CARBON FIBRE REINFORCED SIC MATERIALS BASED ON MELT INFILTRATION

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ABSTRACT

For the manufacture of carbon fibre reinforced SiC materials, three different processes are used in principle: Chemical Vapour Infiltration (CVI), Liquid Polymer Infiltration (LPI), also called Polymer Infiltration and Pyrolysis (PIP) as well as Melt Infiltration or Liquid Silicon Infiltration (MI / LSI). Depending on the different methods for building up the SiC-matrix and embedding the carbon fibres in the brittle ceramic matrix, the resulting C/SiC and C/C-SiC materials vary significantly in their properties as well as in their manufacturing costs. The advantages of the MI processes are their short manufacturing times and the use of low cost raw materials, leading to the most cost efficient Ceramic Matrix Composites (CMC), compared to materials derived from CVI and PIP. In combination with their unique thermal and mechanical properties, MI based CMC`s opened up a wide field of new applications beyond aerospace.

This presentation gives an overview of the manufacturing processes and resulting properties of C-fibre reinforced SiC materials. Typical applications of C/C-SiC or C/SiC materials based on MI processes, like friction materials, hot structures for solid propellant rocket motors and temperature stable structures for optical telecommunication systems are presented.

1. INTRODUCTION

Since the 1970`s various methods for the manufacture of long fibre reinforced CMC materials have been investigated, which mainly differ in the way, the SiC matrix is built up. For carbon fibre reinforced SiC materials, three processes, Chemical Vapour Infiltration (CVI), Liquid Polymer Infiltration (LPI), also called Polymer Infiltration and Pyrolysis (PIP) and, Melt Infiltration (MI) or Liquid Silicon infiltration (LSI) are currently used for industrial production.

CVI and LPI processes could be transferred from C/C (Carbon Fibre reinforced Carbon) technology and were further developed and qualified, leading to improved material properties and a reproducible production of reliable, structural parts. These processes and materials were initially developed for the use in aerospace and military applications, and, due to high material costs, e.g. caused by absolutely vital fibre coatings, and very long production cycle times of several weeks up to months, are still limited to this areas. However, in the late 1980s, cost efficient manufacturing methods based on the infiltration of molten Si in porous C/C preforms have been developed. With this so-called MI / LSI processes, characterized by low cost raw materials and short process times, new application fields for CMC materials beyond aerospace could be opened [1]. Meanwhile, Mi processes are used by most of the CMC manufacturers, worldwide.

2. MELT INFILTRATION MANUFACTURING PROCESSES

The LSI / MI processes are based on the experiences from the manufacture of reaction bonded SiSiC materials, as well as on the manufacture of C/C materials via PIP and can generally be subdivided in three main process steps. In the first step, a CFRP (Carbon Fibre Reinforced Plastic) preform is made, using common technologies, like resin transfer moulding (RTM), autoclave technique or warm pressing. Therefore commercially available carbon fibres in form of 2D fabrics, cut fibres and filament winded or braided preforms as well as high carbon yield precursors, like phenolic resins, are used. In the second step, this CFRP preform is pyrolyzed in inert gas atmosphere at T > 900 °C, and thereby transformed into a highly porous C/C preform. In the third and last process step, molten silicon is infiltrated in this porosity by capillary forces at T > 1420 °C in vacuum. Thereby the silicon immediately reacts with the carbon in the contact areas building up the SiC matrix.

Due to the high reactivity of the molten Si, a direct contact to the C fibres generally has to be avoided. Additionally, a weak embedding of the brittle fibres in the brittle matrix is mandatory to obtain characteristic CMC properties, like high strength, fracture toughness and thermal shock resistance. To ensure both, fibre protection and weak fibre matrix interface, three different methods are used for industrial production up to now, i.e. fibre embedding in carbon matrix via PIP, fibre coating via CVI and in situ fibre embedding in carbon matrix (fig.1):

