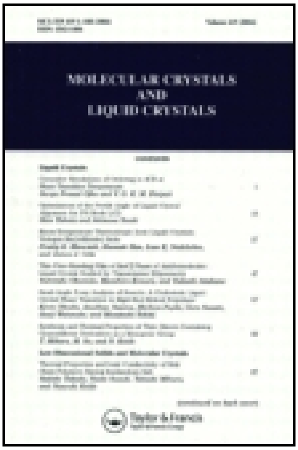

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From Polymer to Ceramics: Low Cost Manufacturing of Ceramic Matrix Composite Materials

Walter Krenkel [a]

[a] German Aerospace Center (DLR), Institute of Structures and Design, 70569, Stuttgart, Germany

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From Polymer to Ceramics: Low Cost Manufacturing of Ceramic Matrix Composite Materials

WALTER KRENKEL

German Aerospace Center (DLR), Institute of Structures and Design,
70569 Stuttgart, Germany

A cost efficient manufacturing route for ceramic matrix composites (CMC) has been developed by DLR. Starting with a carbon fibre reinforced plastic composite and converting the matrix from carbon to silicon carbide via the reaction with liquid silicon, CMC materials of high mass specific properties and of excellent thermal shock resistance can be achieved. Taking advantage of the simplicity of the process and the low raw material costs, C/C-SiC composites offer a wide range of possible applications. Very complex C/C-SiC structures have already been realized and demonstrate the transferability of the material's characteristics from samples to real components. Within industrial cooperation, C/C-SiC materials are being developed as aerospace hot structures and as friction materials for weight saving brake construction. Further prospective products like jet vanes or heat exchangers show new applications where C/C-SiC composites are attractive alternatives to conventional materials.

Keywords: Ceramic matrix composites; CMC; LSI process; brake discs; jet vanes; heat exchanger

1. INTRODUCTION

High performance ceramics are still largely produced via powder routes. The main disadvantage of these materials is their brittle failure behaviour and the thus dissatisfactory damage tolerance of ceramic components. The most favourable way to improve the fracture toughness of ceramics is the introduction of thermally stable continuous fibres.

Different processing techniques are currently in use for the development and prototype production of fibre reinforced ceramic matrix composites. Long manufacturing times, multiple reinfiltration steps and expensive raw materials lead to high material prices which have prevented their breakthrough to terrestrial applications up until now. To overcome these restrictions and widen the applicability of CMCs - in particular, to enter in fields of mechanical engineering -a novel cost efficient manufacturing route has been developed by DLR.

The process is based on the infiltration of a reactive fluid phase into porous carbon fibre preforms. Molten silicon is used as the reactive fluid, which replaces the initial pore volume of the preform and reacts subsequently with the carbon matrix to form silicon carbide.

A one-shot infiltration is sufficient for the densification of the matrix for this liquid silicon infiltration (LSI) process. Therefore, short processing times can be achieved which lead, in addition to the use of commercially available carbon fibres and cheap raw materials like phenolics and granules of silicon, to a C/C-SiC material which promises the lowest manufacturing costs of all CMC materials.

2. THE LSI-PROCESS

Principally, the LSI-process can be split into three processing steps and leads to C/C-SiC composite materials consisting of load bearing carbon fibres and matrices of silicon carbide, carbon and silicon.

2.1 Processing steps

Starting with a polymeric matrix, carbon fibre reinforced ceramics can be fabricated within two high temperature furnace steps where the matrix converts first to a microcracked, amorphous carbon and subsequently to SiC. The carbon fibre preform remains more or less unaffected and constrains high macroscopic changes of the composite during processing.

2.1.1 Green body fabrication

The processing starts with the manufacture of carbon fibre reinforced plastic composites (CFRP) with matrices of high carbon content. Normally commercially available resins like phenolics or other aromatic polymers are used to fabricate laminates by common CFRP techniques like resin transfer moulding (RTM), autoclave pressing or filament winding. These green bodies are produced near net and in simple shapes like rings, discs, panels or tubes.

After curing, the composites are additionally postcured for the complete polymerization of the matrix. Typical values of a bidirectionally reinforced CFRP component with fibre contents of 60 Vol % are densities of 1,49 g/cm^3 and an open porosity of less than 1%.

