tyranno	Si <sub>3</sub> N <sub>4</sub>
Manufacturer	-	Torayca	Torayca	Tonen	Idemitsu	Nippon-Carbon	UBE	Tonen
Composition	-	C: 95%	C: 100%	Pitch	Pitch C: 95% H: 5%	SiC: 65% SiO: 23% C: 12%	Si: 48% C: 28% O: 18% Ti: 4%	Si: 60% N: 37% O: 3%
Price roving/fabric	DM/kg	80/200	250/800	5000/-		1000/2500	1200/2000	
Number of fil.	-	1000-12000	1000-12000	3000	3000	500	400-1600	8000
Diameter	μm	7.0	6.5	10	10	15	11	10
Tensile strength	MPa	3500	2700	3300	3600	2500-3000	2800	2500
Young's modulus	GPa	230	400	700	250	180-200	206	300
Elongation	%	1.5	0.6	0.5	1.5	1.4	1.5-2.0	~1.0
Density ρ	g/cm <sup>3</sup>	1.75	1.80	2.15	2.0	2.55	2.3-2.4	2.5
Spec. electr. resistance ρ	Ωm	20 · 10 <sup>-4</sup>	8 · 10 <sup>-4</sup>		10 · 10 <sup>-4</sup>	10	10	
Coefficient of thermal exp. α	K <sup>-1</sup>	-0.5 · 10 <sup>-4</sup>	-0.5 · 10 <sup>-4</sup>	-1.5 · 10 <sup>-4</sup>		3.1 · 10 <sup>-4</sup>	3.1 · 10 <sup>-4</sup>	
Spec. heat c	J/(kgK)	0.71	0.71			1.14 · 10 <sup>-3</sup>	0.79 · 10 <sup>-3</sup>	
Heat transfer coefficient λ	kJ/(mhK)					41.88		
Dielectric constant ε <sub>2</sub>	-					9		
Temp. of app. T <sub>max</sub> air/inert	°C	400/1700	500/2000	500/2000		-/1200	1000/1300	-/1200

Table 1. Fibers for CMC

Density	g/cm <sup>3</sup>	2.33 - 2.34 (20°C) 2.53 - 2.55 (1420°C)
Melting point	°C	1410 - 1420
Coefficient of thermal expansion	1/K	2.33 - 4.0 · 10 <sup>-6</sup>
Surface stress vs vacuum	N/m	0.72 - 0.75 (1550°C)
Wetting angle	°	30 - 41 (vs SiC/Vacuum) 0 - 22 (vs C/Vacuum)
Viscosity	mPas	0.51 - 0.76 (1440°C) 0.46 - 0.64 (1560°C)

Table 2. Properties of Silicon

Precursor: XP-60	Fiber: T300-plain-weave	Orientation: 0°/90°
Tensile strength	90	MPa
Secant modulus	49	GPa
Elongation	0.22	%
ILSS	23	MPa
Flexural strength	160	MPa
Coefficient of thermal expansion	2.0	10 <sup>-6</sup> 1/K
Porosity	5	%
Fiber content	55	%
Density	2000	kg/m <sup>3</sup>
Temperature of application	1600 - 1800	°C

Table 3. Properties of C/SiC at RT (Status 1991)