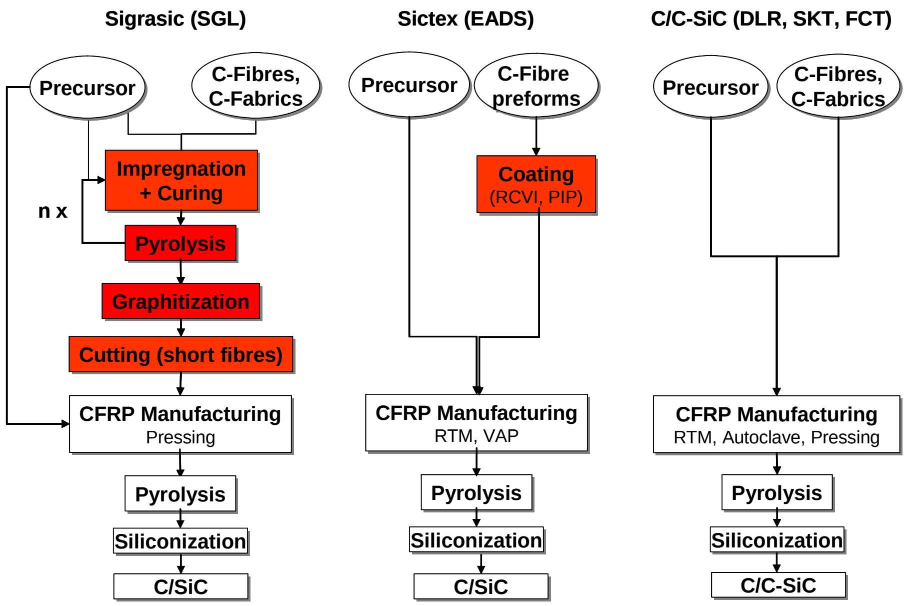

Figure 1. Schematic overview of MI manufacturing processes based on different methods for the build up of fibre protection and weak fibre matrix bonding. Left: Embedding the C-fibres by multiple PIP. Middle: Fibre coating via CVI or PIP. Right: In situ fibre embedding method with no additional coating process.

Fibre protection via PIP is widely used for the manufacture of short fibre reinforced C/SiC brake disks, e. g. leading to so called Sigrasic materials from SGL Carbon AG [2]. Thereby, endless fibre bundles are impregnated with phenolic resin, which is cured and pyrolysed, embedding the fibre filaments in a dense carbon matrix and resulting in a C/C like raw material. Using CVI for fibre coating, a thin layer, (~ 0.1 µm) of pyrolithic carbon is deposited on each fibre filament, resulting in a C/SiC material with the filaments mainly embedded individually in the SiC matrix. This method is used by EADS Astrium for the manufacture of so-called Sictex materials [3]. Time consuming and costly fibre coatings are not necessary at all if particularly suitable precursors, which offer a strong fibre matrix bonding, are used for the manufacture of the CFRP preform [4], leading to a segmentation of each fibre bundle into dense C/C bundles during pyrolysis. This cost efficient method is the basis of the LSI process, which has been developed at DLR and which has already been transferred to FCT Ingenieurkeramik GmbH for the serial production of friction materials. Similar

processes are used by Schunk Kohlenstofftechnik GmbH (SKT), Brembo Ceramic Brake Systems SpA, ECM and M Cubed Technologies Inc..
Due to the low and predictable contraction during pyrolysis, the geometrical stability during siliconization and the fast and homogeneous infiltration process, C/C-SiC parts can be made in near net shape technique with almost no restrictions to size, wall thickness and geometry. Complex shaped, thin walled structures can be realized via in situ joining, whereas different subcomponents are assembled in the C/C stage and joined permanently to integral structures during the subsequent siliconization step [5].

3. PROPERTIES

MI derived CMC materials are relatively dense, multiphase materials. As a basic material, fabric reinforced C/C-SiC XB (DLR) typically consist of a high content of load bearing carbon fibres (~65 Vol.-%), which is significantly higher compared to CVI and LPI materials, amorphous carbon matrix (~11 Vol.-%) and crystalline β-SiC matrix (~16 Vol.-%), with a small amount of metallic Si (~4 Vol.-%). However, the material composition, and therefore the material properties can be adjusted in a wide range by varying the raw materials and process parameters (fig. 2). For short fibre reinforced friction materials, like Sigrasic 6010 GNJ (SGL), highest SiC contents of up to 60 Vol.-%, comparable to CVI and LPI materials, and a Si content above 10 Vol.-% are common [6].

In Table 1 the mechanical and thermal properties of MI C/C-SiC and C/SiC materials are compared to C/SiC materials derived from CVI and LPI. The values can be used as a rough orientation, but cannot be compared directly, due to different evaluation methods used.