2.1.2 Pyrolysis

Within the second step, the CFRP composites are thermally treated under inert atmosphere at 900°C or under vacuum at temperatures up to 1650°C. The pyrolysis of the matrix leads to a contraction of about 60% of the volume of the original polymer, resulting in a carbon/carbon composite material with an interconnecting pore structure which can be described as a translaminar crack pattern with an open porosity of ca. 20%. This shrinkage of the matrix is combined with a considerable gas removal at the component's surface. To effectively achieve a carbon material in a one-shot process, the pyrolysis must be accomplished without inducing stresses that can lead to defects such as delaminations. Consequently, gases from inside the laminate have to travel by diffusion trough a network of cracks to reach the surface. The most critical period of the pyrolysis process is the stage when the evaporation from the surface of the composite falls below the rate at which gases are transported from the interior of the laminate to its surface. Consequently, CFRP composites must be carefully heated up and the allowable heating rates are low, resulting in processing times of more than 100 hours.

2.1.3 Siliconization

The third step represents the final siliconizing process to form the C/C-SiC composite. The process temperature is above the melting point of silicon (ca. 1420°C) so that liquid silicon can penetrate the porous C/C phase, supported by the specific properties of silicon, e.g. good wettability of carbon, high surface tension and low viscosity. The stoichiometrical conversion of molten silicon with solid carbon occurs following the equimolar reaction:

$$1 \text{ mol } Si_l + 1 \text{ mol } C_S \rightarrow 1 \text{ mol } SiC_S$$

That means, for the ideal case, one mole of silicon (28.1 g) reacts with one mole of carbon (12.0 g) to form one mole of silicon carbide (40.1 g).

The period of time for infiltration is a compromise between the necessary uptake of silicon required to fill the cracks in the C/C matrix and the time for a stoichiometrical formation of silicon carbide. The amount of free silicon depends on the heat treatment after silicon infiltration. Temperature and time of the siliconizing process are important parameters to control the formation of silicon carbide and to effect the properties of the CMC material.

Generally, the molten silicon penetrates preferably along the fibre direction. In the case of 2D-reinforcements and high fibre/matrix bondings, layers of SiC occur around segments of carbon fibres resulting in an internal volumetric protection (Figure 1). As an example, the mean Si-uptake of 35% during a two hour siliconization result in a matrix composition of about 62% in mass of SiC, 26% of carbon and 12% of residual silicon.

2.2 Characteristics of C/C-SiC materials

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.

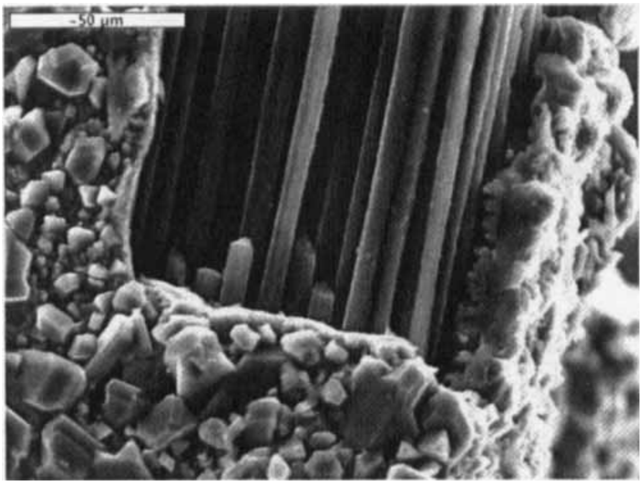

FIGURE 1 Layers of SiC crystals with different sizes create a protection zone around the carbon fibres (magnitude 750x).

2.2.1 Mechanical properties

Typically, C/C-SiC composites are made of bidirectionally woven fabrics which are stacked together or wound to the desired thickness. A macroscopic shrinkage during processing only occurs in the direction perpendicular to the fabric orientation and amounts to less than 7%. An orthotropic behaviour also exists for the mechanical as well as thermophysical properties, which show considerable differences between the in-plane and thickness direction.

With respect to the microstructure, composition and characteristics C/C-SiC composites differ from all other structural materials, in particular from monolithic ceramics, and represent a separate class of material. Three SILCA qualities have been standardized which fit to the requirements of different applications (Table 1):

- SILCA-XB (Basic) shows a level of strength and damage tolerance, which is appropriate for many structural applications
- SILCA-XT (Tenacity) shows an improved fracture toughness with considerable fibre pullout
- SILCA-XD (Density) is a material of higher stiffness and tightness and allows high accuracy during processing

All C/C-SiC composites are characterized by their low densities, their high mass specific properties and low matrix porosities.

TABLE 1 Mechanical and thermophysical properties of 2D C/C-SiC composites at room temperature.