			CVI		LPI		LSI	
			C/SiC	C/SiC	C/SiC	C/C-SiC	C/C-SiC	C/SiC
Manufacturer			**SPS (SNECMA)**	**MT Aerospace**	**EADS**	**DLR**	**SKT**	**SGL (9)**
Density		g/cm^3	2.1	2.1 - 2.2	1.8	1.9 - 2.0	> 1.8	2 / 2.4
Porosity		%	10	10 - 15	10	2 - 5	-	2 / <1
Tensile strength		MPa	350	300 - 320	250	80 - 190	-	110 / 20-30
Strain to failure		%	0.9	0.6 - 0.9	0.5	0.15 - 0.35	0.23-0.3	0.3
Young's modulus		GPa	90 - 100	90 - 100	65	50 - 70	-	65 /20-30
Compression strength		MPa	580 - 700	450 - 550	590	210 - 320	-	470 / 250
Flexural strength		MPa	500 - 700	450 - 500	500	160 - 300	130 - 240	190 / 50
ILSS		MPa	35	45 - 48	10	28 - 33	14 - 20	-
Fibre content		Vol.%	45	42 - 47	46	55 - 65	-	-
CTE Coefficient of thermal expansion	‖	10^{-6} K^{-1}	3(1)	3	1.16(4)	-1 - 2.5(2)	0.8-1.5(4)	-0.3 / 1.8 (5)
	⊥		5(1)	5	4.06(4)	2.5 - 7(2)	5.5-6.5(4)	-0.03–1.36 (6) / 3 (7)
Thermal conductivity	‖	W/mK	14.3-20.6(1)	14	11.3-12.6(2)	17.0-22.6(3)	12 - 22	23–12 (8) / 40-20 (8)
	⊥		6.5 - 5.9(1)	7	5.3 - 5.5(2)	7.5 - 10.3(3)	28 - 35	
Specific heat		J/kgK	620 - 1400	-	900-1600(2)	690 - 1550	-	-

‖ and ⊥ = Fibre orientation; (1) RT - 1000 °C ; (2) RT - 1500 °C; (3) 200 - 1650 °C; (4) = RT - 700 °C; (5) 1200 °C; (6) 200 – 1200 °C; (7) 300 – 1200 °C; (8) 20 °C – 1200 °C; (9) values for fabric/short fibre reinforced material

Table 1. Typical material properties of C/SiC and C/C-SiC materials in dependence of the manufacturing method.

Low cost C/C-SiC materials, based on uncoated fibres, generally show lower tensile strength and strain values, compared to CVI or LPI materials. However, due to the significantly lower open porosity (e`= 1-4 %) obtained by MI processes, the interlaminar shear strength of C/C-SiC is comparable to CVI materials but higher than that of LPI C/SiC materials. Additionally, MI materials are characterized by highest thermal conductivity of up to 40 W/mK, which can be obtained by material types with high contents of SiC and Si.

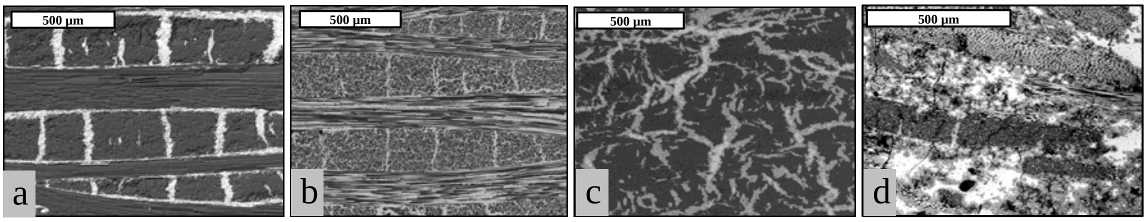

Figure 2. Microstructures of different CMC materials manufactured via MI / LSI. a) 2D fabric based C/C-SiC XB (DLR) characterized by dense C/C bundles (dark grey) embedded in the SiC matrix (grey). b) High density C/C-SiC XD (DLR) based on thermally treated carbon fibre fabrics. c) Short fibre reinforced C/C-SiC SF (DLR). d) Short fibre reinforced Sigrasic 6010 GNJ (SGL), with high SiC (grey) and Si (light grey) content.

4. APPLICATIONS

Due to generally higher material and manufacturing costs, compared to metals or CFRP, CMC materials are used only when there is no alternative. Therefore, high temperature applications in aerospace, are the domain for CMC. However, even in medium and low temperature applications MI C/C-SiC or C/SiC materials can be used, if high performance, regarding e.g. abrasive resistance and low thermal expansion, is required (fig. 3).

MI C/SiC materials were used the first time for the nose cap of the thermal protection system (TPS) of the Buran from the former Soviet Union [7]. The current status of C/C-SiC development in TPS can be demonstrated on the nose cap for the X-38 demonstrator, developed by DLR in the TETRA program (1998 – 2002) [8]. Thereby, maximum temperatures of 1800 °C, high heating rates of several hundred K/s and high thermal gradients are obtained locally during the critical reentry phase, lasting about 20 minutes. Recent developments for novel TPS systems concentrate on facetted structures, based on cost efficient, flat panels [9]. During a reentry test flight in 2005, a first C/C-SiC structure could withstand extreme thermal loads ($T_{max.}$ > 2000 K) at the sharp nose tip as well as at the edges of the structure.

C/C-SiC jet vanes for thrust vector control (TVC) systems have been introduced in military rocket motors, where they have to withstand the most severe thermal and mechanical loads known up to now. However, the service time is very short, usually in the range of a few seconds. The moveable jet vanes are positioned in the exhaust jet stream, which leads to high bending forces in the jet vane shaft, maximum temperatures of up to 3100 K and heating rates of several thousand K/s in the leading edge, as well as to local temperature gradients of up to 200 K/mm in the blade area. Additionally, the erosion of the leading edge, caused by Al_2O_3 particles, impacting at velocities of up to 2000 m/s, can be limited to an acceptable level. Compared to metallic jet vanes, usually made of refractory metals like tungsten, the use of C/C-SiC materials offers weight savings of up to 90 %.

Automotive brake disks are representing the first large scale application of CMC materials. For the first time ever, the up-scaling from a single part or small series manufacture to a reliable industrial production of several 1000, safety relevant components per year was performed successfully by SGL Brakes GmbH, Meitingen, and by Brembo Ceramic Brake Systems SpA, Stezzani. C/SiC brake disks based on short fibre reinforcement and LSI have been presented by DaimlerChrysler [10] and Porsche in 1999, were introduced to serial production by Porsche in 2001 [11] and are now available in almost all Porsche and several Audi models as well as in sports cars from Ferrari and DaimlerChrysler. Compared to cast iron, C/SiC brake disks offer weight savings of up to 50 %. The very high abrasion resistance leads to lifetime brake disks with possible service life of up to 300 000 km. The COF is generally high and stable, even at low temperatures and high humidity, and shows almost no fading after several subsequent emergency stops from maximum speed.

C/C-SiC brake pads for emergency brakes in high speed elevators are in serial production at FCT since 2004 [12] offering low wear, stable COF and high temperature resistance ($T_{max.}$>1200 °C). The high variability of the MI CMC materials also led to the serial production of sliding pads for the high speed hovertrain Transrapid at SKT. In case of a breakdown of the electromagnetic hover system, C/C-SiC pads ensure a safe emergency gliding of the train on the concrete driveway, as well as extreme abrasion resistance and low COF.

Figure 38. Exemplary C-fibre reinforced SiC parts manufactured via MI / LSI. Top left: Nose cap (ca. 740 x 640 x 170 mm^3; t ca. 6 mm; m ca. 7 kg, DLR) for X 38. Rear side showing in situ joint load bearing elements. Top right: Facetted TPS structure, built up by flat panels, mounted on a rocket system. Bottom from left to right: Jet vane (ca. 60 mm x 60 mm) and sealing ring for TVC of missiles (DLR). Porsche Ceramic Brake Disk (PCCB) based on short fibre reinforced C/SiC (Porsche). Elevator emergency brake system with C/C-SiC brake pads 142 mm x 34 mm x 6 mm). In situ joint telescope tube (∅ 140 mm, l = 160 mm, t = 3 mm) for the laser communication terminal in the satellite TerraSAR-X (Zeiss Optroniks / DLR).

Due to the very low CTE, C/C-SiC materials are used for geometrically stable components, e.g. in calibrating plates [13] or optical units. For the laser communication terminal (LCT) of the TerraSar-X satellite, launched in 2007, a C/C-SiC telescope tube with tailored CTE in axial direction, ($\alpha_{||} = 0 \pm 0.1 \times 10^{-6} K^{-1}$) is in service. Thereby, a constant distance between the primary and secondary mirror, in the temperature range of -50 °C and +70 °C can be obtained, ensuring a safe data transfer without transmission losses. Compared to Cerodur, C/C-SiC offers lower density and higher fracture toughness, enabling the near net shape manufacture of thin walled, lightweight structures. Additionally the main drawbacks of CFRP materials, outgasing in vacuum and hygroscopic swelling, can be overcome.