Property	Unit		XB	XT	XD
Density	10^3 kg/m^3		1,9	1,9	2,3
Open porosity	%		3,5	3,5	1,0
Interlaminar shear strength	MPa		28	33	-
Flexural strength	MPa		160	300	80
Tensile strength	MPa		80	190	30
Strain to failure	%		0,15	0,35	0,04
Young´s modulus	GPa		60	60	100
Coefficient of thermal expansion	10^{-6} 1/K	100 °C ǁ	-1	-1	1,5
(Reference temperature 25°C)		100 °C ⊥	2,5	2,5	4,5
		1500 °C ǁ	2,5	2,2	3,8
		1500 C ⊥	6,5	7	7,5
Thermal conductivity	W/mK	200 °C ǁ	18,5	22,6	33,7
		200 °C ⊥	9,0	10,3	18,2
		1650 °C ǁ	17,0	20,8	23,1
		1650 °C ⊥	7,5	8,8	12,4
Specific heat	J/kgK	25 °C	750	690	720
		1400 °C	1550	1540	1450

2.2.2 High temperature properties

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 (see Figure 2).

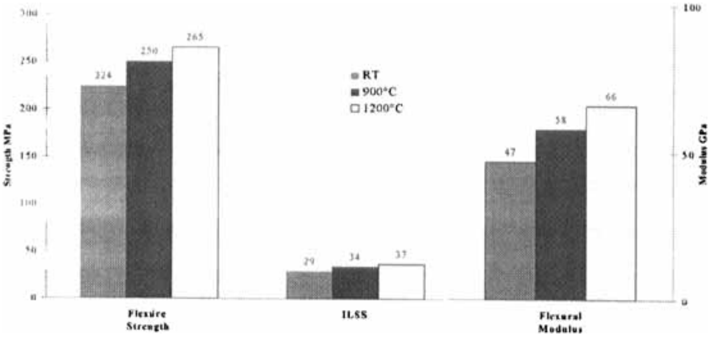

FIGURE 2 High temperature properties of C/C-SiC composites

The maximum temperature of C/C-SiC materials under stationary conditions is limited to 1500-1700°C. However, considerably higher temperatures of up to 3000°C can be applied in cases, where the required lifetime amounts to only a few minutes, e.g. for space or military applications.

3. PROTOTYPE DEVELOPMENT

Ceramic matrix composites fabricated via the LSI process are structural materials which can be used for a variety of lightweight applications particularly under conditions of severe wear, ablation or erosion.

3.1 Aerospace applications

Originally, DLR developed C/C-SiC composites for aerospace structures. Structural ceramic tiles have been developed for space capsules and in a real mission in 1995 the applicability of C/C-SiC for hot structures of spaceplanes was demonstrated [1]. The manufacture of an original-sized nose cap for a test vehicle under the contract of NASA is currently under development.

Within a national technology programme, a demonstrator of an intake flap for a hypersonic propulsion system was developed [2]. The design concept was a differential construction of a five-cell structure with stiffening caps and bushes in the load introduction areas. The flap's geometry was fixed to be about 275 x 265 x 34 mm^3, with wall thicknesses of 3 and 4 mm.

The flap was manufactured as a CFRP component via resin transfer moulding and was subsequently pyrolized to carbon/carbon. The additional reinforcing elements were fabricated separately and inserted into the C/C component. The total arrangement was then siliconized without any additional metallic bolts or ceramic adhesives. The total weight of this structural component amounts to only 1.1 kg. Mechanical tests at room temperature have been carried out in a three point bending test. The fracture load reached 25 kN corresponding to a safety factor of about 2.0. Additionally, thermal tests up to 1270°C have been conducted with temperature gradients of 70 K/s during heating up, meeting all design requirements.

3.2 Jet vanes for rocket propulsion systems

A typical short term application for refractory metals are jet vanes in the nozzle of rockets. Normally, vanes of tungsten are used to improve e.g. the manoeuvrability of missiles with the main drawback of high mass due to their high density (>19 g/cm^3). To withstand the combustion of the solid-fuel, extremely thermal and ablative stability are required combined with a high thermal shock resistance and good mechanical strength. Different aerodynamic shapes of jet vanes have been fabricated from C/C-SiC composites (Figure 3) and were investigated in a test facility. Despite the short burning time of only a few seconds, an additional protection coating of SiC was necessary to withstand the attack of thermal gases and solids. As the position of the vanes is far away from the centre of gravity, the low density of C/C-SiC may come in useful in a new lightweight generation of rocket propulsion systems.

FIGURE 3 Jet vanes made of C/C-SiC for rocket propulsion systems

3.3 Brake discs and clutches

Due to their multiphase matrix composition and the internal SiC layers, C/C-SiC ceramics offer advantages to carbon/carbon with respect to wear and coefficient of friction. In cooperation with industrial partners, DLR is investigating new designs of CMC components for their use in brakes and clutches. C/C-SiC shows extremly low wear and a high coefficient of friction (up to 0.8) which is only slightly influenced by humidity. As the density of C/C-SiC is in the range of 2 g/cm^3, brakes equipped with these CMC materials promise essential weight savings in the unsprung mass of vehicle structures.