5. SUMMARY

Carbon fibre reinforced SiC materials are well known for their unique properties at high as well as at medium and low temperatures. Cost efficient manufacturing processes based on the infiltration of porous C/C preforms with melted silicon opened new application areas for the resulting C/C-SiC and C/SiC materials beyond aerospace. Compared to well established C/SiC materials derived from CVI and LPI, MI based materials offer medium tensile strength and are characterized by low open porosities, leading to high shear strength and high thermal conductivity. Typical application areas are TPS structures for spacecraft, hot structures for rocket propulsion, thermally stable structures and friction materials. The introduction of C/SiC automotive brake disks in serial production was a breakthrough and an important milestone in CMC technology, offering a high potential for the introduction of CMC materials in new industrial application fields.

References:

1. **W. Krenkel, H. Hald**, Liquid infiltrated C/SiC- An Alternative Material for Hot Space Structures, Proceedings of the ESA/ESTEC Conference on Spacecraft Structures and Mechanical Testing, Nordwijk, The Netherlands, 1988.
2. **Winnacker, Küchler**, Chemische Technik: Prozesse und Produkte, Eds. R. Dittmeyer et al, Volume 8, Wiley-VCH, Weinheim, Germany, 11166 -1173, 2005
3. **S. Beyer**: Einsatz von Ceramic Matrix Composites (CMC`s) für Antriebssysteme, DGM Fortbildungsseminar in Bayreuth, DGM, Frankfurt, Germany, 2004.
4. **W. Krenkel, J. Fabig**, Tailoring of Microstructure in C/C-SiC Composites, Proceedings of the 10th International Conference on Composite Materials, ICCM-10, Whistler, Canada, Vol. 4, 601 – 609, 1995.
5. **R. Kochendörfer, W. Krenkel**, CMC Intake Ramp for Hypersonic Propulsion Systems, in: Ceramic Matrix Composites I: Design Durability and Performance, Eds. A.G. Evans, R. Naslain, Ceramic Transactions, Vol. 57, 13 – 22, 1995.
6. Date sheet from **SGL Carbon Group**, SIGRASIC 6010 GNJ – Short Fibtre Reinforced Ceramic, 2005.
7. **V.I. Trefilov**, Ceramic- and Carbon-Matrix Composites, Chapman and Hall, 1995.
8. **H. Hald et al**, Developmentof a Nose Cap System for X 38, in. Proceedings of International Symposium Atmospheric Reentry Vehicles and Systems, Arcachon, France, 1999
9. **H. Weihs, T. Reimer, T. Laux**, Mechanical Architecture and Status of the Flight Unit of the Sharp Edge Flight Experiment SHEFEX, IAF Congress October 2004, I301, Vancouver, Canada, 2004
10. **T. Haug, K. Rebstock**, Neue Werkstofftechnologien für Bremsen, in Breuer, B. (Hrsg.): XIX. Internationales µ-Symposium Bremsenfachtagung 29./30. Oktober 1999, Fortschritt-Berichte VDI Reihe 12, Nr. 405, 40 – 52, VDI-Verlag, Düsseldorf, Germany, ISBN 3-18-340512-1, 1999
11. **R. J. Koehler**, Manuscript of the presentation at the shareholders`meeting of the SGL Carbon Group 2001, Germany, 2001.
12. **H. Abu El-Hija, W. Krenkel, S. Hugel**, Development of C/C-SiC Brake Pads for High-Performance Elevators, Int. Journal of Applied Ceramic Technology, Vol. 2, Issue 2, pp. 105-113, 2005
13. **Renz, R.; Heidenreich, B.; Krenkel, W.; Schöppach, A; Richter, F**, CMC Materials for Lightweight and Low CTE Applications, 4th International Conference on High Tempera-ture Ceramic Matrix Composites (HT-CMC 4), München, 1. – 3. Oktober 2001, in: Krenkel, W.; Naslain, R.; Schneider, H.: „High Temperature Ceramic Matrix Composites“, 839 – 845, Wiley-VCH Verlag, Weinheim, 2001