The prototypes currently under investigation cover the whole range of application fields - from high performance clutches and emergency brakes to brake discs and pads for high speed cars and ultra lightweight vehicles. As the braking procedure is complex to simulate and tribological assessment only possible through trials and service tests, brake discs with differing dimensions must be developed [3][4].

The LSI process enables a modular construction of complex components due to its matrix formation in the fluid phase. Individual prefabricated, pyrolized components can be permanently joined together after siliconization. This in-situ joining technique enabled the manufacture of the first ventilated brake discs with preformed cooling channels between the brake surfaces (Figure 4). A decisive improvement in heat transfer during braking can be achieved through the in operation forced air circulation. The racing car industry, with its readiness towards innovation, has taken a lead in testing this new technology.

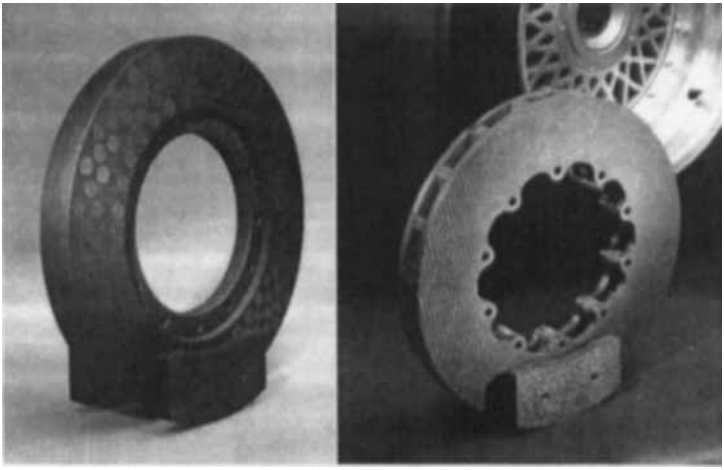

FIGURE 4 C/C-SiC brake discs and pads for automotive vehicles (right: internally ventilated)

3.4 High temperature heat exchanger

A long term but promising aim is to employ ceramic matrix composites for new generation, high temperature heat exchangers. For this application, corrosion resistance and material stability over temperature changes are the main material requirements which are currently being tested on tubular samples (Figure 5).

Metallic heat exchangers are widely used but have reached their limits with respect to temperature capability and corrosion resistance. Therefore a new concept for a ceramic high temperature heat exchanger has been developed [5]. The concept is based on the separation of functions between load bearing fibre reinforced ceramic and gas-tight monolithic ceramic materials. Internally pressurized monolithic ceramic tubes are placed within a C/C-SiC structure which can be subjected to tensile loads and is manufactured in a modular construction via the liquid silicon infiltration process. Due to the mismatch in thermal expansion between the monolithic and the fibre reinforced ceramics a gap filled with a filler material of high thermal conductivity and flexibility (e.g. boron nitride powder) is used to compensate the different coefficients of thermal expansions of the two materials. Prototype manufacturing and thermodynamic measurements are necessary to prove this concept of a new ceramic heat exchanger.

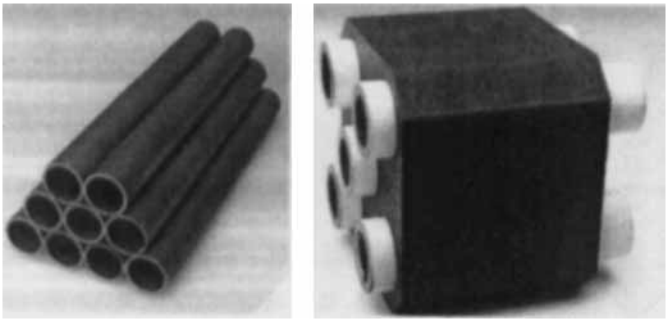

FIGURE 5 C/C-SiC tubes (left) and a prototype of a ceramic heat exchanger substructure

4. CONCLUSIONS

Ceramic matrix composites produced via the LSI process are structural materials which retain their strength at elevated temperatures. These properties combined with their low density make them useful materials for a variety of aerospace as well as non-aerospace applications particularly under conditions of severe wear or erosion. Very complex C/C-SiC structures have already been realized and demonstrate the transferability of the material's characteristics from small samples to real components. As no fibre coating and no reinfiltration steps are necessary, the LSI process offers the potential of cost effective manufacture of CMC due to low raw material costs and comparatively short manufacturing times. The future success of C/C-SiC composites depends upon the realization of a reproducible and economical manufacturing process. Recent cost analyses show the potential marketability of C/C-SiC products - the way to series production is however still far from being achieved, so that daring and farsighted industrial partners are required.

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